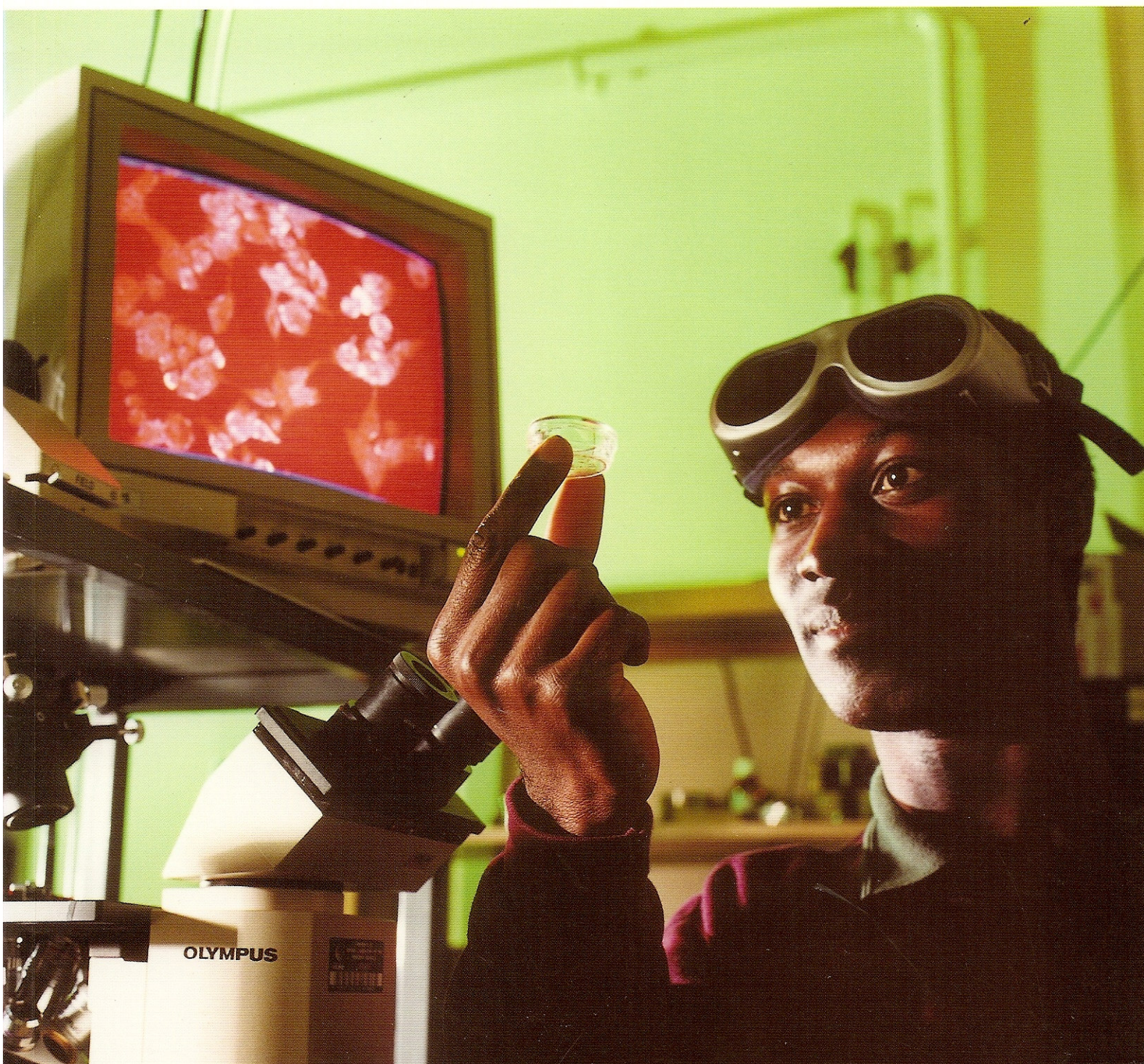




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Central Laser Facility Rutherford Appleton Laboratory Annual Report 2000-2001



Central Laser Facility

Rutherford Appleton Laboratory

Annual Report 2000/2001

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The front cover shows Dr Stan Botchway using the confocal laser microscope to investigate cell-to-cell communication as part of the new life science programme initiative.
(Photograph courtesy of RAL Photographic Section).

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Foreword

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This annual report for the Central Laser Facility (CLF) is an account of work carried out by its users in collaboration with facility staff during the financial year 2000-01.

The Vulcan laser has continued to provide a world-leading facility for the study of the interaction of very intense radiation with matter. The intensities available from the CPA beamline are now approaching 10^{20} W/cm² and this has enabled an extensive programme to be carried out on the study of matter under extreme conditions which is relevant to both microscopic and astronomical objects. Short pulses of energetic electrons and protons produced from laser-irradiated targets have enabled new studies of processes important to particle acceleration and the fast ignition scheme for Inertial Fusion Energy to take place. This has included exciting progress in the development of high-resolution proton radiography, which can detect highly transient electric and magnetic fields in laser-produced plasmas. In addition, the measurement of the highest magnetic fields ever produced in the laboratory have been achieved in laser-plasma interactions at $> 10^{19}$ W/cm². On a different scale, an accurate knowledge of the equation of state (EOS) for planetary constituents under extreme conditions of temperature and pressure is important in developing models of planetary cores and, using the long pulse facility of Vulcan and precompressed samples for the first time, the EOS of water has been studied from the propagation of laser-driven shock waves.

The Astra laser continues to provide a complementary source to Vulcan for the study of high intensity interactions. These have included the dynamics of ionisation and dissociation of atoms and small molecules at high irradiances. The demonstration of efficient guiding of high-intensity pulses in waveguides, by increasing the laser-plasma interaction lengths at high intensities, is a significant contribution to a wide range of processes including harmonic generation, laser wakefield accelerators and x-ray lasers.

A broadly based programme in chemistry, physics and biology has been carried out within the Lasers for Science Facility. These have exploited the sub-picosecond capabilities of the ultra-fast laboratory and the use of Kerr gated transient Raman scattering for the study of photochemical dynamics. In addition, the technique of two-photon fluorescence correlation microscopy has enabled the study of the kinetics of drug distribution and action in situ. The Laser Loan Pool has continued to benefit from the EPSRC-funded capital investment programme in making available advanced laser systems to university users in their own laboratories.

A marked feature of the past year has been the growth of demand from UK and other scientists for access to the Central Laser Facility and this has outstripped the amount of time which can currently be made available.

The quality of the science being carried out within the CLF continues to be of very high quality and has been identified as being world-leading in the EPSRC "Forward Look at Atomic and Molecular Physics" research in the UK. With the commissioning of the Vulcan PetaWatt laser in 2002, I believe we can look forward with confidence to the continuing success of the CLF and its many users.

Overview of the Central Laser Facility

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Laser Facilities for Users

The Central Laser Facility (CLF) is a world leading centre for research using lasers. Facilities available to users include the Vulcan Nd: glass laser which delivers multi- TW beams to two target areas, the Astra ultra- short pulse interaction facility based on titanium sapphire laser technology, a range of state of the art table top laser systems and specialised diagnostic instruments within the Lasers for Science Facility and the Laser Loan Pool.

Vulcan

Vulcan is a highly versatile large scale Nd: glass laser installation which delivers a maximum of 2.5kJ of energy in its six 10cm and two 15cm beamlines to two target areas, each of which is equipped with frequency conversion optics to enable both 1 μ m and 0.5 μ m operation of all beams. A range of pulse durations are available from 100ps to 20ns in various geometries.

A short pulse (700fs) high irradiance ($\sim 10^{20}$ Wcm⁻²) chirped pulse amplification (CPA) capability is available, with vacuum propagation to target and reflective beam focusing optics. Additional low energy beams, including sub- picosecond CPA probes, are provided for diagnostics with high temporal resolution. The system is fully characterised and equipped with advanced diagnostics.

Vulcan Petawatt Project

A 3 year development of Vulcan's CPA beamline to the Petawatt level began in April 1999. The project involves the addition of an additional stage of disc amplifiers, the construction of a large aperture vacuum beam compressor and a new target chamber within a new target area building.

The new building was completed, on schedule, in December 2000. The vacuum compressor and target chamber amplifiers will be installed during the summer. Following vacuum tests and thorough cleaning, the beam optics will be installed ready for the alignment tests and beamline commissioning which will take place early in 2002. Demonstration of Petawatt output is scheduled for the end of June, 2002. The development is funded through an EPSRC research grant.

Lasers for Science Facility (LSF)

The LSF operates a suite of state of the art table- top laser systems and associated instrumentation giving users access to highly tuneable (vuv - ir) and variable pulse width (ns to fs) laser radiation. This includes lasers for ns and ps time- resolved resonance Raman spectroscopy (TR³), a unique dual wavelength kHz femtosecond synchronised pump- probe apparatus based on OPA technology, a high average power laser plasma x- ray source and a fast gated (100ps) confocal microscopy laboratory.

The Ultrafast Spectroscopy Laboratory has recently developed the high brightness PIRATE source (Picosecond Infrared Absorption and Transient Excitation). The Ultrafast Laboratory is heavily subscribed by users for a wide range of experiments in chemistry, physics, biological and material sciences. Demand for beam time is so high that funding is being sought from EPSRC for a second system.

Laser Loan Pool

Compact laser systems are made available to UK researchers for periods of up to 6 months at the user's home institution. Systems available include: nanosecond tunable YAG pumped dye lasers (with frequency up-conversion and down-conversion covering from 205 to 4500 nm), an excimer laser (operating down to 157 nm), a CW frequency doubled argon ion laser and an all solid state femtosecond Titanium Sapphire (680-1020 nm). To complement the lasers, a wide range of ancillary and diagnostic equipment is available.

Astra

The Astra facility is based on titanium sapphire laser technology which gives users access to high intensity laser pulses at 10Hz. Repetition rate.

The facility supplies laser pulses to two target areas simultaneously. Target Area I provides pulses of 50fs duration with an energy of 10mJ, producing irradiance on target in excess of 10^{16} Wcm⁻². The Target Area II currently delivers 300 mJ in 50fs with target irradiance in the 10^{18} Wcm⁻² regime.

Engineering Services

Mechanical, electrical and computing support is provided for the operation of the laser facilities at the CLF, for the experimental programmes on these facilities and for the CLF's research and development activities. Access to mechanical and electrical CAD tools and workshop facilities enable a rapid response to be provided to users.

Access to Facilities

The primary funding source of the Central Laser Facility are the UK Research Councils, who make beam time available for UK University researchers and their overseas collaborators through the responsive mode grant mechanism.

A small proportion of access is available for "Direct Access", to enable rapid access for urgent, topical and proof of principle experiments. Bids for Direct Access beam time are peer reviewed by an expert panel who advise the Director of the CLF on scientific priority, etc. Calls for Direct Access are publicised in scientific journals and on the CLF Web site.

Beamtime is available for European researchers and their collaborators through the EU Access to Large Scale Infrastructure programme organised under the Improving Human Potential (IHP) theme within the Fifth Framework Programme. Calls for Proposals are publicised in Physics Today and on the CLF Web site.

Hiring of the facilities and access to CLF expertise is also available on a commercial basis for industrial research and development.

The Laser Loan Pool is funded directly by an EPSRC rolling programme. These facilities are available to all UK researchers performing work falling within the EPSRC science programme.

CLF Web site

Further information on the CLF, its facilities, and the scientific programmes is available on the CLF Web site at <http://www.clf.rl.ac.uk/>

High Power Laser Programme

- 1) Short Pulse Plasma Physics**
- 2) Long Pulse Plasma Physics and X-Ray Laser Physics**
- 3) Theory and Computation**
- 4) Femtosecond Pulse Physics**

A Multi-MeV proton probe for Inertial Confinement Fusion/ Fast Ignitor studies

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Introduction

In a number of experiments, performed with different laser systems and in different interaction conditions, protons with energies up to several tens of MeV have been detected behind thin foils irradiated with high intensity pulses^{1,2}. In these experiments it was seen that the particle beams are directed along the normal to the back surface of the target, and have a small angular aperture at the highest energies. As proton beams are observed even using targets which nominally do not contain hydrogen, protons are thought to originate from hydro-carbon impurities located on the target surfaces or from bulk contamination of the target. Proposed theoretical models indicate that the protons gain their energy from the enormous electric field ($\sim \text{MeV}/\mu\text{m}$) set up by laser accelerated fast electrons via space-charge at the back target surface³⁻⁵. In particular, Particle-in-Cell simulations suggest that the proton beam charge will be globally neutralized by a co-moving cloud of MeV electrons⁵. The particular properties of these beams make them of great interest for application as a probe in high-density matter investigations. The use of protons as a radiographic source is an idea which has circulated for many years⁶. Applications of proton radiography have been proposed in the biomedical area or in testing of thick systems. Linear or cyclotron accelerators are used to obtain the proton energies required for these applications. Laser-produced proton beams represent a feasible alternative with enormous potential when high spatial/temporal resolution is required.

A particularly interesting application of laser-produced proton beams is the detection of electric and magnetic fields generated during the interaction of intense laser pulses with high density plasmas. In this context, proton imaging can be developed as a diagnostic with great potential for Inertial Confinement Fusion (ICF) studies. For example, the possibility of accessing directly electric field distributions in dense plasmas may shed new light on issues such as hydrodynamic and electromagnetic instabilities highly detrimental for ICF. The technique also has great potential for studying the complex and yet unexplored electric and magnetic field distributions in indirect drive target assemblies. In the Fast Ignitor context, it will contribute to the study of the large transient electric and magnetic fields generated in high-intensity laser-matter interactions. The magnitude and characteristics of these fields are currently the subject of much conjecture in the short pulse, high-intensity plasma physics community.

In this paper the principles of the technique and the results of a series of experimental tests, in which the proton source has been

applied for the first time as a particle probe in a range of laser-plasma interaction conditions, will be presented and discussed.

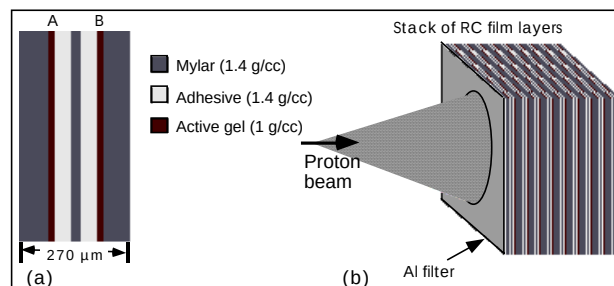


Figure1. Schematic of (a) a layer of Radiochromic film; (b) set-up for spectrally resolved proton beam detection.

Diagnostic set-up

The Vulcan Nd:glass laser operating in the Chirped Pulse Amplification mode (CPA) was used in the experiment. The main targets (used for the production of the proton beams) were Al foils, 1-2 mm wide and 3 - 25 μm thick. The 1.054 mm CPA interaction pulse, 1 ps in duration, with energy up to 100 J was focused by an F/3.5 off-axis parabola (OAP) onto the centre of the main target. The incidence was about 15° off normal. The focal spot varied between 8 and 10 μm in diameter at full width at half maximum (FWHM), containing 30-40 % of the energy, and giving intensities up to $5\text{-}7 \times 10^{19} \text{ W/cm}^2$.

The detector employed in the experimental tests consisted of a stack of several layers of radiochromic (RC) film. As shown in Figure 1(a) the film consists of 270 μm thick plastic containing a double layer of organic dye, which reacts to ionizing radiation⁷. The equivalent dose of energetic protons stopped in the film can be measured from the changes in optical density undergone by the film, yielding information on the number and energy of the protons. By using them in a stack, each layer of film acts as a filter for the following layers. In fact protons deposit energy mainly in the Bragg peak at the end of their range⁸. Due to this, the contribution on each RC film layer will be mainly due to protons within a narrow energy range. The proton energies detectable as a function of the detector's depths are shown in Figure 2. Plastic track detectors were also used on some occasions to confirm that the structures observed were due to protons and not to electrons or x-rays to which the RC film is also sensitive. A 25 μm Al filter was placed in front of the first layer of film giving a minimum detectable proton energy of about 3 MeV.

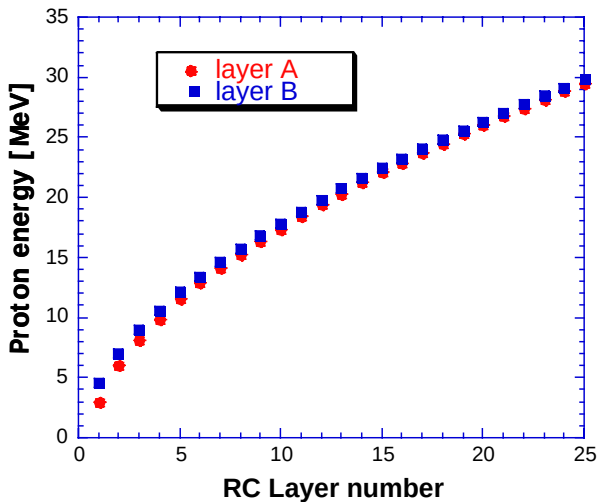


Figure 2. Proton energy detectable as a function of the RC film layer number.

Proton imaging

The laser-produced proton beam was characterized in view of its application as a particle beam probe. The protons were produced by focusing the CPA pulse onto the Al foil, and detected by placing the RC film stack at the back of the target, typically at a distance of about 2 cm. It was found that the proton beams have high brightness, typically with 10^{12} protons with energy above 3 MeV per shot and cutoff energy around 20 MeV (at a laser irradiance of the order of $5 \cdot 10^{19} \text{ Wcm}^{-2}$). As observed in previous experiments, the beams were highly directional, propagating along the normal to the back surface of the target with small angular divergence (about 15° for 10 MeV protons). The energy deposited within each film layer can be extracted from the absolutely calibrated film. By doing this for each film layer and fitting an exponential energy spectrum, an estimate of the proton energy spectrum and total energy can be extracted from the film data⁸⁾. The mean proton energy of the exponential fit is $3.75 \text{ MeV} \pm 0.3 \text{ MeV}$ with a total energy of 2.2 J in an equivalent Maxwellian with a temperature of 2.5 MeV. During the experiments the source size of the proton beam was estimated using a penumbral edge method, setting an upper limit of 15-20 μm diameter for the source of 10 MeV protons.

The proton probe was used in a simple projection scheme, with the object placed between the proton source (i.e. the back side of the primary target) and the detector. With this arrangement some of the advantageous properties of the proton beam were successfully exploited, namely: the small source size, leading to high spatial resolution in imaging applications; the short pulse duration; the low divergence and high brightness of the beam. In addition, spatial and spectral resolution is guaranteed by an

appropriate choice of detector (e.g. RC film stacks), and the proton beam characteristics can be tuned by suitably changing the laser and target parameters. The temporal resolution obtainable with these beams is far beyond the possibilities of beams provided by conventional accelerators. Further, as it will be seen in the following sections, the fact that the beams have a broad spectrum is far from being a disadvantage when probing transient fields. Finally their ease of use and synchronization is a clear advantage in laser-plasma and Inertial Confinement Fusion related experiments; the fact that, being charged, protons can be used for diagnosing electric and magnetic fields, makes proton beam probing a powerful, novel diagnostic method, complementary to techniques such as x-ray radiography.

In general, the intensity distribution cross-section of a proton beam propagating through matter is modified both by collisional stopping/scattering, and by deflections due to electric and magnetic fields. In situations in which scattering/stopping are unimportant (e.g. thin targets) and there are no fields, there is a one-to-one correspondence between the object and detector planes (point projection imaging), as an effect of the small source size. The magnification of the image is simply determined by the ratio of the detector-to-object and object-to-source distances. Deflection due to electric or magnetic fields present in and around the object will introduce perturbations to this projection image. From such distortions, the electric and magnetic fields distribution at the object can be inferred. Depending on the target and irradiation geometry employed, the technique can be made more sensitive to the detection of electric rather than magnetic fields. 3D Particle-In-Cell simulations performed by Dr.H.Ruhl (MBI-Berlin) have studied the propagation of proton beams through plasmas. These simulations have confirmed that electric field structures present in the plasma (as for example those associated with small-scale density non-uniformities) can indeed be imprinted on the proton beam intensity profile. PIC/hydrodynamic simulations, coupled to post-processing via particle ray-tracing, will be fundamental for the retrieval of the field distribution in the more complex situations.

Imaging of cold solid objects

When thick solid obstacles were placed in the beam a shadow of the object was observed in the proton images, due to collisional stopping in the target. However, a shadow was observed even when objects with a thickness much smaller than the proton penetration depth were used, e.g. a mesh formed by 10 μm Cu wires with 25 or 100 μm spacing. The set-up for this particular test is depicted in Figure 3(a). The mesh was parallel to the main target, i.e. perpendicular to the proton beam. The distance between the proton source and the mesh was 1 mm, while the first of the radiochromic film layers was positioned at 22 mm from the source.

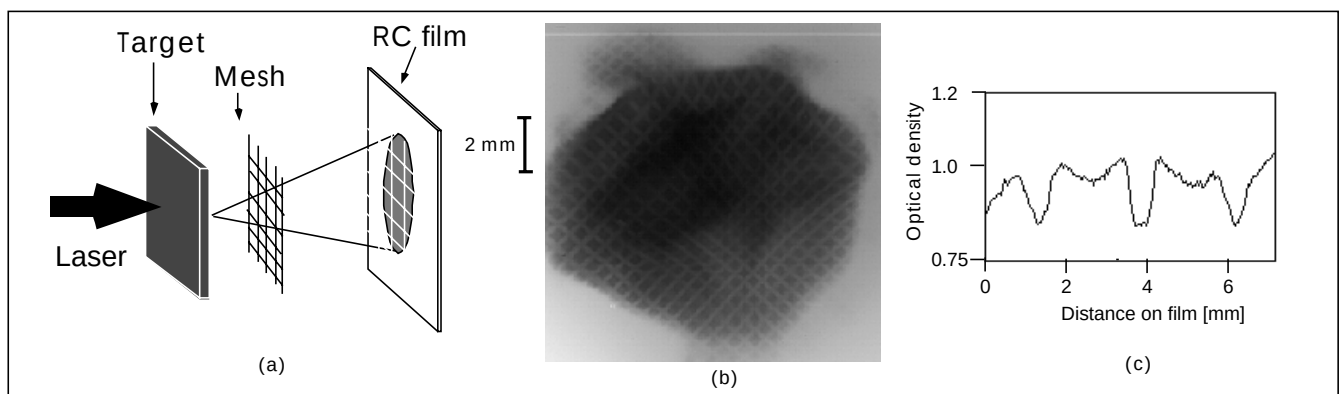


Figure 3. (a) Set up for proton imaging of a mesh; (b) image of a mesh with 25 μm spacing (10 μm Cu wires) obtained with 15 MeV protons; (c) Lineout across image of a mesh with 100 μm obtained with 20 MeV protons.

A shadow of the mesh was observed on the radiochromic film, as shown in Figure 3(b). The image shown in the picture has been obtained with 15 MeV protons and the 25 μm spacing mesh. The shadow of the wires can be observed clearly, the contrast of the picture being quite sharp. Figure 3(c) shows the optical density lineout across the shadow of a different mesh, with 100 μm spacing, obtained with 20 MeV protons. The magnification is consistent with the geometry of the imaging system. The optical density modulation observed is of the order of 0.2. It should be noted that the stopping range of 20 MeV protons in Cu is about 900 μm , and the collisional energy loss for such energetic protons in 10 μm of Cu is just $\Delta E/E \sim 5 \cdot 10^{-3}$. Taking into account the film response, this would lead only to a variation in optical density $\Delta D \sim 5 \cdot 10^{-5}$. Therefore the shadow observed must be due to some different effect. Our present explanation is that the mesh charges up positively, due, for example, to hot electrons preceding the proton beam and expelling a small number of cold electrons from the target via collisions. The deflection of the protons due to the electric field in the proximity of the wires is then responsible for the creation of the mesh shadow on the detector, where pile-up of the deflected protons is observed beside the regions of minimum transmission. An estimate of the linear charge on the mesh can be obtained via particle tracing, giving $\lambda \sim 10^{-6}$ C/m.

Imprinting of the electric field structures on the proton beam is indeed possible even if the beam is globally neutral, as predicted by PIC models. In fact, due to the low density of the proton beam when it reaches the object, and the high temperature of the electrons of the cloud, the Debye length of the ion-electron cloud will be several hundreds of microns (i.e. significantly larger than the spatial scale of the electric field structures).

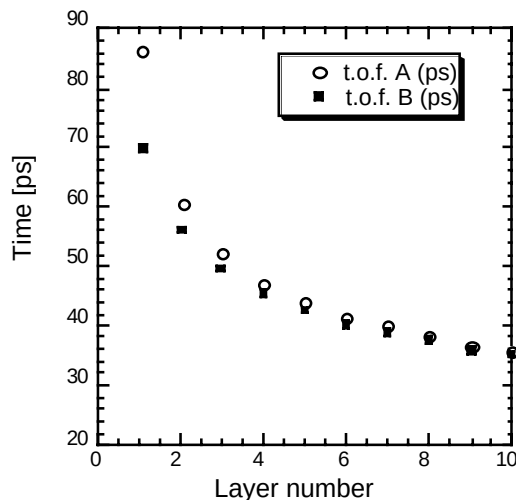


Figure 4. Time of arrival on target versus RC film layer number (data for both active layers A and B of each RC film is plotted).

Imaging of fast-evolving objects

When probing an object undergoing fast changes, the fact that the proton beams are not monochromatic is actually an advantage, as it can be exploited to obtain, in a single shot, information on the temporal history of the object to be probed. In fact, if the object to be probed is situated at a finite distance from the source, protons with different energies will reach the object at different times. By employing a detector that performs spectral selection, the information on the temporal evolution of the target can be retained. This is explained in Figure 4, where the calculated time of arrival on target of the protons produced on the Al foil is plotted versus the RC film layer number (i.e. versus their energy). As can be seen, the presence of the double active layer in each RC film causes a temporal indetermination

which is larger for the first RC layers, but can be removed by mechanically separating the two gel layers after data collection.

By doing so, we were able to confirm the short duration of the proton burst. Figure 5 shows a scan of the two parts of an RC film layer after separation. The object being probed was a solid target (50 μm Ta wire) irradiated with a second CPA pulse. More details about the experimental arrangement for this experiment are given elsewhere in this Annual Report ¹⁰. The target charges up following the interaction, and the proton beam probes a fast evolving electric field pattern. The RC film layer of Figure 5 was the second in the film stack, and the signal of the A and B active layers is mainly due, respectively, to 6 and 7 MeV protons. The temporal difference on target between protons with this energy is about 5 ps. As is clearly visible, the patterns observed in the two layers differ significantly, meaning that the protons producing the pattern have experienced different electric field configuration. From this it can be inferred that the duration of the proton burst at the source is smaller than 5 ps.

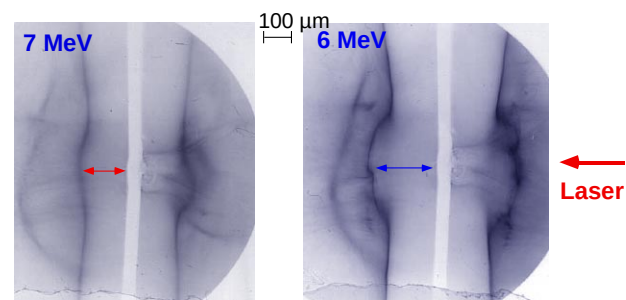


Figure 5. Proton images of a 50 μm Ta wire irradiated by a 10^{19} W/cm² pulse, obtained in the same event with 6 and 7 MeV protons. The spatial scale refers to the target plane.

Conclusion

Proton imaging is a diagnostic with great potential in laser-plasma interaction studies, which can allow diagnostic access to previously inaccessible phenomena. Some applications of the technique are detailed elsewhere in this report ¹⁰. The work was supported by an ESPRC grant. We acknowledge the invaluable contribution to the work provided by the CLF staff.

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Detection of highly transient electric fields following ultra-intense laser interaction with solid targets

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Introduction

We present here the first application of laser-produced protons as a particle probe in high-density matter investigations. By using the recently developed proton imaging technique¹ the first direct demonstration of highly transient electric fields following ultra-intense laser-pulse interaction with plasmas has been obtained. The possibility (previously unavailable) of measuring transient electric fields with high temporal resolution permits the investigation of a range of important phenomena related to the generation and transport of hot electron currents. These issues are of enormous topical interest in view of the development of Fast Ignitor driven Inertial Confinement Fusion. They can now be accessed with a completely different approach, which allows study of the electron current dynamics with an unprecedented resolution in a direct and simple way.

Experimental arrangement

The proton beams were produced by focusing a high-intensity pulse (typically 20 J in 1 picosecond, focused at an intensity of 10^{19} Wcm^{-2}) onto the surface of Al foils. The protons were emitted normal to the back surface of the target with small angular divergence (about 10°), cut-off energy of 10 MeV, temperature of $\sim 1 \text{ MeV}$ (obtained by fitting a Boltzmann exponential to the proton spectrum), from a source with diameter smaller than 10-15 μm .

According to the models, the protons are accelerated for a time of the order of the laser pulse duration, as confirmed by our experimental tests¹. This provides very high temporal resolution for our particle probe, allowing the detection of highly transient phenomena. It should be remembered here that proton beams produced with conventional accelerators have a duration of several nanoseconds at best.

The detector employed consisted of a stack of several layers of radiochromic film (RCF)¹. By employing this technique, we have detected the onset of electric fields in various target configurations². We will discuss here the detection of highly transient fields following the irradiation of a solid target with an ultra-intense, picosecond laser pulse. The experimental arrangement for these measurements is shown in Figure 1.

Two 1 μm , 1 ps pulses (CPA₁ and CPA₂) produced by the Vulcan laser were focused onto separate targets at an intensity of 10^{19} W/cm^2 . The CPA₂ pulse was focused onto an Al foil to produce a beam of protons, while the CPA₁ pulse was focused onto solid targets. The delay between the two pulses could be

varied optically. The angle between proton beam direction and CPA₁ propagation directions was approximately 75° . The distances involved were: 2 mm (Al foil to main target), and 2.7 cm (main target to detector). As explained in Reference 1, the proton probe is used in a point-projection imaging arrangement with the magnification determined by the ratio of detector-to-object and object-to-source distances. The advantages of using an RCF-based detector are also discussed in Reference 1.

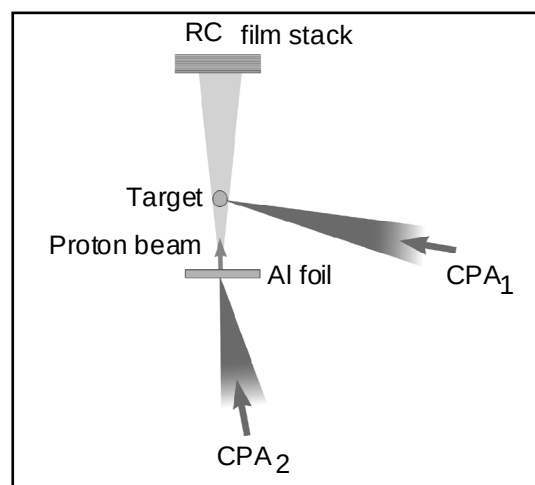


Figure 1. Experimental arrangement for proton probing of ultra-intense laser-target interaction.

Experimental results

In Figure 2 proton images taken (in a single shot) after ultra-intense irradiation of a 150 μm glass micro-balloon are shown. It can be seen (Figure 2(a)) that in coincidence with the interaction, a circular shadow, much larger than the projected target image, is observed in the detector. Here by shadow we mean a region of film unexposed to the proton flux. This shadow is consistent with protons that are deflected away from the target surface by an outwardly directed electric field. As a matter of fact, during the CPA₁ interaction, fast electrons are accelerated in the forward direction by the laser pulse in the interaction region at the front of the target. The energy of these electrons, in the MeV range, is large enough for them to reach the back of the target. Some of the electrons can actually escape from the target, before it charges up, preventing further loss of

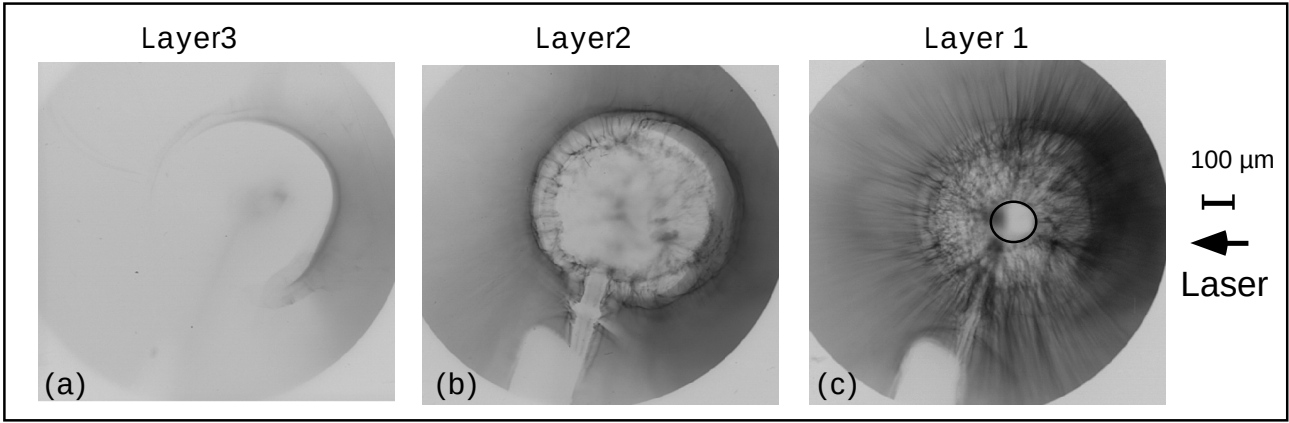


Figure 2. Proton images taken following CPA-irradiation of a 150 μm glass micro-balloon. The original size and position of the target are indicated by the black circle in (c). Each picture refers to subsequent RCF layers (i.e. different proton energy E_p and different probing delay Δt from the interaction): (a) $E_p \sim 8$ MeV, $\Delta t \sim 0$; (b) $E_p \sim 6-7$ MeV, $\Delta t \sim 10$ ps; (c) $E_p \sim 3-5$ MeV, $\Delta t \sim 20-35$ ps. The spatial scale indicated refers to the target plane: distances in the image plane are M times larger ($M \sim 13$ is the geometric magnification).

electrons. The proton deflection we observe is due to this charge.

An analytical expression for the position in the image plane of a proton of the beam can be easily obtained, taking account of the deflection experienced by the proton in the Coulomb field of the charged sphere³⁾:

$$x = d \tan \alpha + L \tan (\alpha + 2 \tan^{-1}(Q/8\pi\epsilon_0 V d \sin \alpha))$$

where V is the energy of the proton in eV, α is the angle formed by the proton with the beam propagation axis, ϵ_0 is the permittivity of vacuum and Q is the charge of the target (SI units). By supposing, for simplicity, uniform proton emission within a cone of aperture α_0 , the proton density distribution in the detector plane can be calculated for an arbitrary Q .

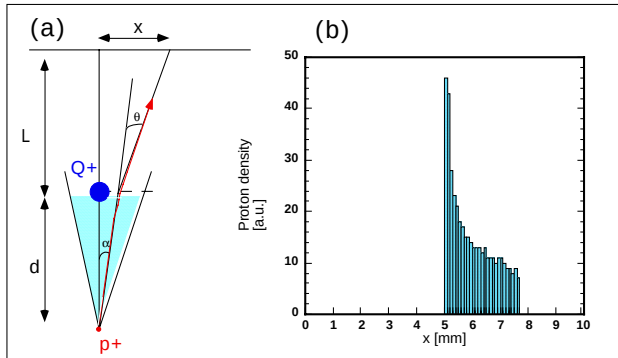


Figure 3. (a) Schematic of proton deflection in presence of a charge Q . (b) Calculated radial proton distribution at the detector plane (for $V = 8$ MeV, $Q = 2 \cdot 10^{-8}$ C), reproducing the experimental data of Figure 2(a).

The radial distribution shows a pronounced peak due to proton pile-up. Matching the peak position with the experimental one yields the value of Q (Figure 3). In this way, the charge at $t = 0$ was estimated to be $Q \sim 2 \cdot 10^{-8}$ C, corresponding to 10^{11} electrons leaving the target during the interaction.

As visible from Figure 2, a rapid discharge of the target was observed following the interaction. By applying the method described above to the different layers, and using data taken with different CPA₁-CPA₂ delays, the temporal evolution of the target's charge could be reconstructed, as shown in Figure 4. The charge decays exponentially, with a time constant of approximately 25 ps. We believe that the observation is consistent with the expelled electrons flowing back into the target. As a matter of fact, the electrons leaving the target will also move in the potential of the positively charged

microballoon. They will reach a maximum distance from the target, after which they will be called back into the target. This is the most likely mechanism able to explain the discharge considering its short timescale.

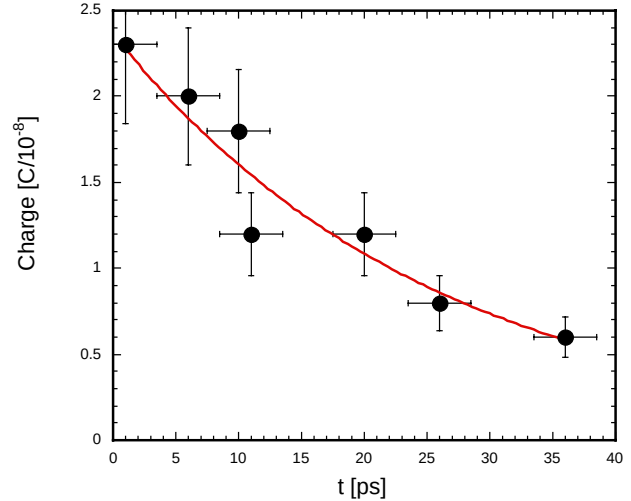


Figure 4. Temporal evolution of the charge of the laser-irradiated microballoon. The solid line represents an exponential fit of the data.

This assumption is supported by another phenomenon clearly visible in the data shown in Figure 2. Simultaneously with the discharge, the onset of filamentary structures at the target surface after the interaction was observed. The filamentary structures are first seen 10-20 ps after the interaction, and appear as striations extending outwards along the normal to the target surface, even far away from the interaction region. This is clear in Figure 2(b) where the filaments start to appear, and in Figure 2(c), where they have fully grown. In Figure 2(c) the filaments are seen both side-on and face-on (as a speckled pattern inside the shadow). The transverse wavelength of the modulation is about 10 μm and is more or less constant over the whole field of observation.

The observations are consistent with the growth, at the surface of the target, of an electromagnetic heat-flow instability⁴⁾, arising in presence of two counterstreaming currents. This takes place when the returning current of hot electrons flows back into the target, and draws an opposite current of cold electrons from the target in order to preserve charge neutrality. Filamentary structures similar to the ones of Figure 2 were observed via optical probing in long pulse experiments about 20 years ago⁵⁾. However, optical probing could only detect density perturbations in the coronal plasma with limited

temporal resolution, and only speculations could be made on the origin and nature of the filaments in that experimental setting.

Heat-flow instabilities have been studied theoretically for a long time due to their potentially detrimental effect on compression in conventional Inertial Confinement Fusion (ICF), and, more recently, due to the renewed interest in fast electron transport associated with the Fast Ignitor Scheme for ICF. The electrothermal instability⁶⁾, which takes place in presence of counter-streaming flows of collisionless hot electrons and cold collisional electrons is particularly relevant to our experimental conditions. As the instability causes magnetized filamentation of both hot and cold currents, the effect is imprinted on the diagnostic proton beam via the associated electric fields, transverse to the filaments. The instability grows at the target surface and the perturbations are transported out by the expanding plasma. Essentially the magnetic fields are frozen into the ablating plasma. Reference 6 provides order of magnitude scaling laws (which are independent from the intensity of the hot electron flux) for the growth rate α and the transverse wavelength λ of the modulation, i.e. $\alpha[s^{-1}] = 2.8 \cdot 10^{-8} n_0 Z / A T_e^{3/2}$, $\lambda[m] = 2.41 \cdot 10^{10} T_e^2 \sqrt{A} / n_0 Z$. n_0 and T_e are density and temperature of the cold electrons, Z and A charge and atomic number of the target material. For example, by using the density of solid glass ($n_0 \sim 5.10^{28} \text{ m}^{-3}$), Z and A for Si (main constituent of the glass target) and $T_e = 500 \text{ eV}$, one obtains $\alpha^{-1} \sim 15 \text{ ps}$ and $\lambda \sim 5 \mu\text{m}$, of the order of the observations. It should be noted that a 500 eV temperature is consistent with the upper bound imposed by the validity condition of the model (cold mean-free path less than collisionless skin depth). Once the magnetic field of the instability has grown sufficiently ($\Omega_0 \tau_c > 1$), the thermal conduction reduces, the condition no longer applies, but the filaments become frozen-in.

Features similar to the ones discussed up to now were observed during the interaction with a range of solid targets. Particularly dramatic effects were observed probing the interaction of the CPA₁ pulse with small diameter metal wires. Figure 5 shows proton images of the interaction with a 50 μm Ta wire. The RCF layers shown (second layers of the RCF stacks, corresponding to proton energies of 6-7 MeV) have been obtained in separate shots for different CPA₁-CPA₂ delays. When the proton probe arrived on target before the CPA₂ interaction pulse (e.g., $t = -10 \text{ ps}$, 1st image in Figure 5), only the shadow of the Ta wire, thick enough to slow down the protons is visible, with some small effect visible in the interaction region due to preplasma present ahead of the interaction. However when the probe is incident with the interaction a dramatic effect is observed, with the protons being deflected away from the wire surface, which again charges up due to hot electron expulsion. Even in this case the charge is seen to decay in a few tens of picoseconds, and filamentary structures are seen to appear. In this case the onset of pronounced horizontal features above and below the interaction axis is also detected. This data is still being analysed. However we think this

structure may be related to the radial expansion of shocks following the interaction, likely presenting non-neutral regions at their leading front. The complex pattern observed with RCF was reproduced when CR39, a nuclear track detector was used. The data of Figure 6 was obtained with a layer of CR39 film placed immediately behind one of the RCF layers shown in Figure 5 (the third from the left). Allowing for the time difference and the lower spatial resolution of CR39, the features are all reproduced, providing further confirmation that all the features observed are due to protons within the estimated energy range.

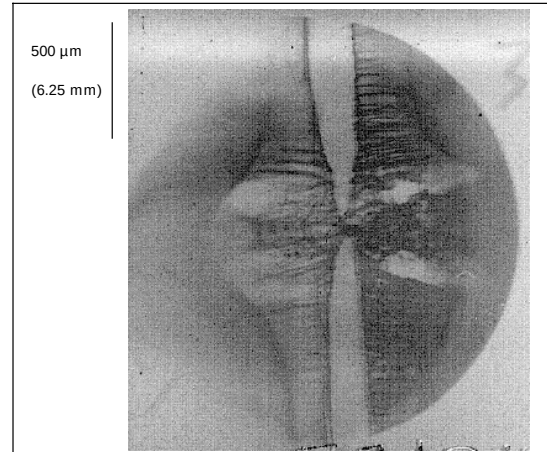


Figure 6. Proton image obtained with CR39 (8MeV protons). The detector was placed immediately after the central layer of Figure 5.

Conclusion

Proton imaging has enormous potential for the diagnosis of fundamental physical problems, which were impossible to explore up to now. By using this diagnostic, for the first time the measurement of very large, highly transient electric fields in plasmas has been obtained, determining their evolution on a picosecond scale with micrometric spatial resolution. In particular, global charge-up of a microscopic target irradiated by a high-intensity laser has been observed for the first time.

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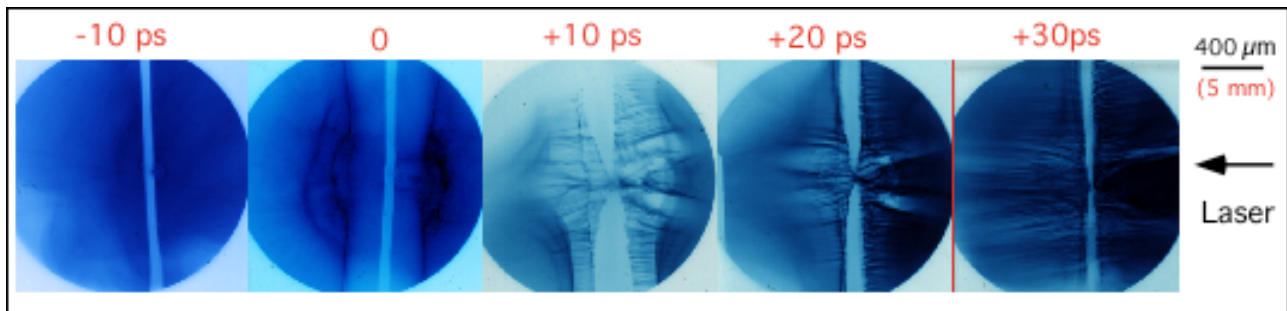


Figure 5. Temporal evolution of proton images of the interaction zone for different interaction-probing delays. The target was a 50 μm Ta wire and the energy of the protons employed was 6-7 MeV. The delay between CPA₁ interaction and probing is indicated above each of the pictures. Spatial scales for both the target and the image plane (between bracket) are indicated.

Macroscopic evidence of soliton formation in multiterawatt laser plasma interaction

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Introduction

Experiments studying the interaction of ultraintense, ultrashort laser pulses with plasmas provide unique laboratory conditions for the study of the collective nonlinear dynamics of a macroscopic system in the relativistic regime. In addition, investigating the structure of the nonlinear coherent modes in the wake of a short laser pulse is of great practical interest as it shows how the laser pulse energy can be transferred to the electromagnetic fields in the plasma and to fast particles. Coherent structures, such as solitons and vortices are fundamental features of this nonlinear interaction. Indeed, analytical and numerical results¹⁻²⁾ have shown that low-frequency, slowly propagating, sub-cycle solitons can be generated in the interaction of ultra short ultraintense laser pulses with underdense plasmas.

A significant fraction of the laser pulse energy can be trapped in these structures in the form of electromagnetic energy oscillating at a frequency smaller than the Langmuir frequency ω_{pe} of the surrounding plasma. The typical size of these solitons is of the order of the collisionless electron skin depth $d_e = c/\omega_{pe}$. The fields inside the solitons consist of synchronously oscillating electric and magnetic fields plus a steady electrostatic field which arises from the charge separation as electrons are pushed outwards by the ponderomotive force of the oscillating fields.

As yet no direct experimental proof of soliton generation in the laser plasma interaction has been obtained. Indeed the experimental detection of such structures poses phenomenal challenges due to their microscopic scale and to their transient nature.

Here we report the experimental observation of bubble-like structures in proton images³⁾ of laser-produced plasmas, which we interpret as the macroscopic remnants of solitons formed during the interaction with the ultra-intense pulse. The observed structures correspond to localized depletion regions in the cross section of a transverse-propagating proton probe beam. We believe that these are the first experimental observations of quasi-neutral cavitated post-solitons. The bubbles appear as the protons are deflected away by the localized electric field at the edges of the cavitated areas. This

interpretation is supported by computational and analytical results.

Experimental arrangement

The experiment was carried out employing the VULCAN Nd:glass laser operating in the Chirped Pulse Amplification mode (CPA). The VULCAN CPA pulse was split in two separate 1 ps, 1 μm , 20 J pulses (CPA₁ and CPA₂) which were focussed onto separate targets in a 10-15 μm FWHM focal spot giving an average intensity of about 10^{19} W/cm². The experimental arrangement is shown schematically in Figure 1. The CPA₁ pulse was used as the main interaction pulse and focused into a preformed plasma. The plasmas were produced by exploding thin plastic foils (0.3 μm thick) with two 1 ns, 0.527 μm laser pulses at a total irradiance of about $5 \cdot 10^{14}$ W/cm². The delay between plasma formation and interaction was typically 1 ns. The CPA₂ pulse was focussed onto a 3 μm Al foil in order to produce a beam of multi-MeV protons, which were used as a transverse particle probe of the interaction region. This is a diagnostic scheme for detection of electric fields in plasmas recently proposed as proton imaging. The delay between the two CPA pulses could be varied optically.

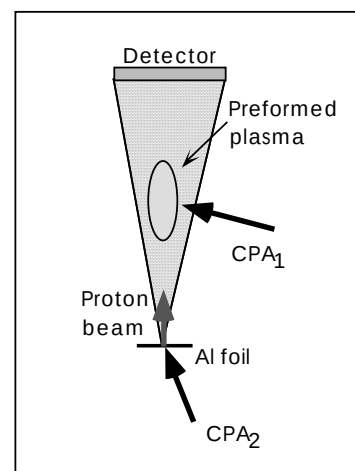


Figure 1. Experimental arrangement.

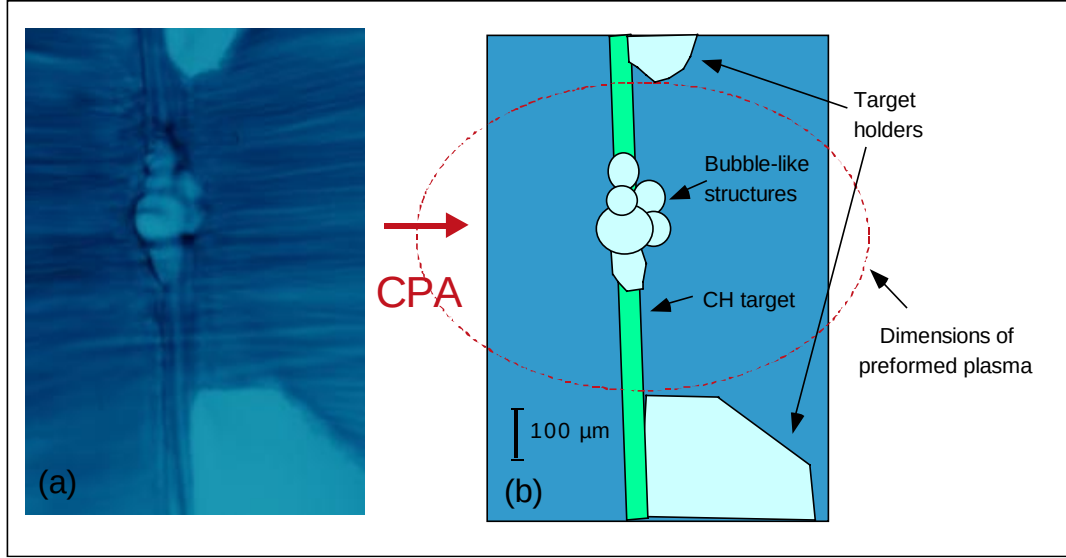


Figure 2. a) Proton image of the preformed plasma taken 20 ps after the CPA₁ interaction with 8 MeV protons. b) Sketch explaining the main features of a).

As the proton source is small, the proton probe could be used in a point-projection imaging arrangement with the magnification determined by the ratio of detector-to-object and object-to-source distances. In our experiment these distances were respectively 2.5 and 22 mm, giving a magnification of about 9.

The proton detector employed consisted of a stack of several layers of radiochromic film (RCF), namely MD-55 GafChromic. The diagnostic use of stacks of RCF for obtaining spectrally selected information on the equivalent dose of the protons stopped is described in Reference 3.

A further, low energy fraction of the CPA pulse was frequency quadrupled and used as a transverse optical probe, alternatively to the particle probe. Interferometry was performed along this line using a modified Nomarsky interferometer, which allowed density characterization of the preformed plasma. The peak density of the plasma was inferred to be $0.1\text{--}0.2\ n_c$ @ $1\ \mu\text{m}$ from self-consistent plasma expansion models⁴⁾ and its longitudinal extension was of the order of a mm. By adjusting the delay between the CPA₁ and CPA₂ pulses, it was possible to probe the plasma with the proton beam at different times following the interaction.

Experimental results

The main feature observed in the proton images (i.e. the proton beam intensity cross section after propagation through the plasma) was the onset of several bubble-like structures closely following the interaction. A proton image of the plasma recorded 20 ps after the CPA₁ interaction, and obtained with 8 MeV protons, is shown in Figure 2. Bubble-like structures are clearly visible at the centre of the plasma. In particular, a large structure with radius of approximately $50\ \mu\text{m}$ is seen at the centre of the picture, with five other smaller structures tightly packed around it. The structures are first observed in coincidence with the interaction and appear to survive until about 50 ps after the interaction. At this time the contrast of the bubble structures is much worse than in Figure 2a), and after this time no such structures are clearly observed. The "bubbles" correspond to unexposed regions of the RCF, i.e. regions of the proton beam cross section from which protons have been evacuated. The area density of the matter crossed by the beam is insignificant compared to the stopping range of the protons employed. Therefore it is reasonable to assume that the bubbles are observed in correspondence with plasma regions where localized electric fields, with a component transverse to the proton propagation direction, are present. The region where the bubbles are present extends for about $300\ \mu\text{m}$ in the transverse direction and for about $150\ \mu\text{m}$ in the longitudinal direction.

They are therefore observed even far away from the interaction axis and the vacuum focal spot region. It should be noted that, in similar interaction conditions, break-up of the laser beam in several filaments diverging at wide angles has been observed⁵⁾. This causes fractions of the laser energy to be spread as far as $150\ \mu\text{m}$ (radially) from the propagation axis in the plasma central plane. In presence of this filamentary behaviour, no efficient channel formation process via Coulomb explosion⁶⁾ following the interaction was observed. It is therefore reasonable to assume that the spatial scale of the area occupied by the bubbles in the proton images is consistent with the dimension of the turbulent region left by the laser pulse in the central part of the plasma.

Data interpretation and modelling

We believe that the observations are consistent with structures (post-solitons) deriving by merging of several solitons, and we have supported this assumption with analytical and computational modelling. Detection of solitary structures on time scales longer than the ion motion time brings into play their dynamics under the action of the electrostatic field due to charge separation. As shown in Reference 2, on time scales longer than $\sqrt{m_i/m_e}\omega_{pe}^{-1}$ the nature of the slow propagating subcycle solitons changes because ions start to expand. As a consequence, a void forms in the ion density and the soliton is changed into a radially expanding post-soliton structure that is largely quasineutral. The void in the plasma forms a resonator for the trapped electromagnetic field with frequency ω_s inversely proportional to the post-soliton radius R . As the hole expands, the amplitude and the frequency of the electromagnetic field decrease adiabatically.

From the adiabatic invariant $\int E^2 dV / \omega_s = \text{constant}$ we see that the electromagnetic field amplitude decreases as $E \propto 1/R^2$. Using a snow-plough model of the ion expansion the characteristic expansion time of the post-soliton is found to be given by $\tau = (6\pi R_0^2 n_0 m_i / \langle E_0^2 \rangle)^{0.5}$ with n_0 the plasma density and $R_0 \sim d_e$ and $\langle E_0^2 \rangle / 8\pi$ the initial soliton radius and electromagnetic energy density. For $t/\tau \gg 1$, the post-soliton radius increases as $R \approx R_0 (2t/\tau)^{1/3}$, and the amplitude of the electromagnetic fields and its frequency decrease as $E \sim t^{-2/3}$ and $\omega_s \sim t^{-1/3}$. Their expansion²⁾ makes the post-solitons merge after a certain time, and eventually they form a bubble much larger than the individual solitons. The bubble can even be larger than the volume traced by the laser pulse due to the soliton motion and to the expansion of the plasma as a whole.

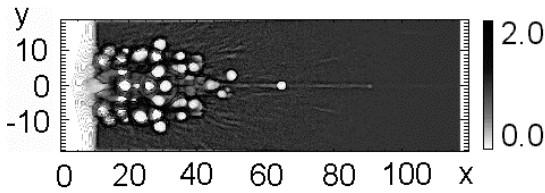


Figure 3. 2-D PIC simulation results: ion density distribution in a cloud of merging post-solitons at $t = 140$.

A laser pulse, wider than a few times d_e , generates a cloud of solitons with conversion efficiency as high as 20% according to the Particle-In-Cell (PIC) results presented in Reference 1. The number N_s of post-solitons depends both on the laser and on the plasma parameters. Figure 3 shows 2-D PIC simulation results, in which a cloud of merging solitons is seen in the wake of a laser pulse. Distances are measured in laser wavelengths λ and times in laser periods $2\pi/\omega$. The laser parameters for these simulations are: dimensionless amplitude $a = 3$, pulse length $l_{||} = 15\lambda$ and width $l_{\perp} = 7.5\lambda$. The laser propagates in an underdense plasma with $n = 0.3n_{cr}$. The figure shows a snapshot of the ion density at $t = 140$. About 30 post-solitons can be seen formed following laser pulse filamentation.

This is a result typically observed in PIC simulations: where the density is not too small compared to the critical density, clouds of solitons are formed, evolve into expanding post-solitons and eventually merge into bigger structures. This process can occur separately at different locations leading to separate macrobubbles. In other words, bubbles appear around each filament if the laser pulse undergoes filamentation inside the plasma. The process of soliton merging is presented in Figure 4, where predictions for an s-polarized pulse with $a = 3$, length $l_{||} = 15\lambda$ and width 7.5λ in a plasma with density $n = 0.3n_{cr}$. The pulse was initialized in such a way as to produce two spatially close solitons, as shown in Figure 4a in the ion density distribution at $t = 80$. As the ions start to move and the two post-solitons expand, their walls intersect going through a transient merging phase that leads to the formation of a new almost circular shell on a time scale of the order of $t = 480$, as shown in Figure 4b.

Similar results appear in the evolution of the ion density pattern shown in Figure 3. At later times than shown in Figure 3, a macrobubble starts to form with a size of the order of the pulse depletion length i.e., of the order of the size of the region inside which the solitons originally formed.

Conclusion

In conclusion the stability, persistence and geometric structure of the "bubbles" observed in the experiment lead naturally to their interpretation in terms of long lived remnants of coherent structures such as solitons, as supported by analytical and PIC modelling. Their "macroscopic" size however is much bigger than the electron skin depth and the time scale over which they are observed implies that the ion dynamics must be accounted for. Post-solitons, and the bubbles formed by their merging, can indeed account for scales much larger than the skin depth and for long expansion times, compatible with the observation time. In addition the values of the electric field that is required in order to account for the proton beam deflection seems to be consistent with the relatively weak electrostatic fields that are expected to occur in the almost quasineutral post-solitons. This field is of the order of the oscillating electromagnetic fields inside the cavity, $E_{||} \approx E_0 a_0 (d_e/R)^4$ and the thickness of the non-quasineutral shell δR is $\delta R/R \sim a_0 (d_e/R)^5$.

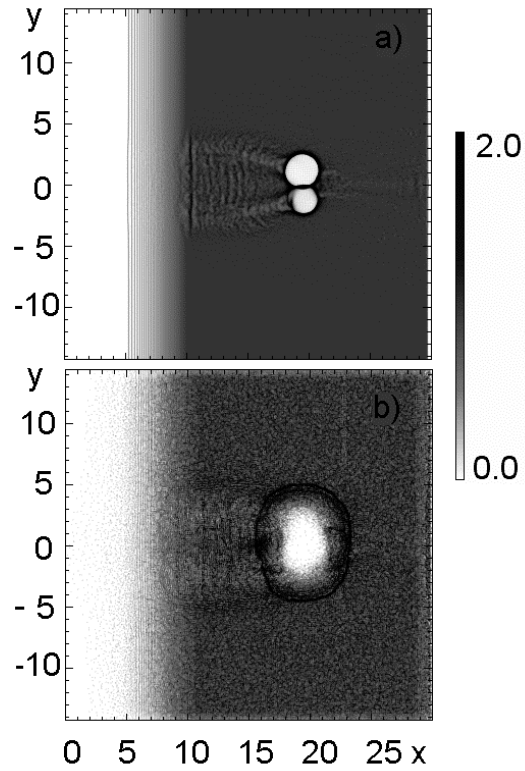


Figure 4. Ion density distributions of two merging post-solitons during (a) and after (b) the merging process, as obtained from 2-D PIC simulations, at $t = 80$ and $t = 480$.

Further modelling is underway in order to support our interpretation, which will include proton tracing through the electric field structures produced by the PIC simulation.

Finally we would like to thank the staff of the CLF for their help and assistance during the experiment.

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High energy electron measurements in relativistic interactions with underdense plasmas

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Introduction

In a previous experiment¹⁾ on the propagation of an intense short pulse (50J, 1ps) in a preformed channel created by a precursor pulse (25J, 1ps) clear evidence was found of a correlation between fast electrons generated by the interaction and the “age” of the channel, i.e. the delay between the channel forming pulse and the interaction pulse. An important issue to be addressed in that experiment was the correlation of those measurements with angular and spectral features of high energy electrons. To this purpose we have designed a multilayer radiochromic-based detector for energetic charged particles (SHEEBA). When exposed to such high energy particles, the active layers within the film absorb energy and change optical density. The exposure to high energy protons also results in nuclear activation of the film, which is monitored using a Geiger counter. The absence of activation in the results shown here is additional evidence that our signal was entirely due to electrons.

Here we report on the first SHEEBA measurements of the spectral and angular distribution of fast electrons generated in the case of interactions of intense CPA pulses with underdense plasmas. Our measurements demonstrate that this simple detector, in combination with appropriate numerical analysis tools, provides a powerful diagnostic technique for this class of experiments.

Experimental setup

The plasma was generated by irradiating a 0.3 μm thick plastic foil (FORMAVAR) with two heating beams ($\lambda = 527 \text{ nm}$,

$\tau = 1 \text{ ns}$, 100J per beam) at $I = 5.10^{14} \text{ W cm}^{-2}$. A CPA laser beam ($\lambda = 1053 \text{ nm}$, $\Delta t = 1 \text{ ps}$, up to 120 J) was focused (off-axis parabola $f/3.5$) on this plasma 1.3 ns after the heating beams. The peak density at the time of interaction was estimated to be $n_c/10$. The density was characterized by Nomansky interferometry using a UV laser pulse ($\lambda = 267 \text{ nm}$, $\Delta t = 1 \text{ ps}$). Finally, the detector (SHEEBA) was placed at 2 cm from (behind) the target on the main laser pulse propagation axis. The layer set-up used for SHEEBA is shown in Figure 1.

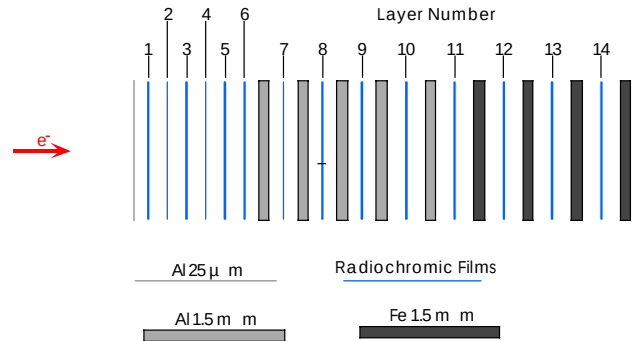


Figure 1. Set-up used for the fast electrons detectors SHEEBA.

Experimental results and discussion

Figure 2 shows the optical density distribution for the various layers of the detector due to exposure to energetic electrons generated by the interaction of a 120 J CPA pulse focused on

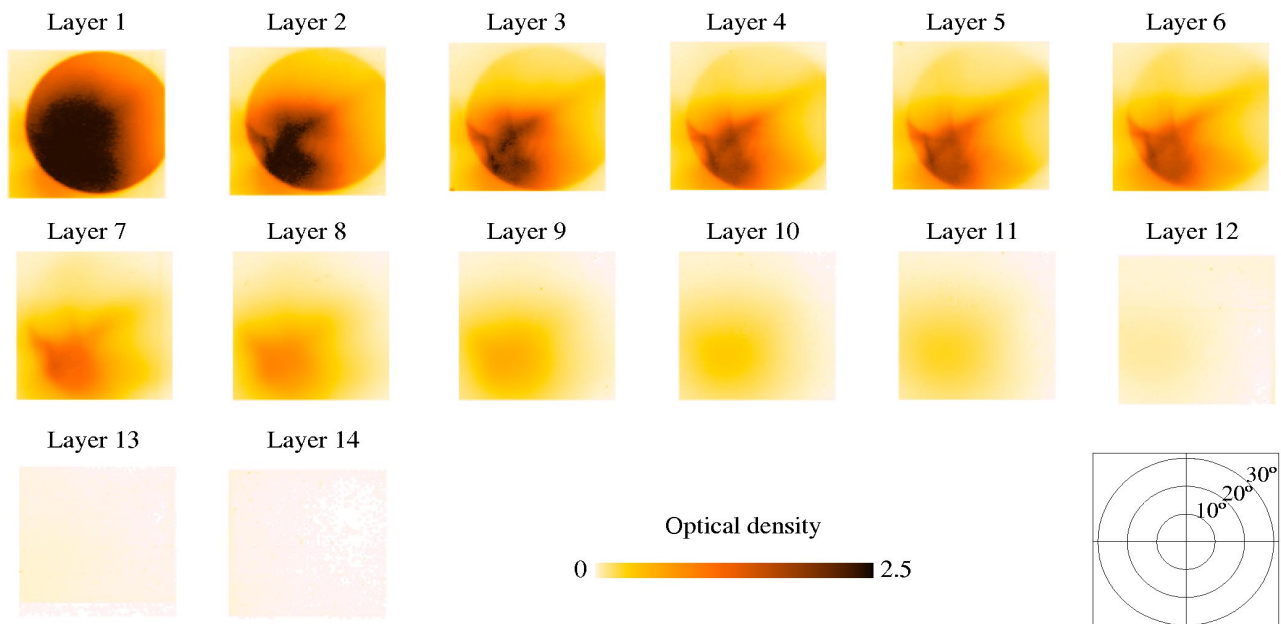


Figure 2. Optical density distribution for the various layers of the detector due to exposure to energetic electrons.

the preformed plasma.

These images clearly show that the electrons are confined in a cone of small aperture, less than 10 degrees. As we proceed from layer 1 to layer 14, the overall optical density decreases and the small scale structures are smoothed out as a result of electron propagation/diffusion through the layers.

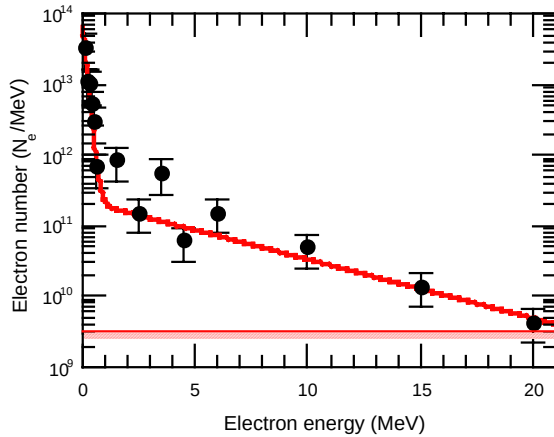


Figure 3. Overall reconstructed spectrum of the electrons from radiochromic films data.

A quantitative analysis of these images has been carried out using a Montecarlo simulation code based on the library GEANT 4.2.0 ⁽²⁾ in order to obtain the spectral distribution of the electrons. Our analysis shows that two populations of electrons exist, which are well characterised by two different temperatures of 133 ± 23 keV and 5.23 ± 0.84 MeV, respectively (see Figure 3). Several physical mechanisms can account for the generation of high energy electrons including direct laser acceleration ⁽³⁾ and acceleration in the plasma waves generated by forward Raman scattering ⁽⁴⁾. In fact, many experiments have been reported in which high energy electrons have been observed where, depending on the interaction conditions, each of these mechanisms is claimed to play a dominant role.

It is interesting to observe that in one of these experiments ⁽⁵⁾ a two-temperature hot-electron energy distribution was already observed in conditions similar to those of our experiment and was ultimately attributed to direct laser acceleration. In that experiment fast electrons were detected using a magnetic spectrometer with a small angular acceptance looking at 45° from the laser axis in the forward direction. In contrast, in our experiment most of the fast electrons were found to be emitted in a narrow cone in the forward direction. This measurement was possible thanks to the large angular acceptance and high angular resolution of our detector. Although the analysis of these data is still in progress, it is clear that our measurements provide basic information for the identification of the physical mechanisms at the origin of high energy electrons and, in particular, of the two-temperature distribution.

Conclusions

We used a detector based on radiochromic film to measure the properties of high-energy electrons generated during ultra-intense laser-plasma interactions. The detector could be placed very close to the target and allowed the angular distribution of the electrons to be measured directly. The spectrum of the electrons was also obtained with the aid of simulations. Our results show that this detection system offers a good alternative to conventional high energy electron spectrometers, usually heavy and bulky and characterised by a small angular acceptance. Also, the angular distribution of high energy electrons can be measured directly in a single shot.

Acknowledgements

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Observation of Relativistic Electron Transport through Dense Preformed Plasmas

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Introduction

The Fast Ignitor scheme¹ for ICF relies on the transport of laser energy to the core of a compressed fuel pellet. It is necessary for an ultra intense laser pulse to propagate through plasma reaching many times critical density via hole boring and induced transparency. In the final stage of energy transport, the laser pulse is converted into relativistic electrons, which then must propagate to the core to ignite the fuel. Studies of propagation of laser pulses and relativistic electrons through hundreds of microns of overdense plasma are of great importance to the realisation of the Fast Ignitor Scheme.

An experimental campaign performed on the Vulcan Laser at the Rutherford Appleton Laboratory, UK has studied the interaction of ultra-intense laser pulses with plasmas several times critical. In previous experimental work², novel use was made of pre-ionised foam targets in an attempt to measure laser propagation through overdense plasma. Here, in an extension of this work, we present observations of the propagation of relativistic electrons through up to 200 μ m of overdense plasmas.

Experimental Arrangement

The set-up is shown in Figure 1. Overdense plasmas were preformed using soft x-ray heating of low-density foam targets. The target composition was triacrylate, doped 10% by weight with chlorine. Washer supported, parylene backed foams with density 20mg/cc and length 50 μ m were used in addition to 200 μ m long, freestanding foams with density 30 mg/cc. The foams were placed 50 μ m behind a pair of 700 Å gold burn-through foils. Two 600 ps heating beams of the Vulcan laser were frequency doubled to 527 nm and focused onto the foils with an intensity of 2×10^{14} W/cm². The soft x-ray emission from the rear of the foils caused volumetric ionisation of the foam within a nanosecond, producing a uniform, overdense

plasma. A picosecond CPA pulse was subsequently focused into the plasma with an off-axis parabola producing an intensity on-target of 5×10^{19} W/cm².

Several diagnostics were employed in the experiment. Soft x-ray pinhole cameras, filtered for radiation below 500eV, were positioned at the front and rear of the target. The rear of the target was imaged at 1054 nm onto a CCD camera using a lens positioned behind the target. In addition, a picosecond UV probe pulse was used to produce a shadowgram of the target at

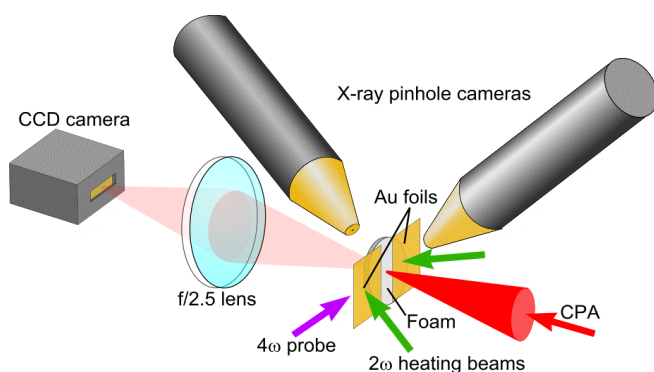


Figure 1. Beam and diagnostic arrangement.

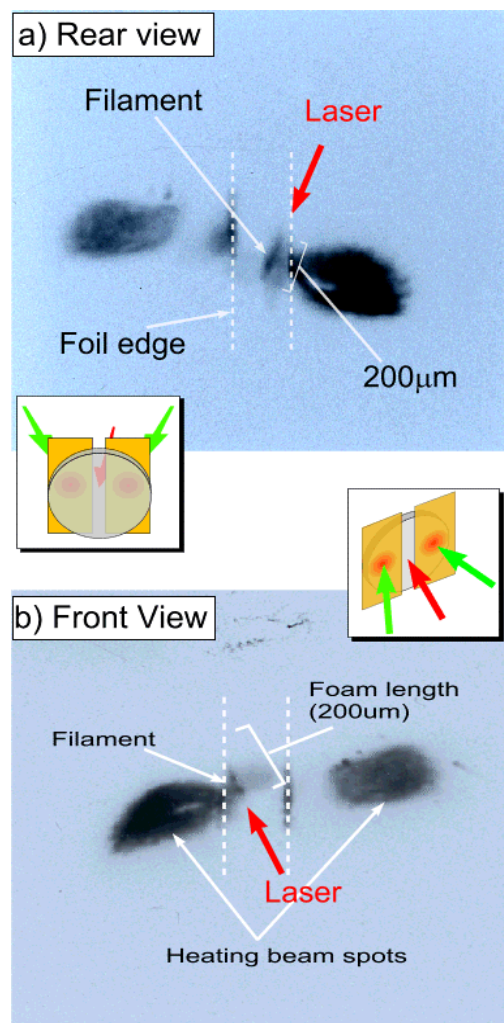


Figure 2. Soft x-ray images of a 30mg/cc, 200 μ m long foam.

varying stages following the interaction.

Results

Figure 2 presents x-ray images recorded by the front and rear pinhole cameras. The overlay shows the position of the inner edges of the two gold foils. The two large dark spots correspond to the x-ray emission from the laser heating of the foils. Between the foils, a dark feature can be seen. This corresponds to the laser direction and appears to extend throughout the target.

Figure 3 presents images from the CCD camera behind the target. In the case of the thinner foams, a compact, bright spot is seen. This corresponds to the position of the laser focal spot when no target is present and is of similar size being less than $20\mu\text{m}$ in diameter. The energy from this emissive spot is very low, representing less than 10^{-5} of the incident laser energy. Figure 3 b) shows an image of the rear of a $200\mu\text{m}$ foam. On this longer foam the spot is broken up and spread over an area roughly $50\mu\text{m}$ in diameter. This breaking-up was not seen in earlier experiments when only the compact emission spot was observed from thinner foams.

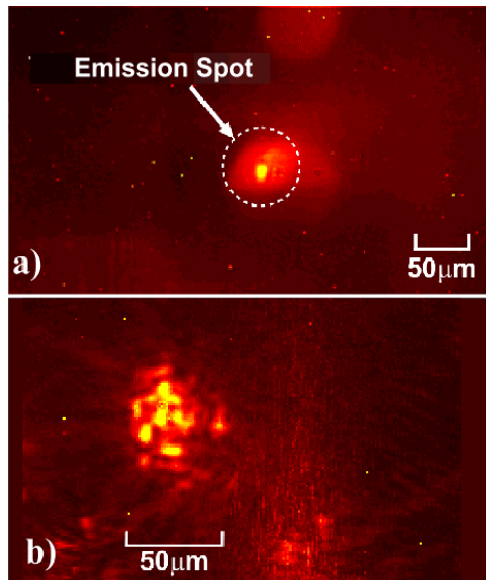


Figure 3. Emission from the rear of a) a 20 mg/cc, $50\mu\text{m}$ long foam and b) a 30 mg/cc, $200\mu\text{m}$ long foam.

Plasma Simulations

The plasma conditions were simulated with the 1D Lagrangian hydrocode, MEDUSA. Figure 4 presents the simulated density profiles at the time of interaction from foams of density 20mg/cc and 30mg/cc. The plasma density is similar for the two targets, reaching 6-8 times the critical density. The $0.1\mu\text{m}$ plastic foil on the rear of the 20 mg/cc foam leads to higher density than would otherwise be the case. This suggests that the CPA interacts with plasmas of similar density when the two target types are used.

Discussion

The emission from the target rear is unlikely to be due to direct laser propagation. In order to propagate, the laser intensity must remain above the threshold for induced transparency throughout the target. This would have resulted in a significant amount of the incident energy being transmitted. It is more likely therefore, that the laser energy is converted into relativistic electrons, which propagate through the target. As the electrons pass through the rear surface, they emit visible radiation, either as transition radiation as they leave the plasma or via synchrotron emission as charge separation accelerates them back onto the target. These processes have been

introduced to explain similar observations in other experiments with solid density targets³⁾.

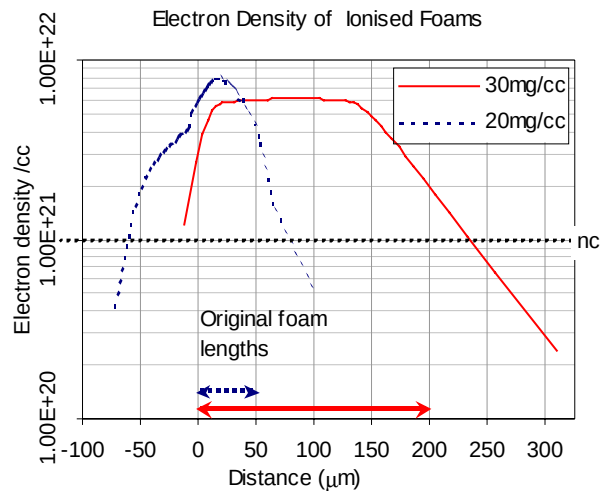


Figure 4. 1D simulation results showing electron density at the time of CPA interaction for two target types.

In thinner foams, $50\mu\text{m}$ long, the electron transport appears to be collimated whilst filamentation takes place over longer propagation distances, up to $200\mu\text{m}$. This lends support to computational studies that predict that the electron stream is unstable as it interacts with the opposing cold return current^{4, 5)}. This return current of background electrons is highly collisional, unlike the relativistic current, which it balances, and it is likely that this produces the x-ray signal on the pinhole cameras.

In addition, previous work²⁾ presented shadowgraphs showing localised expansion of the rear of the target attributable to a hot electron current propagating to the rear side⁶⁾.

Conclusion

These observations represent the first measurements of electron transport in a plasma below solid density and as such are of great relevance to fast ignition studies. We have observed filamentation and break-up of a relativistic electron beam over a $200\mu\text{m}$ length in plasma with 6 to 8 times the critical density for $1\mu\text{m}$ radiation. This effect may have significant impact on the Fast Ignitor where it is desirable for highly collimated electron beams to propagate through high-density plasma. PIC simulations are underway to investigate the electron transport parameters in this density regime.

Acknowledgements

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Proton imaging of E-field structures in laser-produced plasmas

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Introduction

Charge displacement and currents generate electromagnetic fields in plasmas via a wide range of mechanisms. These fields cannot be directly observed by optical probing or X-ray radiography techniques, which are sensitive to plasma density and temperature variations. A more direct measurement could be obtained by using charged particles. MeV protons have a long stopping range in matter, therefore when probing plasmas with small area densities, these particles are not sensitive to plasma density modulations, and their propagation is primarily affected by the presence of electromagnetic fields.

Over the last two years we have been developing a new diagnostic based on laser produced proton beams. Protons with energies of up to several tens of MeV were generated by irradiating thin solid targets at laser intensities in the order of $10^{19} \text{ W cm}^{-2}$ and above. Preliminary experiments were conducted to characterise this proton source¹⁻³. The proton sources have been employed as a particle probe in the development of a novel diagnostic scheme named proton imaging⁴.

Here we report on a series of experiments carried out on the Vulcan laser at the Rutherford Appleton Laboratory, where different plasma conditions of interest to Inertial Confinement Fusion were diagnosed using the laser-produced proton beam as a probe.

Experimental set-up

The proton beam used for imaging was produced by focusing the CPA beam of the Vulcan laser onto a 25 μm Aluminium foil. The pulse had a wavelength of 1 μm and a gaussian temporal profile with duration of 1 ps. A 12 μm FWHM focal spot was obtained by using an $f/3.5$ off-axis parabolic mirror. The intensity generated on target was typically of the order of $5 \cdot 10^{19} \text{ W cm}^{-2}$.

A layered stack of radiochromic film (RCF)⁵ was placed along the normal to the rear surface of the Al foil to collect the protons generated by the CPA interaction. A 25 μm Al filter in front of the RCF stack stopped UV and X-ray radiation below 10 keV.

The plasma to be probed was produced by irradiating 25 μm Al foil targets. These were placed in the propagation cone of the proton beam. The surface of the foils was oriented along or normal to the propagation of the protons to obtain side-on (Figure 1) and face-on images of the plasma. The plasma forming laser beam was a 600ps flat-top pulse. It had a wavelength of 527 nm and was focused with an $f/10$ lens to intensities in the range $10^{14} - 10^{15} \text{ W cm}^{-2}$. The focal spot size was changed from shot to shot by defocusing the lens. Focal spots from 100 μm to 300 μm in diameter were produced to provide different irradiation regimes. On some shots Phase Zone Plates were inserted in the heating beam just after the focusing lens and the focal spot produced had a nominal diameter of 250 μm .

The distance from the proton source to the centre of the plasma was set to 2 mm, and the distance from the source to the detector stack was about 22 mm. The corresponding geometrical magnification was around 10 - 12 times, depending on the RCF layer considered.

In the face-on set-up a 4 ω probe was used to measure by transverse interferometry the plasma density at the time of interaction of the proton beam with the plasma. The probe had a 266 nm wavelength ($n_c \sim 17 \cdot 10^{21}$ electrons/cc) and was 2-3 ps in duration.

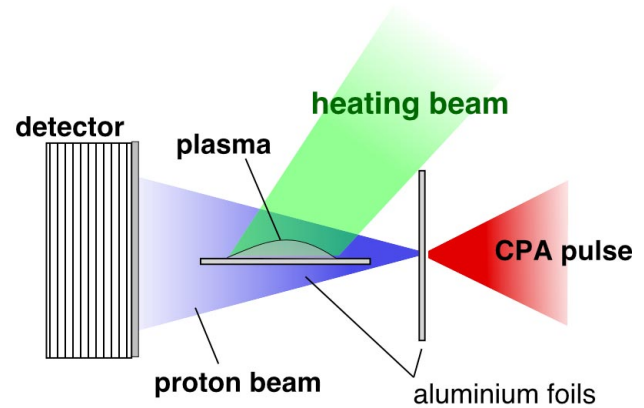


Figure 1. Set-up for side-on probing (top view).

Proton images

Figure 2 presents two RCF layers corresponding to a proton energy of 17.6 MeV.

Panel a) shows the cross section of the proton beam after the propagation through a 25 μm Al foil, as in the face-on set-up. In this laser shot, no plasma was formed on the foil target. The folding structures are caused by inhomogeneities in the electrostatic sheath that accelerate the protons at the rear side of the source foil. The presence of the target in the line of sight is not detected because the area density of a 25 μm Al foil is too low to affect significantly protons with energy of 17 MeV.

Figure 2b) presents a face-on image taken at the peak of the plasma-forming laser pulse: in this case the protons going through the plasma are displaced, scattered or stopped by the e.m. fields generated during the laser interaction.

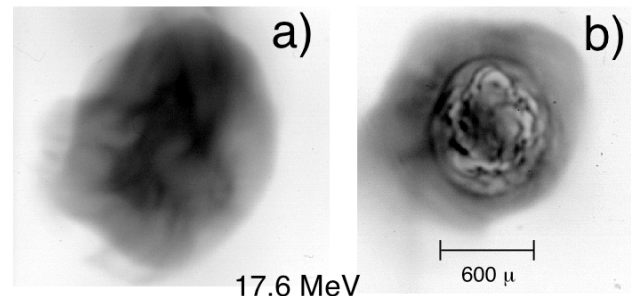


Figure 2. Face-on proton images (a) without plasma and (b) with plasma.

Evolution in time

The temporal evolution of the observed structures was recorded by changing the delay between the plasma forming pulse and the CPA pulse. Images taken at the early stages of the laser interaction show the formation of these structures, which grow and become fully developed towards the end of the pulse

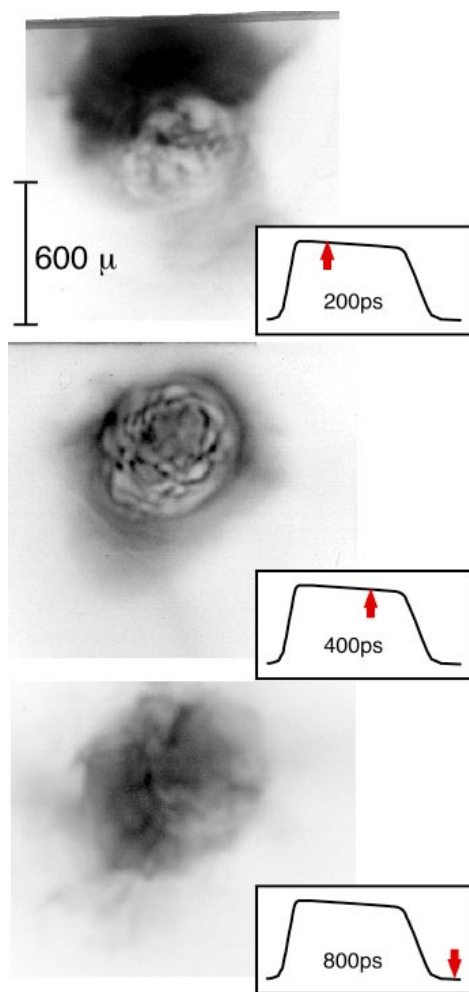


Figure 3. Face-on proton probing at different times; arrows show the time of proton interaction with respect to the plasma-forming pulse.

(Figure 3). Just after the end of the laser pulse, the structures disappear and the pattern is almost indistinguishable from the one observed in absence of plasma. This observation suggests that the e.m. fields in the plasma are set up and sustained by energy input coming from the laser. The time scale for the relaxation of the e.m. fields is less than a few 100 ps.

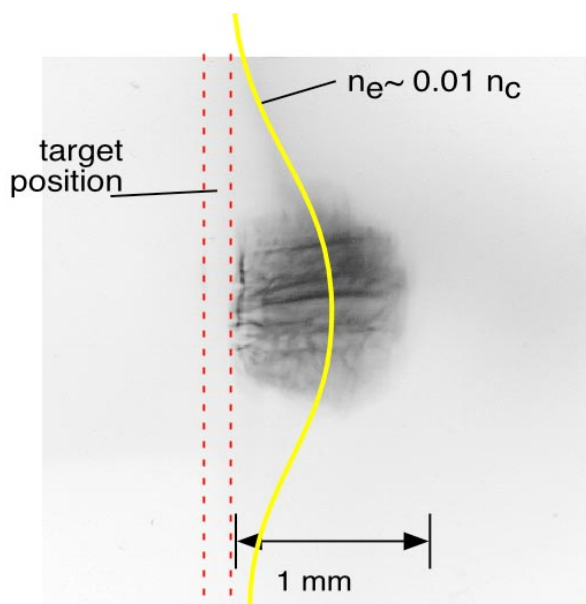


Figure 4. Side-on structures extending into the low density region of the plasma plume.

Figure 4 shows an overlay of a side-on proton image with the density profile obtained from transverse interferometry. The detected structures extend from solid density far out into the coronal region.

Dependence on irradiation parameters

When the irradiation conditions of the target were changed, distinct modifications on the recorded ion pattern were observed. This fact confirms that the fields experienced by the protons are closely related to the interaction of the laser pulse with the plasma.

Face-on images show a fine structure made of cells, the size of which is changing with the properties of the focal spot. In our experiments, tight focus conditions lead to a uniform pattern of small cells about 60 μm in diameter. Larger focal spots correspond to a reduced number of bigger cells (~100 μm).

The presence of a PZP introduces a fine-scale regular modulation on the laser profile, which is transferred to the e.m. field structures inside the plasma, and subsequently detected by the ion beam. Side-on shots reveal a regular modulation in image intensity when PZPs are used.

Simulations

Present day PIC codes can be used to investigate the proton acceleration mechanism in ultra-intense laser interaction with solid targets^{6,7}. However these codes cannot follow the propagation of a proton beam on the centimetre scale of our experiments, due to computational constraints. Therefore we are presently developing a 3D ray-tracing code especially tailored to the parameters of our experiments. We intend to use this code to obtain the order of magnitude of the e.m. fields inside the plasma. Assuming different configurations for the fields, we can investigate the processes potentially accountable for the observed structures, and we could in principle discriminate between the several processes that lead to the formation of the e.m. fields. The basic assumption is that protons propagate inside the plasma as test-particles. Interaction between the different parts of the ion beam is neglected: to support this assumption, we point out that the number density of the proton beam is at least a factor 10^5 smaller than critical density of the plasma, when the protons interact with the target.

Preliminary simulations with a 2D version of the ray-tracing code were carried out assuming tubular E-field structures, like the ones that could be induced by density modulations caused by laser hot spots. We assumed that the tubes had a 60 μm diameter and were 100 μm long. The radial E-field inside the tubes was varied in intensity until the formation of the tubular pattern was observed (Figure 5, next page). This sets a lower limit for the intensity of the electric field. We found that the E-field that could explain the experimentally observed pattern is of the order of $5 \cdot 10^8$ V/m.

At intensities of 10^{10} V/m the protons are deflected so much that the proton beam starts focusing into beamlets (Figure 5c). This invalidates the assumption that the protons propagate independently as test-particles, and sets an upper limit for the E-field under our hypotheses.

Conclusions

For the first time a laser-produced proton beam was used to diagnose a preformed plasma. Direct information about the e.m. field distribution inside the plasma was stored in the ion beam and subsequently recorded on a detector. Maps of the angular distribution of the beam were obtained at selected proton energy ranges. The temporal evolution of the observed structures and the modifications caused by different irradiation conditions were also investigated. Many concurrent phenomena could lead to the observed ion patterns, and therefore extensive modelling and interpretative work is needed in order to identify the

fundamental processes that affect the propagation of the proton beam through the plasma.

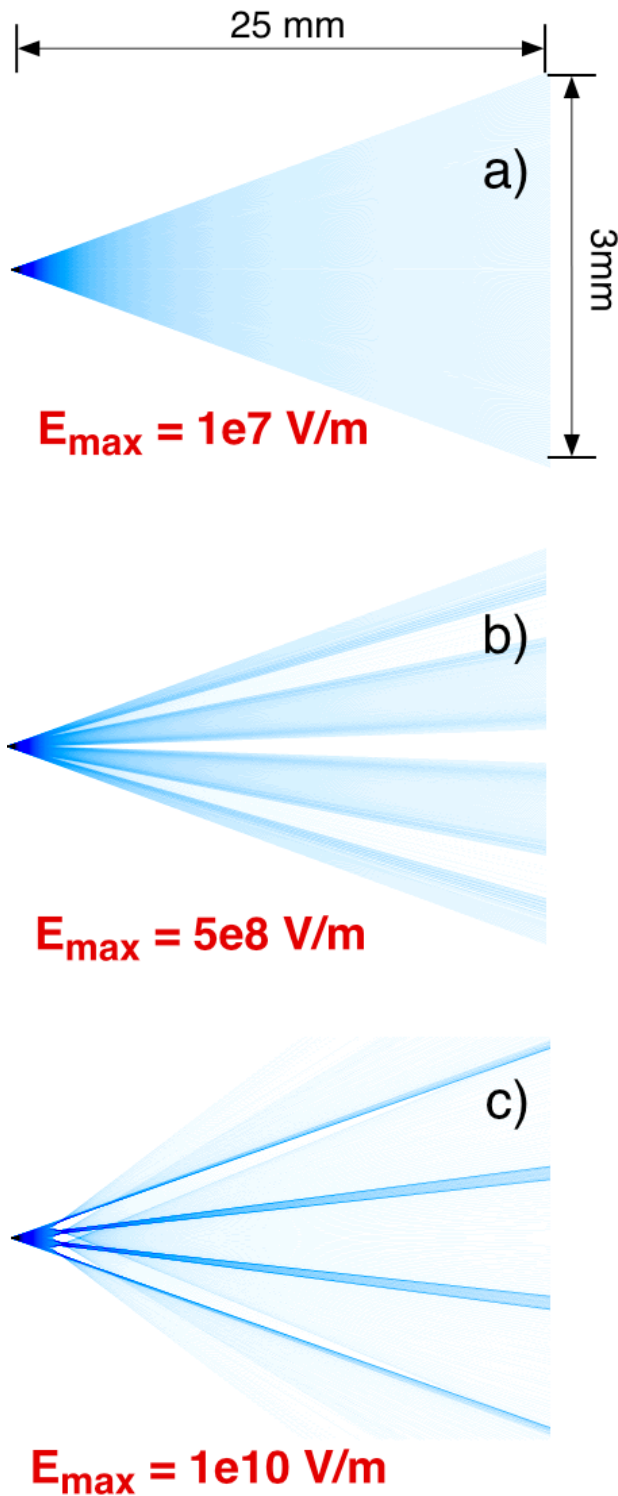


Figure 5. 2D ray-tracing maps for 13MeV protons propagating through tubular structures 100 μm long and 60 μm in diameter.

Acknowledgements

Our thanks go to Prof. M.Haines for the useful discussions and remarks. We would like to acknowledge the contribution to the experiments given by all members of the Central Laser Facility.

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Laboratory measurements of magnetic fields greater than 300 MegaGauss

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Introduction

Recent advances in laser technology have enabled experiments using laser pulses focused to extreme intensities – thus making possible the exploration of new regimes in both atomic and plasma physics¹. For example, when an ultra-high power laser pulse is focused into dense plasma, the generation of magnetic fields up to 10^9 Gauss has been predicted²⁻⁵. Here we report measurements of the highest ever magnetic fields produced in a laboratory, which were achieved during ultra-high intensity ($I > 10^{19}$ Wcm⁻²) laser-plasma interaction experiments. We show that polarisation measurements of self-generated harmonics of the laser provides a convenient method for diagnosing the magnetic field in these interactions – and that our experimental measurements indicate the existence of fields in excess of 300 MegaGauss. Measurements of these fields are important for evaluating the use of intense lasers in various potential applications and perhaps for understanding the complex physics of exotic astrophysical objects such as neutron stars⁶.

Very large magnetic fields (up to 1 GigaGauss) have been predicted by both computer simulations²⁻⁴ and analytical calculations⁵ to exist in the high density region of the plasmas produced during ultra high intensity laser-matter interactions. These fields are predicted to be localised near the critical density surface, i.e., the region where the laser frequency equals the plasma frequency and where most of the laser absorption takes place. Spontaneous magnetic fields can be generated by electron temperature and density gradients⁷ (i.e. $\frac{\partial \mathbf{B}}{\partial t} \propto \nabla n_e \times \nabla T_e$), by the radiation pressure associated with the laser pulse itself⁵, as well as by the current of fast electrons generated during the interaction³. The generation of fields by the above sources becomes similar in magnitude at very high laser intensity.

Existing diagnostic techniques for magnetic fields are inadequate for measurements where the plasma density is very high ($n_e \sim 10^{21}$ cm⁻³) since the steep plasma density gradients in these regions cause unacceptable refraction of external laser probe beams. Until now only the outer low-density plasma ($n_e \sim 10^{19}$ - 10^{20} cm⁻³) magnetic field (less than 10 MegaGauss) has been measured^{8,9} – which is far lower than that predicted to exist near the critical surface. Thus, the development of new diagnostic techniques is required for detecting the highest magnetic fields which may exist only in a very small volume of very high density material and may only last for picosecond durations.

In this article we describe the first observations of the huge magnetic fields near the critical density surface during high intensity ($I > 10^{19}$ Wcm⁻²) short pulse ($\tau \sim 1$ ps) laser-plasma interactions using polarimetry measurements of self-generated harmonics of the laser frequency. High order laser harmonics (up to the 75th) have been previously observed from similar experiments¹⁰ and are produced by the current of hot electrons which is driven by the laser field across the critical surface during the interaction. Since these harmonics propagate out of the high density region isotropically and are generated at the critical surface with the same polarisation as the incident laser beam, we have found that the measurement of the final polarisation of these harmonics is a powerful technique which

can be used to infer the magnitude of magnetic fields through which they travel. In particular, use of self-generated laser harmonics is convenient since they are produced at precisely the same time as the large magnetic fields are generated and propagate so that their k-vectors are perpendicular to azimuthal magnetic fields in the plasma – which greatly simplifies data interpretation (see Figure 1).

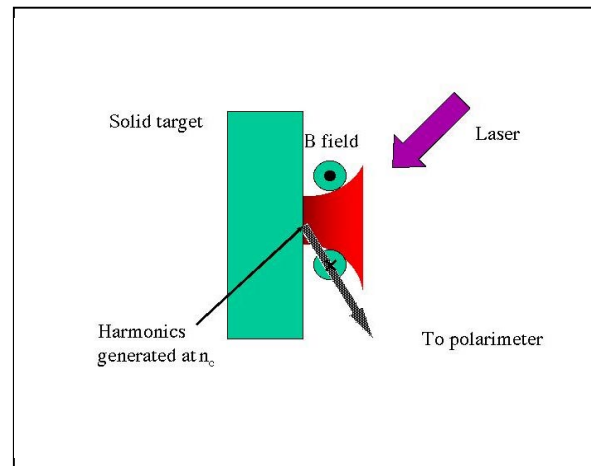


Figure 1. Schematic of experimental set-up.

All of the previous theoretical work²⁻⁵ implies that the largest magnetic fields are in the azimuthal direction about the laser axis of propagation – which is also what is observed here.

Experimental work

In our experiments, we use lower order harmonics (i.e., the 2nd, 3rd, 4th harmonics) generated at the critical surface as well as the 3/2 harmonic generated at the quarter-critical density surface as diagnostic tools to measure the self generated magnetic fields. This measurement is possible since the plasma in the presence of a magnetic field is birefringent and/or optically active depending on the propagation direction of the electromagnetic wave. The former is known as linear anisotropy and produces the Cotton-Mouton effect (an induced ellipticity) and the latter as circular plasma anisotropy which produces the Faraday effect (or rotation of the polarisation vector). An important difference between these two effects at lower field strengths is that the Cotton Mouton effect scales like λ^3 while the Faraday effect scales like λ^2 (where λ is the radiation wavelength). Consequently, comparison of the polarisation states of different harmonics can determine the relative importance of these effects, and measurements of the polarisation parameters of the scattered harmonics (i.e. the Stokes vectors) can precisely determine the transition matrix and hence the magnetic field distribution which connects the initial Stokes vector of the electromagnetic wave (before the plasma) and the final Stokes vector (after the plasma)¹¹.

The results presented here were obtained using the high intensity Vulcan laser system at the Rutherford Appleton Laboratory. This laser delivers pulses at a wavelength of 1.054 μ m, with an energy up to 60 J and a duration of 0.8 – 1 picoseconds. The beam was p-polarised and was focused to a 12 μ m diameter spot producing a maximum

intensity of about $8 \times 10^{19} \text{ Wcm}^{-2}$ on a thin solid target. In order to measure the self-generated magnetic field during the interaction the Stokes parameters of the 4th, 3rd and 2nd harmonics are measured with polarimeters which use high dynamic range CCD arrays as detectors. At the entrance to the polarimeters, interference filters are placed in order to select the desired harmonic. Each polarimeter has four channels consisting of one reference channel, two channels with polarisers set at 0° and 45° respectively and a channel with a polariser at 45° followed by a $\lambda/4$ waveplate. The results of these measurements can thus completely determine the polarisation state of the incident radiation. Calibration shots, i.e. shots without polarisers, are used to measure the efficiency of each channel.

The initial polarisation of the harmonics is linear and is the same as that of the main interaction beam (p-polarised). This was verified experimentally from very low energy shots (less than 1 J). The angle that the harmonics enter the magnetic field (15 degrees) can be determined from the collection optics but can also be calculated experimentally from the initial Stokes parameter from shots at low laser intensity. The uncertainty in this angle is the principal source of error in the measured magnetic field.

Consequently, from each of these measurements we can determine the magnitude of the magnetic field using only a single assumption, i.e. that for the plasma density scalelength – which was estimated from computational simulations of the interaction. It should be emphasised that no other theoretical assumptions or simplifications were used to calculate the field.

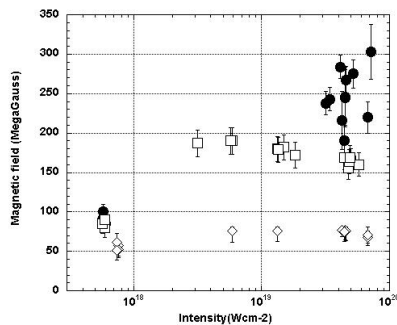


Figure 2. Measured magnetic field vs. incident laser intensity as determined from polarimetry of 2nd (diamonds), 3rd (squares) and 4th harmonics (filled circles).

Figure 2 shows the magnetic field strength versus laser intensity as measured using the 4 ω , 3 ω and 2 ω harmonics of the laser. The peak density used is the relativistically corrected critical density value (e.g. $n_e = 2.4 \times 10^{21} \text{ cm}^{-3}$ for $I \sim 2 \times 10^{19} \text{ W/cm}^2$) which is assumed to decrease exponentially with a scalelength of 1 μm . At low intensities ($I \sim 10^{17} \text{ W/cm}^2$) measurements of all three harmonics give similar results ($B_{\text{max}} \sim 80 \text{ MegaGauss}$) while as the intensity increases, the results diverge. It can be seen that fields in excess of 300 MG are suggested by the measurements of the 4th harmonic.

Plasma density gradients can also produce depolarisation of light^{12,13}. However we estimate that this effect is small since in our experiments the measured radiation is propagating on average along the direction of the density gradient. This effect is also much less important for harmonic (higher frequency) radiation.

It is important to note that there is no change of the state of the polarisation of the 3/2 harmonic (i.e. the 3/2 harmonic was

p-polarised for an incident p-polarised laser beam) which implies that the magnetic field which affects the polarisation of the scattered harmonics is localised between the critical density surface and the quarter critical density surfaces where the 3/2 emission is produced¹⁴. The measured magnetic field is therefore that produced in the very highest density regions. In addition, no significant change of the magnetic field strength was observed when observations were made at different angles. Analysis was also performed to determine the relative importance of magnetic field components parallel to the propagation direction of the harmonics (i.e. the Faraday effect) and these measurements indicated that the $B_{\parallel}$ component is negligible – confirming that the magnetic field produced during the interaction is azimuthal.

Figure 2 can be understood if one considers the effects of extreme magnetic fields on harmonic propagation. When an electromagnetic wave propagates in a plasma with its k vector perpendicular to B , the extraordinary wave (X-wave), i.e. with an electric field vector perpendicular to the magnetic field, can experience cutoffs and resonances, see Figure 3.

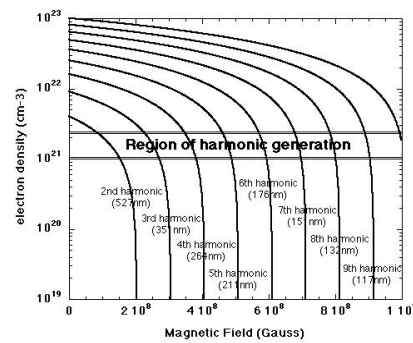


Figure 3. Plot of lower cut-offs for various harmonics of 1.054 μm radiation (in terms of plasma electron density and magnetic field). Harmonics produced at high electron density will only exhibit a cut-off if a very large magnetic field exists in the plasma (i.e. the X-wave cannot propagate across the curve indicated). This plot indicates that this technique may be suitable for measurements of field strengths up to 1 GigaGauss.

Cutoffs occur when the index of refraction is equal to zero and resonances when the index approaches infinity. The X-wave is reflected when it encounters a cutoff and is absorbed in a resonance (at the upper hybrid frequency). For example, the cutoffs for the 4 ω , 3 ω and 2 ω harmonics occur at 341 MegaGauss, 224 MegaGauss and 81 MegaGauss respectively for a density of $n_e = 2.4 \times 10^{21} \text{ cm}^{-3}$. It is consequently impossible to measure fields higher than this using the Cotton Mouton effect – so Figure 2 simply indicates that the harmonics measured are those produced in an extended region of plasma just beyond the extent of the region in which the magnetic field exceeds the cutoff value.

The ordinary wave (with E parallel to B) is unaffected by these cutoffs and resonances. This means that if a field larger than the cutoff field exists in the plasma and if this field extends over a region larger than the location where that particular harmonic is generated – only the ordinary wave will be able to propagate to the detector and consequently only the s-polarised wave can be observed.

This is precisely what is measured in our experiments for the very highest intensity shots. Figure 4 presents data from two high intensity shots ($I \sim 8 \times 10^{19} \text{ W/cm}^2$) for the 4 ω harmonic. Figure 4(A) is a calibration shot where no polarisers were used

and Figure 4(B) is a shot with the polarisers present. There is no signal on the detector on the p-channel in 4(B) (polariser at 0 degrees). This is a clear indication of the 4ω cutoff, implying the existence of a minimum magnetic field of 340 MegaGauss in the plasma – in good agreement with the above analysis. Such fields are more than an order of magnitude larger than any previous observations¹⁵. No assumptions for determination of the magnetic field are required for this technique and these observed cutoffs were clearly reproducible in our experiments – but only at the very highest laser intensities.

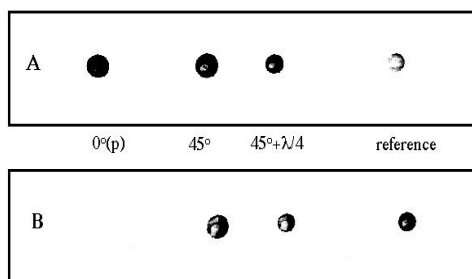


Figure 4. Typical raw data from polarimeter with 4 channels showing existence of 4th harmonic cutoff in plasma. In A) polarisers have been removed and the reference signal level is shown. B) shows the absence of p-polarised 4th harmonic radiation in a full power shot at high intensity – which is indicative of a cutoff – and consequently, the existence of a magnetic field of at least 340 MegaGauss.

In Reference 16 it has been shown that there is a fundamental limit to the maximum field which can be generated in the ablated plasma during such interactions. If one takes $T_e = 10^6$ eV, $n_e = 2.4 \times 10^{21} \text{ cm}^{-3}$ we obtain from this model $B_{\text{max}} \sim 250$ MegaGauss which is in reasonable agreement with the measured fields. This B_{max} will occur at the marginal onset of micro-turbulence and will grow approximately in a time given¹⁶ by $4.2 \times 10^{-13} \text{ sec}^{-1}$ – which is about the laser pulse duration and which can also limit the maximum field.

The magnetic fields which can be produced in these experiments are only an order of magnitude less than that of the oscillating magnetic field of the focused laser pulse itself and begin to approach those required to generate Landau quantisation of electron motion in hydrogen⁶. As the intensity is increased further even higher magnetic fields may be possible, and under such conditions the equation of state and the opacities in the plasma may be affected. Consequently, astrophysical models developed for extreme conditions such as those on the surface of neutron stars and white dwarfs may soon become testable in the laboratory.

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Measurements of plasma propagation instabilities of high current laser produced electron beams

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Introduction

When a high intensity laser pulse is focused onto a plasma, very energetic electrons and ions can be observed from interactions with either gaseous or solid density plasma targets¹⁻³. The onset of this regime is roughly $I\lambda^2 = 1.3 \times 10^{18} \text{ Wcm}^{-2}\mu\text{m}^2$, where the average kinetic energy of an electron oscillating in the laser field becomes equivalent to its rest mass. Currently, the most powerful lasers have been able to achieve focused intensities in excess of 10^{20} Wcm^{-2} with laser pulses containing up to several hundred Joules of energy⁴, indicating that relativistic plasmas can now be easily achieved in the laboratory.

One of the most exciting potential applications for these exotic laser-produced plasmas is in the context of the Fast Ignition scheme⁵ for inertial confinement fusion (ICF). In this scheme, a high power laser pulse generates an intense electron beam at the edge of a cold, highly compressed plasma of deuterium and tritium (DT). This electron beam can then locally heat a region of the DT core to fusion temperatures, which subsequently sparks a burn wave able to propagate throughout the remainder of the pellet. The separation of compression and heating stages in ICF greatly reduces the total energy requirements for the driving beams – and also reduces the symmetry constraints for the initial compression. However, much of the physics involved in this scheme is unknown at present.

In fact, there is a significant difference in scale between the parameters of hot electron “beams” currently produced in experiments and those envisaged for the full Fast Ignitor. Clearly only large-scale experiments will answer all of the questions concerning electron beam generation efficiency, propagation, and energy deposition in such high density plasmas – however, it is possible to estimate the parameters of the electron beams required to heat the necessary hotspot of $\rho r = 0.3 \text{ gcm}^{-2}$ to achieve ignition. For $\rho = 300 \text{ gcm}^{-3}$, one requires $\sim 10 \text{ kJ}$ of energy with $E_{\text{average}} = 1.5 \text{ MeV}$ – which implies 4×10^{16} electrons. The ρr of the hot spot requires a beam diameter of $20 \mu\text{m}$ and implies a beam density of $3 \times 10^{23} \text{ electrons/cm}^3$ – in the case of a 1 ps pulse. This corresponds to the electron density in a $\sim 3 \text{ gcm}^{-3}$ DT (deuterium-tritium) plasma.

The electron beams currently generated in experiments have beam currents significantly above the Alfvén current:

$$I_A = 1.7 \times 10^4 \beta \gamma = 54 \text{ kA for } \gamma = 3,$$

This is the limiting electron beam current in vacuum. In previous experiments, bremsstrahlung measurements at 50 J incident laser energy suggest that $4 \times 10^{12} - 2 \times 10^{13}$ hot electrons are produced (10 - 50% conversion efficiency). The large uncertainty is a result of the uncertainty in the temperature measurement, which indicates hot electron temperatures around $1.5 - 2 \text{ MeV}$ ². The electron current in present experiments is therefore $10 - 50$ times I_A and the electron beam density is $\sim 10^{20} \text{ cm}^{-3}$.

Electron beams greater than the Alfvén current can only propagate in a plasma if they are almost perfectly compensated by a cold return current produced by the background electrons. In present experiments, the forward current density is typically less than 10^{-3} of the target electron plasma density and is easily compensated. However, as the electron beam density increases and approaches the background electron density, it will become much more difficult to compensate for the beam current. Consequently, stable propagation of these beams will be more difficult – especially in the fast ignition regime. Indeed, there are many questions associated with electron beam propagation in this regime which have yet to be studied.

One avenue for investigating these electron beams with present laser systems is to allow the beam generated from a relativistic laser interaction with a solid target to propagate from the solid target into a lower density gas. The electron beam density is then comparable to the density of the cold background electrons. It is also much easier to diagnose low density plasmas than high density ones. Note that the electron beam temperature in our experiments is similar to that envisaged for the Fast Ignitor.

Experiment

These experiments were carried out using the CPA beam of the Vulcan Nd:Glass laser system⁶. The laser has a wavelength of $1.054 \mu\text{m}$, a pulse-length of $0.9 - 1.2 \text{ ps}$ and a pulse energy of $50 - 70 \text{ J}$. The laser beam ($111 \text{ mm} \times 200 \text{ mm}$) was focused onto the target surface using an $f.l. = 600 \text{ mm}$ off-axis parabolic mirror. The laser beam was p -polarised and was incident onto a thin solid target at an angle of 45° . The peak intensity was measured to be about $5 \times 10^{19} \text{ W/cm}^2$. The targets were typically thin foils of aluminium or mylar (CH) and all of the optics for the beam after compression were placed in a vacuum chamber evacuated to less than 10^{-4} mbar pressure.

In this experiment, a gas jet was placed immediately behind the foil target. The gas/plasma was probed transversely using picosecond shadowgraphy and Moiré deflectometry (interferometry) with a picosecond duration 527 nm diagnostic beam to observe plasma density gradients associated with the propagation of the laser-produced electron beam⁷. The supersonic gas jet produced a high density region of gas ($\sim 5 \times 10^{19} \text{ atoms/cm}^3$) of either helium or argon. The electron density in this plasma was around $10^{20} \text{ electrons/cm}^3$ in the case of helium and around $10^{21} \text{ electrons/cm}^3$ in argon.

Electrons in the gas are initially in bound states in atoms and are quickly ionised during the interaction. This process can be observed in Figure 1 which shows a shadowgraph of the ionisation process. This shadowgraph was taken synchronously with the interaction of the main laser beam at the front of the target. The observed filaments are likely due to ionisation of the gas by diverging electron beams produced during the initial phase of the intense laser interaction. Note that it is not possible for the laser radiation to propagate through these aluminium or mylar plasmas – since the targets were generally $50 \mu\text{m}$ thick. Consequently, the structures observed in the

underdense plasma are definitely those due to the propagation of the laser-produced electron beam.

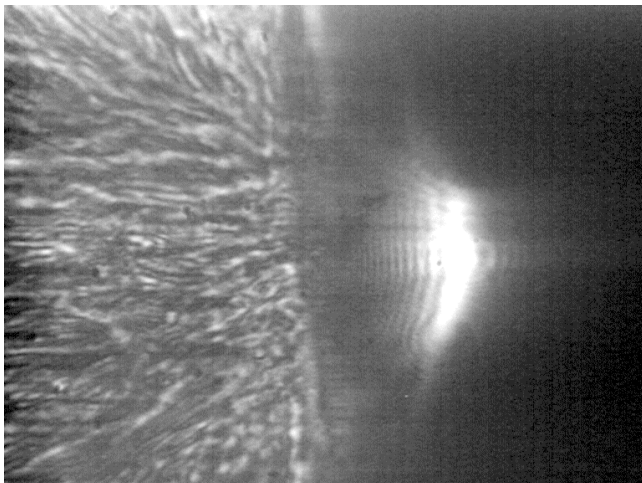


Figure 1. Shadowgraph of rear side of solid/gas target during high intensity laser interaction. Probing time is synchronous with main interaction (1-5 ps) and the laser is incident from the right. The bright region is self-generated second harmonic emission at the front surface. The width of the image is $\sim 250 \mu\text{m}$.

In these experiments, it was also possible to make observations of the energy deposition of the main electron beam. Figure 2 shows the propagation of an electron beam exiting a $50 \mu\text{m}$ mylar target into a helium gas jet. The probe image shown is taken at late time (300 ps after the pulse). The density gradients in the gas are therefore likely to be the signature of the energy deposition by the electron beam as it heats up a region of the gas which then subsequently expands. In Figure 2 the electron beam appears to remain collimated over a short distance after entering the gas after which it filaments and hoses. Significant shot-to-shot variations of the propagation pattern were also observed. However filamentation and hosing of the beam in the low density plasma region was observed for all cases studied. A more detailed analysis of these results will be published in a future paper.

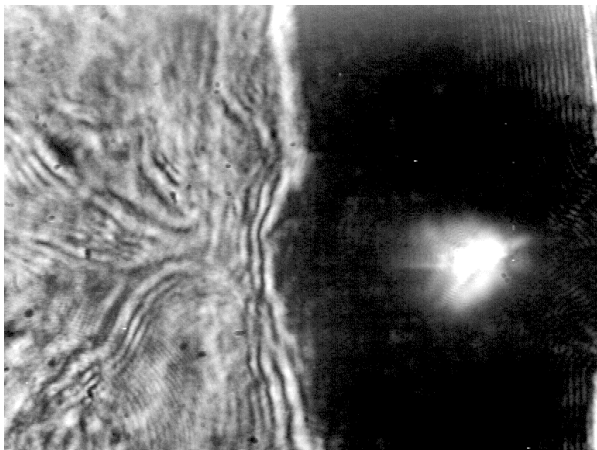


Figure 2. Shadowgraph at late times ($\sim 300 \text{ ps}$ after the main interaction).

Conclusions

We have used an innovative target design to study the propagation of very high current laser produced electron beams in a regime relevant to the Fast Ignition scheme. It is apparent from these results that these electron beams are subject to severe filamentation and hosing instabilities in plasmas where the beam density is close to the background plasma density.

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Excitation of relativistic electron plasma waves by the short-pulse beatwave process

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Introduction

The beatwave scheme has been the subject of investigation for some time as a method for the production of high-energy electron beams with laser-produced plasmas¹⁻³. The process involves the collinear superposition of two laser wavelengths which modulate the wavepacket at the 'beat' frequency; the ponderomotive force associated with the E-field gradient of these beats stimulates the growth of a plasma wave if the wavelength difference is matched to the electron plasma frequency, ω_p , of the target plasma. Charged particles with a velocity similar to the plasma wave phase velocity can gain energy from the longitudinal electric field of the wave and become accelerated⁴.

Growth of the plasma wave is limited by the relativistic mass increase of oscillating electrons⁵, so that ω_p decreases and the beat is no longer resonant. However, if the laser pulse length is much longer than the ion plasma period, electron oscillations couple to ion motion via the modulational instability (MI), and the wave amplitude is instead limited by energy lost into ion acoustic waves⁶. Previous beatwave experiments have used laser pulse lengths of 90 ps or more so that the amplitude is saturated by the MI rather than by relativistic effects. In this experiment, a shorter (3-4 ps) and more intense pulse was employed in order to side-step the modulational instability, so that the wave may be driven to relativistic amplitudes.

Experimental Set-Up

The experiment was performed with the Nd:glass Vulcan CPA laser system at RAL using a Ti:Sapphire mode-locked oscillator. To obtain the two frequencies for the beatwave a mask was placed between the two diffraction gratings of the CPA stretcher (Figure 1). The mask had slits to select two narrow frequency bands from the input bandwidth to pass through the laser amplifier chain: these two bands were thus temporally separated throughout the chain to prevent non-linear interactions within the laser medium⁷.

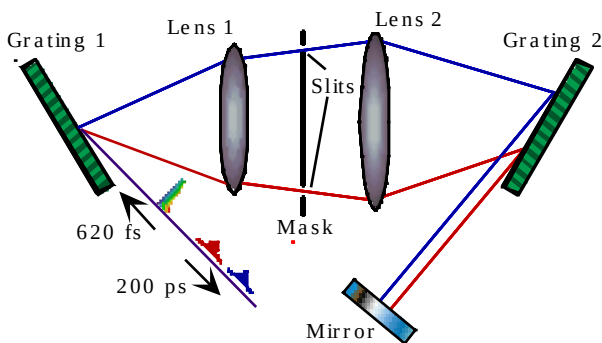


Figure 1. Modifications to the CPA stretcher for the beatwave.

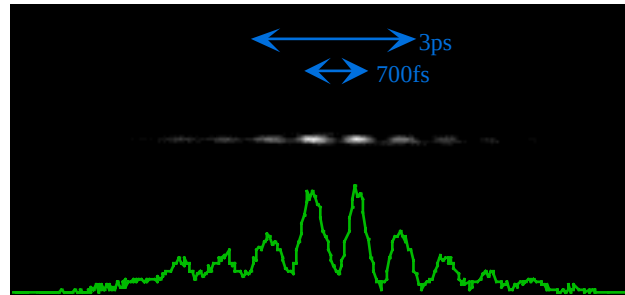


Figure 2. An image from the autocorrelator showing the beats.

The width and separation of the slits could be adjusted to choose the beat frequency and the bandwidth of its component frequencies. A separation of $\Delta\lambda = 5.3$ nm was obtained as a compromise between maximising the beat frequency while keeping both component frequencies within the laser gain bandwidth. Each component had a bandwidth of about 1 nm.

After amplification and recompression, the two components were overlapped temporally and spatially; the compression gratings could also be adjusted to generate a positive or negative chirp on the recompressed pulse. A single-shot autocorrelator showed the intensity modulations due to the beating and could be used to check the overlap - see Figure 2.

The pulse is then focused with a 0.6 m off-axis parabolic mirror into a chamber filled with low pressure hydrogen gas. The transmitted beam was imaged onto an optical spectrometer to determine the forward scattered spectrum.

Results

The average energy on target per pulse was approximately 30 J, delivered into a focal spot with dimensions about $10\mu\text{m} \times 30\mu\text{m}$. The modification of the CPA stretcher had the effect of reducing the output energy and increasing the pulse length due to the reduced bandwidth, and a minimum compressed pulse length of 3 ps was achieved. This resulted in an intensity of about $3 \times 10^{18} \text{ Wcm}^{-2}$ at focus. A measurement of the spectrum of the incoming beam showed that the balance in energy between the two frequencies was about 5:3 in favour of the higher frequency. Given a beat composed of wavelengths at 1050.7 nm and 1056.0 nm, the frequency of the beat envelope was $1.43 \times 10^{12} \text{ s}^{-1}$, which equals the plasma frequency of a gas with electron density of $n_{e0} = 2.55 \times 10^{16} \text{ cm}^{-3}$: assuming that the laser completely ionises the gas without altering its density, this requires an initial gas fill pressure of 0.47 mbar (at S.T.P.).

The presence of the plasma wave was detected by measuring the Raman scattering of the transmitted beam, whereby the plasma wave mixes with the incident electromagnetic waves to produce side-bands in the transmitted spectrum, spaced from the incident frequencies by $\Delta\lambda$. The intensity of these side-bands may be used to estimate the amplitude of the plasma wave. However, two frequencies co-propagating through a non-linear medium (such as the neutral gas between the compression

gratings and the focus) also undergo atomic cross-phase modulation, a process which produces side-bands with the same wavelength separation, and so methods must be found to distinguish between them.

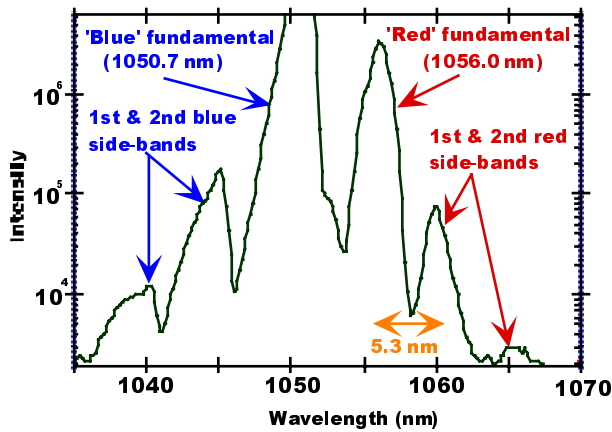


Figure 3. Transmitted beam spectrum showing the incident fundamental frequencies and the scattered side-bands.

A series of shots was taken with the Vulcan laser into hydrogen gas, varying the gas pressure for each shot, and measuring the intensity of the side-bands each time. Figure 3 shows the output from the spectrometer, recorded on a 16-bit Andor CCD camera. A plot of the variation with electron density of the intensity of the first side-band (I_{side}) on each side of the fundamentals is shown in Figure 4. The side-band intensities are scaled against the energy of the laser, to account for shot-to-shot variations, and the electron densities have been scaled to the resonant density derived from the beat frequency. The blue side-bands appear to be more intense than the red; this is probably due to ionisation-induced blue-shifting.

The plot (Figure 4) shows an increase in side-band intensity with electron density, superimposed upon which is a sharp peak at a density of $11.7 n_{e0}$. The underlying increasing trend is most likely to be due to cross-phase modulation in the neutral gas atmosphere, as the non-linear refractive index increases linearly with gas density, but the peak is almost certainly due to the creation of an electron plasma wave by the beatwave process, despite its appearance at a density many times n_{e0} . There is also an apparent peak at $21 n_{e0}$, but more data is needed to find out if that is due to a real plasma effect.

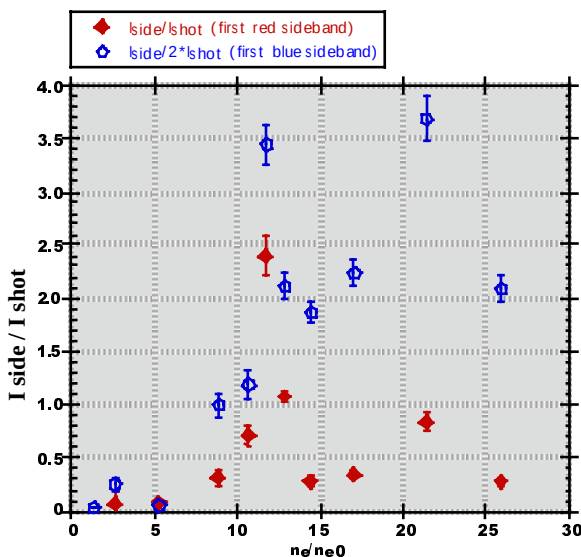


Figure 4. Plot of side-band intensities against electron density.

Discussion

A simple explanation of why the resonance peak in the side-band intensity is shifted to a higher electron density may lie with the effect of the ponderomotive force associated with the radial electric field gradient of the laser focal spot. Assuming that the field strength decreases with distance from the beam axis, this acts to expel electrons from the middle of the beam, creating a density depression there and a density surplus at the beam edge.

Therefore, if the electron density of the plasma is higher than n_{e0} to begin with, the ponderomotive force of the beam could bring it down to a value which is resonant with the beat. A steady-state approximation for the density depression may be calculated by equating the outward ponderomotive force exerted on the electrons by the laser with the inward attractive space-charge force due to the remaining positive ions:

$$\delta n_e = \frac{2E}{\sqrt{\pi} \gamma_e m_e c \tau \sigma^4 \omega_1 \omega_2} \quad (1)$$

for a Gaussian pulse profile with waist σ , length τ , and energy E . With the beam parameters outlined above, an electron density depression of $\delta n_e \approx 10^{16} \text{ cm}^{-3}$ can be expected, which is of the correct order of magnitude to account for the shift in resonance shown in Figure 4.

It can be concluded from this data that the short pulse beatwave process has been successfully demonstrated to generate plasma waves. However, a quantitative measurement of the amplitude of the wave must wait for further modelling work to be undertaken.

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Gamma - radiography using a laser-plasma accelerator

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Introduction

High intensity laser-plasma interactions at intensities greater than 10^{19} W/cm² have recently allowed the exploration of new regimes in plasma physics. Such interactions can produce fast electrons with energies greater than 100 MeV¹⁾, gamma rays of tens of MeV²⁾ and energetic ions of up to several hundred MeV³⁾. There are clearly many potential applications for these energetic particles such as compact accelerators¹⁾, inertial fusion⁴⁾, and as diagnostic probe beams of high density material. The use of these lasers as a source of MeV x-rays for providing deep-penetration radiographs of dense matter has also recently been discussed⁵⁾. This application of laser-produced plasmas is particularly attractive since such sources may soon be scalable to “table-top” sizes and to high repetition rates. It may also be possible to obtain multiple views of an object from arbitrary angles – thus potentially enabling 3-dimensional radiographic “movies” of dense, rapidly moving objects such as inertially confined fusion targets.

Experiment

This report describes experiments conducted at the Rutherford Appleton Laboratory using the ultra-high power Vulcan Laser facility to examine the feasibility of this application. In this work, we compare the use of both high Z solid targets and low density gas jet targets for γ -ray generation. The γ -rays are typically generated in a secondary process – since electrons are initially accelerated during the laser plasma interaction which subsequently emit hard x-rays via bremsstrahlung as they are stopped in solid material. In this work, we show that the gamma rays produced in a laser accelerator configuration are much more collimated and can be generated more efficiently than in a simple solid target interaction.

In these experiments, we used lithium fluoride dosimeters (TLDs) to measure the total radiation output as well as the direction and the spectrum of the radiation. The gamma ray source was then also used to radiograph thick high-density test objects.

The laser interaction region was surrounded by an array of sixteen tungsten collimators to provide complete angular information concerning the x-ray flux. The tungsten collimators were constructed using specially made kinematic mounts so that their positions would be known precisely. The dosimetry was performed by inserting four standard colour-coded TLD plastic pots separated by 4 mm long cylindrical tungsten plugs in a 5 mm diameter 10 cm long cylindrical hole in the centre of each of the collimators. Up to seventeen of these cylinders were distributed around the target chamber and the doses on each TLR were measured using a standard reader.

In addition to the TLD/collimator assemblies which measured filtered dose, a number of TLD pots were fielded to look at the “bare” dose. These were placed inside small perspex cylinders to ensure electron equilibrium and were sensitive to photon energies above 1 keV.

In these experiments the Vulcan⁶⁾ high power beam was transported into an evacuated target chamber where it was focussed by an off-axis parabolic mirror to a spot of about 10 μ m diameter. The maximum intensity was about 5×10^{19} W/cm² in the work described here. In the initial set of experiments a solid target was used which was angled at 45° to the direction of beam propagation.

For simplicity an “effective” energy was assumed for the laser generated electron beam ($V_{\text{effective}}$), and consequently the attenuation values for the TLDs through the collimator could be calculated for each TLD for varying energies from 0.2 MeV to 14 MeV. Target absorption was ignored as an initial approximation. To derive the energy from a particular result, ratios from the first TLD to the others were used since the unattenuated dose was not directly measured. The x-ray spectrum could then be deduced by comparing the ratios of the fielded TLDs to predicted values for a given $V_{\text{effective}}$.

A total of 22 shots was fired with TLDs fielded during this set of experiments and a maximum of 70 TLD containers was used per shot. Background measurements were taken regularly to maintain the accuracy of the TLDs with the lowest readings. Fourteen shots were fired using a solid target of gold or tantalum of differing thicknesses.

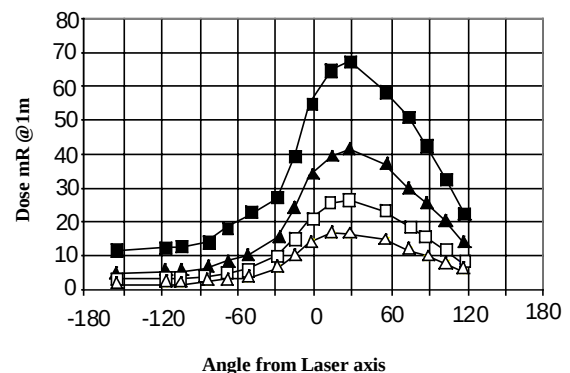


Figure 1. TLD signal levels with respect to angle for a typical solid target shot. The peak signal occurs in the direction approximately normal to the target surface.

Figure 1 shows raw TLD measurements taken from a shot onto solid tantalum targets, 1.75 mm thick and angled at 45 degrees to the laser axis. In general, such shots produce their peak dose at an angle of at least 30 degrees to the laser beam axis. Unfortunately, TLDs could not be fielded at 45 degrees where the peak dose would have been expected due to space limitations. For each angle three values for $V_{\text{effective}}$ could be generated, one from each of the green, blue and yellow TLDs. A weighted average of the data was then taken, skewed towards the front TLDs as these received higher doses and so should be less susceptible to errors.

All of the shots from solid target interactions are broadly similar, with a peak temperature of about 4 MeV (for $V_{\text{effective}}$). The main differences between measured angular distributions for different shots are slight changes in the positioning of the high energy points and the low energy points. In all cases, however, the high energy measurements were made on the TLDs facing the back surface of the target, while significantly lower measurements were obtained from the TLDs facing the front, laser illuminated, surface of the target.

Using the gas target in a laser accelerator configuration as the source of the electron beam has a dramatic effect on the production of x-rays within a high Z target, as shown in Figure 2.

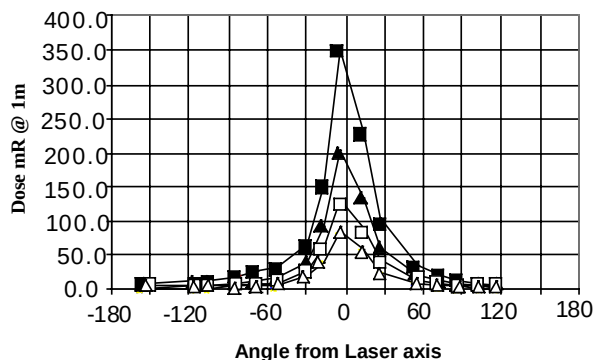


Figure 2. TLD signal levels with respect to angle for a typical gas jet target shot. The peak signal occurs in the direction along the direction of laser propagation.

The peak dose is substantially increased over the x-rays produced from laser-solid target. In fact, the peak dose may well have been higher but has been missed by the positioning of the TLDs. The other notable effect is that the width of the dose distribution is considerably narrower and the direction of the gamma ray beam is directly along the laser axis.

It appears that the high energy electrons which the laser beam generates in the gas jet are self collimated and mono-directional. Evidence for this comes from the shape of the x-ray beam and the difference between the peak doses of these gas jet shots and those without.

All of the gas jet shots have a small ($< 5^\circ$) mean angle. This implies that the gas jet acts as a source of near unidirectional electrons that then hit the heavy metal target. Rough estimates of the total radiated x-ray dose give similar values to the solid and gas jet shots showing that the change in the on-axis dose is purely caused by the mean angle of the electron beam created by the laser. This is in contrast to previous activation measurements of the beam profile – which showed a larger beam divergence of the electrons⁷ and a much higher signal level relative to solid targets – however this was likely caused by the fact that activation measurements only record signals from the highest energy electrons. From the TLD measurements a peak dose of 2.3 R at 1 metre and a $V_{\text{effective}}$ of 4.0 MeV was recorded. This is significantly higher than previous solid-target measurements⁵.

Radiography of test objects was also performed using this source (see Figure 3). It should be noted that no collimation or scatter control measures were employed because of space limitations. Had such techniques been used a substantial improvement in the quality of the radiographic image would have been expected.

The test object was specifically designed to represent a high-density spherical object. It has an inner sphere of lead, 12 mm in radius, surrounded by a tungsten sphere 35 mm in radius which is itself contained within a aluminium sphere of 53 mm

radius. With an incident dose of 156 mR, a density of 0.7 on DEF direct recording x-ray film would be expected. The actual recorded optical density of the central core had a value of 0.9 (of which 0.2 was inherent background optical density) so that good agreement between the calculated values and the radiograph was obtained. An example radiograph is shown in Figure 3. The source size was estimated to be 20 microns. Shown is the central lead core which has a line of sight mass of 118 g/cm². The fuzziness to the edge of the lead core is purely due to the lack of collimation and scatter control employed in this quick set-up arrangement.

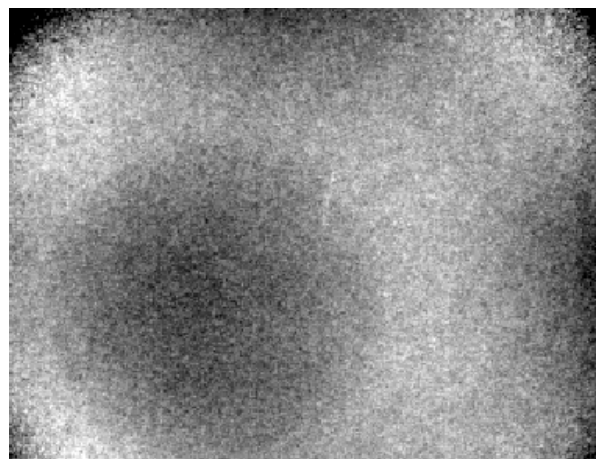


Figure 3. Radiograph of Vulcan test object.

In the case of the Vulcan laser with the above geometry, blur due to the radiographic source spot diameter of 0.03 mm is 0.0069 mm (spot blur). The intrinsic film blur on DEF film for the Vulcan laser projected into the object plane is 0.284 mm.

Conclusions

In conclusion, we have measured the angular direction of the gamma ray emission from both solid target and gas jet interactions and it appears that the use of a laser accelerator configuration greatly enhanced the collimation and the strength of the emitted gamma ray beam.

An important application of these sources may be for non-destructive inspection of materials using high repetition rate lasers. The advantage of using a well controlled gas-jet target has clear advantages over solid targets.

The authors would like to acknowledge the assistance of the operations staff of the Vulcan laser at the Rutherford Appleton Laboratory.

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Dynamics of the Critical Surface in High Intensity Laser-Solid Interactions: Modulation of the XUV Harmonic Spectra

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Introduction

The high intensities available with current lasers ($I \sim 10^{20} \text{ Wcm}^{-2}$) have led to a wealth of novel phenomena observed in solid interactions. These include the generation of relativistic electrons, beams of gamma rays, energetic protons (up to 50 MeV) as well as laser induced nuclear reactions¹⁻⁴. The small spatial and temporal scales ($< 10 \text{ } \mu\text{m}$, $< 1 \text{ ps}$) make it difficult to diagnose these interactions in detail using conventional techniques. Measurements of the emission of high order harmonics of the fundamental laser frequency can be a powerful diagnostic of the physical processes and plasma conditions in the interaction region⁵⁻⁸ in addition to being of interest as a bright source of XUV radiation. Norreys *et al*⁹ using values of $I\lambda^2$ up to $10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$ have observed up to the 75th harmonic of a $1.053 \text{ } \mu\text{m}$ laser with a conversion efficiency of 10^{-6} . The harmonic generation is due to the electrons dragged across the vacuum-solid interface by the electric field of the laser pulse. Harmonic generation can also be understood by a simple model based on the phase modulation experienced by the light on reflection from the oscillating plasma-vacuum boundary¹⁰⁻¹².

In this paper we report the first observations of the modulated spectral structure of harmonics generated from solids. Our results show that at $I\lambda^2 \sim 10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$ the spectrum is modulated with a periodicity of 2 to 4 harmonics. The experimental results are compared to PIC simulations which show that at high intensity the amplitude of the critical surface oscillation increases and is no longer purely sinusoidal at the laser frequency. We show that the modulation results directly from the motion of the reflecting surface. Good agreement is found when the trajectory of the critical surface, derived from PIC simulations, is used with the “moving mirror” model. Consequently the dynamics of the critical surface can be inferred from the experimental observation of the harmonic spectrum and this may prove to be an important diagnostic technique in future high-intensity experiments.

Experiment and simulation

The experiment was performed on the Vulcan laser system at the Rutherford Appleton Laboratory, delivering 0.7 - 1.0 ps pulses at 1.053 microns with energies up to 50 J onto target. The rectangular beam, $20 \times 11 \text{ cm}^2$, was focused by an on-axis parabolic mirror ($f = 22 \text{ cm}$).

The target consisted of an optically polished fused silica slab set at 45° angle of incidence with the beam p-polarized. The energy on target and pulse duration were monitored on a shot-to-shot basis. The focused intensity on target was estimated from the maximum ion energy in the blow-off plasma using CR39 nuclear track detectors^{11,13,14}. Another measure of the shot intensity was obtained from the hole boring velocity of the critical surface measured by the Doppler shift of the harmonics^{5,15}. The intensity (I) on target was up to $1.0 \times 10^{19} \text{ Wcm}^{-2}$.

The laser pre-pulse was determined in a previous experiment to be about 10^{-6} of the peak intensity. The sub-critical plasma produced by this pre-pulse in front of the target was measured by optical probing and found to have a scale-length which was typically less than $10 \text{ } \mu\text{m}$.

The harmonic emission in the specularly reflected direction was observed by a slit-less flat-field XUV spectrometer^{10,17}. This consisted of a gold-coated cylindrical grazing-incidence collection mirror followed by a variable line-spaced grating, also at grazing-incidence. The acceptance angle of the mirror and grating was $1 \times 10^{-6} \text{ sr}$. The mirror and grating were orientated perpendicular to each other to produce an astigmatic line image in the detector plane of the harmonic emitting plasma at the target. The dispersed radiation was split into two wavelength regions and detected separately. The region $540 - 276 \text{ } \text{\AA}$ was intercepted by a plane gold-coated mirror set at 65 degrees incidence and directed onto a double micro-channel plate (MCP) detector coupled to an intensified optical 8-bit charge-coupled-device (CCD). The region $85 - 272 \text{ } \text{\AA}$ was detected by a back-thinned XUV sensitive 16-bit CCD detector. Thus harmonic emission from the 20th to 120th order could be detected simultaneously. The absolute spectrometer response was calculated using the measured mirror reflectivities, the grating calibration¹⁸, the transmission of any filters used and the calibrated MCP/CCD detector response¹⁹. The conversion efficiency of each harmonic was calculated assuming uniform emission into $2\pi \text{ sr}$. This assumption is reasonable in view of previous measurements^{9,20}.

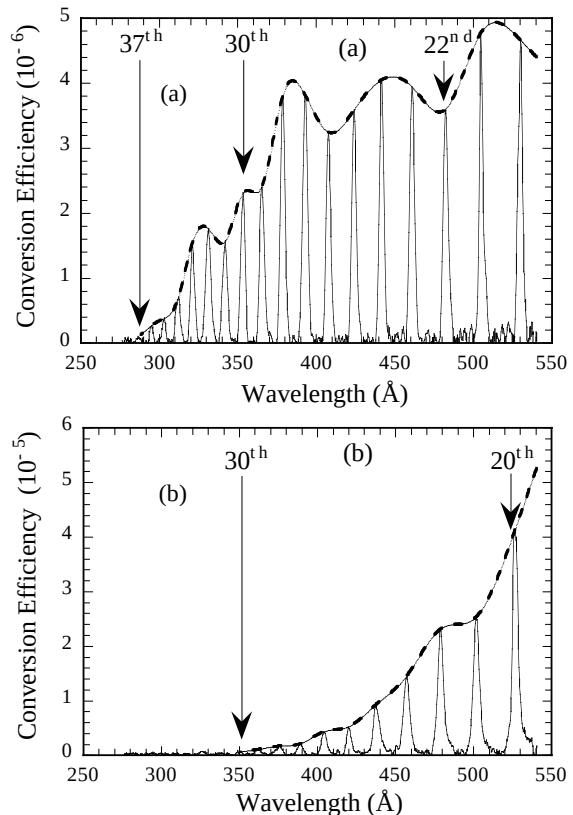


Figure 1. Lineouts of typical harmonic spectra for (a) high intensity $I \sim 10^{19} \text{ W/cm}^2$ and (b) low intensity $I \sim 10^{18} \text{ W/cm}^2$.

A typical spectrum showing the 20th ($526.5 \text{ } \text{\AA}$) to 37th ($284.6 \text{ } \text{\AA}$) harmonics and corrected for the spectrometer response and background is shown in Figure 1a.

The highest harmonic observed was the 60th at 175.5 Å. The conversion efficiency varied from 4.6×10^{-6} at the 20th harmonic and, interpolating between the two detectors, to $\sim 4.0 \times 10^{-8}$ at the 60th. The harmonic spectrum shows modulations at every 2 to 4 harmonics over the entire range on both detectors. It should be noted that the modulations peak at different harmonics for different shots. Figure 1b shows a typical harmonic spectrum at a lower intensity. This shows harmonics only up to the 30th at 351.0 Å. Comparing Figures 1a and 1b it is clear that the modulations in the harmonic spectra are much reduced and that the structure is an intensity dependent effect. The stronger modulations correspond to a higher incident intensity.

The Doppler shift also scales as $(I\lambda^2)^{0.5}$, for $I\lambda^2$ at $10^{18} \text{ W}\mu\text{m}^2\text{cm}^{-2}$, as proposed by Wilks *et al* ¹⁵⁾ and experimentally confirmed by Zepf *et al* ⁵⁾. Below this value a transition from hole-boring to plasma expansion occurs which results in a change from a red to a blue-shift of the harmonics.

The PIC code used in this paper was developed by R. Pfund and R. Lichters and is described in References 11 and 21. It is a fully relativistic one-dimensional code, with oblique incidence treated by transformation to a moving frame of reference in which the light is normally incident^{22, 23)}.

For the simulations here a p-polarized laser beam is incident at 45 degrees onto a one wavelength thick plasma slab with density $n_e/n_c = 13$ (where n_e is the electron density and n_c is the critical density at the laser frequency ω_0). The pulse had a sine-squared temporal profile and a duration of 20 laser cycles. Simulations were performed with both mobile and immobile ions without affecting the results significantly.

The PIC simulations exhibit a similar modulation structure to that observed experimentally with a modulation amplitude which increases with higher intensity. This has previously been reported in PIC simulations by Lichters *et al* ²¹⁾ where the spectrum was found to be modulated with a periodicity of ~ 10 harmonics. The modulations were ascribed to internal reflections of transmitted light due to the finite size of the plasma slab. We tested this hypothesis by performing simulations with various thicknesses of plasma slabs and no effect on the modulation structure was found. This suggests that the modulation structure is intrinsic to the harmonic generation and not related to internal propagation and reflection of harmonic light.

Figure 2 shows the simulated harmonic spectra of the reflected light for high and low $I\lambda^2$, similar to the experimental values in Figure 1. At the lower value of $I\lambda^2$, (Figure 2 b), the conversion into harmonics is low with a smooth unmodulated roll-off. The noise in the spectra is numerical and is reduced when using a higher temporal resolution. The highest harmonic above noise is the 6th which compares to the 30th harmonic observed experimentally. At the higher value of $I\lambda^2$ (Figure 2a) the harmonic emission is enhanced and the spectrum is modulated at every 4 to 5 harmonics. This is to be compared with the 2 to 4 harmonics observed experimentally. The highest harmonic above numerical noise in this case is the 55th.

The oscillatory motion of the critical density surface $x(t)$ for the two simulations is shown in Figure 3. The motion is periodic at the laser frequency ω_0 and the displacement is approximately three times larger for higher $I\lambda^2$. The oscillatory mode at ω_0 is due to the electromagnetic force at the laser frequency and that at $2\omega_0$ is due to the ponderomotive force. These modes are apparent in the power spectrum of Figure 3b at the lower value of $I\lambda^2$. Some energy is coupled to modes greater than $2\omega_0$ by non-linearities. Lichters *et al* ²²⁾ found that these additional modes must be included in the description of $x(t)$ to reproduce the conversion efficiencies observed in the PIC simulations. As $I\lambda^2$ increases, higher surface modes are excited with increasing

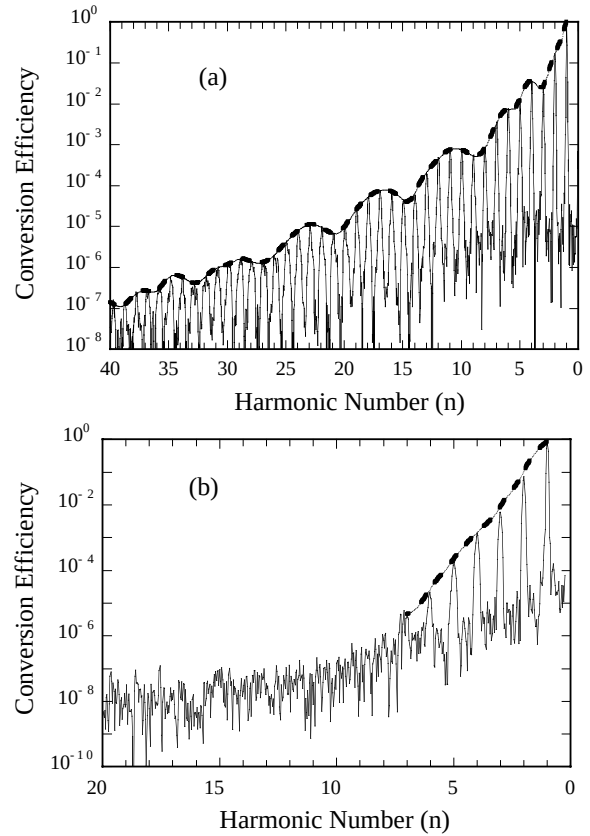


Figure 2. The simulated harmonic spectra for:-

- (a) $I\lambda^2 = 1.23 \times 10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$
- (b) $I\lambda^2 = 1.37 \times 10^{18} \text{ W}\mu\text{m}^2\text{cm}^{-2}$.

The conversion efficiency is given by $2|E(\omega)/E_L|^2$.

amplitudes as shown in Figure 3a. The modes at $4\omega_0$ and $5\omega_0$ become larger and affect the motion of the critical surface significantly.

In order to interpret the PIC results we include in the moving-mirror model all of the oscillatory modes present in $x(t)$ rather than using arbitrary components at ω_0 , $2\omega_0$ and $4\omega_0$ as done by Lichters *et al* ¹¹⁾. This is done by calculating the waveform of the reflected light numerically with the function $x(t)$ taken from the PIC simulation (Figures 3a and 3b). The calculated spectrum of the harmonics for the low and high values of $I\lambda^2$ are shown in Figure 3c. The spectra show the same intensity dependence of the modulation structure as observed experimentally. Furthermore, the shape of the spectrum is in good quantitative agreement with the PIC simulations. This illustrates that the moving-mirror model captures the essential physics of the harmonic generation process.

We have also compared the Fourier transform of the calculated harmonic spectra with the motion of the critical surface from the PIC simulations. The amplitude of the critical surface motion and the degree of non-linearity of the original oscillation is preserved. Consequently the modulation of observed harmonic spectra may be used to determine the dynamics of the critical surface in future experiments. However, this was not done using the experimentally observed spectra in Figure 1 since only part of the spectrum was measured in this work (i.e. that in the soft X-ray/XUV region). Also phase information of the harmonics is lost in the intensity measurements. In the simulations the modulations are greatly suppressed by the addition of a linear density ramp to the slab profile. For this case the conditions were the same as in Figure 2a, with $I\lambda^2 = 1.23 \times 10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$, except that now the density rises from zero to $n_e/n_c = 10$ over 0.5 wavelengths.

The modulation structure of Figure 2a is now not apparent in the harmonic spectrum. The absence of any modulation

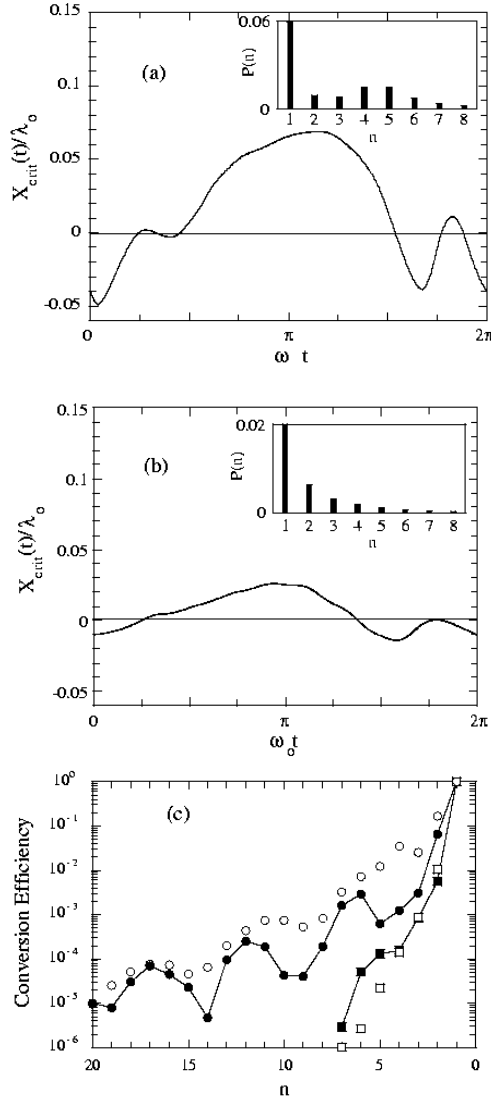


Figure 3. (a), (b), the motion of the critical surface $x(t)$ from the simulations. Inset shows the different modes of oscillation.

(a) $I\lambda^2 = 1.23 \times 10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$

(b) $I\lambda^2 = 1.37 \times 10^{18} \text{ W}\mu\text{m}^2\text{cm}^{-2}$

(c) Calculated conversion into harmonics using the oscillating mirror model. Closed circles correspond to $I\lambda^2 = 1.23 \times 10^{19} \text{ W}\mu\text{m}^2\text{cm}^{-2}$ and closed squares correspond to $I\lambda^2 = 1.37 \times 10^{18} \text{ W}\mu\text{m}^2\text{cm}^{-2}$. The open symbols show the PIC simulation results of Figure 2 for comparison.

structure demonstrates that this effect depends on initial scale-length as well as the incident intensity. The PIC simulation shows that now no single critical surface exists and that layers of ablating plasma gives rise to multiple overdense reflecting layers. Even at lower intensities it has been shown analytically by Kingham *et al.*²⁴⁾ that the reflection of the incident wave is no longer localized at the critical surface in the presence of a ramp and regions above critical density can also contribute to the generation of the harmonic spectrum²¹⁾. For the experimental conditions considered in this paper the scale-length prior to the arrival of the laser pulse is typically in the range of 1 - 6 μm . This is in contrast to the sharp plasma discontinuity that is implicit in the moving mirror model. It is therefore surprising that the moving mirror model and the PIC simulations using a step profile agree so closely with the experimental observations. However, the large laser pressures can lead to significant steepening of the density profile⁵⁾ if the pulse is sufficiently long. At the same time, the laser expels most of the plasma from the focal region, creating the kind of vacuum-plasma boundary that is required to produce the modulation structure.

That this is indeed the case has been shown previously by investigating the conversion efficiency at different pre-pulse levels⁶⁾. For short pulse lengths a rapid drop of the conversion efficiency with increasing pre-pulse was observed. By contrast, experiments with $\sim 1 \text{ ps}$ pulses⁹⁾ were insensitive to the level of pre-pulse and showed conversion efficiencies in good agreement with PIC simulations for short or step-like density profiles. The modulation structure should therefore be a good indicator of high contrast ratios for shorter duration laser pulses ($< 200 \text{ fs}$).

To summarize, the experimentally observed modulation of the harmonic spectrum agrees with the PIC simulation. The modulation is due to the introduction of higher modes of oscillation of the critical surface $x(t)$ and can be described in terms of the moving mirror model. Observations of the modulational structure of harmonic emission from high intensity interactions may be important as a diagnostic tool of the behavior of the critical surface, for example in “fast ignitor” type experiments. Measurements of the modulational structure of harmonic emission from several different angles can potentially provide 3-dimensional information on the critical surface dynamics under intense laser irradiation. Understanding this effect may also be important for determining the suitability of this XUV source for future applications.

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Relativistic Self-Phase Modulation in a Plasma

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Introduction

The rapid development of modern laser systems has led to intensities exceeding 10^{20} Wcm^{-2} , where many new phenomena have been observed in laser-matter interaction experiments. These include the generation of relativistic electrons, gamma rays, energetic protons and laser induced nuclear reactions¹⁻⁴. Also, relativistic non-linear optical effects in the plasma begin to become important⁵ and phenomena such as harmonic generation⁶, relativistic self-focusing and parametric instabilities have been observed⁷⁻¹⁰.

Self-phase modulation (SPM) has been studied extensively in solids and gases¹¹ and is a result of an intensity dependent index of refraction. In plasmas, SPM has been studied theoretically^{5,12} and is predicted to occur when the quiver velocity of an electron in the laser field becomes relativistic ($a = p_{osc}/m_e c > 1$) so that the refractive index is modified by the relativistic increase in electron mass. SPM is the temporal equivalent of self-focusing.

In this report we present the first direct measurements of relativistic SPM of a laser pulse in a plasma. Qualitative observations of SPM have been observed previously in Zhang *et al*¹³. However, to date, no quantitative measurements of this effect have been reported. In our experiments the plasma is produced in front of a solid target by the prepulse (preplasma) of a high power laser. SPM of the light occurs as it travels through the under-dense pre-plasma and alters the spectrum of the incident laser on target, which is reflected in the spectral profile of the harmonics generated in the laser-solid interaction. The harmonics are generated at the relativistic critical density of the laser wavelength, $n_e = \gamma n_c$, where n_e is the electron density, n_c is the critical density for the laser and γ is the relativistic factor. Since scattered light at the fundamental frequency is not at relativistic intensities it will in general not be able to leave the plasma. For this reason observations of the 3rd harmonic, which has a 9 times larger critical density, were used. The spectral profile is compared for two pre-plasmas with different density distributions. The observed SPM agrees well with theoretical predictions. A spectral shift is also observed which is consistent with the motion of the critical surface due to hole-boring^{14,15}.

Experiment

The experiment was performed on the Vulcan laser system at the Rutherford Appleton Laboratory. This laser delivered 0.7 - 1.0 ps pulses at a wavelength of 1.053 μm with energies up to 80 J on target. The beam of dimension $22 \times 11 \text{ cm}^2$ was focused onto target by an off-axis parabolic mirror of focal length $f = 60 \text{ cm}$. The target consisted of an optically polished fused silica slab at 45° angle of incidence with the beam p-polarised. A penumbral imaging camera monitored the soft X-ray spot size and this, combined with the laser energy, yielded the focused intensity. An independent measure of the intensity was obtained by using CR39 plastic nuclear track detectors to measure the maximum ion energies in the blow-off plasma^{12,16}. The pre-plasma produced by the laser pre-pulse was monitored with a 0.633 μm transverse optical probe. The spectrum of the third harmonic, at 351 nm, was observed with a spectrometer viewing along the target normal.

The intensity on target was up to $\sim 3.0 \times 10^{19} \text{ Wcm}^{-2}$. The diameter of the focal spot was $\sim 10 \mu\text{m}$. The bandwidth of the laser was transform limited with $\Delta\lambda = 1.89 \pm 0.16 \text{ nm}$. The laser pre-pulse has been measured previously to be $\sim 10^{-6}$ of the peak intensity at 40 ps before the peak of the pulse¹⁷. With this pre-pulse the scale-length was found to be typically less than 10 μm .

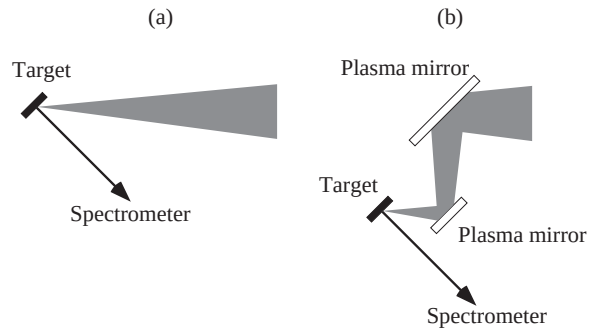


Figure 1. The configuration of the plasma mirrors. (a) Without the plasma mirrors the laser pre-pulse typically produced a $\sim 10 \mu\text{m}$ pre-plasma. (b) With the plasma mirrors the pre-pulse is reduced leading to a smaller scale-length pre-plasma.

In the experiments reported here a smaller scale-length was produced by reducing the laser pre-pulse with a pair of plasma mirrors¹⁸. These consisted of two anti-reflection coated optical flats. The damage threshold of the coatings was $\sim 10^{13} \text{ Wcm}^{-2}$. Incident light at intensities below this value passed through the glass and did not reach the target. The pre-pulse was reduced in this manner by a factor of $10^3 - 10^4$, this limit being due to the residual reflectivity of the glass flat. The set-up is shown in Figure 1.

The laser energy reaching the target was measured with a calorimeter and found to be $\sim 46\%$ of the incident laser energy. The spectrum of the third harmonic was measured as a function of the laser intensity without and with the plasma mirrors, i.e. for large and small scale-length pre-plasmas.

Typical spectra are shown in Figure 2. In both cases the spectrum is broadened and shifted and exhibits a multi-peak structure. This is characteristic of SPM. The broadening and shift are functions of the laser intensity but the individual peaks remain constant with a width of $0.27 \pm 0.04 \text{ nm}$ (FWHM). The resolution of the spectrometer was 0.07 nm. A larger number of peaks is observed in the long scale-length pre-plasma over a broader spectral width.

The spectrum is red-shifted, the shift scaling as $(I\lambda^2)^{0.5}$. This is in agreement with hole boring at the critical surface, as seen in the simulations by Wilks *et al*¹⁴ and measured by Zepf *et al*¹⁵. In the smaller scale-length pre-plasma a slight blue-shift is observed as expected and is due to the plasma pressure exceeding the laser ponderomotive pressure. The transition from a red to a blue shift, depends on the pre-pulse, and is discussed in detail in Kalashnikov *et al*¹⁹.

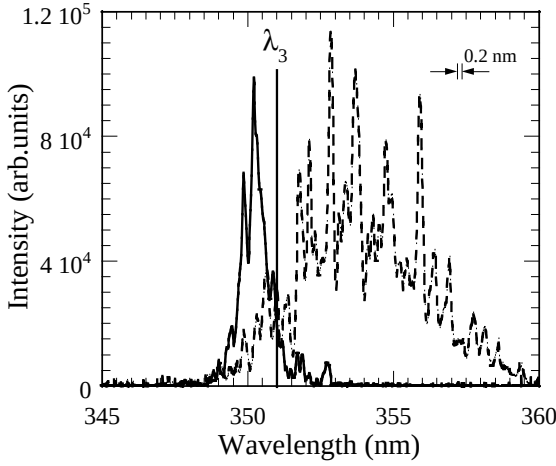


Figure 2. Lineout of typical 3rd harmonic spectra at (a) $I\lambda^2 = 2.0 \times 10^{19} \text{ W}\mu\text{m}^2/\text{cm}^2$ with pre-pulse (dashed line) and (b) at $I\lambda^2 = 2.3 \times 10^{19} \text{ W}\mu\text{m}^2/\text{cm}^2$ with reduced pre-pulse (solid line). The transform limited bandwidth is $\sim 0.2 \text{ nm}$.

The full spectral width is plotted as a function of $I\lambda^2$ for large and small scalelengths in Figure 3. Higher order harmonics up to the 30th at 35.1 nm were observed with a separate detector. The wavelength shift and broadening of the spectral profile was also evident for these harmonics. However, the resolution of the instrument was not high enough to observe the associated multi-peak structure.

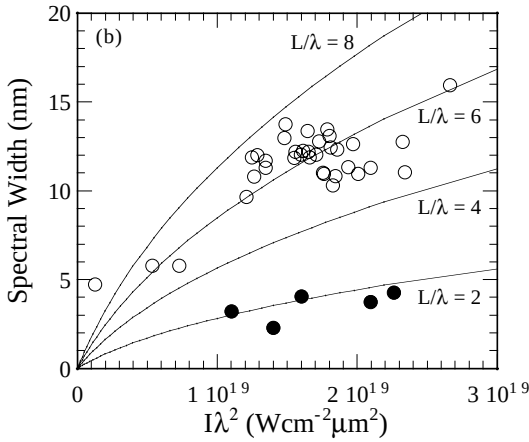


Figure 3. The full spectral width of the third harmonic plotted as a function of $I\lambda^2$. The closed circles represent the data obtained with low pre-pulse. Open circles represent the data obtained for larger pre-pulse. The lines represent the calculated spectral width for relativistic SPM with varying linear ramp scale-lengths.

Relativistic SPM can be calculated as follows. The angular frequency change is ²⁰⁾

$$\Delta\omega(t) = -d/dt \phi(t) \quad (1)$$

where $\phi(t)$ is the phase shift

$$\phi(t) = \frac{\omega}{c} \int_0^{x_c} \eta dx \quad (2)$$

Here $\eta = [1 - n_e(x)/\gamma(t)n_c]^{1/2}$ is the refractive index and

$\gamma(t) = [1 + a(t)^2/2]^{1/2}$ is the relativistic factor.

The index of refraction only requires relativistic corrections to the motion of plasma electrons since the pulse duration is much shorter than typical ion motion timescales. The normalized momentum, $a = p_{osc}/m_e c$, is related to the laser intensity by $I\lambda^2 = a^2 \times 1.37 \times 10^{18} \text{ Wcm}^{-2}$.

For a linearly ramped density profile with $n_e(x) = n_c x/L$ Equations 1 and 2 give :-

$$\delta\omega(t) = -\frac{2}{3} \frac{\omega_o L}{c} \frac{d}{dt} [\gamma(t)] \quad (3)$$

where the integration has been up to γn_c

The frequency change $\delta\omega$ is to the red in the leading part of the pulse and to the blue in the rear. There are thus two times with the same value of $\delta\omega$. At these times the pulse has the same frequency but will have different phase. The multi-peak structure is a result of the constructive and destructive interference of these waves. The full spectral width, calculated from the peak to peak value of $\Delta\omega$ for pre-plasmas of different linear scalelengths, is also plotted in Figure 3. A scale-length of $L/\lambda \sim 6$ matches the experiment when the full laser pre-pulse was used. This agrees well with the scale-length measured by transverse laser probing. With the reduced pre-pulse obtained by use of the plasma mirrors a good fit is obtained for a scale-length $L/\lambda \sim 2$. The number of peaks in the spectral profile is a linear function of the maximum phase change $\phi_{max}^{11)}$. The number of peaks M is given by $\phi_{max} \sim (M-1/2)\pi$. For scalelengths $L/\lambda = 2$ and $L/\lambda = 6$ calculating ϕ_{max} from Equation 2 gives $M = 4$ and $M = 11$ respectively. These are in reasonable agreement with the spectral profiles shown in Figure 2 and corroborates the scalelengths inferred from the data in Figure 3.

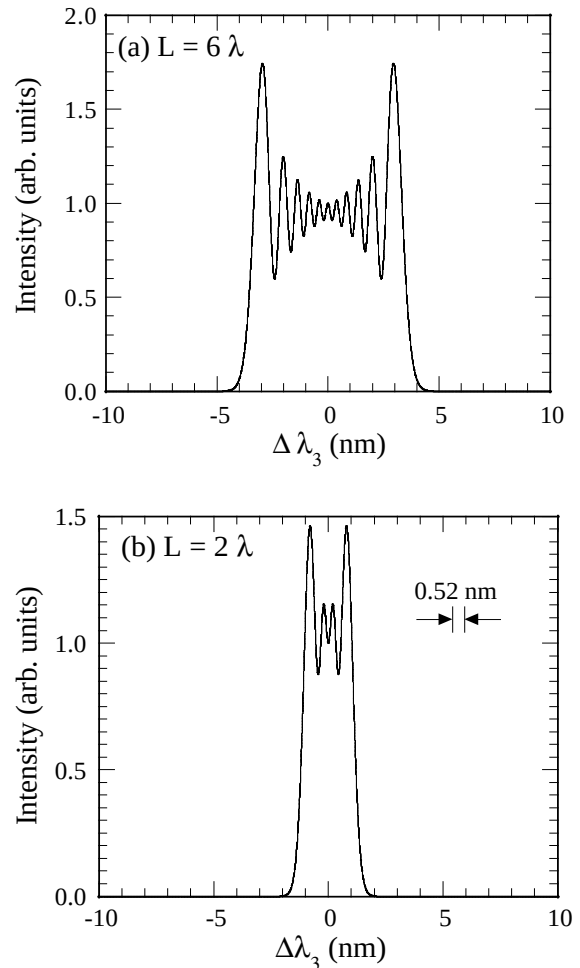


Figure 4. The calculated spectral profile from the Fourier transform of the electric field given for (a) $L = 6\lambda$ and (b) $L = 2\lambda$. The transform limited bandwidth was $\Delta\lambda = 0.26 \text{ nm}$.

The spectral profile can be calculated by taking the square of the Fourier transform of $E(t)\exp(i\phi t)$, where $E(t)$ is the laser electric field and $\phi(t)$ is from Equation 2. This is shown in Figure 4 for linear density ramps with $L/\lambda = 2$ and $L/\lambda = 6$, assuming a Gaussian pulse shape (0.5 ps 1/e intensity half-

width) with peak intensity $I_0 = 1.2 \times 10^{19} \text{ Wcm}^{-2}$. The width of the individual peaks is related to the assumed bandwidth, which for the 3rd harmonic is 0.26 nm. The average measured width of the peaks in Figure 2 is $0.27 \pm 0.04 \text{ nm}$.

The calculated spectrum (Figure 4) has a minimum at the central wavelength whereas the experimental profile (Figure 2) has a maximum. The analysis of Bulanov¹²⁾ found that the spectral profile is a minimum for a non-relativistic pulse ($a < 1$) and a maximum for a relativistic pulse in the situation where a constant uniform plasma density was assumed. This is indeed found to be the case when the integration of Equation 2 is carried out to the critical density n_c . However, when the integration is evaluated up to the relativistic cut-off n_{cr} the resulting profile is a minimum. An analysis of SPM with an exponential density profile $n_e(x) = n_c \exp[-x/L]$ shows a similar behaviour and results. For high intensity laser-plasma experiments the effect of ponderomotive steepening at the critical surface results in extremely short scale-length plasmas^{20, 21)}. Therefore the difference in position of the relativistic and non-relativistic critical densities is likely to be small and may explain the measured spectral profile. A more detailed analysis is needed to fully model the experimental conditions and to include other effects such as the intensity dependence of hole-boring and the time dependence of the density profile $n = n(x, t)$. However, the main effect is clearly due to relativistic SPM.

In addition, the contribution of SPM on the spectrum due to atomic non-linearities is not expected to play a significant role since the susceptibilities for highly ionized atoms are too small²²⁾.

The suitability of the harmonics produced from intense laser-solid interactions as a source of coherent XUV radiation has been shown to be limited by pre-plasma formation²³⁾. This leads to a reduced source brightness at higher intensities due to spectral broadening, a broadened angular emission distribution and reduced conversion efficiencies. The results presented here demonstrate that the formation of pre-plasma is efficiently suppressed by the use of plasma mirrors. This may lead to enhanced brightness characteristics of the high-order harmonics produced in future experiments.

To summarize, observations of the third harmonic spectral profile show varying degrees of shifting, broadening and modulation with different levels of laser pre-pulse. These features are consistent with the effect of relativistic SPM of the fundamental laser light as it travels through the underdense pre-plasma. This is the first quantitative measurement of relativistic SPM in a plasma and demonstrates the importance of relativistic non-linear plasma effects in the high intensity regime. As higher laser intensities are achieved the role of relativistic SPM in laser-plasma interaction experiments will become increasingly important²⁴⁾. For instance the spectral extent of the broadening given by Equation 3 for $I_0 \sim 10^{21} \text{ Wcm}^{-2}$ is such that $\Delta\omega/\omega \sim 1$ implying that the region of laser energy deposition will be greatly enlarged. This will clearly affect hot electron and X-ray production and may have important implications for some of the technological applications foreseen for these lasers. Consequently this confirmation of theory is also important for “fast-ignition” and laser-plasma accelerator research in addition to relativistic non-linear optics.

Acknowledgements

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The effect of target heating on fast ion production during intense laser-plasma interactions

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Introduction

Recent experimental work investigating laser plasma interactions at intensities greater than 10^{19} W/cm² has shown that the plasmas produced during intense laser-matter interactions can potentially be efficient sources of energetic electrons¹, gamma rays², and ions³.

In general, energetic ions produced by these interactions are accelerated by a plasma sheath generated by the hot electron population in the plasma. There are many potential applications for such energetic particles such as compact accelerators⁴ and as diagnostic probe beams of high density plasmas. In addition, the results of these experiments are interesting for technological applications since such sources should be scalable to “table-top” sizes.

Generally, the majority of the energy in the ions is carried by protons which are accelerated preferentially with respect to heavier ions. The lighter protons move at much higher velocities and consequently tend to “short-circuit” the accelerating electric fields – which therefore limits the peak energy of other ion species. In solid target interactions these protons originate from a surface contamination layer on the target – which is largely composed of water and/or vacuum pump oil. Both of these surface contaminants contain hydrogen – which provides the source of the observed protons in the experiments⁵.

In this report, we describe experiments which attempt to remove the contamination layer through heating of the target. Since the boiling/melting points of the thin targets used (aluminium or gold) are typically much higher than that of water or pump oil, we show that this is an effective way to remove the proton component from the accelerated ion spectrum. Using a Thomson parabola ion spectrometer we also show that the total number of protons is significantly reduced and that consequently, the energy of the heavier ions which remain is significantly increased.

Experiment

These experiments were carried out using the CPA beam of the Vulcan Nd:Glass laser system. The laser wavelength was 1.054 μ m, the pulse length was 0.9 – 1.2 ps, and the energy incident on target was 20 – 50 J. The laser beam (111 mm x 200 mm) was focused onto the target surface using an on-axis parabolic mirror of focal length 225 mm. The laser beam was *p*-polarised and was incident on the target at an angle of 45°. The peak intensity was measured to be about 2×10^{19} W/cm². The targets were typically thin foils of gold and the target and all of the optics for the beam after compression were placed in a vacuum chamber evacuated to less than 10^{-4} mbar pressure.

A specially designed target mount was used which was capable of heating a target to a temperature of greater than 400 °C. The target was held in position over a small heating element (filament) which heated the target radiatively. The target temperature was monitored using a thermocouple and was maintained at a constant level prior to each shot.

Energetic ions were measured using a Thomson parabola ion spectrometer which was placed approximately 1 metre from the target and was aligned to the front of the target at an angle of approximately 20 degrees from target normal. CR39 – a nuclear track detector – was used as the detector.

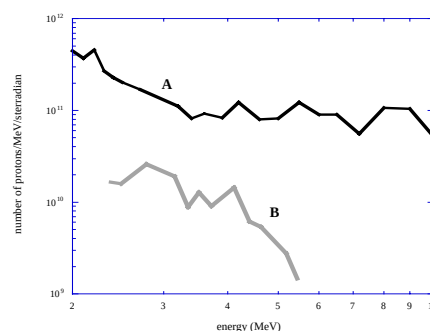


Figure 1. A) proton spectrum from unheated gold target
B) from heated (400 °C) gold target.

Figure 1 shows the measured proton spectrum from the Thomson parabola diagnostic from an interaction at a laser intensity of 2×10^{19} W/cm² with 100 μ m thick gold targets. The number of protons from heated targets (Figure 1B) was reduced by more than an order of magnitude when compared to unheated gold targets at a similar laser intensity (Figure 1A). The peak energy of the measured protons was also significantly reduced and does not approach the diagnostic limit of 11 MeV as in the unheated target.

Although these targets were heated to temperatures greater than 400 °C there were still significant amounts of carbon ions remaining and although the number of carbon ions was reduced – the energy of these carbons was increased significantly.

Figure 2 shows the spectrum of the carbon ions from two consecutive shots – one which used a heated target (Fig. 2B and 2D) and one which did not (Fig. 2A and 2C). Clearly, from the spectra there are still carbon ions present. However in the heated targets the peak energy has increased by more than 10 MeV. While the number of low energy carbon ions has been reduced the entire distribution has been shifted to higher energies. The spectra of the C⁶⁺ ions are shown in Fig 2A and 2B and the C⁵⁺ ion spectra are shown in Fig 2C and 2D. This is in contrast to the fact that the proton number and maximum energy have been radically reduced.

From the Thomson parabola measurements it was also apparent that the number, energy, and ionization stage of the gold ions also significantly increased – although it was not possible to make spectra of this data due to the low signal level and the uncertainty in the ionisation stage (i.e., the parabolas from the many ionisation stages were observed to overlap).

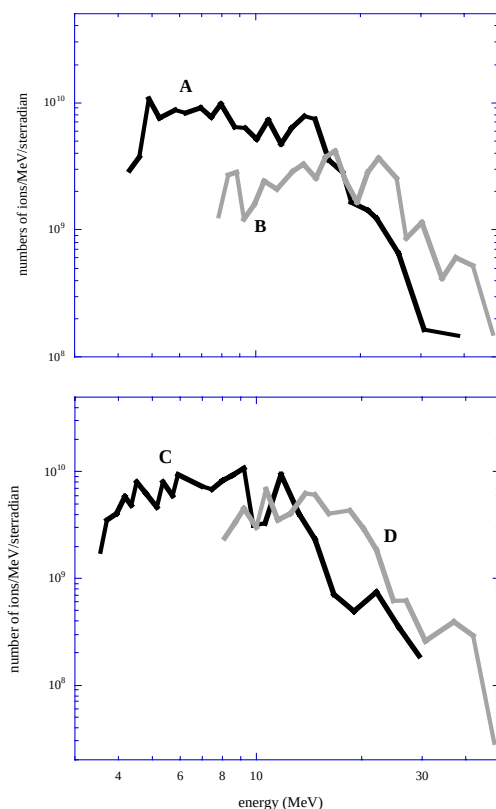


Figure 2. A) C^{6+} spectrum from unheated target B) C^{6+} spectrum from heated target C) C^{5+} spectrum from unheated target D) C^{5+} spectrum from heated target.

In conclusion, it appears that the use of heated targets provides a relatively easy way to increase the energy of the heavy ions produced from intense laser produced plasma. This may allow a more efficient ion source for future heavy ion accelerators – and may perhaps avoid the use of pre-acceleration stages.

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Using Vulcan to Recreate Planetary Cores

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Introduction

An accurate equation of state (EOS) for planetary constituents at extreme conditions is the key to any credible model of planets or low mass stars. However, experimental validation has been carried out only at high pressure (>few Mbar), and then only on the principal Hugoniot. For planetary and stellar interiors, compression occurs due to gravitational force so that the material state follows a line of isentropic compression (ignoring phase separation) to ultra-high densities¹.

An example of the predicted states for water along the isentrope for Neptune is shown in Figure 1. The cutaway figure on the left is from Hubbard², and the phase diagram on the right is from Cavazzoni et al³. Clearly these states lie at quite a bit lower temperature and higher density than single shock Hugoniot states. However they are at higher temperature than can be achieved with accurate diamond anvil experiments.

At extreme densities, material states are predicted to have quite unearthly properties such as high temperature superconductivity⁴ and low temperature fusion⁵. High density experiments on Earth are achieved with either static compression techniques (i.e. diamond anvil cells) or dynamic compression techniques using large laser facilities, gas guns, or explosives. A major thrust of this work is to develop techniques to create and characterize material states that exist primarily in the cores of giant planets and brown dwarf stars.

Typically, models used to construct planetary isentropes are constrained by only the planet radius, outer atmospheric spectroscopy, and space probe gravitational moment and magnetic field data. Thus any data, which provide rigid constraints for these models will have a significant impact on a broad community of planetary and condensed matter scientists.

Recent laser shock wave experiments have made great strides in recreating material states that exist in the outer 25% (in radius) of the Jovian planets and at the exterior of low-mass stars. Large laser facilities have been used to compress materials to ultra-high pressures and characterize their thermodynamic and transport properties (plastic Hugoniot to 40 Mbar, deuterium Hugoniot to 3 Mbar, metallization of “atomic” deuterium on the Hugoniot). To probe material properties at these high pressures, several experimental techniques were developed: high resolution radiography, optical reflectance, pyrometry, and velocity/displacement sensitive interferometry are some of the diagnostics currently used in laser-generated shock EOS experiments.

During our experiments at Vulcan we developed and tested precompressed and multiple shock experimental techniques which allowed us to recreate the extreme core states of giant planets. These experiments compressed water to densities higher than accessible by single shock Hugoniot techniques and showed that the metal-insulator transition of shocked precompressed water is suppressed significantly as compared to

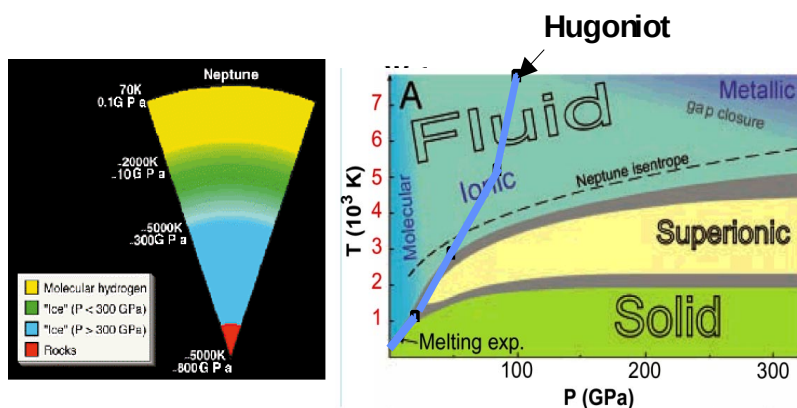


Figure 1. Predicted cutaway of Neptune from Reference 2 and calculated equation of state of water from Reference 3.

uncompressed water. Further, as predicted, the temperature of shocked precompressed water is lower than the temperature of uncompressed water enabling us to determine the metallization mechanism for water near the Hugoniot.

Experimental summary

The double shock target design is sketched in Figure 2. For these experiments, the Vulcan laser was used to ablate CH, launching a shock into an Al step, which unloaded and launched a shock into water or other planetary fluid. Either a 1 ns or 4 ns pulse is used to launch a decaying or steady shock wave respectively. Typically reflectivity can be determined with decaying shocks while Hugoniot data require steady shocks. Rutherford Appleton Laboratory's (RAL) Vulcan Laser in Target Area East generated drive pulses of $10^{13} - 10^{14}$ W/cm² for 1 to 4 ns and with a 400 μ m diameter footprint. The footprint was spatially smoothed with PZP phase plates built at RAL. In these experiments, Vulcan was configured with six 108 mm diameter beams arranged in a hexagonal pattern with each beam incident on the target at 16 degrees from the normal and one additional 150 mm diameter beam at normal incidence. The 4 ns pulse was constructed by temporally staggering four sets of 1 ns pulses from the 7 beams. The 150 mm on axis beam arrived first, followed by pairs of the 108 mm beams that were timed to arrive at 1 ns intervals. The temporal dependence of the pulse shape was measured in situ with a pulse shape monitor.

We generated reflected shock states by reflecting shocks from a fused silica anvil. A sketch of the target design is shown in Figure 2.

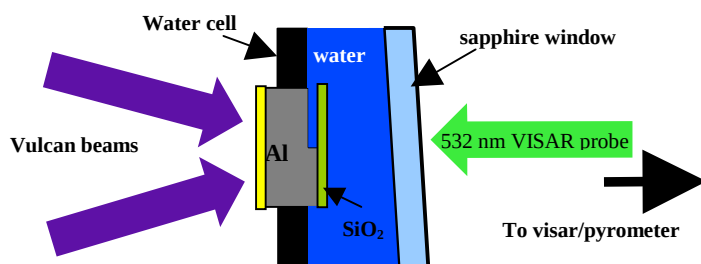


Figure 2. Double shock water cell and experimental configuration.

The water shock transits the gap between the thin Al step and the SiO₂ anvil, and then reflects off of the higher impedance SiO₂ anvil.

Diagnostics

A VISAR (velocity interferometric system for any reflector) diagnostic was used to measure the shock velocity in the water versus time and the average shock velocity in the aluminum across the step⁶. These kinematic observables and the known Al EOS were used to determine the equation of state of water. This diagnostic reflects a probe beam (532 nm 15 ns) off the rear of the target, and relays an image of the target in the reflected beam through an interferometer and onto a streak camera. In most of these cases, after the shock breaks out of the aluminum pusher, light is reflected directly off of the water shock front. The Doppler shift of the light reflected from the shock front, is manifested as a fringe shift at the output of the velocity interferometer. The fringe phase, ϕ , (in radians) produced by the velocity interferometer is related to the velocity, u , of the reflecting surface through the velocity interferometer equation $u = \lambda\phi/4\pi n(1 + \delta)$, where λ is the laser wavelength in vacuum, n is the refractive index of the unshocked water, $\tau = d/c$ is the delay in the velocity

interferometer (c is the speed of light), and δ is a wavelength dependent correction due to dispersion in the etalon⁷. Depending on the experiment we used 3 mm and 7 mm etalons which produced 16.2, and 37.4 ps delay yielding 15.9, and 6.89 μ m/ns/fringe in a vacuum respectively. The precision of this measurement is determined by the accuracy in determining λ , n , τ , and ϕ . Important to note is that this determination is independent of the sweep calibration in the recording instrumentation, and independent of target design and/or metrology. Since we can determine λ , n and τ to a precision of 4 significant figures, the main contribution to experimental error arises in extracting ϕ from the data. The shock velocity in Al is determined from the measured breakout time from each step and the measured step thickness.

An example data record is shown in Figure 3. Before 2.7 ns the stationary fringes are produced from the reflection of the probe beam off the stationary aluminum pusher. At ~ 2.8 ns (3.7 ns) the shock breaks out from the thin (thick) aluminum step, launching a strong shock into the water. As we show below, the reflection shown in Figure 3 after shock breakout from the Al step, is caused from light reflecting off the shock front in water. Also shown in Figure 3 are several lineouts where we have converted phase into velocity.

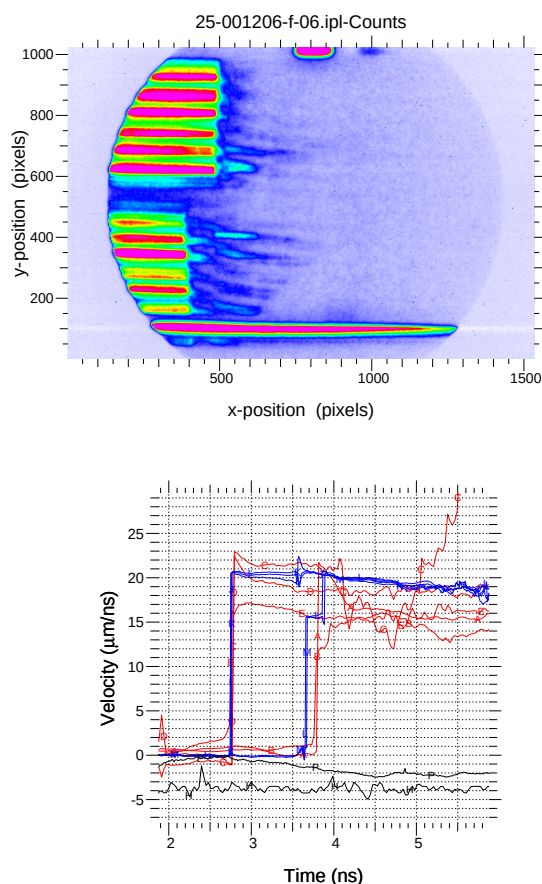


Figure 3. Example of data record from double shocked water experiment.

Equation of state measurements are typically presented as pressure versus density. To determine the shock pressure and density from shock velocities we use the Rankine-Hugoniot relations; $P = \rho_0 U_s U_p$ and $\rho = \rho_0 U_s / (U_s - U_p)$, where ρ_0 is the initial density, P is the shock pressure, and U_p is the particle velocity. We determine U_p (water) by standard impedance matching techniques with aluminum as the standard.

In addition to kinematic parameters, the VISAR diagnostic provides data to estimate the optical properties of shock

compressed dielectrics. In the image shown above, (Figure 3), the strong shock in water reflects light so that we track the shock front velocity and can estimate the reflectance of the shock front. In the case of weaker shocks, the shocked material can be opaque or transparent depending on the shock intensity and intrinsic properties of the material.

Temperature is an important thermodynamic parameter but cannot be determined from the Rankine-Hugoniot equations. Temperature must be measured independently from shock and particle velocities. Typically, temperature of transparent shocked materials is measured from the thermal emission. We extracted T by determining the spectral radiance, $I(\lambda)$ for a gray body Planck spectrum,

$$I(\lambda) = \epsilon(\lambda) \frac{2\pi hc^2}{\lambda^5} \left(\exp \frac{hc}{\lambda k_b T} - 1 \right)^{-1} \quad (1)$$

with T as a fit parameter, c , h , and k_b taking on their usual definitions, and the emissivity, $\epsilon(\lambda)$, estimated from recent multi-wavelength reflectivity data described below.

To determine the spectral radiance from the sample we calibrated the transmission of our optics using a calibrated gray body source and the sensitivity of the streak camera by determining the response to a known intensity of a pulsed laser. An example data record for a double shock target is shown in Figure 4. The temperature plotted in Figure 4 assumes an emissivity of 1. This is clearly not the case. To estimate the emissivity and determine the correct shock temperature we use the reflectance data described above, and use a minimum conductivity model to estimate the collision time and then a Drude model is used to estimate carrier concentration. We then calculate the emissivity using a Drude model with these parameters evaluated at 610 nm.

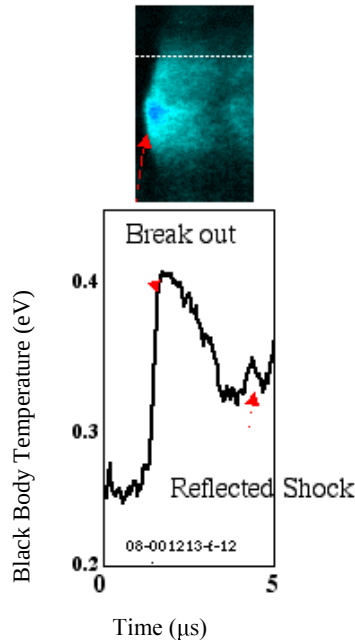


Figure 4. Shock emission at 610nm in water contained in a double shock cell.

Precompressed targets

A novel combination of the laser-driven shock technique with diamond anvil cell compression techniques is shown in Figure 5. With this target we used diamond flats to maintain a pre-compressed volume of our sample material at a static pressure of up to 1 GPa during the experiment. The laser driver geometry described above results in two significant design constraints for achieving Hugoniot data on pre-compressed samples. First, the intensity and short pulse length require that

the anvil through which the laser shock travels be extremely thin—no more than 200 μm . To ensure jump conditions are valid the shock must be steady. In order to have a steady shock wave persist into the sample with a square 4 ns pulse, the shock wave must propagate through the anvil and sample before the end-of-pulse rarefaction catches up. In addition, the shock planarity needs to be adequate for accurate inspection of the shock velocity. Thus, the spot size of the laser must be large enough so that side rarefactions do not erode the shock planarity to more than $\sim 75 \mu\text{m}$. Second, the laser spot size and beam path require a large aperture radius (hence unsupported anvil radius), r , and aperture angle, θ , in the high-pressure cell itself (Figure 5).

In order to satisfy the needs for a thin anvil having a large unsupported aperture, we chose the strongest material known, diamond. Use of a diamond anvil cell is well established and the sample can be probed before and during the experiment due to the optical transparency of the anvil. Hence, the thickness, pressure and other characteristics of the pre-compressed sample can be determined before the Hugoniot experiment.

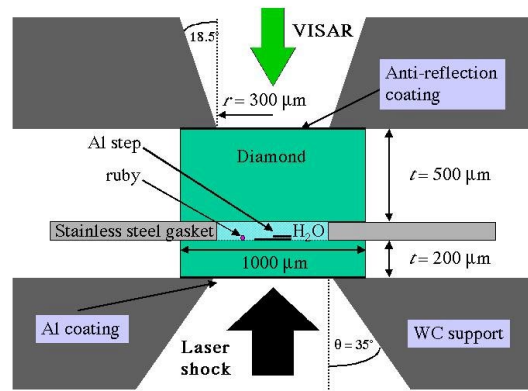


Figure 5. Schematic cross-section of diamond-cell configuration used for laser-driven shock experiments on precompressed samples.

Other features significant in the apparatus shown in Figure 5 are the wide openings (300 μm radius holes) in the tungsten carbide (WC) supports which allow ample shock laser entry ($\theta = 35^\circ$ opening) and VISAR access (18.5 $^\circ$ opening). Thin diamonds are pushed together to apply pressure on a small sample of water ($\sim 30 \text{ nL}$) held in a hole within a stainless steel gasket 100 μm thick. An Al step is glued on the thinnest diamond and used to measure the breakout times (velocities, and ultimately shock pressure) with VISAR⁷. A few ruby grains are placed in the sample chamber for precompression pressure measurements via ruby fluorescence⁸. There is a 1000 $\text{\AA}$ Al flash coating on the rear side of the thinnest diamond to lower the critical depth of shock ablation, and an anti-reflection coating on the thicker diamond for the VISAR measurement.

Plasma generated by ablation of the backing plate is a source of high energy x-rays that can preheat the sample. Also, the blow-off plasma absorbs the laser beam far from the target reducing the shock intensity significantly. In order to avoid preheat, plasma blow-off and laser damage to the DAC, a wide cone angle ($\theta = 35^\circ$) and diamond support hole (300 μm radius) were incorporated into the design of the support plate for the diamond as well as the surrounding diamond cell. This geometry, although accommodating to the laser shock, provides less support for the anvil and is therefore less than ideal for the thin diamond flats.

Characteristics of Thin Diamond Anvils

The diamond flat can be modeled as a uniformly-loaded circular plate, such that a simple relation exists between the maximum

pressure load w and the anvil thickness t ,

$$w = \frac{k_1 S_m r^2}{t^2}$$

where S_m is the maximum stress achieved in the diamond (here, the tensile strength of diamond), r is the unsupported radius and k_1 is a constant equal to 0.833 (simply supported disc) or 1.333 (disc with fixed edges)⁹. For $r = 300 \mu\text{m}$ and $t = 200 \mu\text{m}$ and using the value of tensile strength of diamond⁴, 2.8 GPa, we arrive at a maximum load of between 1.0 (simply supported) and 1.7 GPa (fixed edges).

Determining the initial pressure–density–internal energy conditions (P_0 , ρ_0 , E_0) in the pre-compressed sample is key for Hugoniot measurements. The precompression pressure P_0 was measured in the water via ruby fluorescence⁸. Using the equation of state of water by Saul and Wagner¹⁰, the initial density ρ_0 and energy E_0 were determined.

White-light interferometry was used to determine the product of the index of refraction and distance nd ¹¹. The height of the Al step (known *a priori*) placed into the sample to aid in the VISAR measurements was used as d ; determining the index of refraction for the compressed water sample was therefore straightforward (Figure 6).

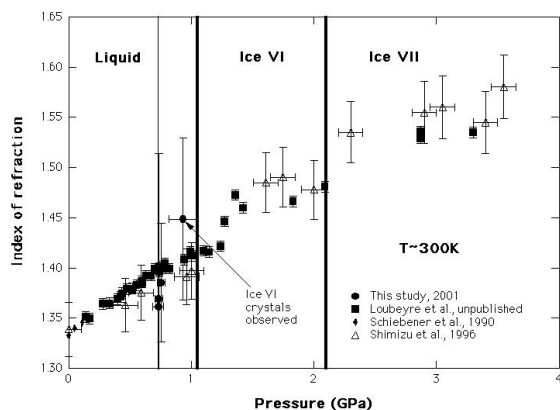


Figure 6. Index of refraction as a function of pressure for H₂O water, ice VI and ice VII at room temperature. The values obtained in the present study (closed circles) compare well with previous results of Loubeyre et al.¹², (closed squares); Schiebener et al., (closed diamonds)¹³; and Shimizu et al., (open triangles)¹⁴. In one run, ice VI crystals were observed at a pressure less than the nominal freezing pressure, indicating a possibly metastable condition¹⁵.

Despite the fragility of the diamond flats, it was possible to pre-compress water to ~ 1 GPa ($\rho_0 \sim 1.2 \text{ g/cm}^3$), as predicted by the above models. These precompressed samples were laser-shocked up to pressures of ~ 200 GPa and temperatures to $\sim 10,000$ K, see References 11, 12. In order to achieve higher initial pressures (and therefore densities), the laser intensity and duration must be increased to allow for thicker diamonds flats. For instance, the maximum load that a $500 \mu\text{m}$ thick diamond flat could withstand is predicted to lie between 6.5 (simply-supported) and 12.5 GPa (fixed-at-edges).

Results and Discussion

To test our experimental setup we compared single shock water EOS data with that collected on the Omega laser facility. The result shown in Figure 7 reveals good agreement between data collected at Omega and Vulcan. The double shock data reached the highest pressure off Hugoniot values. However, for this discussion we will focus on the results of the precompressed experiments.

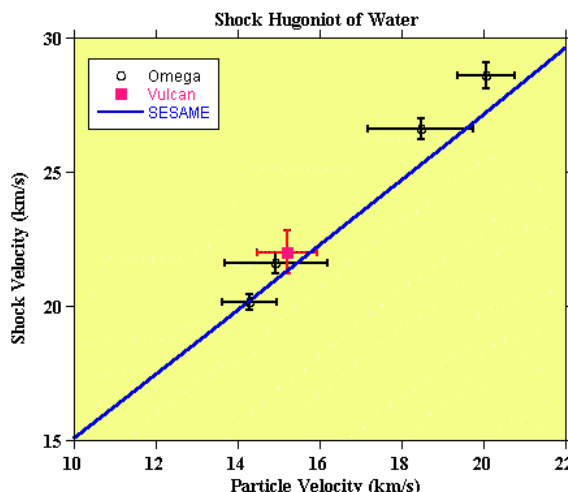


Figure 7. Shock velocity versus particle velocity for water impedance matched to aluminum.

Four successful shots were achieved on pre-compressed targets: the highest pressure shot produced a reflecting shock, the lowest pressure produced shock-compressed material that remained transparent, and the two in between shocked the material into an opaque state, thus straddling the insulator-conducting transition and allowing a comparison with the principal Hugoniot states. All targets were pre-compressed to between 0.7 – 0.95 GPa, giving initial densities of 1.2 g/cm^3 , 20 % above liquid density, and a refractive index of 1.4. An example of a precompressed VISAR data record is shown in Figure 8.

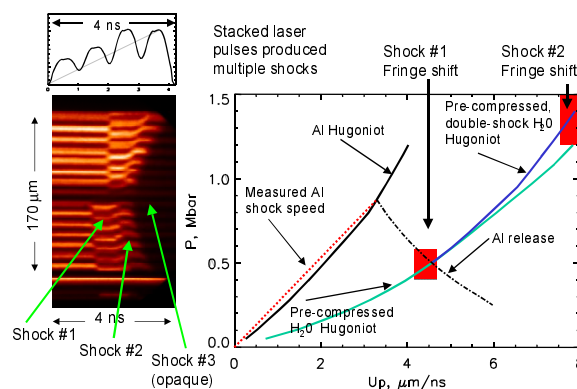


Figure 8. Example of pre-compressed water VISAR data record and analysis.

Shock pressures were determined by:

- (1) the measured break-out times in the aluminum step together with the known step height yield the shock velocity in the Al,
- (2) the shock velocity in the water from the VISAR measurements,
- (3) impedance matching provided a model-based result for the state of shocked water.

On shots where VISAR fringes could be observed either from the reflective water shock front, or from the moving aluminum interface, the pressure could also be determined directly using impedance matching with the known aluminum EOS. These model-based and direct techniques were in agreement for the transparent and reflecting shock states. For the opaque regime, a shock temperature was found for a single shot. This measured temperature was in agreement with the model-based temperature derived from impedance matching to the aluminum shock speed. Within the range explored by this experiment, it

thus appears that the SESAME EOS for water is in agreement with experiment.

The highest pressure shot at ~ 4 Mbar produced a weakly reflecting shock. While the shock reflectivity could not be precisely determined due to the curvature of the shock front, it appeared clear that the reflectivity was significantly less than the 50% value found on the principal Hugoniot at the same pressure.

Pre-compression thus appears to reduce the electronic conductivity. This sheds some light on the mechanism behind the insulator-conductor transition in water. At 4 Mbar, SESAME calculations indicate that the density and temperature are 3.7 g/cm^3 and 3.6 eV on the principal Hugoniot and 4.0 g/cm^3 and 2.8 eV in this pre-compressed shot. If the metal-insulator transition were due to a Mott transition, the higher density in the pre-compressed targets should increase the electronic conductivity of water rather than decrease it. On the other hand, if the transition were due to thermally-induced electron excitations, the lower temperature of the pre-compressed targets would reduce the reflectivity of the shock, as in fact these results show. Our experiments thus provide evidence that the insulator-conductor transition on the principal Hugoniot in water is thermally induced.

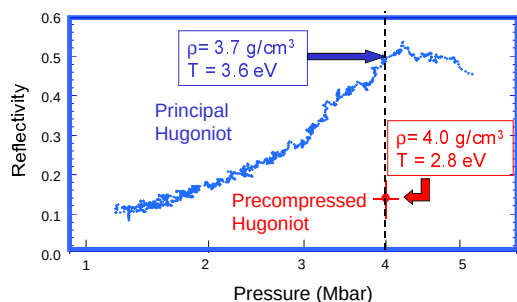


Figure 9. Reflectivity from principal Hugoniot and pre-compressed Hugoniot experiments versus pressure.

At the lowest pressure accessed, a shock of 0.5 Mbar was shown to be transparent to the VISAR probe. This contrasts with water states on the principal Hugoniot, which were found to be opaque above 0.35 Mbar. Such a delayed onset of the transparent-opaque transition in pre-compressed water is consistent with the observation given above that the lower temperatures achieved in pre-compressed water reduce charge-carrier excitation.

An interesting observation in this shot was the effect of multiple shock states. The multiple shocks arose accidentally from the arrangement of stacked laser pulses. In order to produce the 4 ns drive pulse, it was necessary to arrange the seven 1 ns beams in sequence. However, early in the campaign, the pulse widths had not been optimized and gaps still existed between each nanosecond of the 4 ns drive. On this particular shot, the later pulses were stronger than earlier ones, leading to a sequence of shocks of increasing strength that converged in time. The VISAR streak shows these shocks as successive fringe shifts. The initial transparent state at 0.5 Mbar is described above and is confirmed by both SESAME calculations and measured fringe shifts¹⁶⁾. The second shock state can only be inferred from the fringe shift, and is found to be about 1.4 Mbar, based on SESAME. The third shock accesses the opaque state of water at some unknown, higher pressure. The striking result of this shot is that a double-shocked state of pre-compressed water is found to be transparent up to 1.4 Mbar, with a corresponding temperature of 0.3 eV. Combining these results, the two-dimensional P-T diagram of water can begin to be mapped out in terms of the regions of transparent, opaque, and reflecting shocks as shown in Figure 10. Even modest pre-compression of

samples can lead to important extensions in our understanding of material properties.

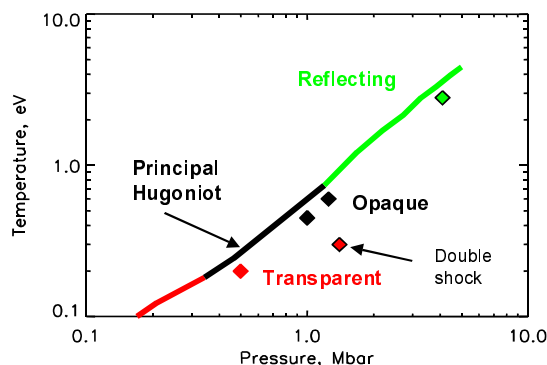


Figure 10. Summary of the optical properties along the principal Hugoniot (line) and precompressed experiments (diamonds) in the T-P plane.

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- Note that in the case of transparent shocks, the fringe shifts correspond to the particle velocity of the shocked water, since the reflection occurs at the aluminum-water interface. Consequently the refractive index of shocked water needs to be taken into account. Based on diamond cell measurements of water at similar densities, it is found that the refractive index of water almost follows Gladstone-Dale scaling, which means that the corrections to the inferred particle velocity are small. In this case they are less than 5 %. It is thus reasonable to assume that uncertainties in the inferred fringe shift due to unknown refractive index effects are in fact small.

Direct observation of strong coupling in a dense plasma

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Introduction

The properties of dense plasmas are of wide interest, for example, to researchers in inertial confinement fusion, laser-ablation, stellar structure as well as planetary physics^{1,2}. An important phenomenon in such plasmas is strong coupling³. This occurs when the Coulomb interaction energy between pairs of ions is greater than their thermal kinetic energy and leads to short range order, as in a liquid metal. This phenomenon is expected to have a significant effect on many plasma properties such as thermal and electrical conductivity. We describe here experiments in which strong coupling of a plasma is observed in a direct way via measurements of the X-ray scattering cross-sections. The measured cross-sections are well reproduced by theoretical simulations. This success points to the possibility of developing the technique of X-ray scattering into a powerful new diagnostic of dense plasmas.

The strong coupling parameter for ions in a plasma was introduced by Brush, Sahlin and Teller⁴, and is given by:-

$$\Gamma = \frac{(Z^* e)^2}{R_i kT} \quad (1)$$

Here Z^*e is the average ionic charge, R_i is the average inter-ionic separation and kT the average ion temperature. For laser-plasmas this parameter is commonly above unity for at least part of the plasma. In order to investigate this phenomenon in a reasonably rigorous way with X-ray scattering methods we have used radiative heating of a thin foil to produce a plasma with relatively uniform conditions at $\Gamma > 1$.

Experiments

The experiments were carried out at the Vulcan Laser Facility of the Rutherford Appleton Laboratory. Figure 1 shows a schematic of the experiment. A brief outline is as follows: the main heating beams were approximately Gaussian in shape with 800ps full-width at half maximum (FWHM) duration. Six beams were used to irradiate the Au foils (3 each side). Each beam delivered ~70J at 532nm wavelength. Focusing with phased-zone plates (PZP) gave a smooth flat topped profile of 1.5mm diameter, resulting in an irradiance of 10^{13} Wcm^{-2} . The gold foils were 1500Å thick with a 0.5µm layer of CH supporting them on the side facing away from the lasers. The X-ray emission from this type of foil has been well characterised by others^{5,6} and is similar to a black body emitting at a radiation temperature of ~66eV for our case. The Au foils were placed facing each other 8mm apart. The experiments were related to earlier work⁷ with single sided irradiation, which was however inconclusive, due to poorer temporal resolution and more severe temperature and density gradients.

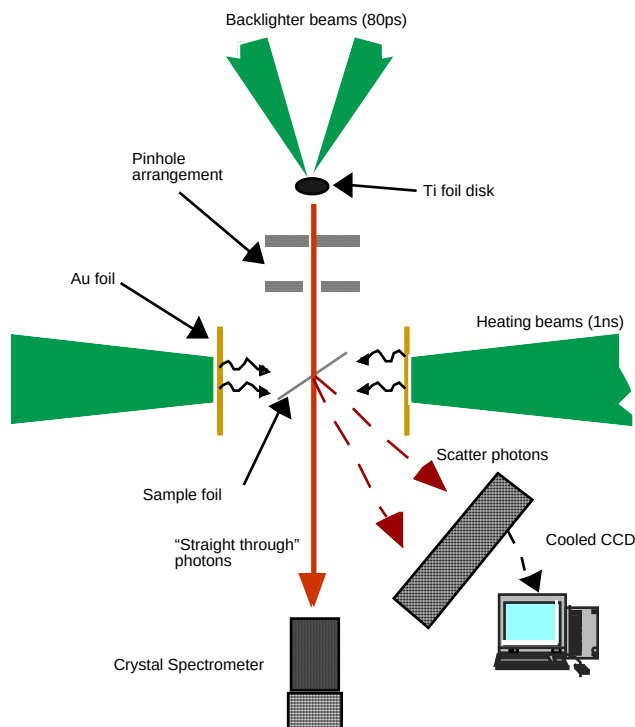


Figure 1. Schematic of the experiment (not to scale). The timing between the main heating pulses and the back-lighter pulses was stable and controllable to ~30ps. X-ray streak measurements showed that the Ti He- α X-ray pulse duration was 80-100ps. Extensive test shots showed that the screening shields (not shown) ensured that only photons scattered from the sample foil were collected.

The sample Al foil was 1µm thick and coated with 0.2µm of CH on each side. The CH coating on both the Au heating foils and on the target absorbed much of the longer wavelength soft X-rays which would otherwise be absorbed close to the Al surface, leading to strong temperature gradients. The CH layer on the sample also helped to constrain the expansion of the Al and thus reduced density gradients. The sample foil was placed between the Au foils and at 45° to them as in Figure 1. The Al samples were 5mmx5mm in size, but only a spot 2.1x2.8mm was probed. Because of the geometry, for parts of the foil away from the centre, the heating is asymmetric. We believe that the lateral non-uniformity caused by this is less important than the axial variations that exist due to the preferential absorption in the outer part of the foil. However, a full analysis of lateral heating variation still needs to be carried out. At a controlled time later, a shorter (80ps) pair of laser pulses were used to heat a Ti foil target. This resulted in a laser-plasma that was a strong source of He-like Ti radiation, in particular the $1s^2-1s2p \ ^1P$ (He- α line) and ^3P transitions at 2.6Å and the associated Li-like dielectronic satellites. This radiation passed

through a pinhole system onto the sample foil in a cone of 6° divergence. Most of this He- α line radiation passed through the sample and into a CCD based crystal spectrometer, for the purposes of monitoring the incident flux. The small number of scattered X-ray photons were detected with a cooled charge coupled device (CCD) placed to cover an 18° angular range in the horizontal plane. The scattering cross-sections were calculated by counting the detected photons and comparing with the number of photons passing through the known thickness of the targets.

The CCD used for detection of scattered photons was a 1024×256 pixel array of $26 \mu\text{m}$ square elements. Filtering of $250 \mu\text{m}$ Be and $25 \mu\text{m}$ Al with $50 \mu\text{m}$ Mylar was used to prevent soft X-rays from the Au foils from being detected. An absorbed photon at 4.75 keV generates ~ 1300 electron-hole pairs and the amplifier was sensitive to $\sim 37 \text{ eV}$ (10 electrons). Thermal, read and shot noise limited resolution further to $\sim 200 \text{ eV}$. The group of lines around the Ti He- α group spans only $\sim 50 \text{ eV}$ in energy and was by far the brightest feature in the keV region and so represented, for our purposes, an effectively monochromatic source. Since the incident photon flux was low, we were able to make histograms of the pixels for each data shot and count how many photons in the He- α group were detected in single pixel events. The likelihood of single pixel detection (as opposed to split-events where the electron cloud, generated by a photon, is split between pixels) was calibrated at 5.9 keV using an Fe^{55} radioactive source. Kraft et al.⁸⁾ show that we can then scale with some confidence to 4.75 keV , giving a single pixel detection efficiency of 0.27 ± 0.02 .

The Si (111) crystal used to monitor the flux of probing photons incident on the sample was also calibrated with an Fe^{55} radioactive source. The integrated reflectivity was half way between that predicted for a mosaic crystal and for a single crystal⁹⁾. Scaling this to 4.75 keV is more problematic than for the CCD but we have assumed that it is also half way for this photon energy. The systematic errors in the overall calibration, due to CCD quantum efficiency, statistical error in photon counts, Fe^{55} source calibration and crystal calibration are estimated to be $\sim 30\%$.

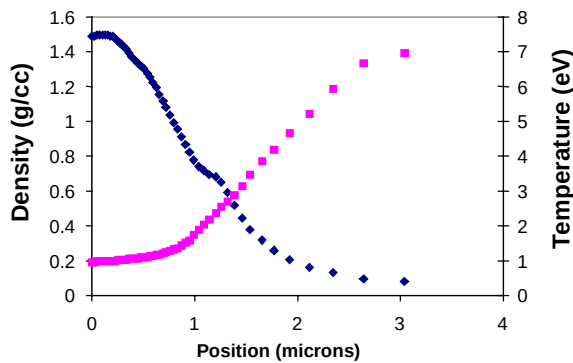


Figure 2. Hydrodynamic simulation of the sample at $t=+0.5 \text{ ns}$ delay relative to the peak of the heating beams. Only one half of the target is shown, since the code uses the symmetry of the experiment as a boundary condition. Only the conditions for the Al are shown. The CH is hotter and is calculated to contribute only $\sim 5\%$ of scatter signal, due to its lower number of bound electrons.

Simulation of the sample plasma formation was carried out using the 2-D NYM radiation-hydrodynamics code^{10,11)}. The nature of our experiment meant that the expansion was expected to be largely 1-dimensional and this was confirmed by the simulation. A line out through the centre of the simulated foils was taken to represent the conditions probed by the experiment. The results of the simulation for early time are shown in

Figure 2. Despite using a thin foil, the gradients present are still quite large and so, for the calculation of theoretical cross sections, the simulated sample foil was divided in three parts of equal mass and the average conditions for each third used to generate a cross-section, the three being then averaged for each probe time. The approximate values of Γ for the averaged thirds are indicated in Figure 2, calculated using the Z^* derived from the INFERNO average atom model¹²⁾.

Figure 3 shows the experimentally determined cross-sections for early and late probe times. We have taken five overlapping data points per shot by integrating over $1/3$ of the CCD for each point (6° resolution) and shifting the centre of measurement by $1/6$ of a CCD screen for the next point. We can see that there is an evolution from the flattened cross section at 0.5 ns delay, towards a more steeply sloping cross section at 2 ns delay. This progression is as expected since, at late time, the plasma is expected to be at lower density and to be fairly weakly coupled. In this case the atomic form factor for individual ion scattering will dominate, resulting in the steeper "fall off" with angle. On the other hand, at 0.5 ns delay, the plasma is expected still to be at higher density and strongly coupled, in which case the collective scattering structure factor for the plasma will be more important and will suppress scatter at lower angles, leading to the flattened curve seen in Figure 3.

In Figure 3 the dashed line is a simulation of the expected temperature and density averaged cross-section, using the INFERNO model combined with a hyper-netted chain model for ion-ion correlation^{13,14)}. The flattened cross-section seen in the data is reproduced well. At 2 ns delay, the simulated cross-section for the weakly coupled plasma conditions seems to fit reasonably well with data. At all times the absolute values seem to agree to within the uncertainty in the experimental calibration.

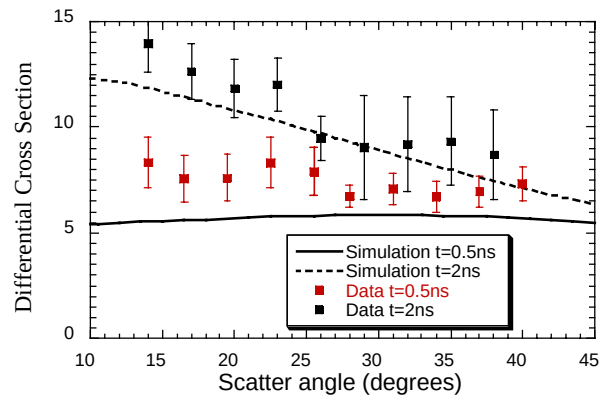


Figure 3. X-ray scatter differential cross sections (barns/Sr) at early and late times. The two CCD positions were chosen to have one angle in common (to within 1°). The curves are simulated cross sections calculated as described in the text.

In an earlier work, with laser-shock compressed plasmas¹⁵⁾, we also reported strong coupling effects on the X-ray scattering cross sections. However, in that work, there was poor agreement between experimental and simulated shapes for the cross-section. This was tentatively ascribed to a lengthening of the electron-ion equilibration time due to degeneracy and strong coupling during the high compression phase. Such effects had been predicted¹⁶⁾ and indeed some evidence for them via optical emission measurements¹⁷⁾ has been reported. Nevertheless, this did not provide a completely satisfactory resolution to the disagreement and would have required this effect to be somewhat larger than currently predicted. This current work, without the high compression phase, represents the first time we have obtained reasonably good consistency between simulation and experiment regarding the shape and absolute value of the cross-sections.

Discussion

In our analysis we also tried the ACTEX¹⁸⁾ ionisation model. For the high density core of the foil at $t=0.5\text{ns}$, ACTEX predicts little or no ionisation and consequently a scattering profile more like the late time curve in Figure 3. However, it should be noted that neither ACTEX nor INFERNO were designed for the plasma conditions of this experiment. The INFERNO model, used to predict ionisation, includes bound states, scattering resonance states as well as free continuum states. Electrons which occupy the resonance states are neither strictly localised or totally free. However, narrow resonances can be viewed as basically bound whereas wide resonances as encountered here for the $t=0.5\text{ns}$ case are better approximated by free electron states¹⁹⁾. At $t=0.5\text{ns}$, in the high density core of the foil, we obtain $Z^*=1.6$ where 0.8 of these electrons are in the wide p resonance states. If we treat these resonance electrons as bound then the effective Γ falls to only ~ 5 and the simulated cross-section at this time is not so well matched to experiment but is closer to the weakly coupled curve.

The significance of this work is that the broad regime we are able to investigate by these means is intermediate between the well researched areas of plasmas and liquid metals and is by no means completely understood theoretically. The occurrence of such matter in a wide range of arenas from astrophysics to pulsed laser deposition, is a strong motivation for further work. Furthermore, for this type of plasma, many methods of plasma diagnosis are difficult. Optical emission and absorption spectroscopy are hampered by high opacity and broadening of spectral features. X-ray absorption spectroscopy is also hampered by the difficulty of distinguishing between low ionisation states. For example, in the current case, K- α absorption spectroscopy is prevented by the filled L-shell of the Al ions. Finally, our analysis shows that this method, (although perhaps in a more refined experiment with better uniformity) may be useful in determining not only the validity of different ionisation models, but also how we interpret the idea of average ionisation in such plasmas.

Acknowledgements

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Saturated x-ray lasers at 196Å and 231Å and imaging of the Ne-like Ni XRL

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Introduction

We demonstrate the reproducibility of Ne-like Ge and Ni soft x-ray lasers and plot a growth curve for the Ge XRL. We also image the Ni XRL from the exit point of the target to look at the spot profile and estimate an absolute number for the output power. A reproducible, saturated and high output power laser is required for future Four Wave Mixing experiments¹⁾.

Experiment

The Ne-like Ni and Ge XRLs were created using the single sided five beam geometry developed at RAL²⁾. The drive beams had a standard 80 ps pulse length with an average energy of 40 J per beam and when distributed across a 100µm x 25mm line focus gave an on-target intensity of 5.10^{13} W/cm². A 20% pre-pulse was set 2 ns ahead of the main drive and the beams were positioned and timed along the target length to simulate a quasi-travelling wave.

The main diagnostic for the Ge and Ni XRLs was an on-axis grazing incidence flat field spectrometer with a 1200 lines/mm aperiodic ruled grating and a 16 bit, back thinned CCD with pixel elements of 13µm. The FFS was used to optimize the output of the Ge and Ni XRLs and to perform a length scan of the Ge XRL, which had not been done before under these conditions. The FFS was then replaced with an x-ray mirror and an imaging system was set up to image the exit plane of the XRL from the target.

The illumination uniformity and the ionization balance were monitored on a shot to shot basis using a crossed slit camera and a space resolving Bragg spectrometer. Figure 1 shows a typical time integrated lineout for Ne-like Ge from the Bragg spectrometer indicating a uniform irradiance across the target.

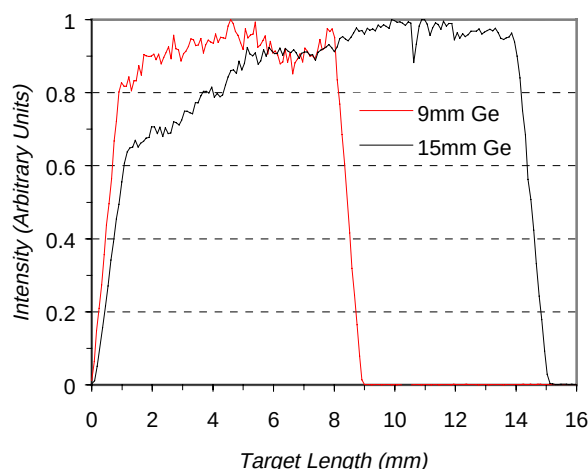


Figure 1. Time integrated Ne-like Ge emission showing line focus uniformity across two different targets.

The Ne-like Ge XRL

A growth curve was obtained for the Ne-like Ge laser by shooting a range of coated (100µm x 1µm thick) stripe targets from 5–25 mm long, see Figure 2. We can also see the analytic growth curve based on the Linford formula³⁾ where the fit indicates an SSG coefficient of 18.5cm^{-1} . The XRL output energy from the 25mm target was 7mJ assuming 1% grating efficiency, tabulated filter transmissions and knowledge of the CCD sensitivity at 196Å.

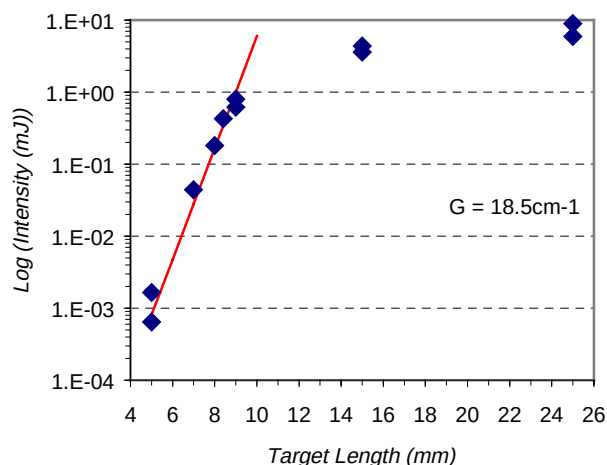


Figure 2. Growth curve for Ne-like Ge XRL at 196Å.

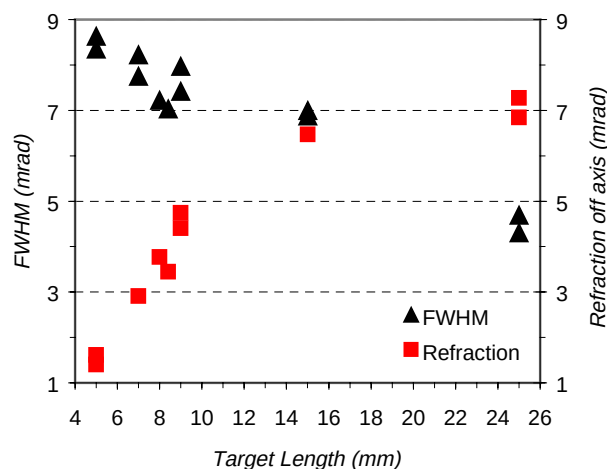


Figure 3. Refraction angle and FWHM divergence as a function of target length.

The divergence and refraction angle of the XRL were also investigated as the target length was varied, see Figure 3. We can see that as the target length is increased the divergence decreases. Also we note that the refraction angle increases with

increasing target length up to the point where saturation takes effect.

The Ne-like Ni XRL

We also shot 25mm Ni slab targets and the output of the Ni XRL was measured at 5mJ assuming 1% grating efficiency, knowledge of the CCD sensitivity at 231Å and from tabulated filter transmissions. The exit plane of the XRL from the target position was then imaged using a spherical multilayer mirror at near normal incidence and a second x-ray mirror to relay the image to the CCD at x40 magnification as shown in Figure 4.

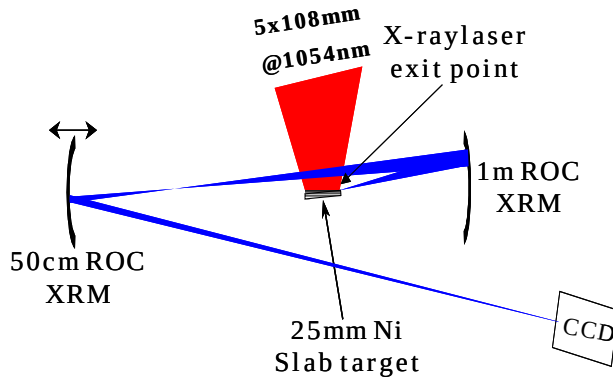


Figure 4. XRL Imaging Setup.

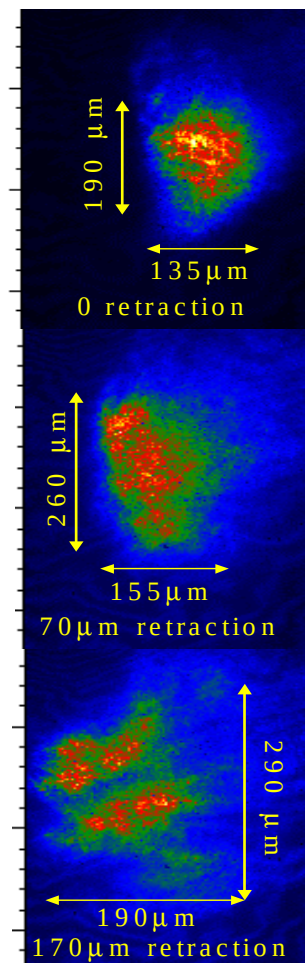


Figure 5. Image of Ne-like Ni XRL at exit point for 0, 70, 170 μm target retractions.

Figure 5 shows images of the XRL at different target retractions (i.e. the target is moved back from best focus) with the FWHM

of the spot size indicated. We can clearly see the increase in spot size as the target is retracted due to a larger area of the pre-plasma being heated by the main drive beams. The output energy of the XRL also increases as the target is retracted and peaks between 70-100μm retraction at ~15mJ, see Figure 6.

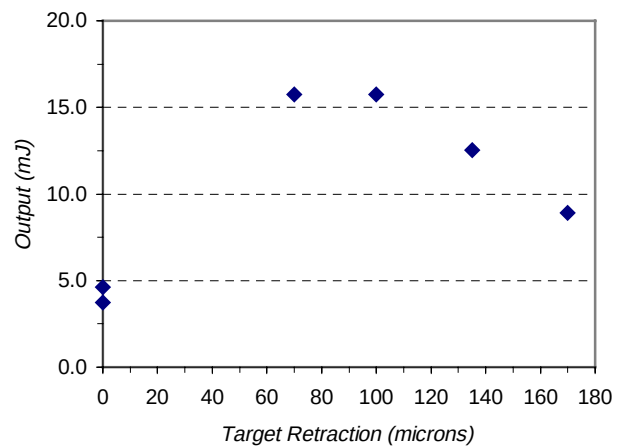


Figure 6. Ni XRL output dependence on target retraction.

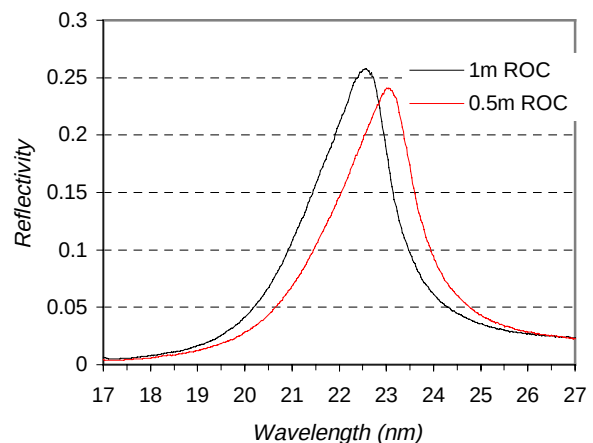


Figure 7. Measured reflectivity of multilayer mirrors.

Conclusions

From the Ne-like Ni XRL images we were able to obtain a value for the XRL output energy. This was based on measured reflectivity (at Queens University, see Figure 7) of the XRLs used in the imaging set-up and knowledge of the CCD sensitivity at 231Å. By comparing this value to the Ni XRL output energy from the FFS it was then possible to estimate the grating efficiency for the FFS, which was found to be 1%. The results from the Ge length scan will be used by York University to model the Ge XRL output energy using EHYBRID⁴⁾ and improve the quality of the simulation.

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Atomic data for modelling of lasers

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Introduction

Large laser amplification in the EUV and X-ray regions has been observed in the past, using particularly the Ne-like and Ni-like ions such as Gd, Se, Ge and Ti. For reliable modelling of the plasmas, atomic data for energy levels, radiative rates and excitation rate coefficients are required. There are many theoretical calculations for the Ne-like ions, but for Ni-like ions there are few - see, for example, Hagelstein¹⁾ and Zhang et al²⁾. Hagelstein has calculated the relevant atomic data for Ni-like Gd XXXVII, whereas Zhang et al have computed these for a series of ions with $60 \leq Z \leq 92$. Although these calculations involve a large number of fine-structure levels including those of $n=4$, and have included configuration interaction (CI) and relativistic effects, the works suffer from two major deficiencies. Firstly, the radiative rates and collision strengths are reported for the resonance transitions only, whereas data are also required for transitions among the excited levels. Secondly, these workers have used the Distorted Wave (DW) code for the computations of collision strengths (Ω), which they have computed at only a few energies above thresholds. Therefore, they have omitted resonances in the threshold region, which are likely to significantly contribute to the calculations of excitation rate coefficients, even at the high temperatures at which the data are required. Therefore, we aim to explore the contribution of resonances to the excitation rate coefficients, and to report the collision data for all transitions. Energy levels and radiative rates are calculated for six Ni-like ions namely, Nd XXXII, Sm XXXV, Eu XXXVI, Gd XXXVII, Ta XXXXVI, and W XXXXVII, whereas computations for Ω and excitation rates have been performed only for Gd XXXVII as a test case.

Energy Levels and Radiative Rates

To generate the wavefunctions, we have used the fully relativistic GRASP code of Dyall et al³⁾, and to calculate Ω the Dirac Atomic R-matrix Code (DARC) of Norrington and Grant⁴⁾. For the computations of energy levels and radiative rates, we have included the lowest 107 fine-structure levels arising from the $(1s^2 2s^2 2p^6) 3s^2 3p^2 3d^{10}$, $3s^2 3p^6 3d^9 4\ell$, $3s^2 3p^5 3d^{10} 4\ell$ and $3s 3p^6 3d^{10} 4\ell$ configurations. The specific list of these energy levels has already been reported^{5,6)}. However, the corresponding calculations for Ω are restricted to the lowest 59 levels because of computational limitations. CI has been included among the above listed configurations, and the option of EAL (extended average level), in which the weighted trace of a Hamiltonian is minimised, is chosen in the GRASP code. The calculations fully include the relativistic effects, and are in the jj coupling scheme.

Our calculated energy levels and radiative rates (A -values) for the above listed ions have already been reported by Aggarwal et al^{5,6)}. Our level energies agree excellently within 1 eV with those of Zhang et al²⁾ and with Fournier⁷⁾ for W XXXXVII. However, the orders of the levels is slightly different in a few instances. This is perhaps a direct consequence of the inclusion of larger CI by Zhang et al, as Hagelstein¹⁾ (who has used the same configurations as us) also obtains the same energy order for Gd XXXVII. However, the level energies of Hagelstein are the highest among the three calculations, and differ up to 5 eV,

corresponding to only $\sim 0.3\%$. Additionally, it must be emphasized here that because of strong mixing, especially among the higher levels, the identification of a particular level is sometimes ambiguous. At present, there is no unique way to identify each level, and the absence of experimental energies complicates this further. Therefore, it is possible that some of the levels may be misplaced.

The comparison of oscillator strengths (f -values) can be made for allowed transitions from the ground level only, as these are the only data available in the literature. Among 13 such transitions, the agreement between our f -values and those of others for the first 11 transitions are highly satisfactory, and are within 10%. However, differences are significantly large for the remaining two transitions. In particular, the f -value of Zhang et al²⁾ for the $1-95 (3s^2 3p^6 3d^{10} {}^1S_0 - 3s 3p^6 3d^{10} 4p_{3/2} {}^1P^o)$ transition in Sm XXXV is larger than ours by a factor of six, while differences in other instances range from 10% to a factor of three. Such large differences partly arise due to the inclusion of larger or smaller CI, but mostly because of the crossing over of the levels. However, neither do we see any indication for sudden enhancement in our calculations nor do we expect it from the general behaviour of f with Z . Inclusion of a larger set of orbitals ($n \geq 5$) in the calculations of Zhang et al²⁾ may be responsible for this abrupt increase in the values of f for some of the transitions. Generally, the inclusion of higher orbitals, and hence larger CI, improves the quality of wavefunctions but limited inclusion may not necessarily do so. To elaborate, it is possible that the inclusion of $n = 6$ orbitals may improve the f -values for the above transitions. However, in the absence of other calculations including larger CI, it is difficult to conclude which one of the two calculations is better. We have obtained accurate energy levels and a good agreement between the length and velocity forms of the oscillator strengths, and therefore, have confidence in our results.

The agreement between the length and velocity forms of our calculated oscillator strengths is within 20% for all the strong (i.e. $f \geq 0.10$) transitions. Exceptions to this are 2 transitions in Nd XXXIII, Sm XXXV and Eu XXXVI, and 1 transition in Gd XXXVII, Ta XXXXVI and W XXXXVII, for which the agreements are within 40%. Not only is this overall good agreement highly satisfactory, but it also gives a clear indication of the accuracy of the results. The agreement between the length and velocity forms for transitions with f -values < 0.10 is much poorer but is not unexpected given the large number of transitions considered. To conclude, the energy levels and the radiative rates reported for 6 Ni-like ions are fairly accurate, and are in excellent agreement with those available in the literature.

Collision Strengths

To compute our collision strengths, we have used the DARC program of Norrington and Grant⁴⁾. This program includes the relativistic effects in a systematic way, in both the target description as well as in the scattering model. It is based on the jj coupling scheme and uses the Dirac-Coulomb Hamiltonian in the R -matrix approach. However, because of the inclusion of fine-structure in the definition of channel coupling, the matrix

size of the Hamiltonian increases substantially, making the calculations computationally more expensive. For this reason, we had to restrict our computations of Ω to the lowest 59 levels. As a test case, we have first performed the calculations for Gd XXXVII. Those for other ions will be performed in future.

The details of the calculations have already been described by Aggarwal et al⁵⁾. To recapitulate, the R -matrix boundary radius has been taken to be 1.64 au, and 20 continuum orbitals have been included for each channel angular momentum for the expansion of the wave function. Contribution from all partial waves with angular momentum $J \leq 40.5$ has been included, Ω have been computed up to an energy of 800 Ryd, more than sufficient for the calculation of accurate excitation and de-excitation rate coefficients up to a temperature of 3×10^7 K.

Collision strengths at 4 representative energies of 200, 400, 600 and 800 Ryd for resonance transitions in Gd XXXVII have been presented and discussed by Aggarwal et al⁵⁾. Corresponding results for remaining transitions and at other energies may be obtained from the first author. At energies below 400 Ryd, the Ω of Hagelstein¹⁾ and Zhang et al²⁾ differ by less than 10% for most of the transitions and by 13% for one transition only (1-25) - see¹⁾ for level identification. However, at the highest electron energy (around 600 Ryd) at which Zhang et al have reported their Ω , the differences with our DARC calculations are rather striking, especially for the 1-3 and 1-5 transitions. For these two transitions, not only the RDW Ω values are higher by up to 25% but also appear to be out of place, as they show a sudden enhancement at this energy in contrast to the smoother variation of Ω at lower energies - see Figures 6 and 7 of Aggarwal et al⁵⁾. Other transitions which show a similar abrupt rise in the value of Ω at the highest energy of Zhang et al's calculations, are those with upper levels 20, 25, 30, 33, and 58. As noticed earlier, the RDW Ω are *higher* by up to 25% at the highest common energy. All of these transitions (including those two discussed above) are electric quadrupole (0^e-2^e) transitions, and hence are forbidden in the jj coupling scheme. The magnitudes of collision strengths for these transitions are comparatively small, and the contribution (if any) of the higher neglected partial waves is negligible. Therefore, we see no reason why the values of Ω for such forbidden transitions should rise at higher energies and conclude that the reported Ω of Zhang et al at the highest energy of their calculations are in error, at least for some of the transitions.

In the threshold energy region Ω have been computed at over 13000 energies in order to delineate resonances. Close to the thresholds the energy mesh is 0.001 Ryd and at energies below 96.50 Ryd, it is not greater than 0.002 Ryd. However, in the remaining threshold region (96.5 to 106.70 Ryd) it gradually but non uniformly increases up to 0.010 Ryd. This means that for transitions whose upper levels J are ≥ 35 (see⁵⁾ for level definitions), the energy mesh is comparatively coarser. However, this should not significantly affect the accuracy of the calculated excitation rates, as no large resonances have been observed in this energy range. The accuracy for rates is normally affected if there are large resonances and have not been resolved in a finer energy mesh in order to have their true widths, and hence may lead to an overestimation. On the other hand, there could be a possibility of missing a few resonances because of the coarser mesh adopted. A few tests made with a finer mesh in the above energy range have not shown any noticeable effects. Since this is contrary to what we observed in the range below 96.50 Ryd, we have confidence in our results.

Excitation Rate Coefficients

The only results available in the literature for the excitation rate coefficients are by Hagelstein¹⁾ for resonance transitions in Gd XXXVII. A comparison made between our presently calculated excitation rates and those of Hagelstein, shows that the resonances have enhanced the values of rates up to an order of magnitude at lower temperatures. But it is interesting to note that even at the highest temperature of the calculations i.e. $T_e = 2500$ eV, the contribution of resonances has enhanced the values of rates by over a factor of five for some of the transitions. For other transitions the effect of resonances has been comparatively smaller, and for transitions with their upper levels $J \geq 35$, the differences between the two sets of rates at the highest temperature are within 25%. The detailed results in the numerical form along with further comparisons will soon be presented. However, in Table 1 we present our preliminary results for some transitions, and the corresponding available results of Hagelstein¹⁾, at the lowest and the highest temperatures, have also been included for comparisons.

Conclusions

In conclusion, we have calculated energy levels and radiative rates among the 107 fine-structure levels of Ni-like ions. The experimental energy values for these levels are not available, but the agreement with other available theoretical energies is within 0.3%. Collision strengths at energies above thresholds have also been computed, for transitions among the lowest 59 levels of Gd XXXVII. The results obtained for Ω have been compared with those available, and are found to be in excellent agreement (within 10%), but at energies below 400 Ryd only. At higher energy, the differences are of up to 25% for some of the forbidden transitions, for which the earlier available RDW Ω are overestimated. Since a large range of partial waves has been included in order to obtain convergence, and relativistic (and CI, although limited) effects have also been included in both the target description and the scattering model, we expect our results of Ω to be accurate to within 10%. The differences among various calculations for the f -values are more pronounced, although the agreement between the length and velocity forms in our calculations is generally within 10%. Excitation rates computed for resonance transitions in Gd XXXVII are found to be enhanced, in comparison with those obtained from non resonant Ω , by about an order of magnitude for many transitions. We hope these new results will be of significant use in laser applications.

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Transition	$T_e=500^h$	500	700	1000	1500	2000	2500	2500 ^h
1- 2	3.283-13	4.782-12	5.494-12	5.270-12	4.268-12	3.411-12	2.778-12	4.638-13
1- 3	1.110-12	1.018-11	1.218-11	1.228-11	1.072-11	9.201-12	8.015-12	2.903-12
1- 4	1.370-13	2.037-12	2.399-12	2.344-12	1.925-12	1.548-12	1.265-12	2.014-13
1- 5	7.666-13	5.788-12	7.034-12	7.203-12	6.402-12	5.571-12	4.906-12	2.053-12
1- 6	2.898-13	2.645-12	3.245-12	3.289-12	2.798-12	2.302-12	1.912-12	4.746-13
1- 7	5.305-13	3.234-12	4.047-12	4.228-12	3.792-12	3.287-12	2.871-12	1.268-12
1- 8	2.132-13	2.149-12	2.659-12	2.704-12	2.300-12	1.888-12	1.565-12	3.517-13
1- 9	9.426-13	6.347-12	8.234-12	9.073-12	8.916-12	8.454-12	8.015-12	3.778-12
1-10	3.678-13	1.592-12	2.044-12	2.169-12	1.937-12	1.645-12	1.398-12	6.265-13
1-11	2.005-13	1.609-12	2.020-12	2.086-12	1.804-12	1.498-12	1.251-12	3.494-13
1-12	2.000-12	7.508-12	1.032-11	1.229-11	1.343-11	1.379-11	1.387-11	8.772-12
1-13	2.827-13	1.611-12	2.058-12	2.192-12	2.007-12	1.767-12	1.561-12	7.379-13
1-14	7.167-14	2.696-13	3.604-13	3.962-13	3.663-13	3.177-13	2.740-13	1.354-13
1-15	3.029-13	1.312-12	1.790-12	2.069-12	2.132-12	2.078-12	2.005-12	1.132-12
1-16	4.018-13	1.331-12	1.799-12	2.035-12	1.995-12	1.843-12	1.688-12	1.105-12
1-17	1.197-13	8.805-13	1.130-12	1.187-12	1.040-12	8.691-13	7.287-13	2.144-13
1-18	4.759-13	8.647-13	1.275-12	1.530-12	1.537-12	1.399-12	1.247-12	9.724-13
1-19	4.942-13	8.517-13	1.274-12	1.564-12	1.634-12	1.549-12	1.433-12	1.127-12
1-20	4.791-13	8.913-13	1.323-12	1.616-12	1.686-12	1.602-12	1.488-12	1.282-12
1-21	3.367-13	7.094-13	1.020-12	1.190-12	1.156-12	1.028-12	8.995-13	6.177-13
1-22	2.926-13	1.491-12	2.048-12	2.281-12	2.113-12	1.826-12	1.568-12	5.874-13
1-23	6.000-13	1.012-12	1.515-12	1.840-12	1.860-12	1.696-12	1.510-12	1.179-12
1-24	3.851-13	7.710-13	1.134-12	1.354-12	1.345-12	1.214-12	1.073-12	7.598-13
1-25	1.092-12	1.396-12	2.285-12	3.151-12	3.846-12	4.116-12	4.195-12	4.238-12
1-26	2.972-13	5.657-13	8.438-13	1.025-12	1.048-12	9.711-13	8.802-13	6.388-13
1-27	9.633-13	1.711-12	2.700-12	3.554-12	4.082-12	4.170-12	4.098-12	3.411-12
1-28	2.483-13	1.909-12	2.608-12	2.870-12	2.609-12	2.222-12	1.885-12	5.192-13
1-29	3.308-13	9.016-13	1.319-12	1.554-12	1.514-12	1.347-12	1.178-12	6.774-13
1-30	6.444-13	9.958-13	1.605-12	2.174-12	2.604-12	2.755-12	2.788-12	2.571-12
1-31	2.939-13	5.079-13	7.704-13	9.454-13	9.653-13	8.859-13	7.926-13	6.349-13
1-32	4.261-13	6.779-13	1.051-12	1.326-12	1.415-12	1.354-12	1.259-12	1.027-12
1-33	4.771-13	7.301-13	1.163-12	1.527-12	1.730-12	1.744-12	1.697-12	1.534-12
1-34	2.777-13	5.216-13	7.769-13	9.337-13	9.300-13	8.383-13	7.396-13	5.411-13
1-35	1.416-11	1.600-11	2.868-11	4.226-11	5.375-11	5.817-11	5.936-11	5.619-11
1-36	1.160-13	1.440-13	2.417-13	3.228-13	3.546-13	3.385-13	3.104-13	2.848-13
1-37	1.102-12	1.099-12	2.273-12	3.909-12	5.952-12	7.326-12	8.230-12	7.011-12
1-38	2.107-13	2.429-13	4.076-13	5.434-13	5.948-13	5.661-13	5.180-13	5.068-13
1-39	6.046-13	6.830-13	1.176-12	1.624-12	1.875-12	1.877-12	1.799-12	1.628-12
1-40	6.398-13	6.750-13	1.138-12	1.521-12	1.663-12	1.579-12	1.441-12	1.436-12
1-41	3.518-13	3.902-13	6.687-13	9.172-13	1.053-12	1.052-12	1.009-12	9.291-13
1-42	6.683-13	6.199-13	1.048-12	1.400-12	1.526-12	1.444-12	1.314-12	1.285-12
1-43	4.582-13	3.946-13	6.621-13	8.778-13	9.499-13	8.947-13	8.114-13	7.173-13
1-44	4.668-13	4.528-13	7.635-13	1.019-12	1.114-12	1.061-12	9.712-13	9.367-13
1-45	4.806-13	3.495-13	5.842-13	7.708-13	8.291-13	7.776-13	7.027-13	6.043-13
1-46	5.285-13	4.288-13	7.251-13	9.671-13	1.051-12	9.927-13	9.016-13	8.268-13
1-47	3.844-13	2.530-13	4.255-13	5.673-13	6.235-13	5.997-13	5.566-13	4.349-13
1-48	8.288-13	8.213-13	1.566-12	2.440-12	3.280-12	3.678-12	3.848-12	3.831-12
1-49	7.041-12	7.056-12	1.413-11	2.319-11	3.319-11	3.902-11	4.238-11	3.832-11
1-50	5.879-13	6.266-13	1.077-12	1.460-12	1.616-12	1.544-12	1.415-12	1.396-12
1-51	3.921-13	3.531-13	6.093-13	8.261-13	9.108-13	8.670-13	7.917-13	7.849-13
1-52	3.443-13	3.263-13	5.600-13	7.557-13	8.297-13	7.876-13	7.177-13	6.882-13
1-53	2.800-13	3.019-13	5.311-13	7.430-13	8.667-13	8.738-13	8.432-13	7.808-13
1-54	2.733-13	2.594-13	4.473-13	6.072-13	6.734-13	6.462-13	5.952-13	5.798-13
1-55	6.835-13	6.816-13	1.311-12	2.047-12	2.746-12	3.069-12	3.202-12	3.201-12
1-56	4.588-13	2.678-13	4.588-13	6.163-13	6.716-13	6.334-13	5.741-13	4.569-13
1-57	8.032-14	8.371-14	1.494-13	2.096-13	2.402-13	2.350-13	2.193-13	2.176-13
1-58	4.416-13	4.231-13	8.460-13	1.375-12	1.928-12	2.221-12	2.370-12	2.325-12
1-59	3.581-11	3.641-11	7.499-11	1.258-10	1.835-10	2.179-10	2.381-10	2.118-10

Table 1. Excitation rates (cm^3/s) for some transitions in Gd XXXVII as a function of T_e (in eV). The superscript h denotes the results of Hagelstein¹⁾. $a \cdot b \equiv a \times 10^{-b}$.

Atoms and molecules in intense laser fields using the R-matrix Floquet approach

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Introduction

The study of multi-electron atoms and molecules in strong laser fields has been one of the areas of atomic and molecular physics that has attracted considerable interest over the last decade. Since the atomic structure is significantly disturbed when the magnitude of the laser field becomes comparable to the magnitude of the inter-particle interactions, many surprising phenomena, such as high-harmonic generation, have been observed experimentally for atoms in strong laser fields. To obtain a coherent understanding of these phenomena, many theoretical approaches have been proposed, ranging from extensive time-dependent calculations^{1,2)} to simple model calculations^{3,4)}.

We are particularly interested in the development of a time-independent method for the description of atoms and molecules in strong laser fields: the R-matrix Floquet approach^{5,6)}. In the R-matrix Floquet approach, the time-dependent wave function of the system is transformed into a time-independent one by the Fourier-Floquet Ansatz. As a consequence of this Ansatz, the net number of photons absorbed or emitted becomes an integral part of the wave function.

In the present report, we describe some recent advances made for two systems in particular, H_2 and Ar^{7+} . A recent paper⁶⁾ discussed R-matrix-Floquet theory applied to molecular multi-photon processes. At present, this theory describes the interaction of intense linearly polarized laser fields with arbitrary multi-electron diatomic molecules, and forms the beginning of a program of work, which aims to complement recent experimental work on multi-photon ionization processes in light molecules. In order to evaluate the merits of the molecular R-matrix Floquet code, we presently concentrate our attention on H_2 .

In addition to molecular processes, atomic processes in intense laser fields are of strong topical interest. For example, highly-charged ions have been studied extensively at the Central Laser Facility⁷⁾. Very few multi-photon calculations have been performed for highly-charged ions, but the characteristics of the R-matrix Floquet approach are such that calculations for highly-charged ions in intense laser fields should be significantly simpler and faster than calculations for neutral atoms in intense laser fields. In response to the experimental interest, we have started a program to examine highly-charged ions in intense laser fields.

Multi-photon ionization of H_2

A comprehensive study of one-, two- and four-photon ionization rates for H_2 has recently been published⁸⁾. Here we examine four-photon ionization rates for H_2 calculated at the frequency of the KrF laser. A one-state approximation is used to describe the H_2^+ target state. The accuracy of this approximation is discussed in more detail in⁸⁾. We present results for four-photon ionization at the KrF laser frequency for a range of intensities and for three internuclear separations, $R=1.2$ a.u., 1.4 a.u. and 1.6 a.u. It is well known that as the laser intensity increases, the ionization potential increases by approximately the ponderomotive energy and in a similar way

also the energy levels of excited bound states increase. Hence as the intensity increases the energy of four-photon absorption relative to the $v=0$ vibrational level of the H_2^+ ground state decreases and so the intensity dependence in Figure 1 is from right to left. The upper axis in Figure 1 gives this intensity dependence for the internuclear separation $R=1.4$ a.u. For $R=1.2$ a.u. and $R=1.6$ a.u. the intensity dependence is only slightly different. The results in Figure 1 indicate that at an intensity of 3.10^{13} W/cm², the KrF laser frequency is close to resonance with the second excited state when $R=1.4$ a.u. However, when the intensity has increased to about $1.7.10^{14}$ W/cm² the KrF laser frequency corresponds to a resonance between the ground state and the first excited state. This gives rise to the large resonance-enhanced multi-photon ionization (REMPI) peak in the $R=1.4$ a.u. curve in the centre of Figure 1. Peaks are also found in the $R=1.2$ a.u. and $R=1.6$ a.u. curves due to the resonance with the first excited state of H_2 . These occur for different intensities and hence different energies relative to the $v=0$ vibrational level of H_2 .

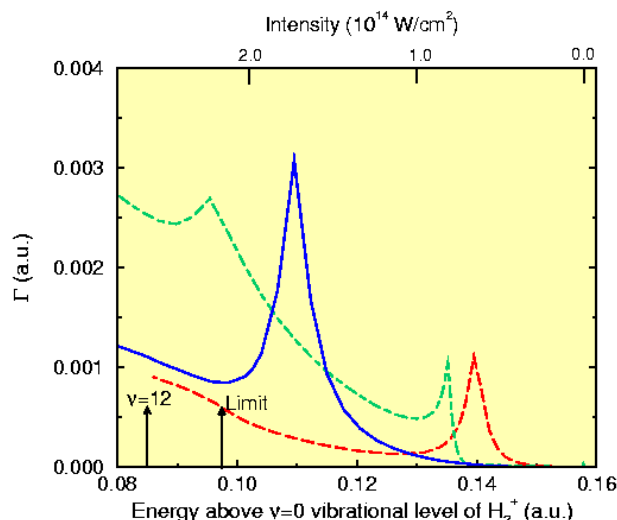


Figure 1. Four-photon ionization rates at the KrF laser frequency are shown for internuclear separations of $R=1.2$ a.u. (green dot-dashed curve), $R=1.4$ a.u. (blue solid curve) and $R=1.6$ a.u. (red dashed curve). The lower axis gives the energy in a.u. above the H_2^+ $v=0$ ground state and the upper axis gives the corresponding intensity of the laser in 10^{14} W/cm² when $R=1.4$ a.u.

Also marked in Figure 1 are the $v=12$ vibrational level of the $H_2^+ \ ^2\Sigma_g^+$ ground state and the dissociation limit. The energy above the $v=0$ level will be divided between the photoelectron and vibronic excitation or dissociation of the residual molecular ion. These results indicate that as the laser intensity (and also frequency) is varied the energy available for these processes also varies. This suggests that varying the laser parameters should enable the population in different vibrational levels of the residual ion to be controlled due to resonance effects. This could be important in a number of ways. Consider, for example, experiments on the multi-photon ionization of the H_2^+ ion.

Since this ion is often formed by the prior multi-photon ionization of H_2 , the vibrational population in H_2^+ could depend critically on the parameters of the laser being used.

In order to gain further information about H_2 multi-photon ionization a more complete non-adiabatic treatment of the nuclear motion is required, analogous to that adopted in field-free studies of electron-molecule scattering⁹⁾. These further investigations, the subject of our current work, should also yield information that will enable the vibrational population of the residual H_2^+ ion to be manipulated in a controlled fashion by varying the laser intensity and frequency.

Multi-photon ionization of Ar^{7+}

Recently, Ar^{7+} has been suggested as a medium in which non-linear effects with X-ray lasers can be observed in a four wave sum difference frequency scheme⁷⁾. Following this interest from experiment, we have started to investigate Ar^{7+} using the R-matrix Floquet approach. Ar^{7+} is Na-like and the atomic structure is therefore quite simple: a single electron outside a closed core. Using the Clementi-Roetti data tables for the 1s, 2s and 2p orbitals¹⁰⁾, it is then straightforward to create a basis set, which is sufficiently accurate to describe the Rydberg states in detail.

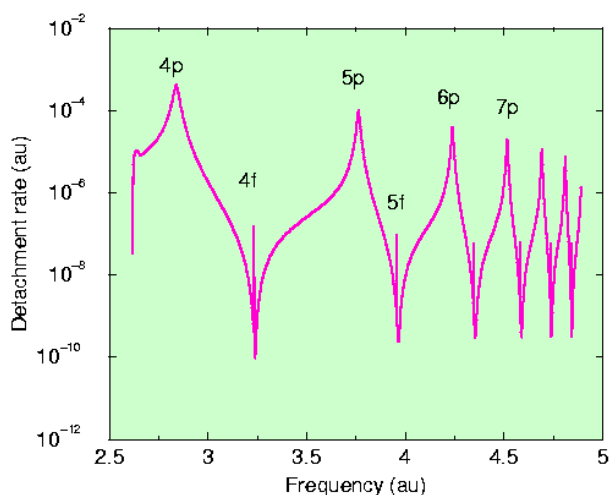


Figure 2. Photoionization rates for the 3s state of Ar^{7+} .

We have started by examining the two-photon ionization rates for Ar^{7+} initially confined to either the 3s and 3p states at an intensity of 10^{15} W/cm^2 . This is a rather large intensity, but it is needed to obtain ionization rates of a reasonable magnitude: when the ionization rates become too small, it becomes very difficult to obtain sufficiently good initial guesses for the position of the initial state. In Figure 2, we show the two-photon ionization rate for the 3s state as a function of frequency. The main resonances in the spectrum belong to the np series, although the excitation of the nf series can also be observed. The spectrum clearly shows that there is a huge influence of the resonances on the two-photon ionization rates.

In Figure 3, we show the two-photon ionization rates for the 3p state. Photoionization can now proceed through two sets of intermediate resonances: the ns and nd Rydberg series. Both series can be identified prominently in the photoionization spectrum. The resonances dominate the photoionization spectrum at this intensity completely: the rapid increases and decreases as one tunes the frequency into and out of resonance indicate that the spectrum is essentially determined by the distance from a resonance. Even then, it can be observed that very small ionization rates can be seen even at an intensity of 10^{15} W/cm^2 : at a frequency of 3.4 a.u., the ionization rate does not exceed $5 \cdot 10^{-10}$ a.u.. Reducing the intensity to lower values would make calculations at these frequencies nearly impossible.

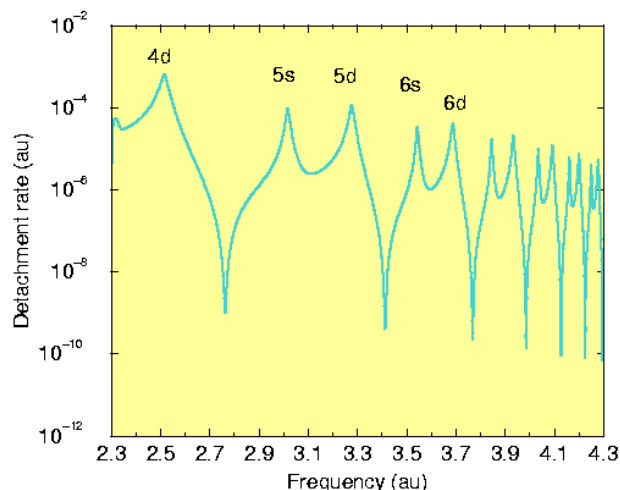


Figure 3. Photoionization rates for the 3p state of Ar^{7+} .

Conclusion

The R-matrix Floquet approach is a valuable tool in describing atoms and molecules in strong laser fields. On the molecular side, we have applied the approach to study four-photon ionization of H_2 . The present results demonstrate the feasibility and the validity of the approach. Building upon this success several new developments can be envisaged: to extend the approach to more complicated diatomic molecules, to treat a laser field direction perpendicular to the molecular axis, and the inclusion of the vibrational motion.

On the atomic side, we have applied the approach to two-photon ionization of Ar^{7+} . Future calculations initially will entail studying the behaviour of the 3s and 3p states in the frequency region corresponding to the Ne-like Nd laser frequency. Subsequently it is envisaged that Ar^{7+} will be studied in two-colour fields using the two-colour R-matrix Floquet approach.

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Interaction of Relativistically Self-Focussed Light Filaments

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Introduction

There is a long history of the study of light filaments trapped or self-focussed by the non-linear refractive index of the medium in which the light is propagating. Non-linearity typically arises from the atomic or thermal properties of the propagation medium and in the case of a plasma there are two quite distinct effects. At very high intensities ($v_0 \sim c$) there is the relativistic non-linearity where the increased mass of electrons oscillating in the intense laser field acts to reduce the plasma frequency and hence increase the refractive index. On longer time scales there is also the ponderomotive effect where plasma electrons are expelled from the laser focus, again reducing the plasma frequency and operating whenever $v_0 \sim v_{th}$.

The threshold and dynamics of self-focussing of single light filaments are well studied, usually using the paraxial approximation for propagation of the light wave and sometimes using variational methods so that the functional form of the distribution of light intensity is assumed and parameters such as the width and central intensity are followed.

Related Work

Investigation of the interaction of multiple light filaments in plasma is rather more limited. Sartang, Evans and Toner¹⁾ followed the evolution of the paraxial wave equation (non-linear Schrodinger equation) in the presence of a ponderomotive type of non-linearity and observed filaments combining and splitting in different circumstances. Wilks et al²⁾ looked at cases of strong self-focussing followed by spreading and beam breakup. Vidal and Johnston³⁾ showed the formation of multiple filaments from a single intense laser but did not follow the interaction of the filaments. Berger et al⁴⁾ simulated filamentation and Brillouin scatter occurring at the same time.

A very comprehensive paper by Schmitt⁵⁾ includes analytic and numerical treatment of filamentation, the break up of single beams into multiple filaments and the statistical effects of changing laser beam patterns as a function of time (ISI). Ren et al⁶⁾ used a fully three dimensional PIC model of laser light in a plasma to demonstrate the mutual attraction of two skew beams which results in the light filaments twisting and forming a braided pattern. The simple dynamics of the braiding were reproduced using a variational method to follow the centroids of two Gaussian beams.

In the non-plasma context Stegeman and Segev⁷⁾ review the interaction of optical solitons

Detailed Interaction of Two Filaments

The work described here uses the same PIC code as Ren et al⁶⁾ (Hemker⁸⁾) but in its 2-1/2 dimensional form, to simulate beams of light with no gradients in the third (x_3) dimension although all three components of E , B , and j exist.

The simulation region is $225c/\omega_p$ units in the direction of propagation (x_1) and $75 c/\omega_p$ in the transverse direction x_2 . Two laser beams are introduced at the $x_1 = 0$ boundary, $10 c/\omega_p$ across and with their centres at $x_2 = 25c/\omega_p$ and $x_2 = 50 c/\omega_p$. The simulation is shown schematically in Figure 1.

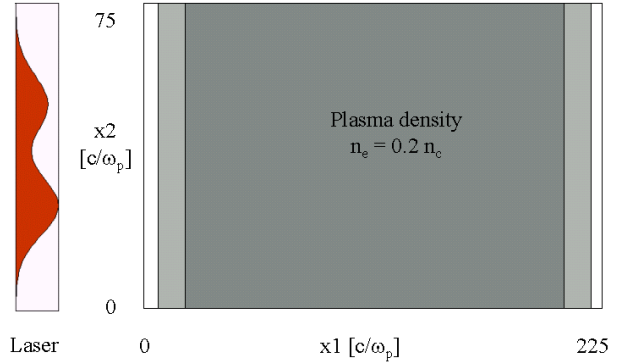


Figure 1. Schematic of the PIC simulation of two laser beams entering a uniform slab of plasma.

The plasma is a uniform slab at $n_e = 0.2n_c$ with two small ‘ramps’ at the entrance and exit planes to minimise surface effects. The laser beams are defined in terms of their dimensionless amplitude $a_0 = (eE/m\omega c)$ and have $a_0 = 2$ and $a_0 = 3$ to provide a degree of asymmetry to the calculation. Both beams are well above the threshold for relativistic self-focussing. The laser beams ‘turn on’ with a risetime of around $20 \omega_p^{-1}$.

The simulation proceeds up to a time $t = 332 \omega_p^{-1}$ at which the laser pulses have propagated across the whole of the mesh. The simulation uses ions with a mass of $1836 m_e$ so $332 \omega_{pe}^{-1}$ is equivalent to $7.8 \omega_{pi}^{-1}$ and there is plenty of time for the ions and electrons to move in response to the ponderomotive forces. The simulation is thus of a mix of relativistic and ponderomotive self-focussing. Figure 2 shows the E_2 field representing the main component of the laser light at $t = 332 \omega_p^{-1}$.

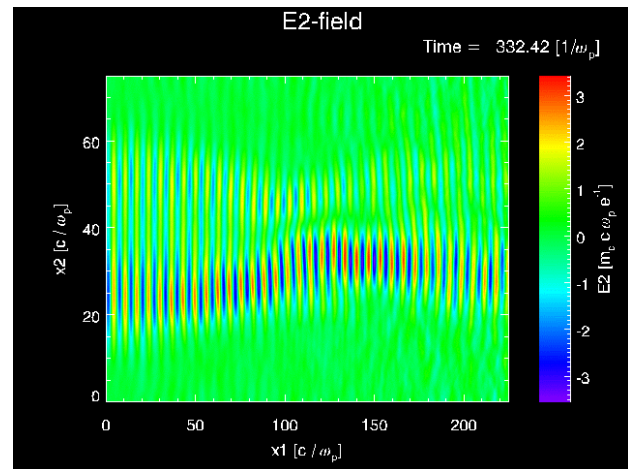


Figure 2. The transverse (E_2) component of the laser waves at a time of $t = 332 \omega_p^{-1}$.

The simulation shows the two filaments attracting each other in the manner of Ren et al⁽⁶⁾ but since the intensities are unequal the phase difference between the two filaments changes and at $x_1 = 140 \text{ c}/\omega_p$ the phase difference has amounted to 180 degrees. From this point on the filaments repel each other and begin to break up. The more intense beam has acquired some of the energy of the less intense beam during the interaction.

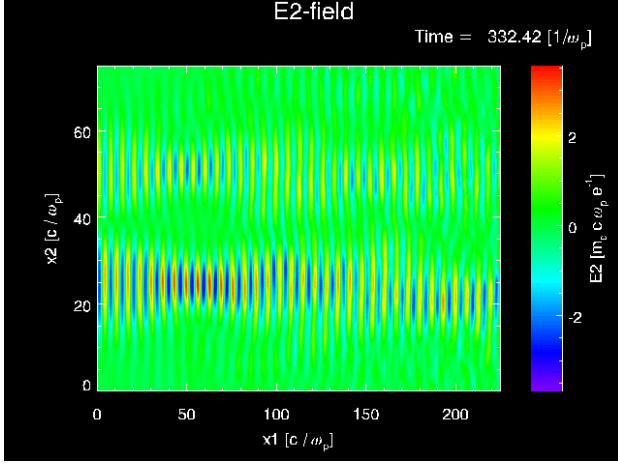


Figure 3. The same simulation as of Figure 2 but with the initial phase of one of the laser beams shifted by 180 degrees.

In Figure 3 we show the results of the same simulation except that the initial phase of one of the beams is changed by 180 degrees. The result is less obvious than the previous simulation but we see that while the relative phase of the beams is close to 180 degrees they repel each other and when the relative phase has drifted back to being closer to 0 degrees they again attract. In this case the attraction and repulsion repeats before the beams start to break up.

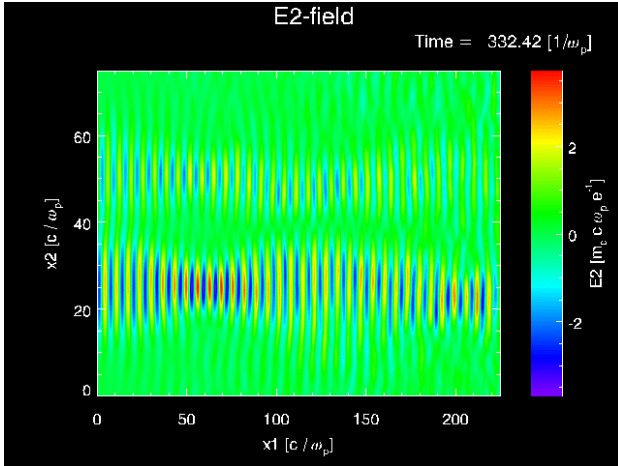


Figure 4. The same simulation as of Figure 2 but with the initial phase of one of the laser beams shifted by 90 degrees.

In Figure 4 we show the simulation repeated with an initial phase difference between the two beams of 90 degrees. The interaction is much weaker but closer examination reveals that the quadrature phase fronts first become out of phase with a weak repulsion before becoming in-phase and attracting each other.

For completeness we show in Figure 5 the ion charge density at the same time as the electric field plot of Figure 3.

The ion density is initially uniform at $0.2n_c$ and we see that the ponderomotive force of each laser beam has produced a density channel down to $n_e = 0.1n_c$ which adds to the strength of the relativistic self-focussing effect.

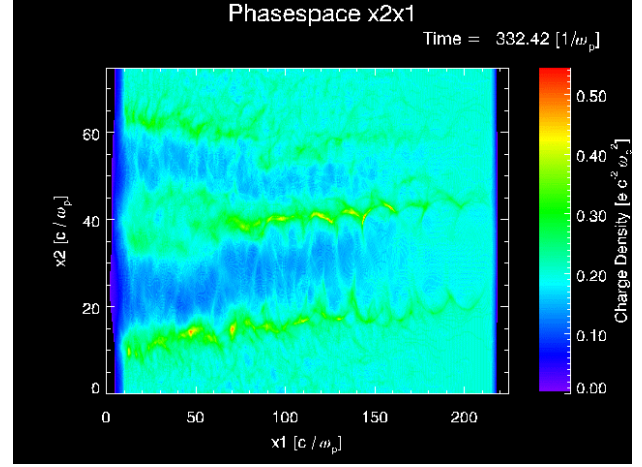


Figure 5. The ion density at the same time as Figure 3 showing the density channels produced by the ponderomotive component of the self-focussing.

Discussion

This change from attraction to repulsion according to the relative phase of the two beams has analogies in the similar behaviour of ideal optical solitons⁽⁵⁾. When the beams are in anti-phase the intensity between the two beams goes to zero and so the intensity and therefore the phase gradient is greater between the beams than outside. Conversely when the beams are in phase the intensity and phase gradient is less in between the beams than outside. The net phase gradient across each beam is a deflecting force towards the side with the greater phase retardation, i.e. inwards when the beams are in-phase and outwards when the beams are out of phase.

If this is an adequate explanation of the effects observed in the self-consistent electro-magnetic plasma calculation we should be able to mimic the effect in a simple model which follows the paraxial propagation in a non-linear medium but which ignores the remainder of the plasma behaviour including Raman side-scattering electron acceleration and ponderomotive self-focussing.

A Simpler Model

Our simple model is based on that of Sartang et al⁽¹⁾ which numerically solves the paraxial (i.e. envelope) equation for the propagation of light in one longitudinal and one transverse direction in a non-linear medium. We include the full form of the relativistic refractive index:

$$\mu = \sqrt{\frac{1 + a_0^2}{1 + a_0^2 - \frac{n_e}{n_c}}}$$

This implies that $\mu \rightarrow 1$ as $a_0 \rightarrow \infty$ i.e. the non-linearity saturates at high intensity in contrast to the simple cubic non-linearity of the ideal soliton. In order to obtain maximum accuracy with a second order Lax Wendroff differencing we need to iterate to a self-consistent value of the non-linear refractive index.

The results are shown in Figures 6, 7 and 8.

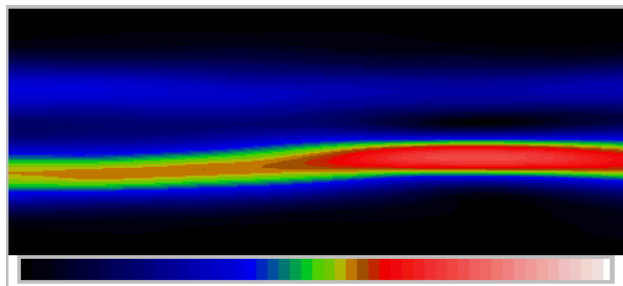


Figure 6. The paraxial simulation of the interaction of two light filaments for the same initial parameters and spatial scales as Figure 2. The colour bar for amplitude a_0 ranges linearly from 0 to 5. The filaments attract but more slowly than in Figure 2.

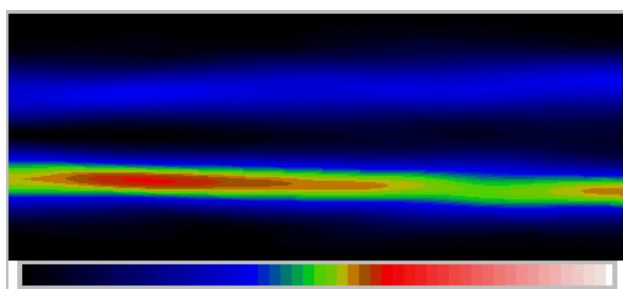


Figure 7. The paraxial simulation repeated but with the initial amplitude of one beam reversed as in Figure 3. The colour scale is as in Figure 5. There is now weak repulsion between the two beams.

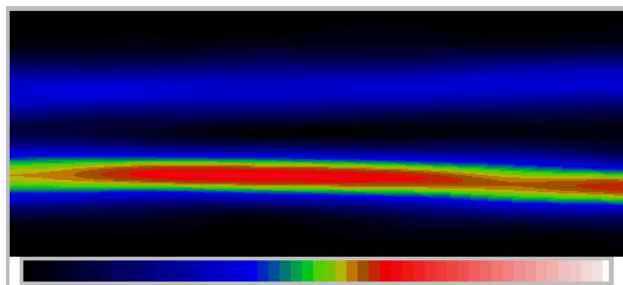


Figure 8. The simulation repeated again but with an initial phase difference between the two beams of 90 degrees. The interaction is initially weaker leading to repulsion at later times.

The simple paraxial model does not reproduce the details of the full PIC simulations but good qualitative agreement is obtained in all three cases. The in-phase case shows the beams attracting and the more intense beam growing at the expense of the weaker beam. The initially out of phase case shows a weaker repulsion of the beams and a second self-focussing. The quadrature simulation shows the weakest of all the interactions leading eventually to weak repulsion. In view of the fact that the simple model has a weaker self-focussing force due to the omission of the ponderomotive effect we consider this overall similarity to give good confirmation that the explanation given earlier of attraction or repulsion of filaments based on their relative phase is essentially correct.

Other work has shown that the influence of the mutual Raman scattering between the beams and the electron currents induced by particle acceleration may be important in some circumstances but to lowest order the two filament interaction appears to be dominated by the simple non-linear optics phenomena.

Acknowledgement

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Magnetic Field Penetration into Warm Plasma – Electron heating and Rayleigh Taylor Instability

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Introduction

This study is motivated by the recent experiment of Woolsey et al¹⁾ at the CLF, designed to produce plasma conditions which would enable the study of a magnetised collisionless shock in the laboratory with application to a variety of astrophysically interesting situations. One of the open questions in that experiment is to what extent an external magnetic field can penetrate a pre-formed laser plasma.

The simplest argument is that the laser plasma is almost collisionless, of high electrical conductivity and so the magnetic field will be shielded out of the interior of the plasma by a skin current. The skin current and the penetration of the field will be limited to a collisionless skin depth c/ω_p . Inclusion of the finite conductivity for the conditions of Reference 1 leads to a penetration of less than twice the collisionless value.

Further consideration²⁾ shows that for large magnetic fields the magnitude of the skin current implies an electron drift velocity greater than the electron thermal speed and the possibility that ion-acoustic turbulence may give rise to an increased resistivity and increased penetration depth. Moreover once the magnetic pressure becomes greater than the plasma pressure there is also the possibility of a Rayleigh Taylor type fluid instability as the ‘low density’ magnetic field attempts to accelerate the ‘high density’ plasma. These two effects occur on different time scales, the ion acoustic turbulence growing on a time scale of $1/\omega_{pi}$ while the Rayleigh Taylor modes will grow on a longer hydrodynamic timescale.

The precise value of the electron drift velocity needed to initiate the ion-acoustic turbulence is not well established under all conditions but if we assume that the condition may be written $v_{crit} = \alpha v_e$ where v_e is the electron thermal velocity and the skin current flows only in a collisionless skin depth c/ω_p then we can derive the interesting relationship

$$(B^2/8\pi)/(n_e m_e v_e^2) = \alpha^2 / 16\pi \quad (1)$$

Most theories of current driven ion-acoustic turbulence give a value for α of the order of $(m_e/m_i)^{1/2}$, i.e. $\alpha \ll 1$, so this equation gives an ordering for the appearance of the turbulent skin current and Rayleigh Taylor instabilities. If the pressure of the magnetic field is smaller than the plasma electron pressure by more than the factor of $\alpha^2/16\pi$ then neither of the instabilities should occur. As the magnetic pressure increases first the current driven instability appears when the magnetic pressure is still much less than the plasma pressure but the Rayleigh Taylor instability will not appear until the magnetic pressure becomes comparable to the plasma pressure and is capable of imparting significant acceleration to the plasma.

This situation is related to the tearing modes of magnetically confined plasmas and the disruption phenomena that initiate solar flares. In all cases the initial magnetic field energy is destroyed by instabilities which break the original symmetry much faster than would be deduced from purely collisional time scales.

Simulations

While the Rayleigh Taylor aspects of the above problem can be simulated using MHD methods which are more efficient for long time scale problems we have taken advantage of the availability of the PIC code Osiris²⁾ which runs efficiently on

multiple parallel processors and simulated the problem for long enough to observe both effects described above.

There is an intrinsic difficulty in setting up the problem described above since the source of the magnetic field is typically of dimensions much larger than can be included self-consistently in the model. Attempting to initialise a magnetic field at $t=0$ is not viable since it assumes just that which we are trying to calculate. Instead we have introduced additional particle species into Osiris which form a current sheet and which can be accelerated by fictitious external forces. The initial condition with $j = 0$ is then field-free and as the current sheet grows the magnetic field propagates away from the source at the speed of light and interacts with the test plasma to form a self-consistent solution.

We have chosen to make the particles of the skin current very massive and so resistant to any back reaction from the plasma. In the real world problem the reaction back on the field sources is largely irrelevant due to the transit time delays.

The magnetic field rise time must be slow, ie $10 - 100 \times \omega_p^{-1}$ so that there is little magnetic energy in the Fourier components with frequencies greater than the plasma frequency which can directly penetrate the test plasma.

The initial conditions of the PIC simulation are shown in Figure 1 with the dimensions in units of c/ω_p . x_1 and x_2 are the space coordinates of the simulation while all x_3 derivatives are zero.

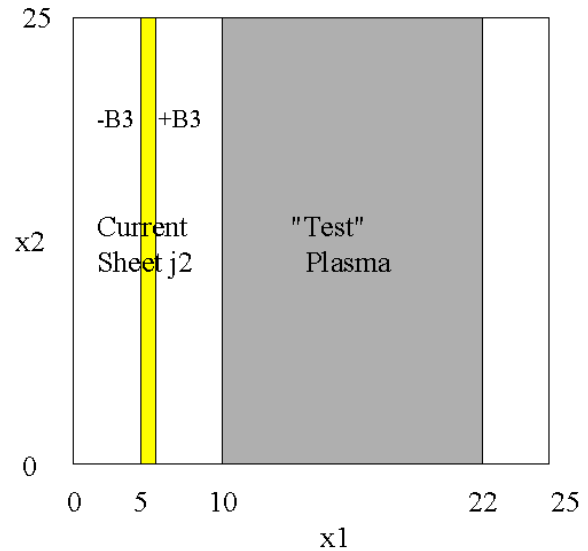


Figure 1. Schematic of the Osiris simulation.

The simulation evolves with the current sheet growing from $J = 0$ at $t=0$ to a steady value at $t=100\omega_p^{-1}$ which gives a magnetic field of $0.7 m c \omega_p / e$ between the current sheet and the test plasma.

As the simulation proceeds the expected skin current appears (Figure 2) and this skin current eventually becomes turbulent (Figure 3).

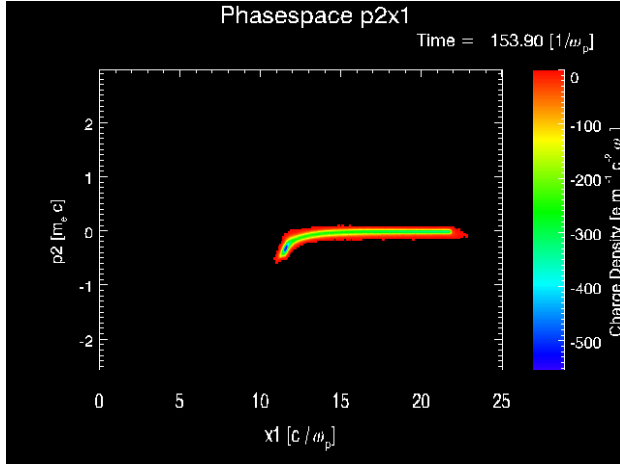


Figure 2. Electron phase space at $t = 153.9 \omega_p^{-1}$ showing the skin current in the test plasma in the x2 direction induced by the applied magnetic field B3 and decaying over the collisionless skin depth c/ω_p .

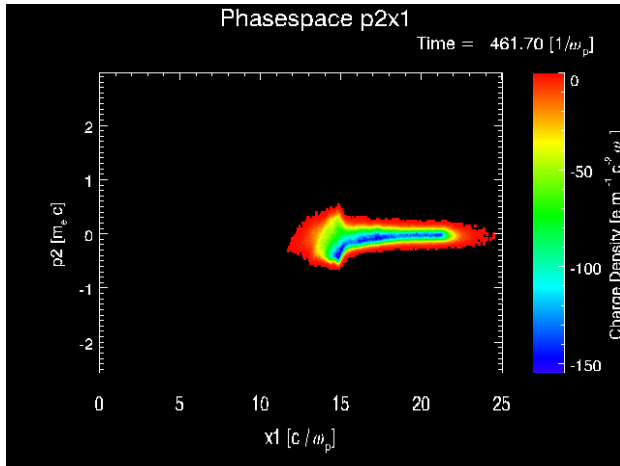


Figure 3. Electron phase space at $t = 461 \omega_p^{-1}$ showing the spread in electron velocities as turbulence develops in the transverse skin current.

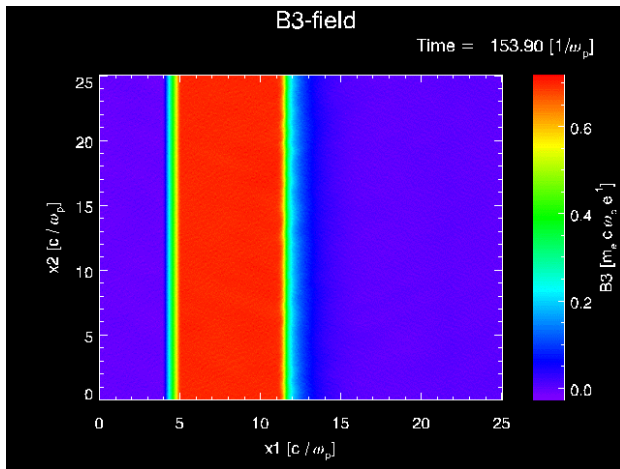


Figure 4. Magnetic field out of the plane of the simulation at $t = 153.9 \omega_p^{-1}$ showing the almost planar interface with the test plasma.

At the same time that turbulence and heating has been developing in the region of the induced skin current, the test plasma has been accelerating under the influence of $j_{\text{skin}} \times B$.

The profiles of B3, the main component of applied magnetic field, show a development of surface ripples reminiscent of the Rayleigh Taylor fluid instability. This sequence is shown in Figures 5, 6 and 7 with the characteristic non-linear Rayleigh Taylor behaviour that small wavelength modes grow fastest but also saturate soonest leaving longer wavelength modes dominant at later times.

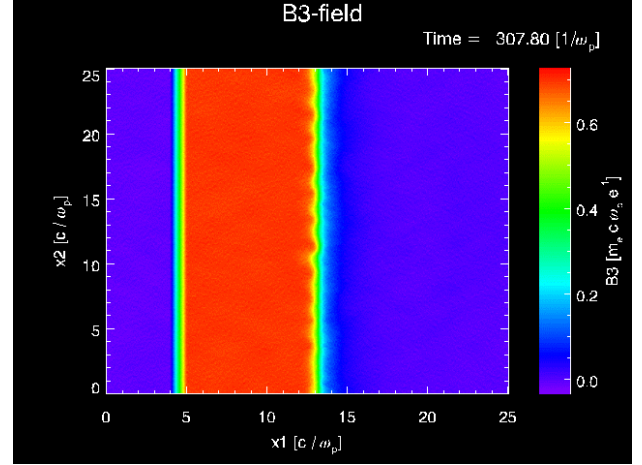


Figure 5. Magnetic field at $t = 307.8 \omega_p^{-1}$ showing the instability developing with a wavelength around $2 - 3 c/\omega_p$.

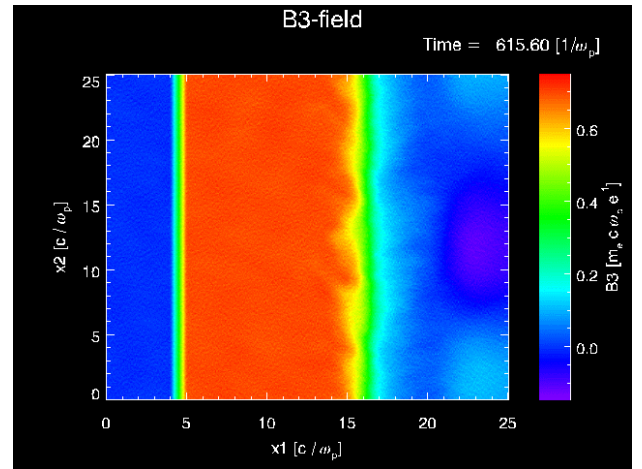


Figure 6. At $t = 615 \omega_p^{-1}$ the instability of the interface is most developed at longer wavelengths around $5 c/\omega_p$.

The characteristic wavelength of the ‘Rayleigh Taylor’ modes grows from about $2 c/\omega_p$ to about $5 c/\omega_p$ between $t = 307 \omega_p^{-1}$ and $t = 615 \omega_p^{-1}$.

Apart from the very latest times where the influence of the right hand boundary has clearly perturbed the test plasma we see almost no penetration of the applied field beyond the region of the turbulent skin current. The electron drift instability has generated strong turbulence and electron heating but without making significant changes to the effective resistivity and magnetic diffusion.

The electron phase space at this time shows similar perturbations to the magnetic field plots (Figure 7).

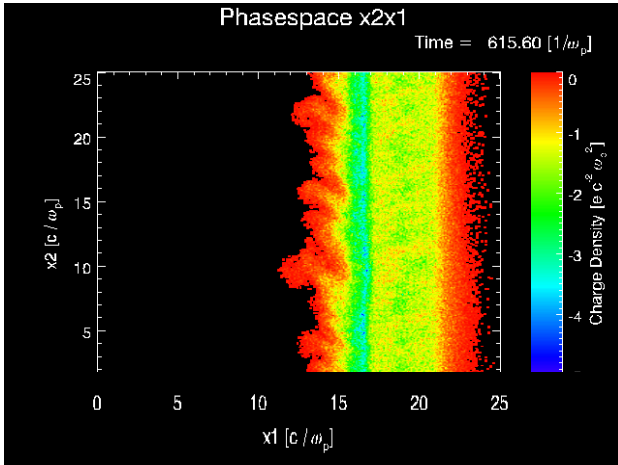


Figure 7. The electron density plot at $t = 615\omega_p^{-1}$ showing similar structure to the interface in the magnetic field plot.

On the other hand the ion phase space shows more structure including what we believe to be a succession of shock waves as the test plasma is impulsively accelerated by the magnetic field (Figure 8).

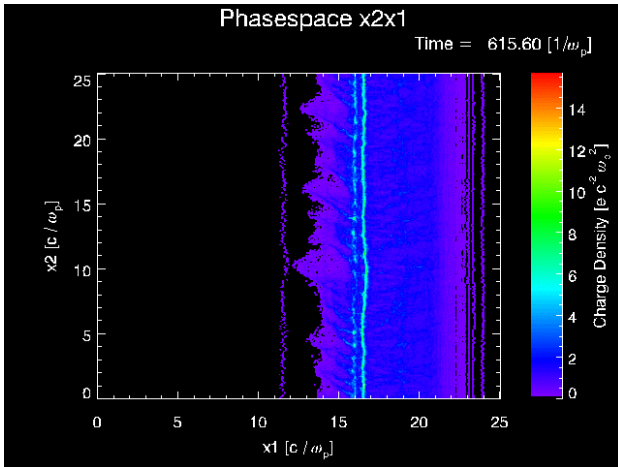


Figure 8. Ion density plot at $t = 615\omega_p^{-1}$ showing more small scale structure than the equivalent electron density plot.

Acknowledgement

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Conclusion

These simulations contain a wealth of information that need more detailed analysis but already show the viability of the PIC approach to these long time scale problems given fast modern computers.

An immediate conclusion regarding the Woolsey et al experiment is that there is unlikely to be any significant magnetic field penetration into the flowing plasma and that the turbulent skin current may confuse the observation of magnetised collisionless shocks. On the other hand the possibility exists of measuring the turbulence in the skin current which is itself of considerable interest given its close connection with other laboratory and astrophysical plasma conditions. The observation of a magnetic Rayleigh Taylor instability is also an interesting prospect.

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Theory for Magnetised Exploding Foil Experiments

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This note presents analytical modelling of the simplest aspects of ongoing experiments using the Vulcan laser to simulate astrophysical shocks by producing collisions between two exploding foils¹. The purpose is to understand the basic dynamics of the plasma and the magnetic field in these experiments, and to gain some analytical insight into the output from numerical simulations of the experiments using the MEDUSA¹) and POLLUX²) codes. Specifically, we try to clarify why the plasma flow becomes supersonic even though it is purely thermally driven; how nonuniformities imparted by the laser beam can survive in the plasma while its transverse dimension expands by a factor of several thousand; and whether the magnetic field can penetrate into the plasma despite the small collisional and collisionless skin depths.

Hydrodynamics

The simplest model of an exploding foil is that furnished by the isothermal, one-dimensional fluid equations,

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial(nu)}{\partial x} &= 0 \\ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} &= -\frac{c_s^2}{n} \frac{\partial n}{\partial x} \end{aligned} \quad (1)$$

where n is the electron number density, u the velocity, and $c_s = (T_e/m_e)^{1/2}$ the isothermal sound speed. The electron pressure is taken to dominate over the ion pressure since the electrons outnumber the ions. The magnetic field does not affect fluid-like aspects of the plasma dynamics if $\beta = 2\mu_0 nT/B^2 \gg 1$. These equations have solutions with Gaussian density profiles and linear velocity profiles³,

$$n(x, t) \propto L^{-1}(t) e^{-x^2/2L(t)} \quad \text{and} \quad u(x, t) = \frac{x\dot{L}}{L} \quad (2)$$

where the scale length $L(t)$ satisfies

$$t = \int_{L_0}^{L(t)} \frac{ds}{\sqrt{\dot{L}_0^2 + 2c_s^2 \ln s}} \approx \frac{L}{c_s \sqrt{2 \ln(L/L_0)}} \quad (3)$$

The last, approximate, equality holds if the initial velocity, $\dot{L}_0$, vanishes and if $L(t) \gg L(0) = L_0$. This solution, which might reasonably describe the early stages of the exploding foil experiments before the two foil plasmas have had time to interact, enables us to understand two features of the experiments: the supersonic nature of the plasma expansion and the possibility of density fluctuations remaining in the plasma for a relatively long time. The initial foil thickness is about $L_0 = 0.1 \mu\text{m}$, and the flow speed at the time of the collision, when $x = L = 0.5 \text{ mm}$, thus becomes $u \sim 4c_s$, in rough quantitative agreement with the Mach number observed in the simulations. The expansion is thus strongly supersonic although it is purely thermally driven. In this respect the flow is rather similar to the solar wind. Now suppose that the plasma is filamented at $t=0$, perhaps because the laser irradiation is non-uniform. We expect sound waves to flatten filaments that have the scale length λ (or smaller) in the time λ/c_s . However, since the Mach number exceeds unity, at the time (3) when the collision occurs this still leaves filaments with scale lengths

$$\lambda \geq \frac{L}{\sqrt{2 \ln(L/L_0)}} \approx 0.1 \text{ mm} \quad (4)$$

intact, as indeed observed in the experiments.

Magnetic field penetration

A question of prime importance is whether the magnetic field produced by Helmholtz coils surrounding foils penetrates into the plasma. Insofar as the plasma is ideally conducting, only the field initially frozen into the plasma would be present there. This field would become very weak as it is attenuated by a factor $L/L_0 \sim 5000$ when the plasma expands. The collisionless skin depth is very small in the experiment, $\delta_e = c/\omega_{pe} \sim 2 \mu\text{m}$ if $n = 10^{25} \text{ m}^{-3}$, and the resistive skin depth is also small, $\delta_{\text{skin}} = c/\omega_{pe} = (\eta t/\mu_0)^{1/2} \sim 10 \mu\text{m}$ for $T_e = 1 \text{ keV}$ if the Spitzer value is used for the resistivity η . While this may suggest that the plasma is indeed ideal, Spitzer resistivity is, in fact, not applicable since the electron mean-free path is of the order of 0.3 mm , which is much larger than δ_{skin} . We are thus led to consider other mechanisms which control the resistivity of the plasma. One such mechanism is micro-turbulence excited if the current density becomes high enough. This turbulence gives rise to an anomalous resistivity which acts to limit the current to stay below some value related to the sound speed, $j < \alpha n c_s$, and determined by the constant α ⁴). If the electrons drift faster through the plasma than indicated by this limit, ion acoustic or lower-hybrid waves become unstable. This instability is then strong enough to scatter the electrons and thus reduce the current to near the stability threshold. If this limiting current is smaller than the Spitzer skin current, this implies enhanced magnetic field penetration since it limits the sharpness of magnetic field variation. Indeed, Ampere's law in a slab, $dB/dx = \mu_0 j$, then implies the following lower bound on the penetration scale length

$$L_B > \frac{B}{\alpha n e c_s \mu_0} = \delta_i \sqrt{\frac{2}{\alpha^2 \beta}} \quad (5)$$

where the collisionless ion skin depth $\delta_i = (m_i/m_e)\delta_e$ is about 0.1 mm if $n = 10^{25} \text{ m}^{-3}$. The factor α is believed to be somewhat larger than unity, but not very large and certainly smaller than $(m_i/m_e)^{1/2}$ since this would correspond to a current comparable to the electron thermal speed, leading to the excitation of a two-stream instability. As the magnetic field reaches tens of teslas in the experiments, the factor β is not very much larger than unity, suggesting that $L_B \sim \delta_i$, so that anomalous resistivity could allow the magnetic field to penetrate into the plasma.

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A General Dispersion Relation for the Parametric Instability of Ultraintense, Circularly Polarized Laser Light

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Introduction

Circular polarization is often assumed to facilitate analysis when studying the propagation of laser light in plasma at intensities where the electron quiver velocity is strongly relativistic. This is because there is an exact analytic form for large amplitude circularly polarized plane waves due to the vanishing of the $\mathbf{v} \times \mathbf{B}$ force. This wave is a pure transverse electromagnetic wave in which electrons move in circles at constant speed and relativistic mass increase. In contrast, ultraintense linearly polarized laser light is a longitudinal-transverse anharmonic wave with oscillations in the electron longitudinal motion and electron mass increase. In the case of both polarizations, such pulses are rapidly unstable to fluctuations in density and mass increase. The general treatment of the parametric instability of ultraintense, linearly polarized laser light has proved elusive until recently^{1,2}. For this reason, much current theory has assumed circularly polarized laser light^{3,4}. Even so, the extension of stability theory to arbitrarily high intensities and valid for any accessible density is not straightforward. Quesnel et al⁴ first obtained a general solution for the parametric instability of circularly polarized laser light. They derived and numerically solved a system of fourth order difference equations, which involved 7-dimensional unknowns and coefficients, which were 7x7 matrices. We present here a much-simplified representation for this case in the form of a system of fourth order difference equations for a single scalar unknown with scalar coefficients.

The Difference Equation

The circularly polarized vector potential for the laser light is

$$\mathbf{a}_0 = e\mathbf{A}_0/m_e c^2 = a_0(0, \sin \eta, \cos \eta)$$

where the phase $\eta = k_0 x - \omega_0 t$. The electrons have momentum $\mathbf{p}_0 = m_e c \mathbf{a}_0$, constant relativistic mass $\gamma_0 = (1 + a_0^2)^{1/2}$ and constant speed $v_0 = ca_0/\gamma_0$. The mass increase gives a reduced plasma frequency $\omega_{pr} = \omega_{p0}/\gamma_0^{1/2}$. The dispersion relation is modified to $\omega_0^2 = \omega_{pr}^2 + k_0^2 c^2$.

Let $\Psi = (n/\gamma)_1$ be the first order fluctuation in the ratio of density to mass increase (effectively the ‘relativistic’ plasma frequency $4\pi n e^2/m_e \gamma$). From linear theory² we eventually derive the 4th order linear difference equation for Ψ

$$\sum_{m=-2}^2 \alpha_m(\omega, \mathbf{k}) \Psi(\omega + m\omega_0, \mathbf{k} + m\mathbf{k}_0) = 0$$

where the coefficients are

$$\alpha_0 = \frac{\varepsilon(\omega)}{D(\omega, \mathbf{k})} + \frac{v_0^2}{4c^2} (k_\perp^2 c^2 + 2\omega_{pr}^2) \left(\frac{1}{D(\omega_+, \mathbf{k}_+)} + \frac{1}{D(\omega_-, \mathbf{k}_-)} \right)$$

$$\alpha_{\pm 1} = -\frac{k_\perp v_0}{2} \left(\frac{\omega}{D(\omega, \mathbf{k})} + \frac{\omega}{D(\omega_\pm, \mathbf{k}_\pm)} \right)$$

$$\alpha_{\pm 2} = \frac{k_\perp^2 v_0^2}{4} \frac{1}{D(\omega_\pm, \mathbf{k}_\pm)}$$

and $\varepsilon(\omega) = \omega^2 - \omega_{pr}^2$, $D(\omega, \mathbf{k}) = \omega^2 - \omega_{pr}^2 - k^2 c^2$, $\omega_\pm = \omega \pm \omega_0$, $\mathbf{k}_\pm = \mathbf{k} \pm \mathbf{k}_0$. $k_\perp$ is the perpendicular wavenumber. Solutions depend only on the two parameters $\omega_{pr} v_0/\omega_0 c$ and $k_\perp v_0/\omega_0$. This form is entirely equivalent to that of Quesnel et al⁴ but

involves only a scalar unknown Ψ (instead of a 7 dimensional vector) and scalar coefficients α_0 , $\alpha_{\pm 1}$ and $\alpha_{\pm 2}$ (instead of 7×7 matrices). The coefficients of the difference equation correspond to a doubly infinite, symmetric, penta-diagonal matrix.

The one-dimensional dispersion relation ($k_\perp = 0$) is given by $\alpha_0 = 0$ and represents a closed coupling between modes ω and $\omega_\pm$. (This is also the same form as for the approximate 4-wave linearly polarized case valid when $a_0 < 1$.) This case has been analyzed in detail by Guérin et al³ showing the various mixes of the relativistic modulational instability, forwards and backwards stimulated Raman scattering. The closed system prevents the occurrence of higher order processes, such as stimulated harmonic generation.

This is no longer the case for 2/3-dimensional processes involving obliquely propagating modes where the off diagonal elements couple an infinite hierarchy of modes. As such it describes additionally the relativistic filamentation instability, stimulated (Raman) side scattering and the two-plasmon decay instability as well as higher order processes such as stimulated Raman harmonic generation. However, it is a routine exercise to solve the dispersion relation, i.e. to evaluate and solve the determinant of the coefficients of this symmetric penta-diagonal system (truncated to include sufficient coupled modes).

This form allows approximate analytic formulae to be deduced for the growth rates in special cases, such as for low density ($n \ll n_{cr}$, where $n_{cr} = \gamma_0 n_c$ is the relativistic critical density accessible by self-induced transparency due to the electron mass increase) or for weakly relativistic regimes ($a_0 \leq 1$). For example, expressions for three-wave Raman growth rates are routinely derived:

$$\Gamma = \frac{kv_0 \omega_{pr}}{2} \left(\frac{1 - k_\perp^2 / 2k_s^2}{\omega_{pr}(\omega_0 - \omega_{pr})} \right)^{1/2}$$

where $k_s^2 c^2 = \omega_0(\omega_0 - 2\omega_{pr})$, $k^2 = k_x^2 + k_\perp^2$ and $k_x = k_0 \pm k_{sx}$. In terms of the scattering angle θ , this takes the form

$$\Gamma = \frac{k_0 v_0}{2} \left[\frac{\omega_{pr}}{2(\omega_0 - \omega_{pr})} \left(1 + \frac{k_s^2}{k_0^2} - 2 \frac{k_s}{k_0} \cos \theta \right) \left(1 - \frac{\sin^2 \theta}{2} \right) \right]^{1/2}$$

Conclusions

A simpler form than has hitherto been available to describe the dispersion characteristics of all electronic parametric instabilities for circularly polarized light has been deduced. Within the constraints as a cold plasma model, it is valid for arbitrary density and laser intensity.

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Spatially Resolved Atomic Ionisation Processes in High Intensity Femtosecond Laser Pulses

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Introduction

Ionisation of xenon up to Xe^{6+} has been investigated using a Z-scan technique to spatially resolve individual processes within the focused laser spot. Experimental data has been described well by considering the relative volume contributions from each ionisation stage within the confocal volume.

Experimental Configuration

Experiments are performed using 65fs 800nm (10Hz) laser pulses from the Astra femtosecond laser facility. A 25cm lens is used to shallow focus the pulses, resulting in a large confocal volume. Pulse integrity is monitored using a frequency resolved optical gating (FROG) technique and shot to shot fluctuations are discriminated at a 5% level.

Z-scan experiments are performed using a modified interaction chamber of the ion beam apparatus,^{1,2)} as shown in Figure 1.

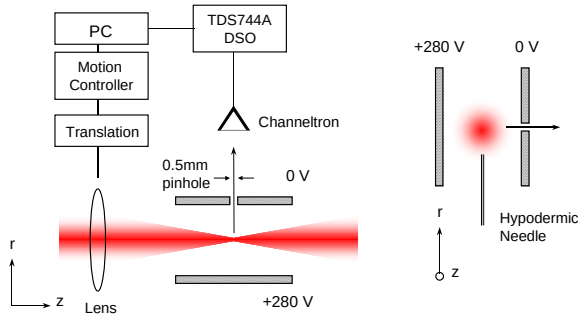


Figure 1. Schematic diagram of z-scan apparatus.

Target gas is effused into the vacuum chamber via a hypodermic needle, located 10mm beneath the interaction region, to a typical pressure of 10^{-7} mbar. Ions produced during the laser interaction are extracted through a 0.5mm slit and detected using conventional time of flight techniques. The laser focal spot position along the z-axis is controlled by a Newport motion controller driving a lens mounted to a sub-micron precision translation stage. This allows excellent z-scan resolution of the confocal volume.

Confocal Volume Characteristics

Laser pulses are assumed to be Gaussian in r and Lorentzian along z ³⁾, isointensity contours are calculated using (1).

$$r = \left(-\frac{\omega_0^2}{2} \left[1 + \left(\frac{z}{z_0} \right)^2 \right] \ln \left[\frac{I_s \left(1 + \left(\frac{z}{z_0} \right)^2 \right)}{I_0} \right] \right) \quad (1)$$

Here z_0 is the Rayleigh range and I_s is the process saturation intensity. The n^{th} ionisation stage (A^{n+}) will be bound between the saturation contours for A^{n+} and $A^{(n+1)+}$. These contours take the distinctive form of peanut-shape lobes, as shown in Figure 2. The volume unique to each ionisation stage $V'(A^{n+})$ is given by:-

$$V'(A^{n+}) = V(I_s(A^{n+})) - V(I_s(A^{(n+1)+})) \quad (2)$$

where $V(I_s)$ is given by:

$$v = \frac{\pi^2 \omega_0^4}{\lambda} \left[\frac{2}{9} \left(\frac{I_0}{I_t} - 1 \right)^{\frac{3}{2}} + \frac{4}{3} \left(\frac{I_0}{I_t} - 1 \right)^{\frac{1}{2}} - \frac{4}{3} \tan^{-1} \left(\left(\frac{I_0}{I_t} - 1 \right)^{\frac{1}{2}} \right) \right] \quad (3)$$

When the 0.5mm slit is present, only a thin slice (Δz) of the confocal volume is observed. In this case, the volume equations must be modified⁴⁾ to calculate the individual ionisation stage volumes observed through the slit.

$$V_{\Delta z} = \frac{\pi}{2} \omega_0^2 \Delta z \left[1 + \left(\frac{z}{z_0} \right)^2 \right] \ln \left[\frac{I_0}{I_s} \left(1 + \left(\frac{z}{z_0} \right)^2 \right)^{-1} \right] \quad (4)$$

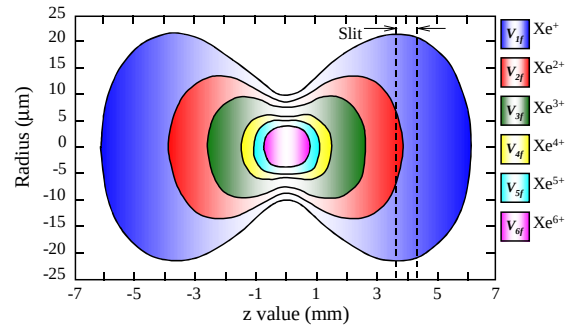


Figure 2. Cross section through the laser confocal volume showing sequential ionisation stages bound by corresponding isointensity contours.

Results and Analysis

Depending on the region of the confocal volume exposed to the detector through the slit, different ionisation stages will be observed with different relative strengths. Figure 3a shows a typical time of flight spectrum for xenon where no slit is present and the whole confocal volume is exposed to the detector. Conversely, with the slit present and situated close to the focus, higher charge states will dominate with little contribution from singly and doubly ionised channels. This is illustrated in Figure 3b.

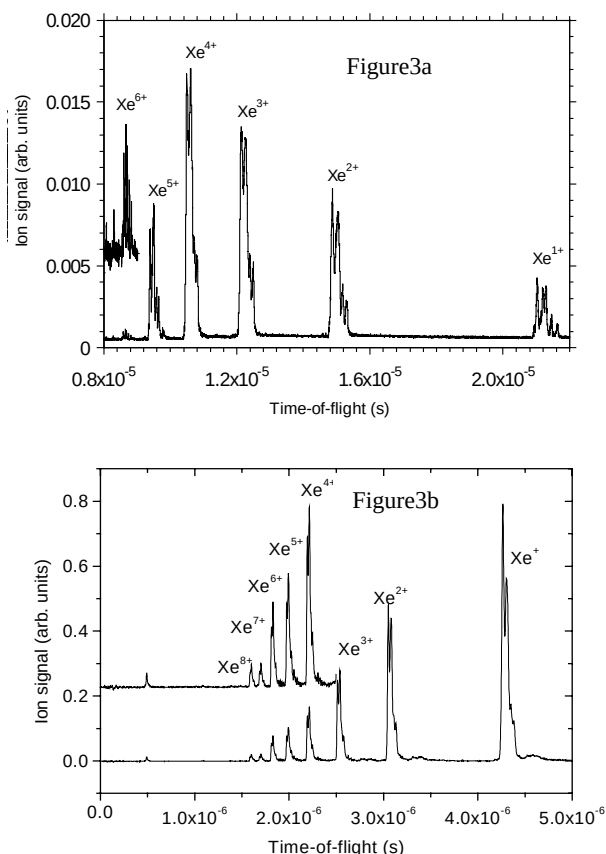


Figure 3. (a) Time of flight spectrum for xenon with full confocal volume exposed to the detector. The presence of Xe⁸⁺ indicates a peak intensity of the order $8 \times 10^{15} \text{ Wcm}^{-2}$, see Reference 4. (b) Time of flight spectrum with slit located at the laser focus showing relative enhancement of higher charge states.

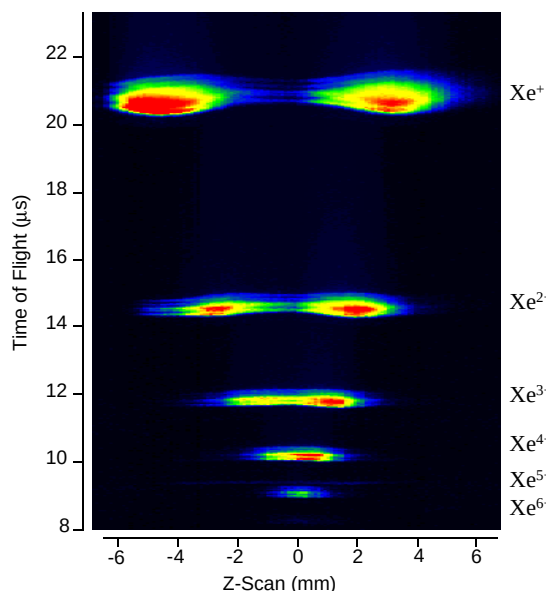


Figure 4. Z-scan matrix illustrating spatial characteristics of ions within the confocal volume up to Xe⁶⁺. The temporal streaking observed within each ionisation stage is attributed to the resolution of xenon isotopes by the TOF spectrometer.

By recording spectra over the full z range, a z -scan matrix (Figure 4) is constructed, clearly showing the spatial characteristics of each ionisation stage within the confocal volume.

Theoretical volume curves have been generated as a function of z -position using Equation (4) and fitted to experimental ion

yields for the first four ionisation stages of xenon⁵⁾, as shown in Figure 5.

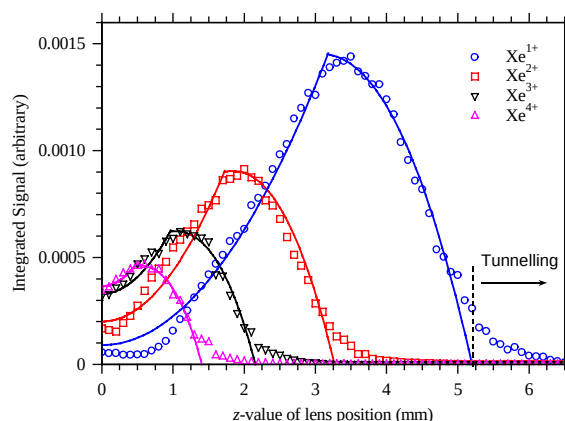


Figure 5. Cross section along the z -axis showing expected volume behaviour (solid lines) normalised to experimental z -scan data (data points) for ionisation stages up to Xe⁴⁺.

Agreement between theory and experiment is good for the bulk of the dataset but fails dramatically at the tails of each distribution. This is due to the calculated volume curves only accounting for saturated (unity ionisation probability) signal. This consequently indicates that the experimental tail must originate from an unsaturated tunnelling ionisation process at low relative intensities.

Each volume curve is shown to peak at a z -position corresponding to the onset of the next ionisation stage. For smaller z , the relative volume contribution decreases due to both the absolute reduction in confocal volume and the subtraction of volume belonging to higher ionisation stages. This inner curve of the z -scan depends primarily on the saturation intensity of higher ionisation stages, making it critically dependent on the diffraction limit of the laser pulse. Thus, in addition to facilitating spatially resolved ionisation studies, z -scanning can provide a simple experimental technique for calculation of the laser diffraction limit.

Conclusion

The z -scan technique has been shown to be a versatile experimental technique allowing detailed characterisation of intensity dependent processes within the confocal. Z -scans have also been employed as a convenient means to gauge laser diffraction limit.

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Ion Momentum Imaging of Carbonyl Sulphide in High Intensity Femtosecond Laser Pulses

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Introduction

Following recent work on the geometry modification and laser induced molecular reorientation of H_2O ¹⁾ and CO_2 ²⁾, we report on the Coulomb explosion dynamics of OCS in high intensity femtosecond laser pulses using time of flight momentum imaging techniques. Unlike CO_2 and H_2O , OCS is a highly asymmetric molecule. This makes it an ideal candidate for studies of geometry modification in high intensity laser pulses, as subtle changes in both bond length and bond angle will appear more pronounced relative to other symmetric triatomics using this momentum imaging technique.

Experimental results have indicated the presence of a non-linear Coulomb explosion geometry with bond lengths approximately twice equilibrium internuclear separation, in agreement with enhanced ionisation theory. Experimental results have been confirmed using Monte Carlo simulations and a two-dimensional classical field ionisation model.

Experimental Configuration

The time of flight mass spectrometer and laser system remain largely unchanged from previous studies¹⁾, and so will only be described briefly.

Laser pulses of 790nm, 55fs (10Hz) were reflection focussed into the Wiley-McLaren type spectrometer using an f/5 spherical mirror to produce a focus with peak intensity $2 \times 10^{15} \text{ Wcm}^{-2}$ and a waist of $12 \mu\text{m}$. The target gas was effused directly into the interaction region via a hypodermic needle to a fill pressure of 10^{-7} mbar (background 10^{-10} mbar). Laser pulses were gated (5% discrimination) to reduce fluctuations. Polarisation of the incoming pulses was computer controlled via a Newport precision rotation stage housing a $\lambda/2$ -plate. Good signal-to-noise ratio allowed each time of flight spectrum, as shown in Figure 1, to be constructed from an average of 100 laser pulses.

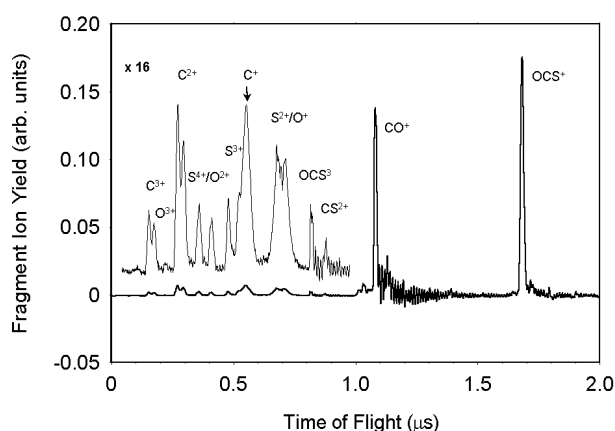


Figure 1. Typical time of flight spectra for OCS with laser polarisation axis parallel to the detection axis.

Results

Prior to the ion momentum imaging of carbonyl sulphide, a covariance map³⁾ was generated to assist identification of

observed ionisation channels. The covariance map shown in Figure 2 was built up over 10^4 individual laser shots. During this period the target gas pressure was reduced to 4×10^{-9} mbar in order to reduce the possibility of false coincidences by ensuring that, on average, only a single molecule undergoes Coulomb explosion per laser shot.

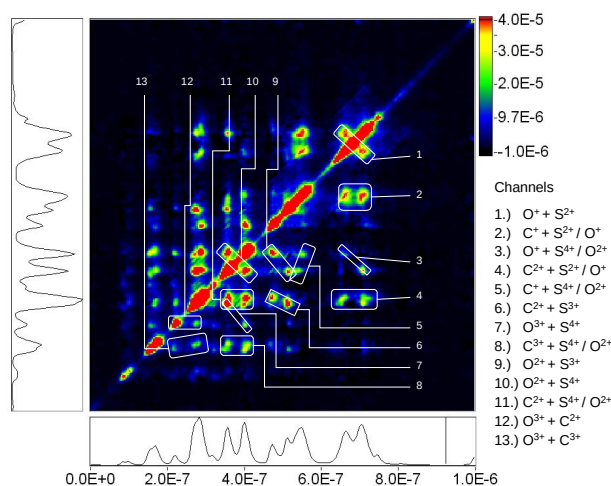


Figure 2. Covariance map of carbonyl sulphide. 10^4 laser pulses of 55fs duration at 790nm, and peak intensity of $2 \times 10^{15} \text{ Wcm}^{-2}$.

Production of ion momentum maps requires sequential time of flight spectra to be recorded as a function of laser polarisation angle (θ) with respect to the detection axis, forming a time of flight matrix. The time of flight matrix for OCS, shown in Figure 3, was constructed using 100 shot averaged spectra and extends from 0° (parallel) to 360° in 2° increments.

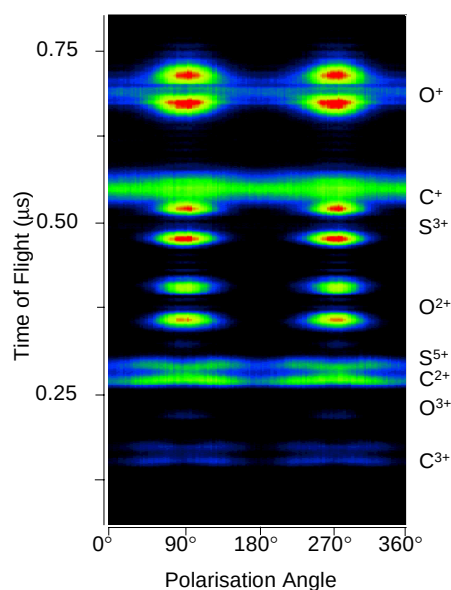


Figure 3. Time of flight matrix for OCS.

Following a correction to account for the low momentum detector bias¹⁾ due to the finite solid angle of collection, individual ion signals within time of flight matrix are converted to ion momentum maps, as shown in Figure 4a-c.

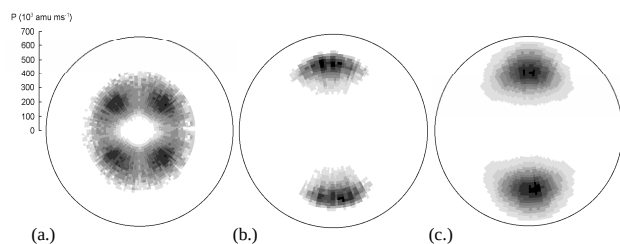


Figure 4. Ion momentum maps for (a.) C^{3+} , (b.) O^{3+} and (c.) S^{3+} from the Coulomb explosion of carbonyl sulphide. Laser polarisation axis acts vertically in page.

The momentum maps show the terminal oxygen and sulphur ions acting primarily along the polarisation axis. Conversely the C^{3+} ion exhibits an unusual four-lobe structure which, via conservation of momentum, is indicative of a non-linear geometry. This implies a bend angle is induced during the transition from equilibrium geometry to final Coulomb explosion geometry.

A more quantitative analysis of the ion momentum maps may be made using a Monte Carlo technique to simulate the fragmentation process and comparing the simulated maps with experimental results. Each simulation is run over 10^4 iterations, with bond length (R), bond angle (θ) and alignment (ϕ) distributions varied until a good fit with experimental data is obtained. Individually simulated ionisation channels (q_1 , q_2 , q_3) are subsequently combined using least square fitting to form an ensemble of channels for a particular ion, allowing direct comparison with the experimental ion momentum maps, as shown below in Figure 5.

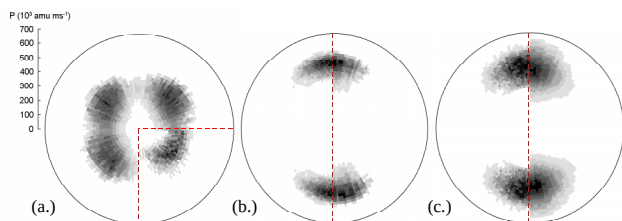


Figure 5. Experimental and Monte Carlo momentum map comparisons for (a.) C^{3+} , lower-right quadrant simulated (b.) O^{3+} and (c.) S^{3+} left-hand side simulated.

The lack of signal in the simulated C^{3+} map about the poles (0° and 180°) is thought to result from the time of flight degeneracy of C^{3+} and O^{4+} ions. The distributions derived from the simulation of these momentum maps are shown in Figure 6.

Despite the initial large equilibrium asymmetry of carbonyl sulphide, both bond lengths are shown to double ($R_c/R_{eq}^{OC} = 2.01$ and $R_c/R_{eq}^{CS} = 2.07$), in good agreement with the enhanced ionisation model^{4,5)}. The Coulomb explosion bond angle is shown to peak at 170° , indicating an enhancement of the most probable instantaneous zero-point bend angle of 175° ⁶⁾. Finally, the molecular alignment distribution about the laser polarisation axis is shown to extend to a maximum of 40° and fits well to a $\cos^{10}(\phi)$ function, indicating the presence of laser induced molecular reorientation prior to Coulomb explosion.

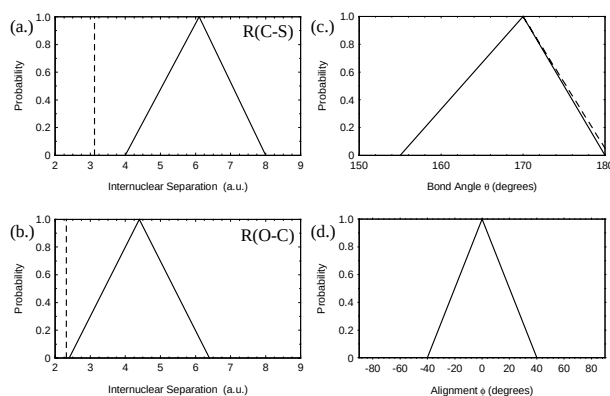


Figure 6. Monte Carlo distributions: (a.) bond length R_{CS} , (b.) bond length R_{OC} , (c.) bond angle and (d.) alignment for OCS at onset of Coulomb explosion.

Conclusion

Carbonyl sulphide has been shown to undergo significant laser induced molecular reorientation before Coulomb exploding with a non-linear bond angle peaking at 170° and bond lengths in agreement with enhanced ionisation. This has been confirmed through Monte Carlo simulation and a two-dimensional classical field ionisation model, which will be discussed in detail in a future publication. The results described here are in good general agreement with previous work on CO_2 , which also exhibited an enhancement of the zero-point geometry prior to Coulomb explosion.

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High Intensity Femtosecond Laser Interactions with a Fast H_2^+ Beam

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Introduction

Recently reported by this collaboration was the first observation and measurement of both neutral and charged dissociative products from the interaction of a fast H_2^+ molecular ion beam with a high intensity femtosecond laser pulse¹⁾. In this report we compare angular distributions to neutral targets, and discuss fragment yields in terms of the effective interaction volume for both the dissociation (0,1) and Coulomb explosion (1,1) processes.

Experimental Configuration

Both the laser and ion beam apparatus have been discussed in detail elsewhere²⁾. Consequently only salient points will be mentioned here.

H_2^+ ions are formed in a plasma discharge source with a standard Franck-Condon vibrational distribution and are extracted and momentum selected before acceleration to 1kV. Laser pulses of 65fs, 790nm (10Hz rep.) with a focused intensity of $5 \times 10^{15} \text{ Wcm}^{-2}$ and a waist of $10 \mu\text{m}$ intersect the ion beam perpendicularly in the interaction region. Deflector plates prior to the interaction region allow ion beam steering and pulsing to avoid detector saturation. Neutral products are detected on-axis using conventional time of flight techniques with the laser polarisation orientated parallel to the ion beam axis. Conversely, ions are electrostatically deflected through a 45° parallel-plate analyser to the ion channel electron multiplier with laser polarisation perpendicular to the ion beam axis. The residual primary beam is dumped in a Faraday cup.

Results and Analysis

Experimental results confirm the presence of two fragmentation channels, namely dissociation (1) and Coulomb explosion (2).

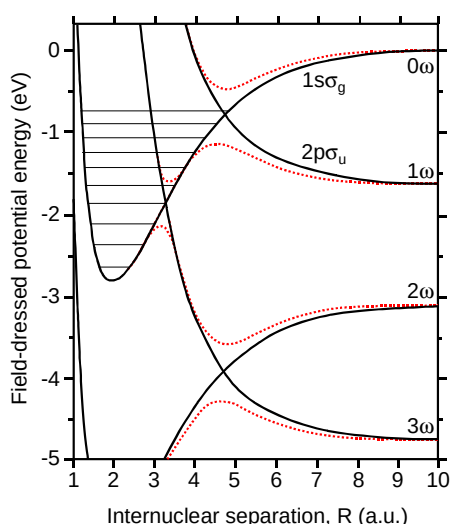
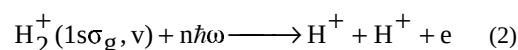
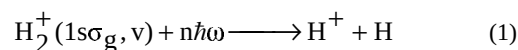


Figure 1. Dressed potential diagram for H_2^+ highlighting the one, two and three-photon adiabatic avoided crossings for intense 800nm radiation.



The dissociation mechanism is best understood by considering a dressed potential model³⁾ with an adiabatic avoided crossing of the 1 photon resonant $1\sigma_g$ and $2p\sigma_u$ potential curves, whilst the Coulomb explosion channel results from enhanced ionisation⁴⁾ at the critical distance.

Angular distributions of the neutral dissociation products have been measured by rotating the laser polarisation axis with respect to the detection axis and recording neutral yield as a function of angle (θ), as shown in Figure 2.

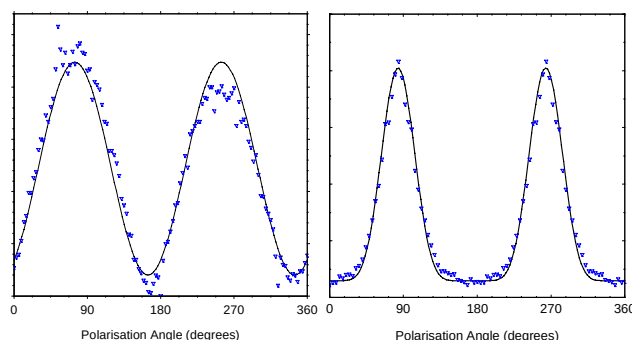


Figure 2. Neutral yield from dissociation of H_2^+ (left) and proton yield from H_2^+ formed from a neutral H_2 molecular precursor (right).

Dissociation products from the molecular ion fit well to a $\cos^2(\theta)$ form, which is indicative of the absence of laser induced molecular reorientation. Conversely the dissociative product yield from neutral H_2 fit a tight $\cos^7(\theta)$ distribution indicating the presence of laser induced alignment. This discrepancy between the pure molecular ion and the molecular ion formed from H_2 in the leading edge of the evolving laser pulse is currently believed to result from the prompt dissociation of the pure molecular ion early in the laser pulse. In contrast, the neutral molecule must undergo primary ionisation at a threshold intensity of $3 \times 10^{13} \text{ Wcm}^{-2}$ prior to dissociation⁵⁾.

Consideration must also be given to the temperature of the targets. Rotational excitation, which will compete against laser induced alignment, for a thermal H_2 target will be very small in comparison to the H_2^+ molecular ions formed in a hot plasma discharge source.

Neutral dissociation products and protons from the (1,1) Coulomb explosion channel have also been investigated as a function of peak laser intensity, as shown in Figure 3.

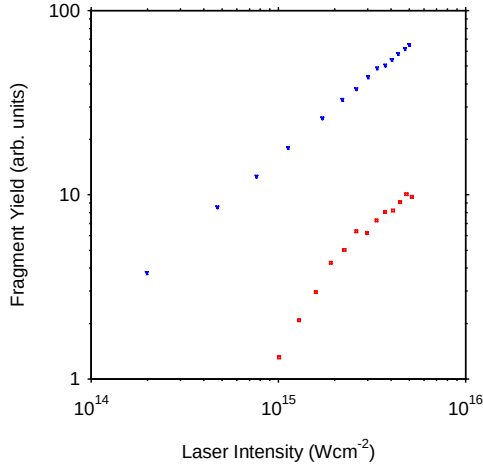


Figure 3. (0,1) dissociation (∇) and (1,1) Coulomb explosion ($\square$) channels from H_2^+ as a function of peak laser intensity.

Unlike the primary ionisation of H_2 , which has a well defined, relatively high threshold intensity, the photodissociation of H_2^+ has a very low threshold ($2 \times 10^{11} \text{ Wcm}^{-2}$)⁶, and may even be considered in terms of a one photon resonance with H_2^+ ($1s\sigma_g$, $v = 9$). Consequently significant interaction volume will lie beyond the Airy disk. Apertures present in the optical system mean laser pulses will undergo diffraction, resulting in Fraunhofer fringing on the low intensity wings of the pulse, as shown in Figure 4. Although too weak to contribute to the (1,1) Coulomb explosion channel, the fringe region will contribute heavily to the (0,1) dissociation channel due to the large relative interaction volume. This point has also recently been considered by Frasinski⁶.

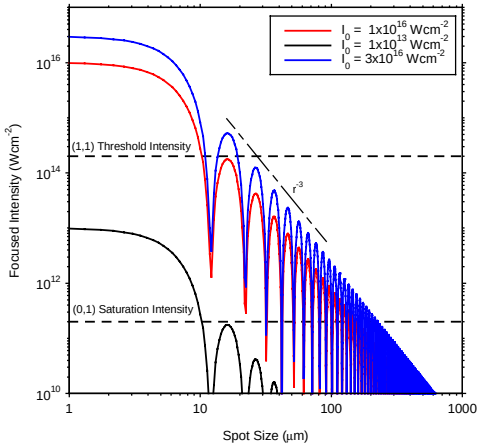


Figure 4. Typical diffracted laser pulses for various peak intensities. The radial behaviour of fringes beyond the Airy disk falls like r^{-3} . Superimposed on these graphs are the (0,1) and (1,1) process thresholds.

Whilst the radial intensity dependence $I(r)$ within the Airy disk still behaves in a Gaussian fashion, diffraction causes the fringed region to fall like $I(r) \propto r^{-3}$. The common interaction volume of the crossed ion and laser beams, known as a Steinmetz volume, is found to scale like $V(r) \propto I^{2.66}$ with laser radius, assuming a fixed ion beam diameter.

Thus the effective interaction volume of the fringe region behaves like $V(I) \propto I^{2.66/3}$ or $I^{0.88}$. As illustrated in Figure 5, this linear volume expansion in log-log space fits the (0,1) channel well, indicating the (0,1) process originates from the low intensity diffracted wings of the laser pulse.

The Coulomb explosion threshold intensity is sufficiently high to ensure all signal is confined within the Gaussian Airy disk. Volume as a function of laser intensity for this region is given

analytically by (3) below. However, if the laser spot size is larger than the ion beam dimensions, the bound form (4) of the equation must be used.

$$V = \frac{\pi^2 \omega_0^4}{\lambda} \left[\frac{2}{9} \left(\frac{I_0}{I_t} - 1 \right)^{\frac{3}{2}} + \frac{4}{3} \left(\frac{I_0}{I_t} - 1 \right)^{\frac{1}{2}} - \frac{4}{3} \tan^{-1} \left(\left(\frac{I_0}{I_t} - 1 \right)^{\frac{1}{2}} \right) \right] \quad (3)$$

$$V = \frac{\pi^2 \omega_0^4}{\lambda} \left[\left(\frac{1}{3} \delta^3 + \delta \right) \ln \left(\frac{I_0}{I_t (1 + \delta^2)} \right) + \frac{2}{9} \delta^3 + \frac{4}{3} \left(\delta - \tan^{-1}(\delta) \right) \right] \quad (4)$$

Here I_0 and I_t are the peak and threshold intensities respectively and δ is the ratio of the ion beam radius to the Rayleigh range.

The (1,1) channel also fits well for a threshold intensity of $8 \times 10^{14} \text{ Wcm}^{-2}$, implying a saturated (1,1) process originating entirely from within the Airy disk.

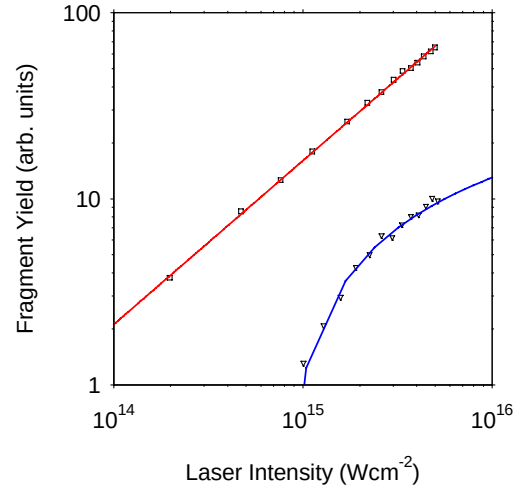


Figure 5. Effective interaction volume fits to (0,1) dissociation channel (red), and (1,1) Coulomb explosion channel (blue).

Conclusion

Significant differences in the angular characteristics of the H_2^+ molecular ion and the molecular ion formed from neutral H_2 have been identified and discussed. The (0,1) and (1,1) mechanisms in H_2^+ have been described in terms of the effective interaction volume produced by a diffracted laser pulse.

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First demonstration of guiding of high-intensity laser pulses in a hydrogen-filled capillary discharge waveguide

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Introduction

Optical guiding of laser pulses with intensities of $10^{15} \text{ W cm}^{-2}$ or greater is important for increasing the laser-plasma interaction length in applications such as harmonic generation¹, laser wakefield accelerators^{2,3}, and x-ray lasers^{4,5}. A wide variety of techniques for guiding intense laser pulses has been investigated, including grazing-incidence reflection at the walls of a hollow capillary tube⁶⁻⁸, relativistic and ponderomotive channelling^{9,10}, and several types of plasma waveguide¹¹⁻¹⁹. However, no single approach has been shown to be capable of guiding high-intensity laser pulses over long lengths with low coupling and propagation losses, minimal distortion of the duration or spectral content of the pulse, and a long device lifetime.

In the present paper we report the first demonstration of guiding of high-intensity laser pulses in a new type of plasma waveguide: the hydrogen-filled capillary discharge waveguide²⁰. We have achieved guiding of femtosecond laser pulses with a peak input intensity of greater than $10^{16} \text{ W cm}^{-2}$ through 20 and 40 mm-long hydrogen-filled capillaries, with pulse energy transmissions of 92% and 82% respectively. The waveguide also has a long shot lifetime: in these experiments more than 10^3 laser pulses were guided through the same device.

Before describing our experiments, we briefly discuss the background to this work. In an ideal plasma waveguide a channel is formed in which the radial electron density profile is parabolic:

$$N_e(r) = N_e(0) + \Delta N_e(r/r_{ch})^2$$

where $N_e(r)$ is the electron density at radius r . In the absence of further ionization of the plasma by the guided laser pulse, and where ponderomotive and relativistic effects can be neglected, a Gaussian laser beam will propagate through the guide with a constant spot-size W_M , provided that:

$$W_M = [r_{ch}^2 / (\pi r_e \Delta N_e)]^{1/4}$$

where r_e is the classical electron radius. Plasma waveguides have been formed by hydrodynamic expansion of a laser-produced cylindrical plasma¹¹⁻¹⁴, ablation of a capillary wall by a slow electrical discharge¹⁵⁻¹⁷, and formation by the pinch effect in a fast capillary discharge¹⁸⁻¹⁹.

The hydrogen-filled capillary discharge waveguide

The hydrogen-filled capillary discharge is illustrated schematically in the inset to Figure 1. The two electrodes were mounted at the ends of an alumina capillary of internal diameter 300 μm . Gas was flowed into the capillary through two groups of six, 50- μm diameter holes located 2 mm from each end of the capillary. The discharge was initiated by switching a thyatron so as to connect across the electrodes a 1.7 nF capacitor charged to a voltage between 20 kV and 30 kV.

We have previously measured the radial electron density profile formed in this device and found it to be approximately parabolic²⁰, with a matched spot size of 37.5 μm . The average ionization Z^* of the plasma for $t = 60 \text{ ns}$ after the initiation of the discharge was determined from these measurements to be 0.99 ± 0.12 .

Magneto-hydrodynamic (MHD) simulations²¹ of the electron density profiles are in good agreement with the measurements, and demonstrate that under the conditions of the present

experiment the pinch effect is negligible. Instead, the guiding electron density profile is formed by conduction of heat to the capillary wall by the plasma electrons. Since radial pressure variations are rapidly equalized, the radially-decreasing plasma temperature corresponds to a radially-increasing electron density. The simulations show the guiding channel to be parabolic near the axis, and predict the hydrogen to be fully ionized for $t > 55 \text{ ns}$.

Guiding experiments

Figure 1 shows the experimental arrangement employed for the present experiments. Pulses from the Astra Ti:Al₂O₃ laser were focused at the entrance of the capillary by a 1.6-m focal-length off-axis paraboloid used at $f/27$. Considerable care was taken to remove small amounts of astigmatism in the Astra beam by reflecting it from a mirror with an adjustable radius of curvature in one (chosen) dimension. As a result, a high-quality focus was achieved with a measured spot size of 29 μm and $M^2 \approx 3$. During the present experiments the average pulse energy of the laser was 230 mJ. The pulse duration (FWHM) was measured to be $(120 \pm 40) \text{ fs}$.

The measured energy, duration, and spot size of the input laser pulses correspond to a mean peak input laser intensity of $1 \times 10^{17} \text{ W cm}^{-2}$. However, several months after the completion of our experiments it was discovered that, under certain conditions, the output pulses from the Astra laser system contained significant temporal structure, namely a train of approximately 8 short pulses separated in time by $\sim 100 \text{ ps}$. It is not known whether or not this unwanted temporal structure was present during our experiment. However, even if it had been, the peak intensity of the most intense of the sub-pulses would have been greater than $10^{16} \text{ W cm}^{-2}$. (The conditions under which multiple pulses occur are now understood and procedures are implemented to ensure that only single pulses are present.)

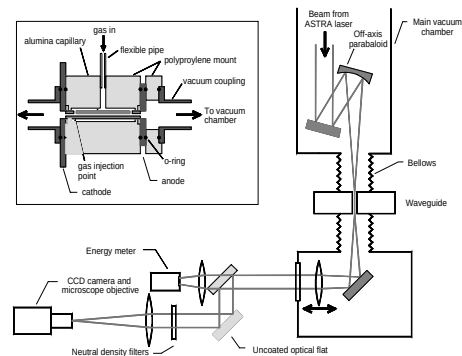


Figure 1. Schematic diagram of the experiment. Inset: Schematic diagram of the hydrogen-filled capillary discharge waveguide.

Radiation leaving the capillary was reduced in intensity by reflections from wedged optical flats and imaged onto a CCD camera. The pulse energy transmission T was measured using energy meters located behind beam-splitters placed before and after the capillary.

For each shot, hydrogen was either flowed into the capillary continuously, or pulsed for 2 s, commencing 1 s before the discharge was initiated.

Results

Figure 2 shows the measured transmission as a function of the delay t for a 20 mm-long capillary waveguide, together with the temporal variation of the discharge current, for a hydrogen pressure of 67 mbar. Note that the small current pulse prior to the main current arose from charging of the coaxial cable connecting the electrodes to the rest of the circuit, and did not pass through the capillary.

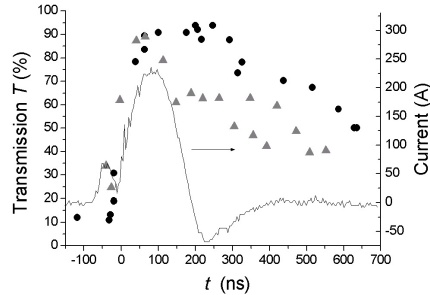


Figure 2. Measured transmission T as a function of the delay t for 20 mm (circles) and 40 mm (triangles) long capillaries. The solid line shows the discharge current for the 20 mm-long capillary.

For the 20 mm-long capillaries it is seen that prior to the initiation of the discharge T is approximately 12%, the low transmission resulting from ionization-induced defocusing of the laser pulse by the neutral hydrogen inside the capillary. The transmission rises to approximately $(92 \pm 3)\%$ within 60 ns of the onset of the current pulse, and is maintained at this value for t up to approximately 270 ns. For longer delays T decreases slowly.

Figure 2 also shows the measured temporal variation of T for a 40 mm-long capillary. In order to achieve gas breakdown the charging voltage of the storage capacitor was increased to 30 kV, limited by the thyatron, and the initial hydrogen pressure was reduced to 30 mbar. The temporal profile of the discharge current was very similar to that recorded with the 20 mm capillary, the peak current being 300 A. However, the discharge breakdown was less reliable, which may explain the increased scatter in T . It is seen that for the 40 mm capillary the temporal variation of T is broadly similar to that of the 20 mm capillary, although the duration of very high transmission appears to be shorter. The best transmission occurs for t between approximately 40 and 120 ns, during which $T = (82 \pm 5)\%$.

Figure 3 shows transverse intensity profiles of the laser pulse measured in the plane of the capillary entrance (with the capillary removed), and in the exit plane of the 20 mm-long capillary for several values of t . It is seen that prior to the onset of the discharge current the transmitted laser pulse energy is low, and distributed across the entire diameter of the capillary. For $t > 0$ the transmitted pulse energy initially increases with t , and becomes constrained to the axial region of the capillary. For example for the pulse recorded at $t = 206$ ns, the output beam spot size is $33 \mu\text{m}$, $T = 92\%$, and the peak axial fluence is 70% of that of the input laser pulse. For longer delays the transmission and spot size of the exiting beam decrease and increase respectively.

Discussion of results

Our previous measurements and MHD simulations have shown that the guiding electron density profile is formed within 60 ns of the onset of the discharge current. This is consistent with the observed rapid increase in T immediately after the onset of the discharge. The MHD simulations show that the curvature of the electron density profile evolves only slowly during the current pulse. This explains the fact that for the 20 mm capillary high

pulse energy transmission is maintained for approximately 200 ns before a decrease in the degree of ionization, loss of plasma, and changes in the curvature of the electron density profile cause the transmission to be reduced, and the transverse profile of the transmitted beam to deteriorate. It is likely that changes in the guiding electron profile are more critical when guiding over 40 mm, which may be the reason that the very high transmission was found to last for a shorter interval in this case.

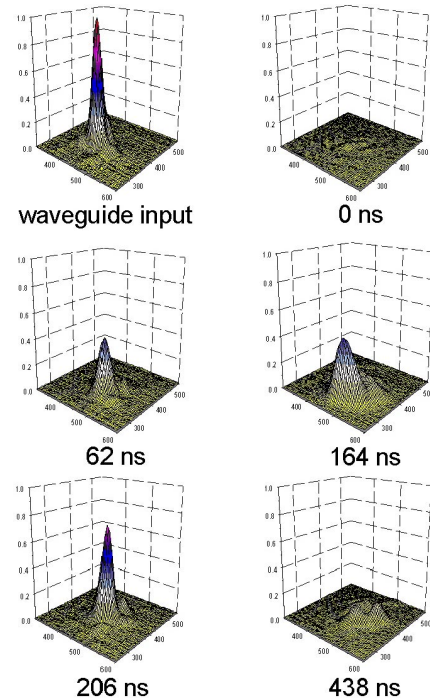


Figure 3. Fluence profiles of the pulses transmitted through a 20 mm-long capillary as a function of the delay t , together with that of the input pulses. The profiles have been normalized to the mean peak fluence of the input pulses.

It should be emphasized that the plasma channel formed by the hydrogen-filled capillary discharge waveguide is essentially fully ionized, and parabolic. As such ionization-induced de-focusing will not occur, and the channel should operate as an almost perfect plasma waveguide. Any mis-match between the input spot size W_0 of the laser pulses and the matched spot size W_M of the waveguide will cause the spot size of the guided laser pulse to oscillate with propagation distance, but the corresponding oscillations in the axial intensity of the guided pulse are relatively small.

Since the guiding channel is essentially fully ionized, temporal distortion of the pulse due to ionization should not occur, and pulse-stretching is restricted to modal dispersion (if the input spot size is mis-matched), and group velocity dispersion (GVD) in the plasma. Calculations show that pulse-stretching caused by GVD is less than 1 fs for the conditions of the present experiment.

As discussed above, it is not known whether unwanted temporal structure on the laser pulses was present during our experiments. However, since the plasma channel is essentially fully ionized, the effect of any individual sub-pulse on the plasma channel would have been negligible: the peak intensity of any sub-pulse would have been too low for any movement of the plasma by the ponderomotive force to occur; and heating of the plasma by ionization, or by inverse bremsstrahlung heating,

would be negligible. Hence, it is expected that if such temporal structure were present each sub-pulse would propagate through the plasma independently. The fact that for the 20 mm-long capillaries the measured pulse transmission was as high as 92% is further evidence for this.

Finally, we note that during these experiments more than 10^3 laser pulses were guided through a single 20 mm capillary at the full input intensity, with no apparent degradation of the guiding performance.

Conclusions

The hydrogen-filled capillary discharge waveguide combines several important features. The plasma channel is composed of fully ionized hydrogen, and so does not suffer from ionization-induced de-focusing²²⁾, or temporal and spectral distortion of the laser pulse. The device is relatively simple: no auxiliary lasers are required; and since the plasma channel is long lived, the discharge circuit does not require very low jitter triggering. Furthermore, since the capillary is not ablated by the discharge current, the capillary lifetime is long.

In summary, we have reported the first demonstration of the guiding of high-intensity laser pulses in a new type of waveguide: the hydrogen-filled capillary discharge waveguide. Low-loss guiding of femtosecond laser pulses with a peak input intensity of greater than $10^{16} \text{ W cm}^{-2}$ was demonstrated. More than 10^3 laser pulses were guided though the same device with no degradation of the guiding performance.

Finally, we note that very recently we have completed new guiding experiments with Astra in which the unwanted temporal structure which may have existed in the present experiments did not occur. An initial analysis of those results indicates that laser pulses with a peak input intensity of at least $10^{17} \text{ W cm}^{-2}$ were guided over distances of up to 50 mm with a pulse energy transmission similar to that reported here. These new results will be described in more detail in a future publication.

Acknowledgements

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Femtosecond OPCPA in the UV

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Introduction

So far intense femtosecond laser pulses in the spectral range of short wavelength visible (SVIS) and UV have been generated via second harmonic and sum frequency generation. However, due to the dispersion and related problems in nonlinear crystals the requirement of broadband frequency conversion limits the achievable energy of the generated pulse. Also, the narrow spectral gain of the readily available excimer laser amplifiers limits the bandwidth of amplification¹⁻²⁾ while the relatively broadband newly developed solid state materials exhibit a small gain only³⁾. During the past few years papers have been published about successful experiments on optical parametric chirped pulse amplification (OPCPA), in which short pulse NIR and IR laser pulses were efficiently amplified using femtosecond or nanosecond pump lasers⁴⁻⁹⁾.

In this first experiment we demonstrate efficient amplification of broadband, stretched femtosecond pulses at 400 nm, to our knowledge for the first time, using non-collinear optical parametric amplification pumped by picosecond 267 nm pulses. The effect of saturation and the geometry of the interacting pulses on the spectral gain are also investigated.

Experimental

In our experiment a part of the 800 nm fundamental beam of Astra laser was used (Figure 1). The stretched and amplified pulses with a bandwidth (FWHM) of 20 nm were left slightly over-compressed resulting in a pulse length of 1.85 ps. A small fraction of this beam generated the signal pulse at 400 nm in a 100 μm BBO crystal while the majority was used to obtain the pump pulse at 267 nm in a two-stage frequency converter. The generated pump pulse was further stretched in double pass by a 68° fused silica prism pair and subsequently spectrally filtered providing a smooth spatial profile. Two CCD cameras were used both measuring the beam waist of the pump and signal pulses giving 550 μm and 140 μm , respectively and monitoring their spatial overlap in the 12 mm long BBO amplifier.

The temporal width and phase of the fundamental (800 nm) pulse were established from the spectrum by using a fitting algorithm to a multiple shot autocorrelation measurement (Figure 2). The pump (267 nm) pulses were similarly characterised from their spectra and a cross correlation measurement with the fundamental pulse. The signal (400 nm) pulse was assumed to inherit the phase of the signal pulse¹⁰⁾, so it could be obtained from measuring the spectra only. The temporal width (Figure 2c) and the resulting peak intensity of the negatively stretched signal and pump pulses are 1.2 ps, 0.1 MW/cm² and 3.5 ps, 2 GW/cm², respectively.

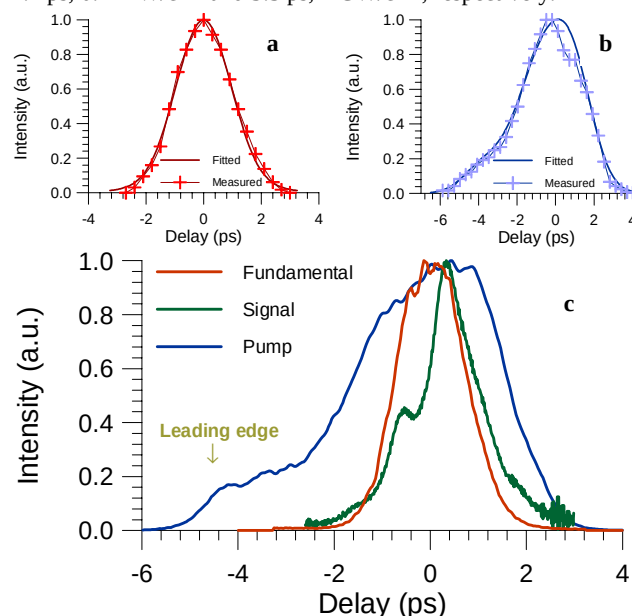


Figure 2. (a) Autocorrelation and (b) crosscorrelation of the fundamental and the pump pulses, respectively, and (c) the temporal shape of the retrieved pulses.

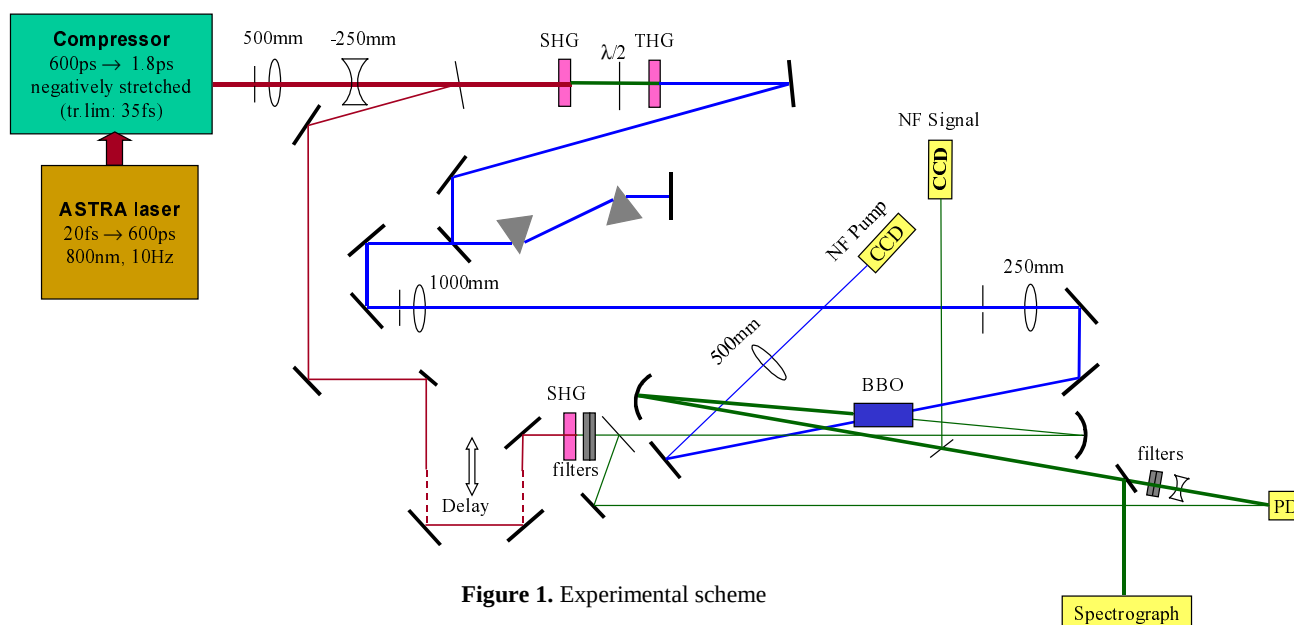


Figure 1. Experimental scheme

Results and discussion

Figure 3 shows the recorded spectra at different intensities of the input signal. The highest gain corresponds to the lowest input signal while the lowest gain was recorded when the pump was depleted (see also Figure 4). When the amplification is not saturated then the amplified spectra fits very well to the input spectrum along the whole spectral range of 392 nm - 408 nm (Figure 3a). In the case of pump depletion, however, the more enhanced shorter wavelength side of the spectrum (Figure 3b) resulted in the 3.8 ps group delay between the pump and signal pulses in the BBO crystal and the inherent feature of optical parametric processes: the peak of the spectrum cannot be amplified further, moreover, its energy is transformed back to the pump. The slight asymmetry in amplification between the shorter and longer wavelength side of the spectrum, which is significant only in the depleted case, corresponds well to the slightly non-flat spectral gain¹¹⁾.

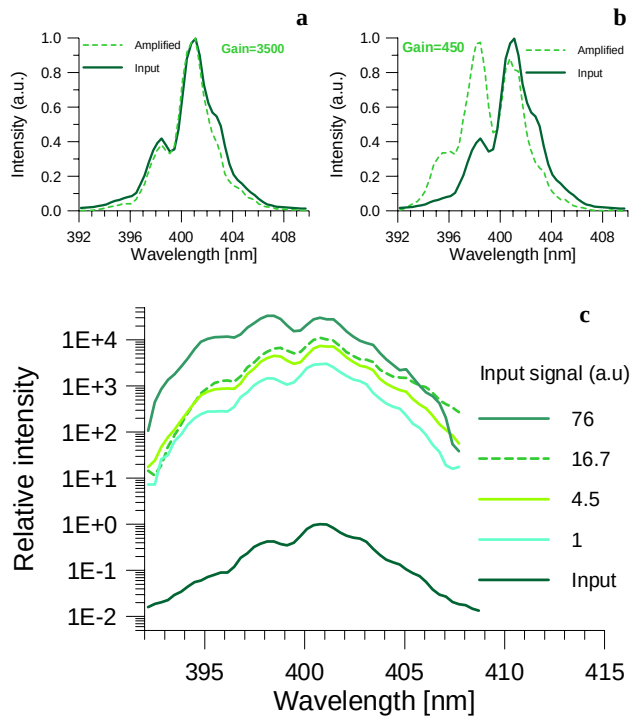


Figure 3. Spectra of the amplified signal at different input powers at a pump intensity of 2 GW/cm².

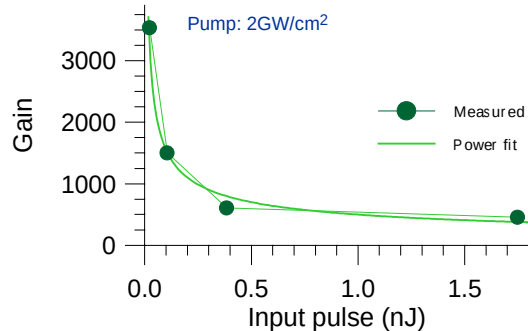


Figure 4. The measured gain vs. input signal.

Because of the shot-to-shot instability of the Astra laser in energy ($\pm 10\%$), pointing direction (± 0.1 mrad) and spectrum especially in the wings, all the spectra displayed above are an average of three measurements. Since the combined effect of these three is not really predictable and hard to distinguish, a way to give an impression for the accuracy of the experiment is to display the spectra of three subsequent amplified signals and their average (Figure 5a).

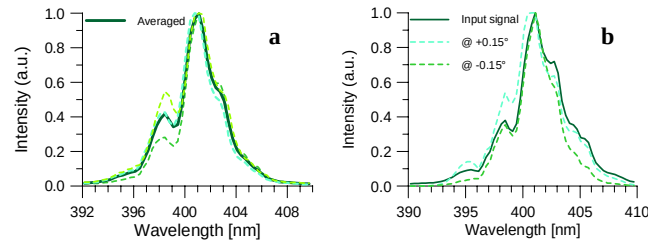


Figure 5. Spectra of the amplified signal at different input powers at a pump intensity of 2 GW/cm².

The effect of angular misalignment is shown in Figure 5b. For the available bottom-to-bottom signal bandwidth of 17 nm the theory¹¹⁾ allows for a deviation of 0.02° for the noncollinear angle from the optimal one. As can be seen, the tolerance of alignment for the amplified spectra is better than could be expected from the theory. One reason for this is that due to group delay difference between the signal and pump pulses the effective crystal length upon amplification is much less than the available physical length of 12 mm.

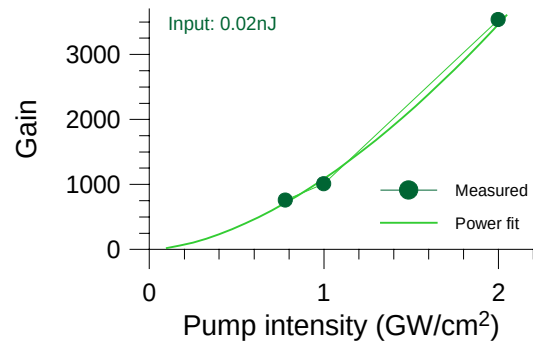


Figure 6. The measured gain vs. pump intensity.

The gain was also recorded at different levels of pump intensity for weak input signals (Figure 6). It has to be mentioned that very strong two photon absorption (TPA) of the pump beam in BBO was observed resulting in only 30% transmission at the peak and hence lower gain. The fact that apart from TPA the gain can, according to the theory, be fitted by the power of pump intensity, gives the other reason for assuming a reduced effective crystal length.

Acknowledgement

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Lasers *for* Science Facility Programme

1) Chemistry

2) Biology

3) Physics

Using Ultrafast Time-resolved Infrared Spectroscopy to Probe the Nature of the Excited States of d⁶ and d⁸ Transition Metal Complexes

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Introduction

We are currently developing the PIRATE (Picosecond Infrared Absorption and Transient Excitation) facility in the Ultrafast Spectroscopy Laboratory. This has provided a tunable source of ultrashort pulses in the mid-IR fingerprint region (1000 – 3000 cm⁻¹). The output can be generated in two modes: (i) narrowband (ca. 25 cm⁻¹ FWHM) 1 ps pulses for pumping specific IR transitions and (ii) broadband (ca. 150 – 200 cm⁻¹ FWHM) 150 fs pulses for use in spectrally dispersed time-resolved infrared (TRIR) spectroscopy, using 64-element linear IR array detectors. The IR pulses are perfectly synchronised with the UV/visible/NIR pulses from the existing OPAs, thus providing the opportunity to perform both conventional TRIR experiments and more complex 3-colour experiments such as UV pump-IR pump-TR³ probe. A more detailed description of the PIRATE apparatus is given in the Laser Science and Development Section of this report (page 165). In this paper we present some applications of broadband multichannel TRIR spectroscopy using the PIRATE system to probe the excited states of d⁶ and d⁸ transition metal complexes.

TRIR Spectroscopy of d⁶ Transition Metal Complexes: Infrared Probes for DNA

TRIR spectroscopy is a powerful probe of the excited state nature of transition metal complexes¹, particularly those which possess strong IR reporters, such as CO or CN, bound to the metal centre. The positions and bandwidths of ν(CO) and ν(CN) IR absorptions are extremely sensitive to electronic and molecular structure. Thus by monitoring changes in the IR absorption spectra upon photoexcitation, we are able to directly probe the electronic redistribution occurring in the excited state.

There is currently considerable interest in the design of transition metal complexes which interact strongly with DNA. Once bound to the DNA helix, they have the potential to act as probes of the structural changes and electron transfer processes that can occur along the helix. Traditionally, research in this area has focussed on complexes of Ru(II), Rh(III) and Cu(I) with polypyridine ligands, particularly the strong intercalator dppz (dppz = dipyrro[3,2-a:2',3'-c]phenazine)². These complexes are known to possess low lying metal-to-ligand charge transfer (MLCT) excited states. This property enhances their ability to act as reporters of their surroundings via the molecular 'light switch' effect³. Our strategy has been to design a family of neutral and charged complexes based on *fac*-[(dppz-R,R')Re(CO)₃(L)]^{0,+} (see Figure 1) and assess their suitability to act as IR probes of DNA. These complexes have the advantage of possessing a tricarbonyl moiety, which offers a structural probe with which to investigate the nature of their lowest excited states.

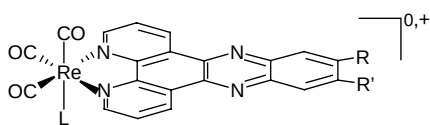


Figure 1. A series of *fac*-[(dppz-R,R')Re(CO)₃(L)]^{0,+} complexes have been studied using ps-TRIR spectroscopy.

Before studying the complexes in the presence of DNA it is necessary to elucidate their photophysical properties in solution, which until now have remained somewhat ambiguous. We have therefore used broadband ps-TRIR spectroscopy to probe the effect of ligand substitution on the nature of the lowest excited states of this family of complexes, with a view to ultimately designing Re-dppz complexes with tunable excited states that are suitable for DNA probing.

Figure 2 shows the ps-TRIR spectra recorded in the ν(CO) region for two of the complexes studied. The spectrum obtained with the charged complex, *fac*-[(dppz)Re(CO)₃(py)]⁺[PF₆]⁻ is given in Figure 2(a). The two negative bands correspond to a depletion of the ground state upon photolysis. Two positive bands, corresponding to a new species, are observed at lower frequencies relative to the ground state. The positions of these bands are characteristic of a dppz based π → π* excited state. This is because the π* orbitals of dppz are slightly more electron donating than the π orbitals. Thus, population of the dppz π* orbitals in the excited state causes a small increase in π-back bonding from the metal to the CO ligands and a characteristic negative shift in the ν(CO) vibrations.

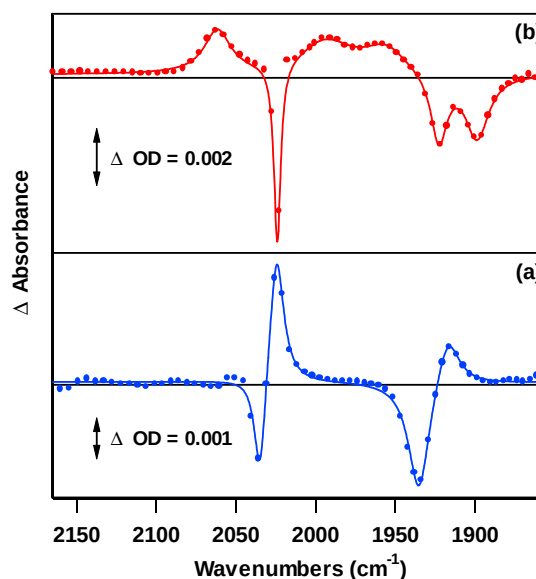


Figure 2. TRIR spectra of (a) *fac*-[(dppz)Re(CO)₃(py)]⁺[PF₆]⁻ in MeCN and (b) *fac*-[(dppz)Re(CO)₃Cl] in CH₂Cl₂, recorded 100 ps after 400 nm photolysis.

Replacing the pyridine ligand with Cl⁻ yields the neutral complex, *fac*-[(dppz)Re(CO)₃Cl]. The TRIR spectrum of this complex, recorded 100 ps after 400 nm photolysis, is shown in Figure 2(b). The negative bands indicate depletion of the ground state species and three new bands are observed, shifted to higher frequencies relative to the ground state bands. Such a positive shift in the ν(CO) bands is characteristic of a dπ(Re) → π*(dppz) MLCT excited state. This is because in an MLCT excited state there is a reduction of electron density at the metal centre, causing a corresponding reduction in π-back donation and thus a strengthening of the CO bonds.

In both cases discussed above, the excited state bands were observed to appear within the laser flash and were stable over the timescale of the experiment (1.5 ns). Although a complex possessing a low lying MLCT excited state was produced, this species was neutral. It is highly desirable for a DNA probe to be positively charged since this would enhance its ability to bind to the DNA base pairs in the helix. Work is currently in progress to study a large series of charged complexes with the PIRATE system and these will be the subject of a forthcoming publication. The experiments presented above have demonstrated that ps-TRIR spectroscopy is an extremely powerful technique for studying the nature of the lowest excited states of transition metal carbonyl complexes.

TRIR Spectroscopy of d^8 Transition Metal Complexes

The majority of transition metal complexes that have been studied using TRIR spectroscopy¹⁾ have been based on d^6 chromophores, e.g. Re^I , Ru^{II} or Os^{II} . It is surprising that relatively few d^8 complexes have been studied using TRIR since these species have the potential to act as DNA intercalators and building blocks for supramolecular electron/energy conducting units. However, the short excited state lifetimes of d^8 chromophores have been a limiting factor in the application of TRIR to these systems.

In addition to the strong metal bound IR reporter ligands, CO and CN, it has previously been shown that peripheral IR reporter groups, such as carboxylic acids and esters, bonded to other ligands can also be used as spectroscopic handles in TRIR investigations⁴⁾. We have used the PIRATE facility to probe the excited state dynamics of $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ by following changes in the electronic density on the peripheral ester groups (shown as red bonds below) bound to the α -diimine ligand.

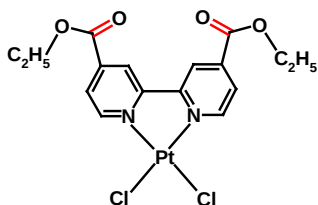


Figure 3(a) shows the ground state FTIR spectrum of $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ in CH_2Cl_2 . It exhibits a strong $\nu(\text{CO})$ band at 1733 cm^{-1} due to the ester groups bound to the bipyridyl ligand. A series of ps-TRIR spectra recorded at time intervals between 500 fs and 200 ps following 400 nm photolysis is presented in Figure 3(b). There is an instantaneous bleaching of the parent absorption concomitant with the production of a new $\nu(\text{CO})$ band at ca. 1707 cm^{-1} . The bleach and transient bands both decay back to the baseline on a 100 ps timescale. The decay of the transient band is accompanied by a small shift of the band maximum to higher frequency, which is characteristic of a vibrational cooling of the excited state.

The negative shift of the $\nu(\text{CO})$ absorption upon photolysis reflects an increase of electronic density on the ester groups of the diimine which causes a weakening of the $\text{C}=\text{O}$ bonds. The magnitude of the shift is consistent with that observed previously⁴⁾ upon formation of the MLCT state in $[\text{Ru}(\text{bpy})_2(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})]^{2+}$, thus supporting the assignment of the excited state of $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ as MLCT.

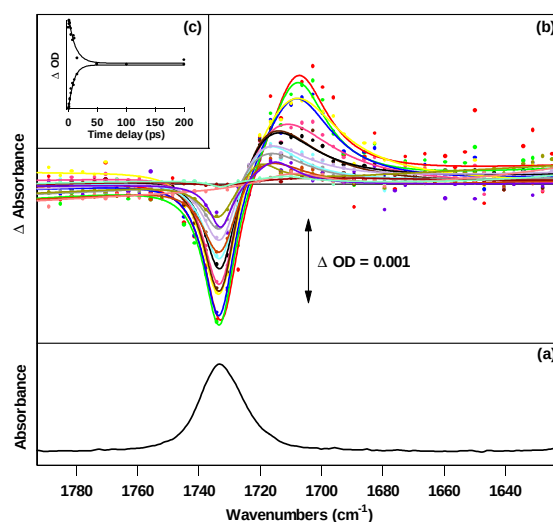


Figure 3. (a) FTIR of $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ in CH_2Cl_2 . (b) TRIR spectra of this solution from 500 fs to 200 ps after 400 nm excitation. (c) Kinetic decay traces for the transient and bleach, obtained from Lorentzian curve fits.

The dynamics of the excited state process have been analysed by performing multi-Lorentzian curve fits of the data at each time delay. Assuming that the transient band is composed of one vibrationally hot and one vibrationally cool component, the resulting kinetic traces for the transient and bleach are shown in Figure 3(c). These reveal that the lifetime of the MLCT excited state and thus the rate of back electron transfer is $10.2 \pm 1.5\text{ ps}$. This is consistent with $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ being non-emissive in fluid solution at room temperature. Analysis of the hot and cool transient band heights reveals that the vibrational cooling of the MLCT excited state occurs with a time constant of 1.9 ps.

Conclusions

In this paper we have demonstrated the potential of the PIRATE system for broadband ps-TRIR spectroscopy. Using PIRATE we have studied the excited states of a series of d^6 transition metal carbonyl complexes, which are potential probes of DNA. We have shown how a subtle change in the ligand set allows us to tune the nature of the excited state, thus allowing the design of complexes for specific applications. We have also reported the first ultrafast TRIR study of a d^8 transition metal complex. In this experiment we probed the excited state dynamics by monitoring the IR absorptions of organic reporter groups attached to an α -diimine ligand. Changes in the IR spectral profile on the picosecond timescale allowed the nature of the lowest excited state of $[\text{Pt}(\text{4,4'}\text{-(COOEt)}_2\text{-2,2'-bpy})\text{Cl}_2]$ to be assigned as MLCT. It is clear that the PIRATE facility will prove to be an invaluable addition to the Ultrafast Spectroscopy Laboratory, providing access to the complementary technique of ps-TRIR.

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Early photochemical dynamics of charge transfer excited organometallic complexes: Ultrafast CO dissociation from Charge-Transfer Excited States of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ and $[\text{Mn}(\text{Br})(\text{CO})_3(^i\text{Pr-DAB})]$

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Introduction

In previous articles^{1,2}, we have described mechanistic studies of the photochemistry of various transition metal complexes containing low-energy charge transfer excited states. In particular, we have investigated the behaviour of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ and *fac*- $[\text{Mn}(\text{Br})(\text{CO})_3(^i\text{Pr-DAB})]$ with time-resolved visible absorption spectroscopy on the ultrafast (femtosecond – picosecond) timescale. The mechanisms we have proposed in the past, however, have been suggested on the basis of kinetic data and by comparison with slower time-resolved techniques. Direct structural characterisation of the species involved with the photochemistry of the aforementioned chromium and manganese complexes has only recently been made possible by the application of the newly developed PIRATE time-resolved infrared spectroscopy apparatus at the Rutherford Appleton Laboratory's Lasers for Science Facility.

The results we describe here represent one of the first uses of the PIRATE system to study the mechanisms of photochemical reactions.

Carbonyl photodissociation from $[\text{Cr}(\text{CO})_4(\text{bpy})]$

It is known that CO loss from $[\text{Cr}(\text{CO})_4(\text{bpy})]$ proceeds via a dissociative mechanism from a Cr→bpy metal-to-ligand charge transfer (MLCT) excited state¹. The quantum yield for the process varies from 0.02 to 0.2, depending on excitation wavelength and temperature³. In the past, studies involving time-resolved visible absorption spectroscopy have identified two unreactive (trapping) MLCT states which decay to the ground state, thereby decreasing the quantum yield from the theoretical maximum of one. We have also determined that the outcome of the photochemistry of the complex (*ie.* the branching ratio between the reactive and unreactive pathways) is determined at the very earliest times after excitation (≤ 400 fs). The aim of the PIRATE study was to probe this mechanism using infrared spectroscopy by directly observing the presence of the photoproduct after short time delays and monitoring the decay of the MLCT trapping states to the ground state.

We recorded the infrared absorption spectrum of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in CH_2Cl_2 at various time delays (1 ps to 1 ns) after irradiation with 500 nm laser pulses of 150 fs width (FWHM) (see Figure 1). At early times after excitation the spectrum consists of a set of bands at negative Δ absorbance which accurately represent the ground state infrared absorption spectrum of the complex (1827, 1884, 1900 and 2009 cm^{-1}). At higher stretching frequencies than this, a very broad absorption extending from 1925 to 2070 cm^{-1} is seen. This signal decays over time, disappearing completely within 500 ps. Positive shifts of carbonyl ligand stretches, relative to the ground state, are characteristic of a reduction in electron density at the metal centre⁴. Accordingly, we assign the 1925 – 2070 cm^{-1} absorption to one or more MLCT states of $[\text{Cr}(\text{CO})_4(\text{bpy})]$. The decay of the band over time fits reasonably well to a double exponential decay function with lifetimes $\tau_1 \approx 80$ ps and $\tau_2 \approx 2$ ps, which is in broad agreement with the results of a previous time-resolved visible absorption study¹. Crucially, it is found that the bleach absorption due to depletion of the ground

state reforms with the same kinetics, implying that the decay of the excited states is, indeed, to the ground state.

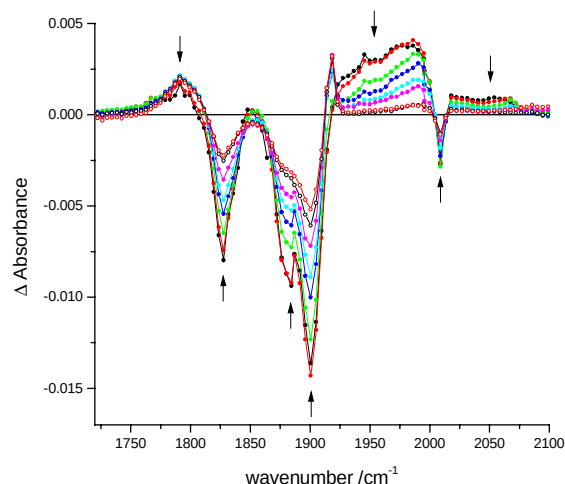


Figure 1. Time-resolved infrared spectra of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ in CH_2Cl_2 following 500 nm, 150 fs FWHM laser excitation. Time delays: ● 1 ps; ● 2 ps; ● 10 ps; ● 30 ps; ● 50 ps; ● 100 ps; ○ 200 ps; ○ 1000 ps.

A reasonably sharp band at 1791 cm^{-1} is observed. This is shifted down in frequency relative to the ground state and is fully developed at 1 ps after excitation, showing no evolution over the first nanosecond. Additionally, a sharp band at 1919 cm^{-1} is seen in spectra measured at delay times of 30 ps and longer. It is possible that this band is also present in the spectra measured between 1 and 20 ps being as it is obscured by the more intense ground-state bleach absorption at 1900 cm^{-1} . As the ground state is reformed over time and the bleach absorption bands decrease in intensity, the 1919 cm^{-1} band is revealed. Accordingly the 1919 and 1791 cm^{-1} bands are assigned to the photodissociation product *fac*- $[\text{Cr}(\text{sol})(\text{CO})_3(\text{bpy})]$ (sol = CH_2Cl_2) by comparison with previous ns-TRIR studies.⁴ The presence of this band at the earliest times after excitation suggests that CO loss does indeed occur in the very shortest times following MLCT excitation and is not a consequence of the decay of a ³MLCT trapping state.

It should be emphasised that the signals assigned here to the transient species formed by the MLCT excitation of $[\text{Cr}(\text{CO})_4(\text{bpy})]$ consist of many separate, overlapping IR absorption bands. The existence of two $[\text{Cr}(\text{CO})_4(\text{bpy})]$ excited states and one *fac*- $[\text{Cr}(\text{CO})_3(\text{bpy})]$ photoproduct species makes a complete spectral deconvolution a difficult task.

Carbonyl dissociation from *fac*- $[\text{Mn}(\text{Br})(\text{CO})_3(^i\text{Pr-DAB})]$

CO loss is known to be the initial step in the *fac*→*mer* isomerisation of *fac*- $[\text{Mn}(\text{Br})(\text{CO})_3(^i\text{Pr-DAB})]$. This is accompanied by migration of bromide to the equatorial plane. In non-coordinating solvents, fast recombination of the metal fragment with CO occurs, thus yielding the *mer* isomer of the

complex. This thermally isomerises to the more stable *fac* isomer on a timescale of seconds. In contrast to this, when irradiation is carried out in strongly coordinating solvents (eg. pyridine), the dissociated CO is replaced by solvent and the dicarbonyl complex *cis,cis*-[Mn(Br(sol)(CO)₂(ⁱPr-DAB)] (sol = solvent) is formed (see Figure 2).

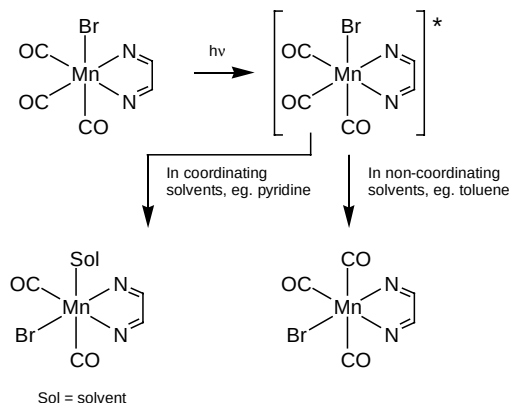


Figure 2. Photochemistry of *fac*-[Mn(Br)(CO)₃(ⁱPr-DAB)].

Although the precise mechanism of this chemistry has not yet been fully explained, it is known that the reaction is triggered by the excitation of an electron from a mixed character metal-halide molecular orbital into a π^* orbital of the ⁱPr-DAB ligand; so called MLCT/XLCT excitation. Density functional theory (DFT) calculations of the MLCT/XLCT excited state potential energy surfaces along various coordinates have indicated the presence of large, insurmountable barriers towards the dissociation of both the equatorial and axial CO ligands⁵. These calculations have also suggested that the most likely carbonyl loss pathway involves dissociation of an equatorial CO, concerted with migration of the bromide ligand into the equatorial plane, albeit still involving a large energy barrier. To overcome this, the authors of the study⁵ propose that the reaction involves resonance coupling between the excited and ground states, thus facilitating tunneling through the barrier. This process is expected to occur with a reduced probability, compared with the direct loss of CO from, say, [Cr(CO)₄(bpy)]¹¹. Hence the primary photochemical step in the dissociative isomerisation is expected to occur on a timescale considerably longer than the 20-400 fs range known for direct CO dissociation⁶.

From previous time-resolved UV/visible absorption studies on the ultrafast timescale², we have established the presence of a single species immediately after excitation (absorbing at 600 nm) which decays with a lifetime of 11 ps to form a second species (absorbing at 560 nm). This is a clean conversion displaying a clear isosbestic point. However, due to the difficulty in distinguishing excited states and photoproducts from each other, using UV/visible spectroscopy alone, we are left with at least two mechanistic interpretations:

- (i) Guided by the DFT calculations⁵, the 600 nm band is attributed to the MLCT/XLCT excited state and the 11 ps process to the concerted CO dissociation and bromide migration.
- (ii) Alternatively, if it is assumed that the CO ligand dissociates in an ultrafast manner (in a similar fashion to the aforementioned [Cr(CO)₄(bpy)] complex), the 600 nm band can be ascribed to the CO loss product [Mn(Br)(CO)₂(ⁱPr-DAB)] with the 11 ps process representing solely Br migration.

As we have seen from the case of [Cr(CO)₄(bpy)], time-resolved infrared absorption spectroscopy is a powerful technique for discriminating between excited states and dissociation photoproducts. In the situation where an excited state is present after excitation, we would expect to see a set of

CO stretching bands of identical pattern to the ground state, but shifted to higher frequency. In the case of the photoproduct being present at early times, a new pattern of bands should appear at lower frequencies.

The time-resolved infrared absorption spectrum of *fac*-[Mn(Br)(CO)₃(ⁱPr-DAB)] in pyridine solution 2 ps after 150 fs (FWHM), 500 nm excitation is shown in Figure 3. The absence of any new bands at higher energies than the highest ground state band (2025 cm⁻¹) precludes the possible existence of a charge transfer excited state directly after excitation and thus excludes hypothesis (i), above.

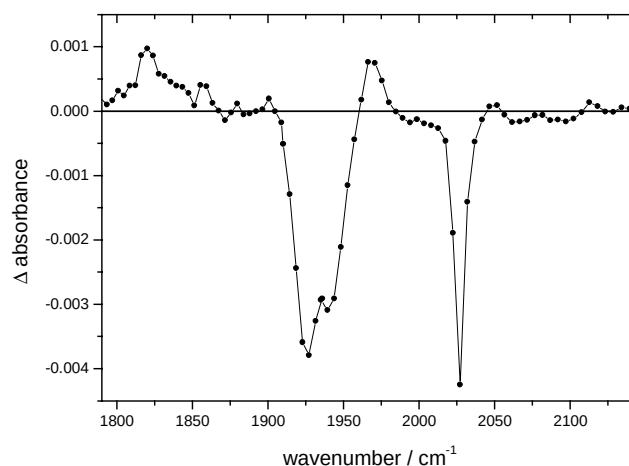


Figure 3. Time-resolved infrared spectrum of *fac*-[Mn(Br)(CO)₃(ⁱPr-DAB)] in pyridine solution 2 ps after 500 nm, 150 fs (FWHM) excitation.

The appearance of a photoproduct with $\nu(\text{C-O})$ bands at lower stretching frequencies than the ground state is tentatively assigned to the CO loss photoproduct [Mn(Br)(CO)₂(ⁱPr-DAB)], formed by ultrafast dissociation of CO from an excited state.

This experiment suggests that the movement of Br into the vacant equatorial position is not concerted with CO loss, as predicted by theory, but is a separate event, most likely occurring with a lifetime of 11 ps. However, the role of vibrational excited states is still being investigated.

Conclusions

The PIRATE facility at the Rutherford Appleton Laboratory has provided the users of the LSF with an invaluable tool for the structural characterisation of excited states and transient photoproducts which, until now, have only been observable by means of their electronic-absorption UV/visible chromophores.

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TR³, Kerr-gate emission and PIRATE study of Interligand Electron Transfer in [Re(MQ⁺)(CO)₃(dmb)]²⁺

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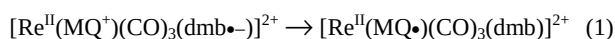
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Introduction

Irradiation of [Re(MQ⁺)(CO)₃(dmb)]²⁺ (MQ⁺ = *N*-methyl-4,4'-bipyridinium, dmb = 4,4'-dimethyl-2,2'-bipyridine) in the near UV region (330–400 nm) populates simultaneously Re→dmb and Re→MQ⁺ MLCT excited states, (Figure 1), abbreviated hereinafter MLCT(dmb) and MLCT(MQ⁺), respectively. The MLCT(dmb) state can be viewed as [Re^{II}(MQ⁺)(CO)₃(dmb•-)]²⁺. Its population is followed by an inter-ligand electron transfer:



which produces a relaxed MLCT(MQ⁺) excited state formulated as [Re^{II}(MQ•)(CO)₃(dmb)]²⁺, see Figure 1.

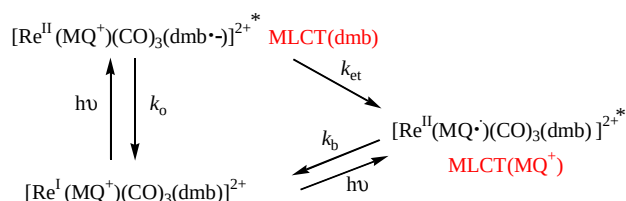


Figure 1. Excited state reaction pathways.

In order to understand the dynamics of this reaction, we have studied fs-ps TR visible absorption spectra in acetonitrile and ethylene glycol. The spectra show a weak absorption in the 420–470 nm region due to the MLCT(dmb) excited state [Re^{II}(MQ⁺)(CO)₃(dmb•-)]²⁺ and a very strong absorption band centred at 640 nm, which belongs to the MQ• chromophore of the MLCT(MQ⁺) state, that is the [Re^{II}(MQ•)(CO)₃(dmb)]²⁺ ET product. Time constant of the MLCT(dmb) → MLCT(MQ•) inter-ligand ET was determined¹⁾ as 8.3±0.4 ps in CH₃CN and 14.0±1.6 ps in ethylene glycol.

Time Resolved Resonance Raman (TR³)

Although the fs-ps TR visible absorption spectra have afforded a straightforward mechanistic picture and accurate kinetic data, some important information about the inter-ligand ET is still missing: (i) Are some of the high-frequency vibrations activated during the inter-ligand ET and does this activation persist on a longer time-scale? (ii) Is the ET product formed vibrationally relaxed or hot (excited)? (iii) Are the vibrational relaxation dynamics solvent-dependent? (iv) Is the Re(CO)₃ moiety affected by the inter-ligand ET?

To answer these questions, it is necessary to resort to time-resolved vibrational spectroscopic techniques, namely to ps-TR resonance Raman (TR³) and IR absorption. Shown in Figure 2 are the TR³ spectra of [Re(MQ⁺)(CO)₃(dmb)]²⁺ in CH₃CN. The spectra were measured with the Raman probe wavelength of 600 nm, that is in resonance with the MQ• absorption band. They show only Raman bands due to vibrations of the MQ• ligand:²⁾ V(CC)_{ir}/V(CC) 1648 cm⁻¹, V(CN)/V(CCH) 1516 cm⁻¹, V(CCH)/V(CC)_{ir} 1352 cm⁻¹ and V(CCN)/V(CN) 1018 cm⁻¹.

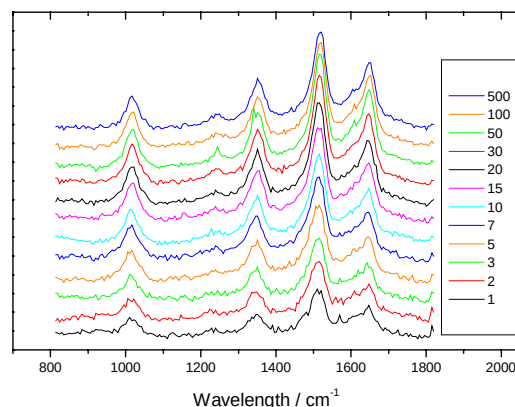


Figure 2. TR³ spectra of [Re(MQ⁺)(CO)₃(dmb)]²⁺ in CH₃CN measured between 1 and 500 ps after laser pulse excitation at 400 nm. The spectra were measured with the Raman probe wavelength of 600 nm.

(CC)_{ir} denotes the inter-ring C-C bond. All the MQ• Raman peaks are present already in the spectra measured at 1 ps with low intensities. Their integrated intensities then grow with a time constant approximately corresponding to the ET time. The Raman peak positions show a dynamic shift by 4–7 cm⁻¹ with time to higher wavenumbers. This shift depends exponentially on the time for all bands studied and the corresponding lifetime depends on the particular peak and the solvent. In CH₃CN time constants of 24.2 ± 2.2, 16.1 ± 2.2 and 15.1 ± 3.1 ps were determined for the peaks at 1516, 1352 and 1018 cm⁻¹. Raman peak widths decrease with time constants slightly lower than those found for the peak shifts: 17.3 ± 3.4, 10.0 ± 4.1, 12.4 ± 4.1 ps, respectively. Surprisingly, kinetics of peak shifts and narrowing in ethylene glycol are faster than in CH₃CN, occurring in the range 11–16 ps and 1–7 ps, respectively. The absolute values of the dynamic peak shifts being very small in both solvents, it is obvious that all the Raman peaks observed occur very close to their final positions already at the earliest time delays measured, 1–2 ps. Moreover, no anti-Stokes peaks were observed in the ps TR³ spectra. Hence, it can be concluded that the promoting high-frequency modes relax faster or alongside the dmb•-→MQ⁺ interligand ET. There is no evidence for a specific activation of high-frequency vibrations in the ET product [Re(MQ•)(CO)₃(dmb)]²⁺. At the same time, the small upward dynamic shifts and broadening of the MQ• Raman peaks show that the extra energy discharged in the ET reaction (ca. 0.5 eV) is rapidly redistributed into many low frequency vibrations, leaving the [Re^{II}(MQ•)(CO)₃(dmb)]²⁺ ET product initially vibrationally hot. A final relaxation then follows on a time scale of a few tenths of picoseconds.

Time Resolved Emission Spectra

The Kerr Gate was used to measure the temporal evolution of the emission profile.

Time-resolved emission (Figure 3) shows a strong, broad absorption centred around 530 nm, which decays, while

another, much weaker band centred at 680 nm grows. These correspond to MLCT(dmb) and MLCT(MQ⁺) respectively as seen from the transient absorption spectra.

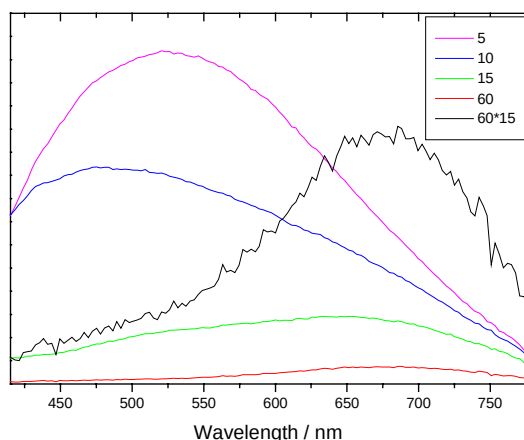


Figure 3. Time –resolved emission of $[\text{Re}(\text{MQ}^+)(\text{CO}_3)(\text{dmb})]^{2+}$ in CH_3CN .

Time Resolved Infra-Red Absorption (PIRATE)

The final piece of mechanistic information on the interligand ET reaction (1) came from picosecond TR IR absorption spectra (Figure 4). Optical excitation of $[\text{Re}(\text{Et-py})(\text{CO})_3(\text{dmb})]^+$ populates an MLCT(dmb) excited state, which can be described as $[\text{Re}^{\text{II}}(\text{Et-py})(\text{CO})_3(\text{dmb}\bullet-)]^+$. Accordingly, the ps IR absorption pattern shows three bands shifted to higher frequencies (1970(w), 2011(w), 2060(s) cm^{-1}) relative to their ground state positions (1930(br), 2034(s), cm^{-1} , the former comprising two unresolved bands). This is caused by the depopulation of $\text{Re}(\text{d}\pi)$ orbitals on $\text{Re} \rightarrow \text{dmb}$ MLCT excitation which diminishes the $\text{Re} \rightarrow \text{CO}$ π back donation. The ps TR-IR spectra show just a small upward shift and narrow during the first 10 ps due to relaxation. Excited state bands do not change further, in accordance with a long $^3\text{MLCT}$ excited state lifetime. TR-IR spectra of $[\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb})]^{2+}$ measured at early times after excitation show the typical MLCT(dmb) spectral pattern (1960(vw), 2010(vw), 2060(m) cm^{-1}) due to initial formation of $[\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb}\bullet-)]^{2+}$. In addition, a weak band at 2100 cm^{-1} is already present at 1 ps. Subsequently, its intensity increases with a time constant approximately equal to that of the ET reaction (1). Intensity of the $[\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb}\bullet-)]^{2+}$ bands decreases concomitantly. The new spectral pattern (1997(vw), 2100(s) cm^{-1}) corresponds to the ET product $[\text{Re}^{\text{II}}(\text{MQ}\bullet)(\text{CO})_3(\text{dmb})]^{2+}$. The large difference between the IR spectral patterns of $[\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb}\bullet-)]^{2+}$ and $[\text{Re}^{\text{II}}(\text{MQ}\bullet)(\text{CO})_3(\text{dmb})]^{2+}$ is rather surprising. It shows that the structure and electron distribution in the $\text{Re}(\text{CO})_3$ fragment are both strongly affected by the interligand ET. The upward shift of the highest $\text{V}(\text{CO})$ band indicates a decrease of electron density on the metal, presumably due to a higher localization of the excited electron on the $\text{MQ}\bullet$ ligand as compared with $\text{dmb}\bullet-$. It is also interesting to note that the position of the highest $\text{V}(\text{CO})$ band of $[\text{Re}^{\text{II}}(\text{MQ}\bullet)(\text{CO})_3(\text{dmb})]^{2+}$ does not change with time after 2 ps. This shows that the ET reaction is accompanied by very fast redistribution of vibrational energy to low-frequency modes and solvent librations. This conclusion agrees with the TR^3 results discussed above.

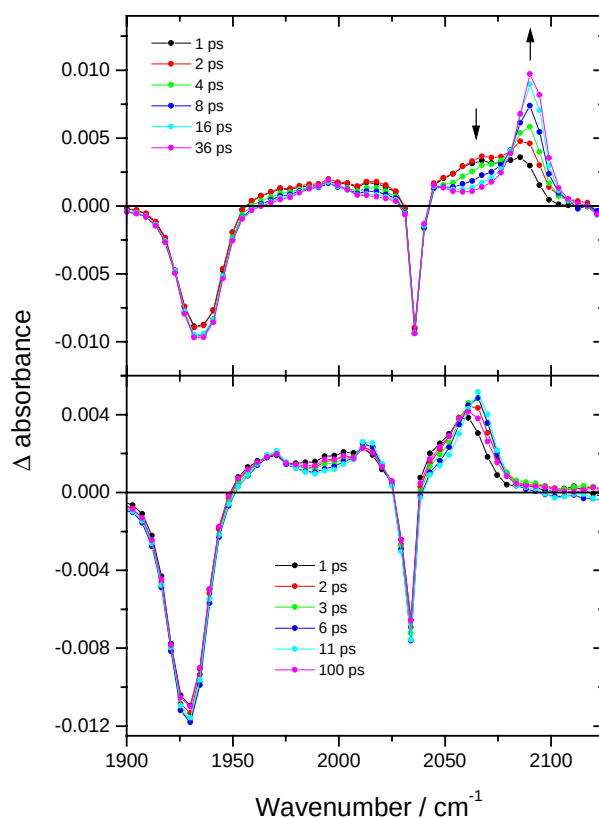


Figure 4. Top: TR-IR spectra of $[\text{Re}(\text{MQ}^+)(\text{CO}_3)(\text{dmb})]^{2+}$ in CH_3CN . Bottom: TR-IR spectra of $[\text{Re}(\text{Et-py})\text{CO}_3)(\text{dmb})]^+$ in CH_3CN .

Conclusion

The picosecond TR visible absorption spectra of $[\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb}\bullet-)]^{2+}$ allowed us to determine accurately the kinetics of the inter-ligand ET (1) and to identify both excited states involved. The latter was possible due to the fact that the $\text{dmb}\bullet-$ and $\text{MQ}\bullet$ chromophores present in the initial and final state, respectively, have characteristic visible absorption bands. TR vibrational spectra confirmed this mechanism and brought additional information on the molecular details of the ET reaction. The ps TR-IR and TR^3 have shown that the ET is accompanied by very fast energy dissipation from $\text{V}(\text{CO})$ and $\text{MQ}\bullet$ -localized high-frequency vibrations. The small time-dependent shifts of Raman peaks observed by TR^3 show that at least part of this energy is redistributed intramolecularly, into low-frequency skeletal modes. Moreover, TR-IR spectra indicate that the interligand ET is accompanied by structural changes of the $\text{Re}(\text{CO})_3$ moiety and increasing localization of the excited electron.

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Structure of the Intramolecular Charge Transfer State of 4-Dimethylaminobenzonitrile (DMABN): Determined by Time-Resolved Resonance Raman Spectroscopy

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Introduction

The structure of the intramolecular charge transfer (ICT) state of DMABN, formed only in polar solvent, has been a subject of speculation for more than 40 years¹. Monomolecular models interpreting the nature and structure of the ICT state fall into four main classes: TICT (Twisted ICT)², WICT (Wagged ICT)³, PICT (Planar ICT)⁴, and RICT (Rehybridisation ICT)⁵. All have an ICT mechanism in common but they differ in modes related to the ICT reaction.

Direct experimental evidence for the structure of the ICT state of DMABN in solution has recently been obtained using time-resolved infrared (TRIR)⁶⁻⁸ and picosecond Kerr gated time-resolved resonance Raman (ps-K-TR³) spectroscopy^{9,10}. The observation of the ICT state C≡N stretching mode at ~2100 cm⁻¹ rules out the RICT model as this model predicts a ~1650 cm⁻¹ C≡N stretch frequency which is far away from that observed by both TRIR and ps-K-TR³. This leaves the remaining three models in dispute. With the aim of discriminating between the TICT and PICT models Dryer and Kummrow¹¹ have performed full optimization *ab initio* CASSCF calculations. They conclude that an experimental determination of the frequency of phenyl-amino stretching mode, $\nu(\text{ph-N})$, will allow a final decision between the TICT and PICT models to be made. The TICT model predicts a downshift of the $\nu(\text{ph-N})$ frequency relative to the ground state whilst the PICT model requires an up-shift. However, The crucial $\nu(\text{ph-N})$ mode has to date not been identified until our recent ps-K-TR³ study. We report here the ps-K-TR³ results of the ICT state of DMABN and its isotopic labeled analogous DMABN-N¹⁵, DMABN-d₄, and DMABN-d₆ in order to help vibrational mode assignments. The results provide new evidence and shed light on the determination of the ICT state structure.

Experimental arrangements

The experiments were carried out using a TR³ system based on optical parametric amplifiers (OPAs), described elsewhere¹⁰ with 90° collection configuration¹². The pump wavelength was 267 nm. Probe wavelength of 330 nm was used in resonance with the strong electronic transitions of the ICT state of DMABN¹³. Pump and probe beams had 5-10 and 1-5 μJ energy/pulse, respectively, ~1 ps pulse-length, and parallel polarisations. Solution filter of *trans*-stilbene was placed in front of the spectrometer to block the Rayleigh lines and scattered pump light. Details of acquisition methods and the Kerr gate are given in Reference 14. Here we used an improved system based on benzene with throughput up to 30 % (excluding polariser losses). Each spectrum shown is the sum of 3 individual background-subtracted spectra with accumulation times typically of 2000 seconds. The filters attenuated all bands below 900 cm⁻¹.

Since both the ground and ICT state of DMABN absorb in the 330 nm region, transient resonance Raman (TR²) spectra of the ICT state were obtained also by single-color pump probe method. The 330 nm laser, ~20 ns pulse duration, was

generated by frequency doubling of 660 nm dye (DCM) laser pulse pumped by 308 nm excimer laser. The detail of obtaining the TR² spectra can be found in Reference 15.

Acetonitrile Raman bands were used to calibrate all the spectra with an estimated accuracy of $\pm 10 \text{ cm}^{-1}$ and $\pm 3 \text{ cm}^{-1}$ in absolute frequency for the ps-K-TR³ and TR² spectra, respectively. The spectra are not corrected for variations in throughput and detector efficiency.

Spectroscopic grade solvents were used as received. Commercial available DMABN was re-crystallized three times before use. DMABN-N¹⁵, DMABN-d₆, and DMABN-d₄ were synthesized according to References 3, 16, 17, and their purities confirmed by NMR and mass spectroscopic analysis. Sample concentrations were $5 - 10 \times 10^{-3} \text{ mol dm}^{-3}$ for the ps-K-TR³ and TR² experiments.

Results

Figure 1 shows Ps-K-TR³ spectra of the ICT state of DMABN, DMABN-N¹⁵, DMABN-d₆, and DMABN-d₄ in methanol obtained at 50 ps delay time between pump and probe pulses.

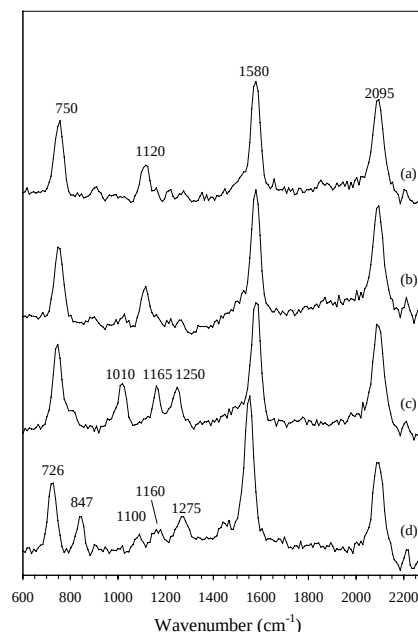


Figure 1. Ps-K-TR³ spectra of the ICT state of (a) DMABN, (b) DMABN-N¹⁵, (c) DMABN-d₆ and (d) DMABN-d₄ obtained with 267 nm pump, 330 nm probe wavelengths at 50 ps delay time in methanol.

Figure 2 shows the TR² spectra of the four compounds. The close resemblance of all spectral features in the TR² to the corresponding ps-K-TR³ spectra demonstrates that they originate from the same state, the ICT state of DMABN. This observation is also supported by the position of the cyano C≡N stretching frequency, which serves as a marker band to identify the state being probed^{6,7,9}.

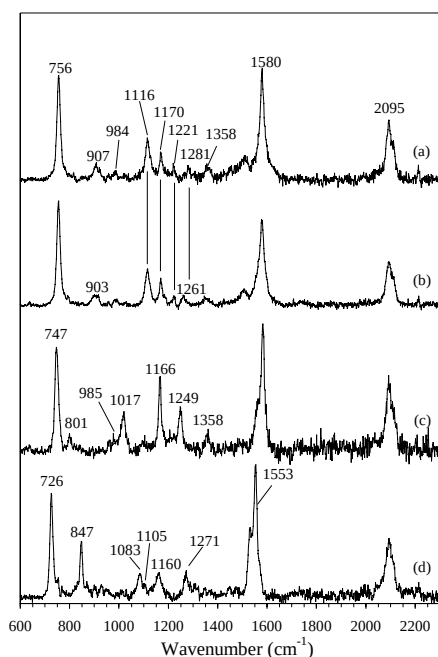


Figure 2. TR² spectra of the ICT state of (a) DMABN, (b) DMABN-N¹⁵, (c) DMABN-d₆ and (d) DMABN-d₄ obtained with 330 nm excitation in methanol.

The TR² data offer superior spectral resolution. For example, for DMABN and DMABN-N¹⁵, the broad strong asymmetric ~1120 cm⁻¹ band observed using the picosecond apparatus is resolved into two bands at ~1170 and ~1116 cm⁻¹, and the weak features observed in the corresponding ps-K-TR³ spectra all appear more clearly in the TR² spectra, such as the bands at 907, 984, 1221, 1281 cm⁻¹ for DMABN and 903, 987, 1221, 1261 cm⁻¹ for DMABN-N¹⁵ (Figure 2). Band frequencies and relative intensities computed from Lorentzian fitting of the spectra displayed in Figure 2 are listed in Table 1 with their tentative assignment included. The assignments were made based on comparison with frequencies and isotopic shifts of corresponding modes of the ground state compounds. Vibrational analysis based on *ab initio* DFT calculation for DMABN and its various isotopic labeled analogues has been reported very recently by Okamoto et al.¹⁸ and ourselves¹⁹.

Assignment	DMABN	DMABN-N ¹⁵	DMABN-d ₆	DMABN-d ₄
C≡N	2095(1.00)	2095(1.00)	2095(1.00)	2095(1.00)
C=C (8a)	1580(1.19)	1578(1.50)	1581(1.15)	1553(1.03)
	1502(0.60)	1504(0.36)		
C=C (19a)	1446(0.17) ^b		1448(0.13) ^b	
	1358(0.12)	1352(0.11)	1358(0.11)	
v(ph-N) (13)	1281(0.08)	1261(0.09)	1249(0.28)	1271(0.22)
v(ph-CN) (7a)	1221(0.06)	1221(0.04)	1212(0.21)	1105(0.07)
CH bend (9a)	1170(0.18)	1170(0.25)	1166(0.41)	847(0.30)
ρ ^s _{Me}	1116(0.44)	1115(0.51)	1017(0.33)	1160(0.45)
CH bend (18a)	984(0.06)	987(0.07)	985(0.05)	
v ^s (NC ₂)	907(0.17)	903(0.22)	801(0.11)	899 (0.01)?
ring breath (1)	756(0.84)	755(1.13)	747(0.81)	726(0.71)
1+ρ ^s _{Me}	1856 ^c	1864 ^c	1765 ^c	

Table 1. Frequencies and provisional assignments of resonance Raman bands of the ICT state of DMABN, DMABN-N¹⁵, DMABN-d₆ and DMABN-d₄.^a

a: Relative intensities of bands are indicated inside parentheses

b: From Reference 10

c: Bands are from ps-K-TR³ spectra shown in Figure 1

? band with uncertain assignment.

Discussion

Frequencies of C≡N stretching and ring local modes, observed at 2096, ~1580, ~1221, ~1170, ~984, and ~756 cm⁻¹ for the ICT state of DMABN are found to be very similar to those of the benzonitrile radical anion recorded at: 2093, 1592, 1268, 1178, 991, and 760 cm⁻¹.²⁰ This implies that the benzonitrile subgroup in the ICT state of DMABN resembles the benzonitrile radical anion, which is consistent with a full charge transfer mechanism from the dimethylamino to the benzonitrile group suggested by the TICT model. Frequency downshift of the ring CC stretching modes, such as Δν = ~28 cm⁻¹ for the Wilson 8a C=C vibration, on-going from the ground state to ICT state indicates loosening of the ring skeleton upon the ICT state formation. In addition, the substantial increase in difference between the Wilson 8a and 19a C=C modes of the ICT state (131 cm⁻¹) in comparison with the ground state (79 cm⁻¹)^{18,19} implies that the ICT state structure gains some quinoidal character when compared with the ground state structure.

Three bands of the ICT state, 1281, 1116, 907 cm⁻¹ were found to be sensitive to the amino group substitutions. They were attributed consequently to modes dominated by vibrations of the v(ph-N), methyl rocking (ρ^s_{Me}) and symmetric N-(CH₃)₂ stretching (v^s(NC₂)). It is important to note that, comparing with the ground state, the v^s(ph-N) frequency shifts down by ~96 cm⁻¹ for the ICT state.

It has been shown by extensive studies of the geometry and electronic conformation of aromatic amino compounds that the v^s(ph-N) mode could be viewed as a good probe for evaluating the bonding configuration around the amino N atom and the electronic distribution of the aromatic amine compounds^{21,22}. The frequencies of typical single and double C-N bonds are ~1200 and ~1600 cm⁻¹, respectively. Structure of the ground state DMABN has been determined by X-ray diffraction and microwave spectroscopy to be slightly pyramidal with ~11-15° wagging angle^{23,24}. Its amino conformation is therefore similar to well studied closely related compound dimethylaniline (DMA, ~27° wagging angle)^{21,22}. The electronic coupling between the amino nitrogen lone pair electrons and the phenyl ring π system (nπ conjugation) is quite extensive in the ground state of DMABN as indicated by the 1377 cm⁻¹ v^s(ph-N) frequency^{18,19}. Thus, the ~96 cm⁻¹ down shift of this mode on going from the ground state to the ICT state implies a substantial decrease in the nπ interaction and electronic isolation of the amino from the benzonitrile subgroups. This is in good agreement with the minimum overlap principle of the TICT model but contrary to the strong electronic coupling proposed by the PICT model. It is also consistent with the TICT model v^s(ph-N) frequency shift predicted theoretically by Dryer and Kummrow¹¹.

In addition, we found that the frequencies and isotopic shifts of the amino related modes, the v(ph-N), ρ^s_{Me} and v^s(NC₂) of the ICT state of DMABN are similar to those of DMA-H⁺ (1245, 1132, 900 cm⁻¹). For DMA-H⁺, involvement of the nitrogen lone pair in an N-H bond leads to substantial electronic decoupling from the ring π system. The amino group of DMA-H⁺ has thus been suggested to be a pure pyramidal sp³ hybridization conformation²⁵, different from the planar or near planar sp² hybridization conformation of neutral DMA and ground state of DMABN. The resemblance of the amino related modes of the ICT state of DMABN to DMA-H⁺ indicates on the one hand, the electronic isolation of the amino group from the rest of the molecule which lends further support to the TICT model; on the other hand, an sp³ pyramidal character of the ICT state amino group. Theoretical studies show that a wagging motion of the DMABN amino group alone cannot lead to a stable high polar excited state²⁶. However, a mainly twisting structure combined with some wagging of the amino group might be a realistic conformation for the ICT state. Such a

structure has been suggested by CASSCF study of DMABN performed by Serrano-Andres *et al*²⁷⁾. We notice that a full optimisation of the ICT state structure considering both the twisting and wagging motion and also including possible solvation effects is still lacking. It is hoped that the data presented here can stimulate this much needed work.

Conclusion

The ~96 cm⁻¹ downshift of the mode dominated by $\nu(\text{ph-N})$ stretching and close resemblance of $\text{C}\equiv\text{N}$ stretching and ring local mode frequencies of this state to those found in the benzonitrile radical anion provide unequivocal experimental evidence of a full charge transfer from the amino to the benzonitrile subgroup. This is consistent with the electronic decoupling TICT model. However, because the spectroscopic evidence shows similarities with protonated dimethylaniline (DMA-H^+), the results also suggest some pyramidal character for the ICT state amino conformation.

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Time-resolved Study of the Triplet State of 4-dimethylaminobenzonitrile (DMABN)

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Introduction

The triplet state of DMABN has been extensively studied experimentally¹⁻⁴, and theoretically^{5,6}. Intersystem crossing (ISC) has been shown to be the principal non-radiative deactivation channel for singlet excited states, the LE and ICT state, irrespective of solvent polarity^{2,7,8}. However, the electronic and structural properties of the lowest triplet ($^3T_1$) state and their sensitivity to solvent polarity thus remain unclear. Although most work suggests a planar $\pi\pi^*$ nature for the $^3T_1$ state irrespective of solvent polarity¹⁻³, the view is challenged by TRIR studies performed by Hashimoto and Hamaguchi which identify a twisted charge transfer triplet state (^3TICT) in polar solvent⁹. In particular, no vibrational bands of $^3T_1$ have previously been reported, other than the $C\equiv N$ stretch. Although the frequency of this mode reflects the extent of negative charge localization on the cyano group, it alone can not be used to determine structure, which is mostly related to the conformation of the dimethylaniline subgroup. Frequencies of the amino nitrogen-phenyl ring stretching mode ($\nu(\text{ph-N})$) and ring modes, such as $C=C$ stretching vibrations, are essential in evaluation of its bonding configuration¹⁰⁻¹². The lack of structural data has led to controversy on both the triplet geometry (planar or TICT) and the ISC mechanism. Here we present and discuss time-resolved resonance Raman (TR³) and transient absorption (TA) data that directly resolve these issues.

Experimental arrangements

Experimental detail is described in Reference 13. In short, the ns-TR³ spectra were obtained with 308 nm pump and 532 nm probe wavelengths. Pump and probe energies were between 0.5 and 1 mJ, the repetition rate was 10 Hz. The spectra were accumulated over 20-100 min. with pump only and probe only spectra being subtracted. Argon bubbling conditions were used on the sample solution to remove oxygen. Acetonitrile Raman bands were used to calibrate the spectra with an estimated accuracy of $\pm 5 \text{ cm}^{-1}$ in absolute frequency. Transient absorption was measured using the arrangement described in Reference 14, with a pump wavelength of 267 nm, under "magic angle" conditions.

Spectroscopic grade solvents were used as received. Commercially available DMABN was re-crystallized three times before use. DMABN- N^{15} , DMABN- d_6 , and DMABN- d_4 were synthesized according to References 15, 16, 17, and their purities confirmed by NMR and mass spectroscopic analysis. Sample concentrations were $1 - 5 \times 10^{-3} \text{ mol dm}^{-3}$ for the TA and TR³ experiments.

Results

TA spectra of DMABN in ethanol from 400 to 700 nm recorded at various delay times are displayed in Figure 1. A broad band peaking at $\sim 550 \text{ nm}$ grows in as the $\sim 420 \text{ nm}$ peak decays on a timescale extending to 3 ns. An isosbestic point at $\sim 450 \text{ nm}$ indicates conversion between two distinct states. Referring to the TA and flash photolysis measurement performed by Okada et al.¹ and Köhler et al.², the early time $\sim 420 \text{ nm}$ band was attributed to $S_n - S_1$ absorption from the ^1TICT state, while the later time $\sim 550 \text{ nm}$ band was attributed to $T_n - T_1$ absorption

from the $^3T_1$ state. It is important to note that the temporal evolution of the TA spectra shows clearly the precursor-successor relationship between the ICT singlet and the triplet state of DMABN. The time-dependence of the ^1TICT to $^3T_1$ conversion is consistent with the $\sim 2 \times 10^8 \text{ s}^{-1}$ ISC rate constant reported before^{7,8}. As the $\sim 550 \text{ nm}$ $T_n - T_1$ absorption was also observed in nonpolar solvent², we chose 532 nm as probe wavelength for the TR³ experiments.

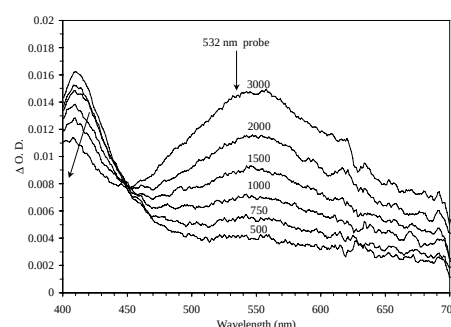


Figure 1. Transient absorption spectra of DMABN in ethanol obtained with 267 nm excitation.

ns-TR³ spectra of the $^3T_1$ state of DMABN in nonpolar solvent hexane and polar solvent methanol are shown in Figure 2. The resemblance seen in Figure 2 between the spectra in the two solvents is striking evidence that the same state is formed in both solvents. The $\sim 2040 \text{ cm}^{-1}$ frequency of the $C\equiv N$ band coincides with the TRIR $C\equiv N$ frequency recorded by Hashimoto and Hamaguchi⁹ in butanol at $\sim 100 \text{ ns}$ delay time and we conclude we are probing the same state here, in both methanol and hexane. However, our observation of the same $C\equiv N$ frequency also in nonpolar solvent is different from the TRIR study which presents one unusually broad and low intensity IR absorption band at $\sim 2000 \text{ cm}^{-1}$ in hexane and attributed to an alternative triplet state.

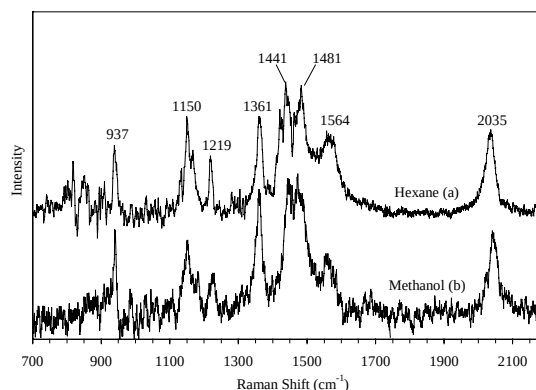


Figure 2. ns-TR³ spectra of the $^3T_1$ state of DMABN in hexane (a) and methanol (b) obtained by using gated O-SMA diode array detector with 308 nm pump and 532 nm probe wavelengths at 100 ns delay time.

In order to help assignment of the observed Raman band and gain structural information of the $^3T_1$ state, ns-TR³ experiments were carried out also on DMABN-N¹⁵, DMABN-d₆ and DMABN-d₄. Their spectra together with that of DMABN are displayed in Figure 3. Band frequencies and relative intensities computed from Lorentzian fitting are listed in Table 1 with their tentative assignment included. The assignments were made based on comparison with frequencies and isotopic shifts of corresponding modes of the ground state compounds.

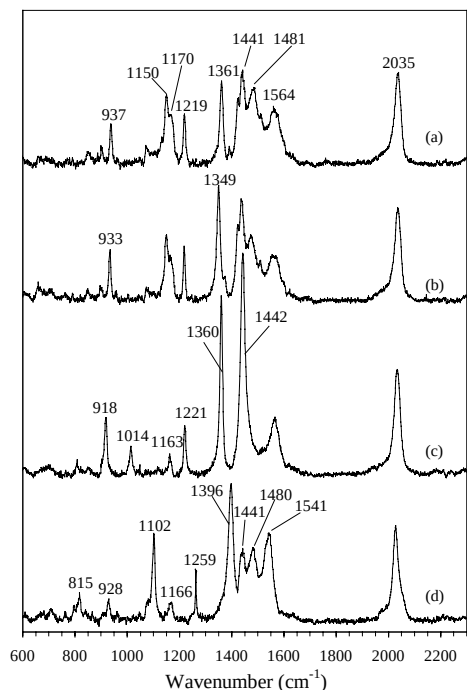


Figure 3. ns-TR³ spectra of the $^3T_1$ state of (a) DMABN, (b) DMABN-N¹⁵, (c) DMABN-d₆ and (d) DMABN-d₄ obtained by using a CCD detector with 308 nm pump, 532 nm probe wavelengths at 50 ns delay time in hexane.

Assignment	DMABN	DMABN-N ¹⁵	DMABN-d ₆	DMABN-d ₄
C≡N	2035(1.00)	2035(1.00)	2033(1.00)	2028(1.00)
ring C=C (8a)	1564(1.10)	1562(0.90)	1562(0.87)	1541(1.13)
ring C=C (8b)	1513(0.08)	1510(0.07)	1513(0.08)	
methyl def.	1481(1.13)	1475(0.86)		1480(0.98)
ring C=C (19a)	1441(0.63)	1438(0.62)	1442(1.62)	1259(0.23)
methyl def.	1422(0.15)	1422(0.17)	1132?	1441(0.38)
v(ph-N)	1361(0.43)	1349(0.65)	1360(0.69)	1396(1.10)
v(ph-CN)	1219(0.17)	1218(0.15)	1221(0.16)	1102(0.38)
CH bend (9a)	1170(0.23)	1168(0.21)	1163(0.07)	815(0.12)
ρ_{Me}^s	1150(0.47)	1149(0.36)	1014(0.12)	1166(0.12)
ρ_{Me}'	1086(0.27)	1080(0.10)	918(0.24)	1079(0.08)
$\nu^s(\text{NC}_2)$	937(0.15)	933(0.17)	808(0.05)	928(0.10)

Table 1. Frequencies and provisional assignments of resonance Raman bands of the $^3T_1$ state of DMABN, DMABN-N¹⁵, DMABN-d₆ and DMABN-d₄.^a

a: Relative intensities of bands are indicated inside parentheses ? bands: with uncertain assignments.

Discussion

Frequencies of the ring modes and dimethylamino group related modes of the $^3T_1$ of DMABN and their isotopic shifts upon the methyl and ring deuteration are found to closely resemble the corresponding modes of radical cation of dimethylaniline (DMA⁺)^{10,11}. For example, the 1564 (C=C), 1361 (v(ph-N)), 1150 cm⁻¹ (methyl rocking, ρ_{Me}^s) have their corresponding

bands of DMA⁺ at 1568, 1366, and 1166 cm⁻¹. This implies that the dimethylaniline subgroup of the $^3T_1$ of DMABN possesses a similar property to DMA⁺ and a full charge separation from this group to the cyano group in the $^3T_1$ of DMABN. This is also supported by the strikingly low frequency of the C≡N stretching at 2035 cm⁻¹, corresponding to ~185 and 65 cm⁻¹ downshift from the ground state (~2220 cm⁻¹) and ICT state (~2100 cm⁻¹), respectively. The reduction in C≡N frequency reflects a significant decrease of the C≡N bond order that can be interpreted to be due to intensive localization of the transferred charge on the C≡N antibonding orbital in the $^3T_1$ state. In addition, because frequencies of the amino related modes are similar in the $^3T_1$ and S₀ state of DMABN, it is reasonable to infer that it is the ring that acts as the donor from which charge is transferred onto the cyano group upon the formation of the $^3T_1$. This charge separation leads to substantial weakening of the ring π bonding strength with the amino group remaining almost intact.

The charge-separated character of the $^3T_1$ proposed here is consistent with previous results. It accounts for the substantially higher dipole moment of the triplet state (12 D) than of S₀ (6 D)¹⁵. It is also in full agreement with the ESR measurements of Köhler *et al*²) and Wagner *et al*⁴) who found a charge-separated 1,4-biradicaloid structure for the $^3T_1$ of DMABN with high spin density on the cyano group, the amino group acting as π -delocalizer conjugated with the ring.

Experimental and theoretical studies of resonance Raman spectra of DMA⁺ and its isotopic analogue show that it possesses a conjugated planar structure with quinoidal character. According to the similarity in vibrational frequencies of related modes, we suggest the same structure for conformation of the dimethylaniline subgroup in the $^3T_1$ state of DMABN. Increased quinoidal character of the $^3T_1$ state comparing with the ground state of DMABN is reflected by the larger difference between the C=C modes the Wilson 8a and 19a for the $^3T_1$ state (142 cm⁻¹) than the ground state (79 cm⁻¹).

The proposed structure is also in good agreement with previous work. For example, Köhler *et al*²) and Günther *et al*³) suggest the same structure for the triplet based on the similarity of phosphorescence and $^3T_n - ^3T_1$ transient spectra from DMABN and forced planar DMABN derivatives. It is also supported by results of several recent theoretical investigations^{5,6}).

As to the ISC mechanism and its response to solvent polarity, the temporal evolution of the transient absorption spectra presented by us (above) and Okada *et al*¹), the ns to ms time scale $^3T_n - ^3T_1$ spectra presented by Wang⁴) and Köhler *et al*²), and the phosphorescence measurements^{2,3}), are all consistent with the $^3T_1$ state being the only intermediate involved in the non-radiative deactivation channels of the singlet excited states of DMABN, independent of solvent polarity. Therefore, ISC deactivation channels of the singlet excited state of DMABN in the solution phase can be described as: $^1LE \rightarrow ^3T_1 \rightarrow S_0$ and $^1TICT \rightarrow ^3T_1 \rightarrow S_0$. Due to the significant difference in electronic and structural properties of the four states involved, the processes occur through multi-charge-transfer accompanied by multi-structural reorganization.

Conclusion

Nanosecond time-resolved resonance Raman spectra of the triplet states of DMABN, DMABN-N¹⁵, DMABN-d₆ and DMABN-d₄ have been obtained over the frequency range from 700 to 2300 cm⁻¹. Isotopic shifts identify modes associated with the dimethylaniline subgroup. There is no significant difference between spectra recorded in polar and non-polar solvents implying that the lowest triplet state ($^3T_1$) has only one form. Our results characterize it as planar in structure with a high negative charge localization on the cyano group and a substantial loosening of the ring skeleton with conjugation extending to the amino group. Non-radiative deactivation of the

singlet intramolecular charge transfer state through ISC is discussed in relation to the transient absorption spectra.

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ps-TR³ Observation of the Iso-CH₂Cl-I and Iso-CH₂I-Cl Photoproducts from the “Photoisomerization” Reactions of CH₂ClI in the Solution Phase

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Introduction

Many polyhalomethane molecules exhibit characteristic transient absorption bands after ultraviolet excitation in condensed phase environments. A combination of nanosecond transient resonance Raman experiments and density functional theory computations has begun to be used to identify clearly and characterize the photoproduct species that give rise to these transient absorption bands for a number of polyhalomethanes containing iodine and bromine atoms²⁻⁵. Excitation of either A-band or B-band CH₃I and CH₂BrI produces the same iso-CH₃I and iso-CH₂I-Br species respectively^{2,3}. This suggests that the production of iso-polyhalomethane species does not occur for a particular transition and probably happens generally after ultraviolet excitation of $n \rightarrow \sigma^*$ transitions localized on C-X bonds in the condensed phase. The lifetime or stability of the iso-polyhalomethane species produced can vary considerably and this will likely affect the chemistry of these species. We note that we could not detect any isomer species associated with CH₂ClI in room temperature solutions on the nanosecond time scale² although the iso-CH₂Cl-I species was readily observed in low temperature (12 K) matrices^{6,7}. A recent femtosecond transient absorption study for the ultraviolet photolysis of CH₂ClI in room temperature acetonitrile solutions has been reported⁸. This study observed fast formation of a strong band at 460 nm and a weaker band ~710 nm that decayed with time constant of ~100 ps. This was followed by formation of a new species that had a band at ~370 nm (strong) and ~725 nm (weak). The first transient absorption bands (at 460 nm and 710 nm) were attributed to formation of the iso-CH₂Cl-I species which has a lifetime of ~100 ps and the second transient absorption (at ~370 nm) at longer times was tentatively assigned to an ICl species⁸.

Here we report picosecond time-resolved resonance Raman (ps-TR³) experiments to investigate the identity and formation of the two photoproduct species observed in the recent femtosecond transient absorption study of the ultraviolet photolysis of CH₂ClI in room temperature solution. We utilize the results of density functional theory computations for several proposed photoproduct species and compare them to the experimental results to identify the two photoproduct species as iso-CH₂Cl-I and iso-CH₂I-Cl. Our ps experimental results indicate the iso-CH₂Cl-I species is formed first within several ps via recombination within the solvent cage of the initially produced CH₂Cl and I photofragments. The iso-CH₂Cl-I species then decays to form either the more stable iso-CH₂I-Cl species or parent molecule via isomerization reaction(s)¹.

Experiment

The experiments were carried out using a ps-TR³ apparatus based on optical parametric amplifiers described in detail elsewhere⁹. Briefly, an 800 nm pulse generated from a femtosecond Ti:Sapphire oscillator is amplified to 2 - 3 mJ at 1 kHz in a regenerative amplifier. The output from the

amplifier was frequency doubled in a 2 mm type I BBO crystal to generate the 400 nm probe pulses for TR³ spectroscopy. The 267 nm pump wavelength was the third harmonic of the regenerative amplifier. Typical pump and probe pulse energies at the sample were ~ 5 - 15 μ J with ~ 1 ps pulse duration (FWHM).

Results and Discussion

Figure 1 shows the ps-TR³ spectra obtained for the photoproduct(s) following 267 nm photoexcitation of CH₂ClI in acetonitrile solution using 400 nm probe wavelength. The Raman spectra appear to be composed of the fundamentals, overtones, and combination bands of several Franck-Condon active modes. Closer inspection of Figure 1 shows that a Raman band at ~174 cm⁻¹ appears first and as it decays (between 3 and 500 ps) a new Raman band ~207 cm⁻¹ begins to appear at later times (between 300 ps and 2000 ps). This suggests that a second photoproduct species is formed following decay of the first photoproduct species.

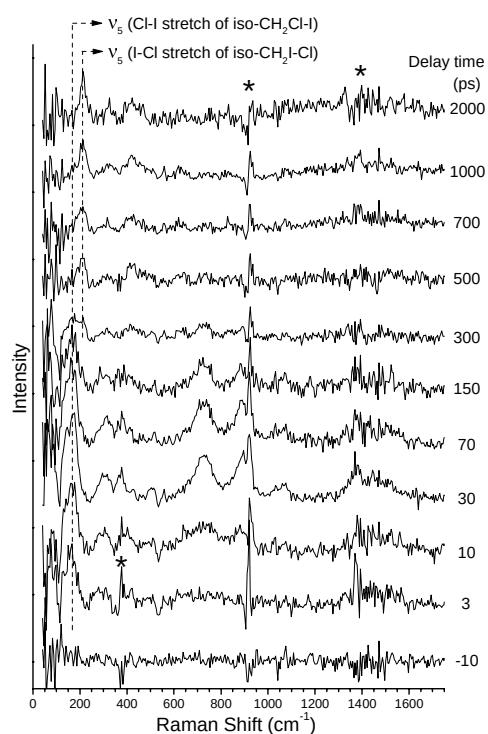


Figure 1. ps-TR³ spectra from ultraviolet excitation of CH₂ClI in acetonitrile. Asterisks “*” mark parts of the spectra where solvent subtraction artifacts are present.

The first photoproduct species that appears after several ps has four fundamental bands at ~141 cm⁻¹, 174 cm⁻¹, 376 cm⁻¹, and 724 cm⁻¹ (values from the 30 ps spectrum in Figure 1). These bands appear to have overtones and/or combination bands with

Experiment Fig 1. 30ps spectrum	Experiment Fig 1. 500ps spectrum	Calculated iso-CH ₂ Cl-I B3LYP/Sadlej-PVTZ	Calculated iso-CH ₂ I-Cl B3LYP/Sadlej-PVTZ	Calculated CH ₂ ClI ⁺ cation B3LYP/Sadlej-PVTZ	Calculated CH ₂ Cl B3LYP/Sadlej-PVTZ
724		A' v ₁ , sym. CH str. 3119	A ₁ v ₁ , sym. CH str. 3114	A' v ₁ , sym. CH str. 3002	A' v ₁ , CH sym. str. 3134
174	207	v ₂ , CH ₂ scissor 1409	v ₂ , CH ₂ scissor 1361	v ₂ , CH ₂ def. or sciss. 1321	v ₂ , CH ₂ def. or scissor 1361
141	105 ^a	v ₃ , C-Cl stretch 975	v ₃ , C-I stretch 794	v ₃ , CH ₂ wag 1103	v ₃ , C-Cl str. 827
		v ₄ , CH ₂ wag 760	v ₄ , CH ₂ wag 686	v ₄ , C-Cl stretch 783	v ₄ , CH ₂ wag 242
		v ₅ , Cl-I stretch 194	v ₅ , I-Cl stretch 236	v ₅ , C-I stretch 379	A'' v ₅ , CH asym. str. 3307
		v ₆ , C-Cl-I bend 136	v ₆ , C-I-Cl bend 113	v ₆ , I-C-Cl bend 191	v ₆ , CH ₂ rock 978
		A'' v ₇ , asym. CH str. 3276	A'' v ₇ , asym. CH str. 3254	A'' v ₇ , asym. CH str. 3050	
		v ₈ , CH ₂ rock 1020	v ₈ , CH ₂ rock 869	v ₈ , CH ₂ twist 1050	
376		v ₉ , CH ₂ twist 420	v ₉ , CH ₂ twist 494	v ₉ , CH ₂ rock 527	

^aValue obtained from subtraction of vibrational frequency for v₅ from the combination band v₅ + v₆ in the 500 ps 400 nm Raman spectrum.
str.=stretch; sym.=symmetric; asym.=asymmetric; def.=deformation

Table I. Comparison of the experimental fundamental vibrational frequencies (in cm⁻¹) found from the ps-TR³ spectra (this work) to the calculated B3LYP/Sadlej-PVTZ density functional theory vibrational frequencies.

each other. The four fundamental Raman bands exhibit good agreement with the computed vibrational frequencies for iso-CH₂Cl-I but not the other probable photoproduct species shown in Table I. For instance, the ~141 cm⁻¹, 174 cm⁻¹, 376 cm⁻¹, and 724 cm⁻¹ experimental vibrational frequencies agree better with the values computed for iso-CH₂Cl-I (at 136 cm⁻¹, 194 cm⁻¹, 420 cm⁻¹ and 760 cm⁻¹ respectively) compared to those for iso-CH₂I-Cl (at 113 cm⁻¹, 236 cm⁻¹, 494 cm⁻¹ and 686 cm⁻¹ respectively). The first photoproduct species clearly shows two low frequency Raman bands at ~141 cm⁻¹ and 174 cm⁻¹ that have a combination band ~303 cm⁻¹. However, the CH₂ClI⁺ cation has only one low frequency mode below 200 cm⁻¹ at ~191 cm⁻¹ (see Table I) and can be ruled out as the species responsible for the first photoproduct resonance Raman spectra shown in Figure 1. Similarly, the CH₂Cl radical has no low frequency modes below 200 cm⁻¹ and can also be ruled out as the identity of the first photoproduct species. The computed electronic transition energies and oscillator strengths¹⁾ are consistent with the assignment of the first photoproduct species to the iso-CH₂Cl-I species but not the other species examined. Comparison of our experimental results for both the vibrational frequencies and the electronic absorption transition observed in a recent femtosecond study at ~460 nm⁸⁾ clearly demonstrates that the first photoproduct species is the iso-CH₂Cl-I species. This is consistent with the proposed assignment of Åkesson and co-workers⁹⁾. Thus, we assign the vibrational fundamentals of the first photoproduct species (iso-CH₂Cl-I) as follows: the 141 cm⁻¹ fundamental to the v₆ C-Cl-I bend mode, the 174 cm⁻¹ fundamental to the v₅ Cl-I stretch mode, the 376 cm⁻¹ fundamental to the v₉ CH₂ twist mode and the 724 cm⁻¹ fundamental to the v₄ CH₂ wag mode.

The second photoproduct species that begins to appear as the first photoproduct species disappears in the 300-500 ps region also has at least two low frequency fundamental modes. The CH₂Cl radical can thus be ruled out as the second photoproduct species. Since there appear to be at least two fundamental vibrational modes, this also rules out the possibilities of diatomic photoproduct species like the ICl⁻ ion or ICl molecule. The CH₂ClI⁺ cation does not seem too likely for the following reasons: the computed 379 cm⁻¹ mode is fairly far away from the experimentally observed 312 cm⁻¹ Raman band, the computed electronic absorption transitions¹⁾ are also far from the experimental ~370 nm transient absorption band observed for the second photoproduct species in a recent femtosecond study⁹⁾, and the oscillator strengths for the computed electronic transitions¹⁾ are relatively weak. The most likely candidate for the second photoproduct is the iso-CH₂I-Cl species if we assume the 312 cm⁻¹ Raman band in the experiment is a combination band of two lower frequency modes as was observed in the iso-CH₂Cl-I species ps-TR³ spectra. This would give a ~105 cm⁻¹ fundamental frequency which forms a combination band with the strong 207 cm⁻¹ fundamental. The 105 cm⁻¹ fundamental can be assigned to the iso-CH₂I-Cl computed 113 cm⁻¹ v₆ C-I-Cl bend mode and the experimental

207 cm⁻¹ Raman band could be assigned to the computed 236 cm⁻¹ v₅ I-Cl stretch mode. The iso-CH₂I-Cl computed electronic transition position at 332 nm¹⁾ is reasonably close to the experimental transient absorption band ~370 nm observed in the femtosecond experiments⁸⁾ and the calculated oscillator strength (0.4008) for this transition is large. The B3LYP/Sadlej-PVTZ density functional theory computational results indicate the iso-CH₂I-Cl species is about 4.54 kcal/mol more stable than the iso-CH₂Cl-I species¹⁾. This is consistent with our assignment of the first photoproduct (which has a lifetime of ~100 ps) to the iso-CH₂Cl-I species and the second photoproduct species (which has a longer lifetime on the order of hundreds of ps to nanoseconds) to the iso-CH₂I-Cl species. We note that this situation is similar to that found for the iso-CH₂Br-I and iso-CH₂I-Br species. The iso-CH₂I-Br species was computed to be more stable by ~4.1 kcal/mol and was the only species with a sufficiently long lifetime to be observed in nanosecond transient resonance Raman study³⁾. We note that the assignment of the second photoproduct species to iso-CH₂I-Cl is not as clear cut as the first photoproduct species assignment to iso-CH₂Cl-I. However, the assignment of the second photoproduct to iso-CH₂I-Cl is consistent with the experimental and computational data available at this time.

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ps-TR³ Observation of the iso-CH₂I-I Photoproduct from the “Photoisomerization” Reaction of CH₂I₂ in the Solution Phase

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Introduction

Polyhalomethanes have been observed in the atmosphere and are potentially important sources of reactive halogen species in the atmosphere. Polyhalomethanes are also of interest in synthetic chemistry for cyclopropanation reactions. Ultraviolet excitation of gas phase polyhalomethanes usually leads to a direct carbon-halogen bond breaking reaction(s). Molecular beam anisotropy measurements show these primary reaction(s) typically occur in a time much less than the rotational period of the parent molecule and photofragment translational spectroscopy experiments for CH₂I₂, CH₂BrI, and CF₂I₂, indicate that the polyatomic photofragment typically receives large amounts of internal excitation of their rotational and vibrational degrees of freedom. This is consistent with the observation that the direct photodissociation reactions proceed along multidimensional reactions coordinates as deduced from resonance Raman (RR) investigations of the short-time photodissociation dynamics in both gas and solutions.

While the ultraviolet photodissociation reaction of CH₂I₂ in the gas phase appears relatively well understood, the situation for its photodissociation in condensed phases remains murky with many conflicting reports. Ultraviolet excitation, direct photoionization and radiolysis of CH₂I₂ in condensed phase environments leads to formation of characteristic absorption bands ~385 nm (strong intensity) and ~570 nm (moderate intensity) that have been assigned to several different probable photoproduct species like trapped electrons², the CH₂I₂⁺ cation³ or the iso-CH₂I-I⁴ species. Several femtosecond transient absorption experiments have been done to follow the formation and decay of the photoproduct species²⁻⁴. Although the three different femtosecond studies exhibited similar results with a fast rise followed by a fast decay and then by a slower rise, three different interpretations were given because of their differing assignments for the photoproduct species responsible for the 385 nm and 570 nm transient absorption bands. A recent nanosecond transient resonance Raman (ns-TR²) and density functional theory (DFT) investigation⁵ demonstrated that the iso-CH₂I-I species is mostly responsible for the intense ~385 nm transient absorption band.

In here, we report picosecond time-resolved resonance Raman (ps-TR³) experiments that probe the initial formation of the hot iso-CH₂I-I photoproduct following ultraviolet excitation of CH₂I₂ in room temperature solutions. These experiments establish a connection between the ultrafast time scale and the longer ns time scale observation of the iso-CH₂I-I photoproduct.

Experiment

The experiments were carried out using a ps-TR³ apparatus based on optical parametric amplifiers described in detail elsewhere⁶. Briefly, an 800 nm pulse generated from a femtosecond Ti:Sapphire oscillator is amplified to 2 - 3 mJ at 1 kHz in a regenerative amplifier. The output from the amplifier was frequency doubled in a 2 mm type I BBO crystal to generate the 400 nm probe pulses for TR³ spectroscopy. The 267 nm pump wavelength was the third harmonic of the regenerative amplifier. Typical pump and probe pulse energies

at the sample were ~ 5 - 15 μJ with ~ 1 ps pulse duration (FWHM).

Results and Discussion

The ps-TR³ spectra obtained for photoproducts produced from ultraviolet excitation of CH₂I₂ are shown in Figure 1 (Stokes and anti-Stokes spectra) for experiments carried out in cyclohexane solution and in Figure 2 for experiments in acetonitrile solution. Figure 3 compares a ns-TR² spectrum of iso-CH₂I-I in cyclohexane solution (obtained with 309 nm pump and 416 nm probe excitation wavelengths) to the ps-TR³ spectra with 30 ps and 500 ps pump-probe time delays in cyclohexane solution and 15 ps and 100 ps pump-probe time delays in acetonitrile solution.

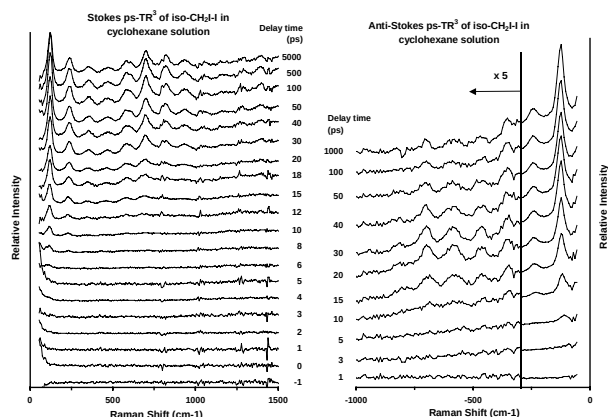


Figure 1. ps-TR³ spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of CH₂I₂ in cyclohexane.

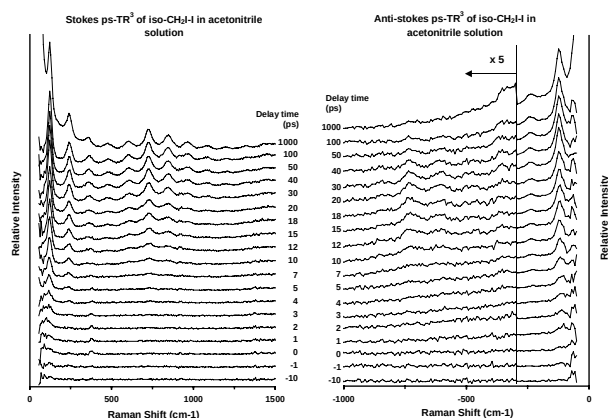


Figure 2. ps-TR³ spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of CH₂I₂ in acetonitrile.

Inspection of Figure 3 shows that the RR spectra are all similar to one another and suggests that the same photoproduct species is observed in the ns-TR² spectrum and the ps-TR³ spectra. Table I compares the experimental fundamental vibrational frequencies (ns-TR² spectrum, ps-TR³ spectra and previously

reported infrared spectra) to the DFT computations done for several species (iso-CH₂I-I, CH₂I₂⁺ radical cation or CH₂I radical) proposed to be the photoproduct responsible for the ~385 nm transient absorption observed after ultraviolet photoexcitation of CH₂I₂ in the condensed phase. Inspection of Table I shows that the fundamental vibrational bands of the RR and infrared spectra have values that agree well with those computed for the iso-CH₂I-I species but not with either of the other proposed species (the CH₂I₂⁺ and the CH₂I). We also note the experimental Raman bands assigned to the nominal C-I stretch (v₃) and CH₂ wag (v₄) fundamental of the photoproduct species exhibit very good agreement with the infrared bands observed for iso-CH₂I₂ in low temperature solid matrices. Isotopic shift data from ns-TR² spectra and infrared spectra as well as DFT computed electronic absorption transition energies and oscillator strengths are all consistent with the assignment of the photoproduct to the iso-CH₂I-I species. Therefore, the RR spectra in conjunction with results from DFT computations unequivocally indicate the iso-CH₂I-I species is predominantly responsible for the ps to ns ~385 nm transient absorption band in solution. Comparison of the resonance Raman spectra shown in Figures 1-3 indicates that this is true for ultraviolet excitation of CH₂I₂ in nonpolar solvents like cyclohexane as well as in polar solvents such as acetonitrile.

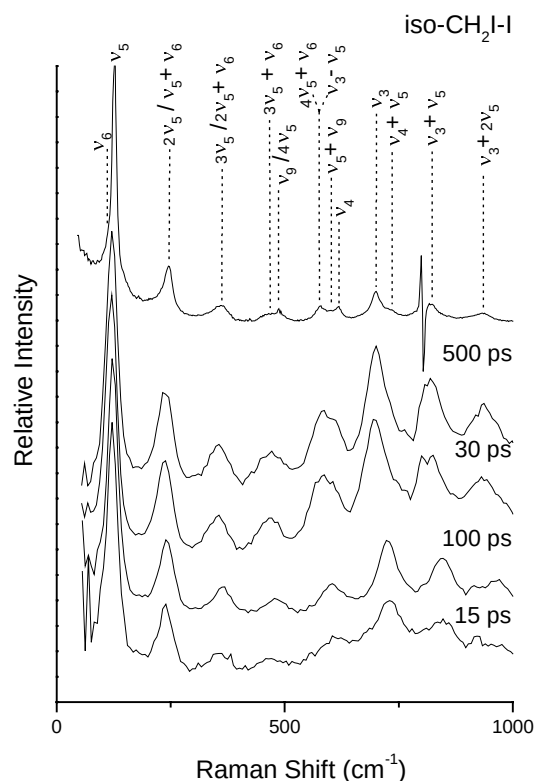


Figure 3. A comparison of RR spectra of iso-CH₂I-I.

Examination of the ps-TR³ spectra in Figures 1-2 indicates that Raman bands attributable to the iso-CH₂I-I photoproduct begin to appear within several picoseconds (~8 ps in cyclohexane solution and ~5 ps in acetonitrile solution) after ultraviolet excitation of CH₂I₂ in the solution phase. These RR bands grow in intensity as time increases and appear to shift somewhat to higher vibrational frequencies. Examination of Figures 1-2 shows that the RR bands tend to shift from lower to higher vibrational frequency and become more intense as the iso-CH₂I-I Raman bands appear in the 4 ps to 20 ps time scale. The vibrational frequency shifts are only readily apparent at times between 4 ps and 18 ps in both cyclohexane and acetonitrile solvents although the changes seem to occur somewhat faster in acetonitrile. Our ps-TR³ results show a good correlation with changes found in the femtosecond transient absorption spectra observed by Åkesson and coworkers⁴) in acetonitrile solvent at

times between 3 ps and 50 ps that they tentatively ascribe to vibrational cooling of the hot iso-CH₂I-I photoproduct. Their transient absorption spectra between 3 ps and 50 ps show absorption in the range 350 to 500 nm that is relatively flat, broad and weak at 3 ps that begins to sharpen and becomes more intense from 3 ps to 50 ps with most of this change occurring between 3 and 20 ps. This behavior is very similar to what we observe in our ps-TR³ spectra with most of the vibrational frequency shifts and intensity changes occurring in the first 20 ps or so with some additional sharpening of the Raman bands and increase of intensity at longer times. Our ps-TR³ results confirm that the iso-CH₂I-I photoproduct is formed vibrationally hot within several picoseconds and then undergoes subsequent vibrational cooling between 4 ps to 50 ps. Examination of the anti-Stokes spectral changes as a function of time in cyclohexane solvent (Figure 1) and acetonitrile solvent (Figure 2) provides additional support for this interpretation. Between 5 ps and 100 ps in the anti-Stokes RR spectra obtained in cyclohexane solvent, the v₃, v₃+v₅, 4v₅+v₆/v₃-v₅, 4v₅ and 3v₅ first grow in intensity and then decrease in intensity until they are similar to that observed at 1000 ps. This behavior also indicates a highly excited iso-CH₂I-I species that is vibrationally cooling between 5 ps and 50 ps. The anti-Stokes RR spectra in acetonitrile solvent (Figure 2) also exhibit similar behavior.

Vibrational Mode	B3LYP/ Sadlej TZVP	ns RR in C ₆ H ₁₂ (ref. 5)	IR in low T solid	30 ps RR in C ₆ H ₁₂
CH₂I-I (CD₂I-I)				
A' v ₁ , CH ₂ sym. str.	3131 (2260)	-----	3028 (2213)	
v ₂ , CH ₂ scissor	1340 (1011)	-----	1373 (1041-1033)	
v ₃ , C-I stretch	755 (645)	701 (640)	714/705 (645)	694
v ₄ , CH ₂ wag	619 (476)	619 (496)	622-611 (498-486)	606
v ₅ , I-I stretch	128 (128)	128 (128)	-----	121
v ₆ , C-I-I bend	99 (93)	? (~110)	-----	
A'' v ₇ , CH ₂ asym. str.	3281 (2451)	-----	3151 (2378)	
v ₈ , CH ₂ rock	865 (697)	-----	-----	
v ₉ , CH ₂ twist	447 (318)	487 ? (352 ?)	-----	
CH₂I₂⁺				
A ₁ v ₁ , CH sym. str.	3103 (2246)			
v ₂ , CH ₂ def.	1365 (1003)			
v ₃ , CI sym. str.	551 (522)			
v ₄ , ICI bend	114 (114)			
B ₁ v ₅ , CH asym. str.	3220 (2401)			
v ₆ , CH ₂ rock	755 (576)			
A ₂ v ₇ , CH ₂ twist	983 (696)			
B ₂ v ₈ , CH ₂ wag	1080 (813)			
v ₉ , CI asym. str.	517 (490)			
CH₂I				
A ₁ v ₁ , CH sym. str.	3126 (2252)			
v ₂ , CH ₂ def.	1309 (974)			
v ₃ , C-I stretch	614 (576)			
B ₁ v ₄ , CH ₂ wag	234 (180)			
B ₂ v ₅ , CH asym. str.	3288 (2457)			
v ₆ , CH ₂ rock	832 (619)			

str.=stretch; sym.=symmetric; asym.=asymmetric; def.=deformation

Table I. A comparison of fundamental vibrational frequencies (in cm⁻¹) of three proposed products of photo excitation of CH₂I₂ in solution.

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Kerr Gated ps-TR³ Study of Porphyrin-Oligonucleotide Exciplex Formation

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Introduction

Water-soluble cationic (metallo)porphyrins complexed with nucleic acids are widely investigated owing to their possible use in photodynamic therapy of cancer. Besides the promising medical applications, cationic porphyrins are interesting also as specific probes of local nucleic acid base pairs and/or sequence composition, structure, conformation and dynamics^{1,2)}.

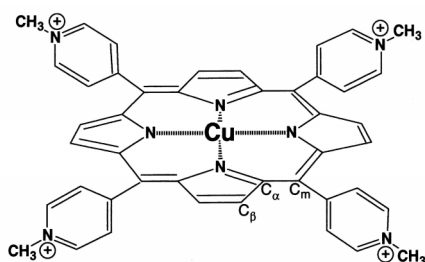


Figure 1. Structure of Cu(II) 5,10,15,20-*meso*-tetrakis(4-N-methylpyridyl) porphyrin (CuP).

Among (metallo)porphyrins studied in complexes with nucleic acids, the copper(II) derivative of cationic 5,10,15,20-*meso*-tetrakis(4-N-methylpyridyl) porphine (CuP, see Figure 1) has recently attracted particular interest because of its ability to form, in excited state, transient axially coordinated complex (exciplex) with an oxygen-containing ligand from its close proximity^{1,2)}. Since a C=O group of thymine (uracil) was identified as the CuP axial ligand¹⁾, formation of the CuP*·C=O exciplex can serve as an indicator of the proper distance and appropriate orientation between the C=O group and the centre of the CuP macrocycle, thus providing valuable structural information about the CuP microenvironment. Besides the CuP*·C=O species, formation of a concurrent CuP*·H₂O exciplex (having water molecule as its fifth axial ligand) was approved²⁾ in aqueous solutions containing free CuP. As both exciplex species exhibit virtually identical Raman features²⁾, they cannot be discerned by nanosecond pulse excited resonance Raman spectra, if the system contains fractions of both complexed and free CuP. Nevertheless, the CuP*·H₂O and CuP*·C=O species can be distinguished by their picosecond time-resolved resonance Raman (ps-TR³) spectra due to different relaxation kinetics, as their corresponding lifetimes differ in orders of magnitude (~10 ps and ~ 1-3 ns, respectively²⁾).

Previously, exciplex formation was studied preferentially with *double-stranded* polynucleotides and natural dsDNA having regular double-helical structure. Apart from the studies¹⁻⁴⁾ showing that CuP exciplex can be formed also with *single-stranded* poly(dT), poly(rU) and some oligothymidylates (d(pT)_n), no systematic investigation was carried out with corresponding nucleosides and mononucleotides. Especially challenging was a question whether and under which conditions interaction with deoxythymidine (dT) or deoxythymidine 5'-monophosphate (dTMP) units would be sufficient for exciplex formation, or whether some secondary structure, provided by sufficiently long oligonucleotide, is required. Our recent spectrophotometric titration (will be published),

monitored by absorption in the CuP Soret band, revealed that CuP mixed with dTMP yields two distinct types of molecular complexes having 1:1 (CuP·dTMP) and 1:2 (CuP·(dTMP)₂) (or even higher but spectroscopically indiscernible) stoichiometries, the latter being spectroscopically very close to the CuP complexed with d(pT)₉ (CuP·d(pT)₉). The aim of the present study was to show that this spectroscopic resemblance reflects some common structural features, i.e. that a local environment favourable for exciplex formation in complexes with single-stranded oligomers can be mimicked by molecular complexes with mononucleotides.

Results and Discussion

Titration of the CuP solution (fixed total concentration of ~ 3 × 10⁻⁵ M) with dT, dTMP and d(pT)₉ was monitored by the probe-only (Δt = -50 ps) and pump-and-probe (Δt = +50 ps; to eliminate contribution from the fast relaxing CuP*·H₂O species) ps-TR³ spectra. Nucleotide concentration was increased stepwise to cover fully the interesting region of the nucleotide-to-porphyrin ratio (R). Instead of pumping *via* relatively weak CuP Q-band (~ 550 nm) used in the recent ps-TR³ study²⁾, a single colour arrangement (λ_{pump} = λ_{probe} = 420 nm) with excitation in the CuP Soret band (~ 424 nm) was applied to increase conversion of the CuP into its excited state. Undesired Raman scattering from the intense pump pulses (pulse energy of ~ 9 μJ at the sample) was rejected by means of a Kerr gate (3 ps resolution). Details of the experimental setup and the Kerr gate were given elsewhere⁵⁾. The ps-TR³ spectra were normalized using an internal intensity standard (~ 982 cm⁻¹ Raman band of the 0.2 M SO₄²⁻ present in all samples).

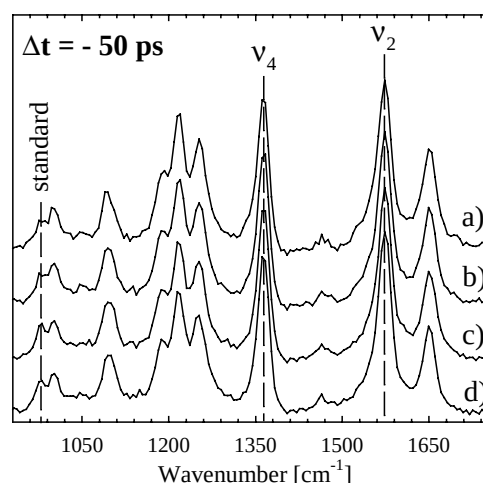


Figure 2. Normalized probe-only ps-TR³ spectra of the CuP mixed with dTMP. Nucleotide-to-porphyrin ratio of ~ 10 (a), ~ 100 (b), ~ 600 (c) and ~ 5000 (d).

As illustrated by the CuP mixed with dTMP (Figure 2), probe-only excitation yields CuP ground-state Raman features (v₂ and v₄ bands) regardless of the nucleotide-to-porphyrin ratio R, whereas the pump-and-probe spectra (Figure 3) exhibit also

CuP exciplex features (ν_2^* and ν_4^* bands), the relative intensity of which increases with R.

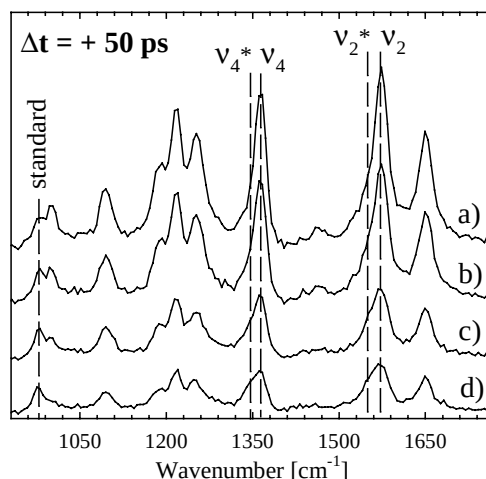


Figure 3. Normalized pump-and-probe ps-TR³ spectra of the CuP mixed with dTMP. Nucleotide-to-porphyrin ratio of ~ 10 (a), ~ 100 (b), ~ 600 (c) and ~ 5000 (d).

For all (oligo)nucleotides studied, detailed analysis of the ps-TR³ data by means of a factor (SVD) analysis revealed gradual spectral changes in their probe-only ps-TR³ spectra as well. The changes reflect an increasing fraction of the complexed CuP. Under experimental conditions used in the present study, the extent of the spectral changes in the pump-and-probe ps-TR³ spectra (overall decrease of the total Raman signal and intensity ratio between exciplex and ground-state features) for the CuP complexed with dTMP at R ~ 5000 was found to be virtually identical with that of CuP complexed with d(pT)₉, R > 10 (i.e. [d(pT)₉]/[CuP] > 1). Thus, at extremely high concentrations of mononucleotide, the CuP can form molecular complexes providing an environment similar to that generated by a secondary structure of the oligonucleotide. Nevertheless, since two distinct molecular complexes of 1:1 and 1:2 (or higher) stoichiometries can be formed with dTMP (and dT), effectiveness of the exciplex formation (evaluated directly from the pump-and-probe ps-TR³ spectra by means of the factor analysis) was confronted with their relative fractions.

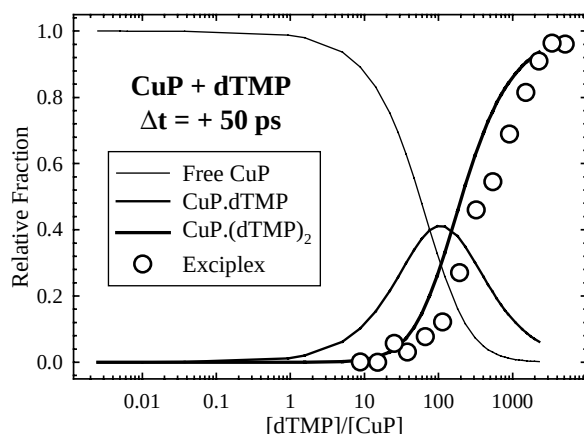


Figure 4. Distribution of the CuP complexes as a function of the dTMP-to-CuP ratio vs. effectiveness of the CuP*C=O exciplex formation.

A close match between exciplex effectiveness and distribution curve of the CuP.(dTMP)₂ complex (Figure 4) clearly identifies species responsible for exciplex formation. Nevertheless, slight deviation from the CuP.(dTMP)₂ distribution seems to suggest substantial participation of the complexes of stoichiometries

higher than 1:2. Concerning the complexes with dT, similar behaviour was observed as for complexes with dTMP.

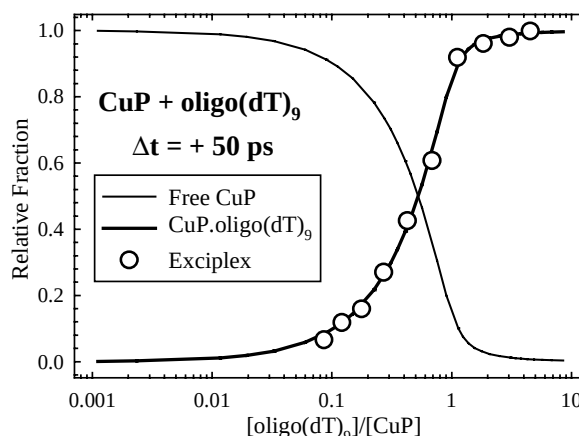


Figure 5. Distribution of the CuP complexes as a function of the d(pT)₉-to-CuP ratio vs. effectiveness of the CuP*C=O exciplex formation.

In the case of d(pT)₉, a single spectral species attributable to a 1:1 CuP.d(pT)₉ complex was revealed by spectrophotometric titration (will be published). As shown on Figure 5, the same complex is fully responsible for the CuP exciplex formation.

Conclusions

By means of the Kerr gated ps-TR³ spectroscopy it was shown that CuP*C=O exciplex can be effectively formed in molecular complexes with dTMP as well as dT. Nevertheless, among two spectroscopically distinct complex species formed with mononucleotides, only molecular complexes of higher stoichiometries than 1:2 seem to provide a microenvironment favourable for exciplex formation. Considering contemporary thoughts about requirements for axial coordination giving rise to exciplex^{1,2}, some structural features of the CuP molecular complexes with mononucleotides can be suggested:

The 1:1 species can be characterised by a more-less «coplanar» arrangement of the porphyrin macrocycle and thymine planes, thus stabilised mainly by stacking interactions. It is formed preferentially in the CuP mixtures with dT and dTMP at low nucleotide-to-porphyrin ratios, and is not favourable for the CuP*C=O exciplex formation.

The 1:2 (and higher) species is characterised by a more-less «perpendicular» arrangement of the porphyrin macrocycle and thymine planes. It is stabilised by van der Waals's interactions of other types than stacking and formed preferentially in the CuP mixtures with dT and dTMP at extremely high nucleotide-to-porphyrin ratios. Its structure seems to be favourable for CuP*C=O exciplex formation.

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Nanosecond Laser Flash Photolysis and Time-Resolved Resonance Raman Spectroscopy of Carotenoid Neutral Radicals

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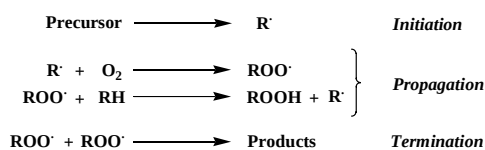
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Introduction

In recent years we have been engaged on a research programme directed towards characterisation of the free radical scavenging properties of carotenoids and the properties of the carotenoid radical products arising from such reactions¹⁻⁵. Epidemiological evidence suggests that diets rich in fruit and vegetables can reduce the risk of cardiovascular disease and certain types of cancer. Dietary carotenoids are constituents of fruit and vegetables and there is much interest in their potential protective properties. One possibility is that carotenoids function as free-radical scavenging antioxidants, intercepting oxygen-centred radicals (Scheme 2) such as peroxy radicals, which arise as propagating species during lipid peroxidation (Scheme 1) for example. Hence, it has been suggested that carotenoids may act as chain-breaking antioxidants thereby reducing oxidative stress in organisms by scavenging damaging peroxy, alkoxyl and other radicals. We have previously combined nanosecond laser flash photolysis, pulse radiolysis and TR³ to study the kinetics of carotenoid reactions with numerous free radicals as well as advancing understanding of the reaction mechanisms and properties of carotenoid radicals¹⁻⁵.



Scheme 1. The principal steps involved in free-radical induced lipid peroxidation.

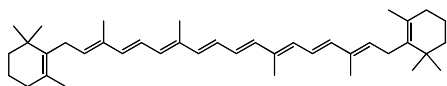
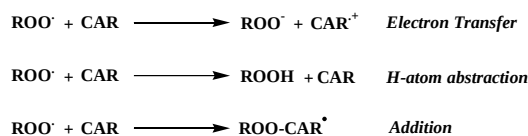


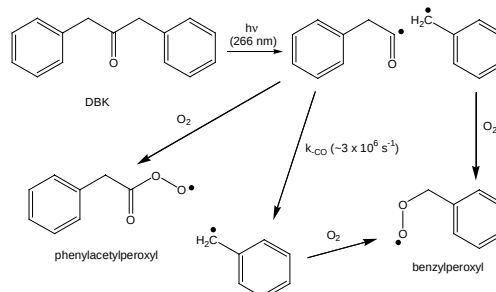
Figure 1. Structure of 7, 7'-dihydro-β-carotene (77DH).



Scheme 2. Possible reactions of carotenoids (CAR) with peroxy radicals.

For carotenoids to act as antioxidants in this way, the carotenoid radicals produced must not be capable of propagating free-radical chain reactions, which could result in pro-oxidant behaviour. In order to address this issue it is necessary, first of all, to establish whether carotenoid radicals react with oxygen.

The work reported here focuses on the spectroscopic and kinetic properties of the different types of carotenoid radicals that are formed as a result of scavenging reactive peroxy radicals derived from carbonyl pre-cursors (Scheme 3) in polar and non-polar environments. The methods used include nanosecond laser flash photolysis coupled with kinetic UV-VIS-NIR absorption spectroscopy and TR³.



Scheme 3. Generation of peroxy radicals by laser photolysis of dibenzyl ketone (DBK).

Results and Discussion

Laser excitation (266 nm) of dibenzyl ketone (DBK) in hexane or methanol containing carotenoid leads to the α-cleavage products shown in Scheme 3. In the absence of oxygen the carotenoid is stable to the experimental conditions and no bleaching of the ground state absorption is evident, indicating low reactivity towards benzyl radicals. However, in the presence of oxygen rapid bleaching of the carotenoid absorption is observed in both methanol and hexane with bimolecular quenching rate constants in the range of 10⁹ M⁻¹ s⁻¹ (measured directly or by competition kinetics using a free radical probe). Detailed studies of the oxygen concentration dependence of the extent of carotenoid bleaching strongly suggests that phenylacetylperoxy (PAP) radical is primarily responsible for the observed carotenoid reactions and that the contribution from reaction with benzylperoxy radical is insignificant under these conditions.

Contrasting behaviour is observed in methanol and hexane, despite the fact that the reactions are rapid in both solvents. In methanol transient absorption features are observed in the visible and near infrared, and there are at least two near infrared absorbing carotenoid radical species (at ~690 and ~780 nm for 77DH, Figure 3) displaying different kinetic behaviour. In hexane no near infrared absorption features are observed, but strong visible absorption bands are apparent (Figures 2 and 4).

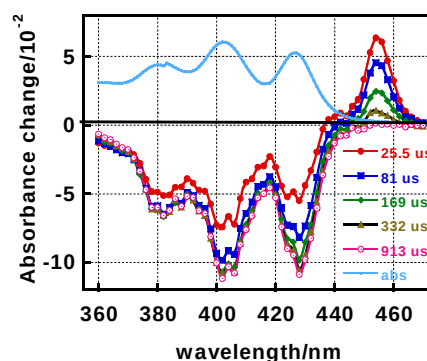


Figure 2. Transient absorption spectra for 77DH (~10⁻⁵ M) following 266 nm excitation of DBK in air-equilibrated hexane. The spectrum in light blue is the absorption spectrum of 77DH.

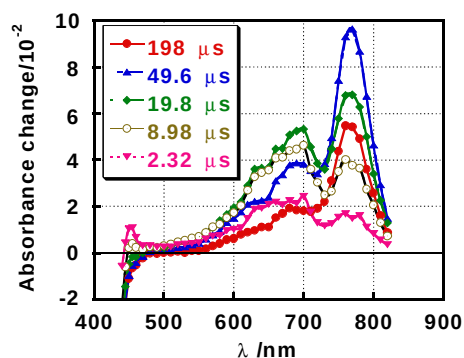


Figure 3. Transient absorption spectra for 77DH ($\sim 10^{-5}$ M) following 266 nm excitation of DBK in air-equilibrated methanol.

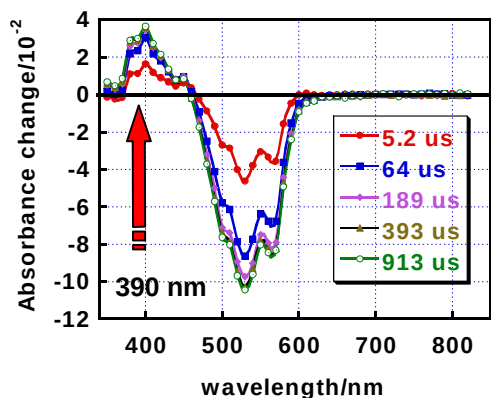
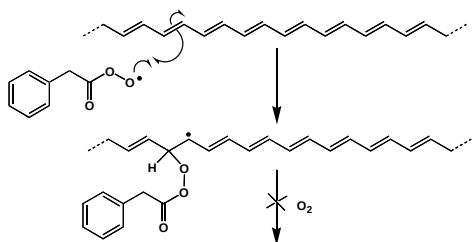


Figure 4. Transient absorption spectra for DODEC ($\sim 10^{-5}$ M) following 266 nm excitation of DBK in air-equilibrated hexane.

Kinetic evidence suggests that in hexane a carotenoid radical adduct is formed, which decays by 1st order kinetics, possibly leading to an epoxide (Scheme 4). The radical adduct is not scavenged by oxygen, probably due to extensive resonance stabilisation. The lack of oxygen scavenging discounts a pro-oxidant effect for these types of radicals. However, the fragmentation of the radical may give rise to other peroxy radicals (e.g. benzylperoxy in this particular case), which could contribute to pro-oxidant effects.



Scheme 4. Radical addition of PAP to the polyene chain of a carotenoid.

In methanol near infrared absorption bands characteristic of the carotenoid cation radical are observed (780 nm for 77DH). However, other absorption features are observed in the red/near infrared and in the visible region.

Resonance Raman Spectra

The TR³ spectra of the PAP-CAR radical adducts are dependent on the carotenoid. For 77DH the ground state band corresponding to the C=C stretch at 1553 cm⁻¹ moves to lower wavenumber (~ 1495 cm⁻¹, see Figure 5) in the radical adduct, reflecting a decrease in the C=C bond order. In contrast (Figure 6), the C=C stretch of the DODEC-PAP radical adduct

is at higher wavenumber (~ 1565 cm⁻¹) than the DODEC ground state (1508 cm⁻¹), reflecting an increase in C=C bond order. These differences between 77DH (8 conjugated double bonds) and DODEC (19 conjugated double bonds) may be due to differences in the site of attack on the polyene chain between these two carotenoids. However, theoretical calculations are required to assess the impact on C=C bond order of radical addition at different sites.

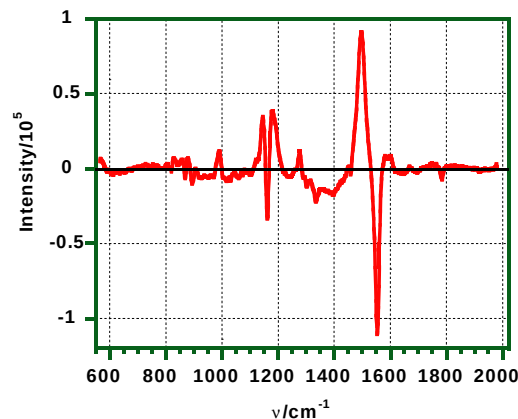


Figure 5. Time resolved resonance Raman spectrum of the 77DH-PAP radical adduct using DBK in hexane with 266 nm pump (0.8 mJ) and 455 nm probe (1.2 mJ) at a time delay of 5 μ s. The spectrum is corrected for background fluorescence, but not for ground state bleaching.

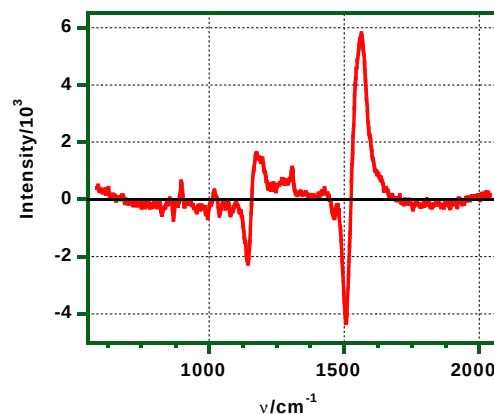


Figure 6. Time resolved resonance Raman spectrum of the DODEC-PAP radical adduct using DBK in hexane with 266 nm pump (0.75 mJ) and 390 nm probe (1.1 mJ) at a time delay of 10 μ s. The spectrum is corrected for background fluorescence, but not for ground state bleaching.

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Picosecond Kerr Gated Time-resolved Raman Spectroscopy of Solids: Capabilities and Limitations for Fluorescence Rejection

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Introduction

Raman spectroscopy is an extremely powerful tool for characterizing the physical and chemical properties of materials. It is widely employed as both a research and a routine analytical tool in industrial and academic laboratories, and ongoing developments in laser, optical and detector technology mean that it will continue to grow in importance. However, in some cases intense fluorescence swamps the weak Raman signal. This, along with possible laser-induced sample damage, is the major disadvantage of what is otherwise a very versatile tool.

The usual approach to avoid fluorescence is to change the laser wavelength to avoid electronic excitation, but it is not always possible to find an effective wavelength. Sometimes this necessitates using a near-IR (NIR) laser and an interferometer detector (Fourier Transform Raman spectroscopy). However, NIR-excited Raman spectroscopy is inherently insensitive, giving relatively low signal/noise (S/N) data, and a number of systems still fluoresce strongly or decompose under NIR laser excitation. Also, self-absorption in organic and aqueous systems can significantly distort spectral intensities and make quantitative analysis difficult. Therefore, alternative ways to obtain Raman spectra from highly fluorescent samples are still needed.

One “generic” solution that has been under development for three decades is to use a pulsed laser and time-resolved detection to allow the Raman photons to be discriminated from the broad fluorescence background. The Raman interaction time is virtually instantaneous ($\ll 1$ ps), whereas fluorescence emission is statistically relatively slow, with hundreds or thousands of picoseconds elapsing between electronic excitation and radiative decay. If we illuminate a thin transparent sample with a very short (~ 1 ps) laser pulse, all of the Raman photons will be generated within 1 ps, whereas most of the fluorescence photons will be emitted at much longer times (nanoseconds). If the detection system is gated so as to detect only those photons scattered or emitted during the laser pulse, we will collect all of the Raman photons but reject the majority of the fluorescence.

Two rather different time-resolved approaches have been most effective in yielding high quality Raman data from highly fluorescent materials. The first used a streak-camera to provide time-resolved Raman data (~ 10 ps resolution, up to 2 kHz repetition rate)¹. This gave an estimated improvement of ~ 280 for a fluorophore with $\tau_f \sim 4$ ns. The second method used a Kerr gate with ~ 3 ps full width at half maximum (FWHM) and 650 Hz repetition rate. The Kerr gate was used to time-resolve the light that is allowed to pass into a spectrograph-CCD combination². This system achieved three orders of magnitude suppression of the background from a fluorophore with $\tau_f \sim 2$ ns, and produced excellent Raman signals that were completely obscured in the ungated spectra.

Both of the systems noted above have been demonstrated to work well using liquid samples that were doped with fluorescent dyes. However, many industrially relevant samples are clear or opaque solids (powders, films, fibres...), where there is potential for (a) multiple reflections that can blur the

time response and (b) laser absorption and damage. The latter is a concern because although the average laser power of an OPA may be only a few mW, the peak power can be rather high (MW), which raises the possibility of non-linear absorption and damage. The aim of this work was therefore to establish whether this same technology provides useful Raman data from industrially-relevant materials, and to study the effect of multiple scattering / reflections in heterogeneous materials.

Experimental

Spectrometer

The laser and Kerr-gated detector system used in this work were designed and constructed at the Rutherford Appleton Laboratory, Oxfordshire, UK, and have been described in detail elsewhere^{2,3}. In the experiments on solid samples described here, the original collection mirror has been replaced with a 10 cm focal length, $f/2$ collection lens. In all of the experiments described in this article, the exciting laser wavelength was fixed at 400 nm, with a pulse rate of ~ 1 kHz, a pulse width of ca 1 ps, a peak pulse power of between 1 - 5 MW and an average power of 1 - 5 mW at the sample. The beams were focused to a spot diameter of 200 - 400 μm , and scatter was collected at $\sim 90^\circ$ geometry with respect to the probe beam. Before this work it was not known whether the high peak pulse powers would cause significant degradation of solids, since in the past it has only been used on flowing liquids. Therefore, we tested the system using a number of solids that fluoresce under visible excitation. Spectra were obtained in gated mode, and also from the same sample with the gate permanently “open” (by rotating the polarizer after the Kerr cell to be parallel to the one before the cell and turning off the laser beam that drives the cell). For bands at around 1600 cm^{-1} , the spectrometer transmission in the ‘open’ state was about a factor of 3 lower than for gated operation. This is because in the gated configuration, the polarizer after the Kerr gate is aligned with the spectrometer axis of maximum transmission. The presented data are not corrected for this difference. It should also be noted that the throughput of the gate, given by the efficiency with which the beam polarisation can be rotated, could in theory reach 100 %, but is typically $\sim 40\%$ for liquids. The efficiency for light scattered from solids is typically lower, and can vary with sample geometry. The precise origin of this has not been investigated.

For one of the samples, comparative Raman data were also obtained using a Perkin Elmer 1760 FT-Raman spectrometer (1064 nm laser), operating with 100 mW of laser power on the sample and acquiring data at 16 cm^{-1} resolution.

Samples

Three polymer films were examined in these studies, namely PEEK (poly(aryl-ether-ether-ketone)), $\sim 250\text{ }\mu\text{m}$ thick, a polyimide (Upilex SGA, $\sim 25\text{ }\mu\text{m}$ thick), and a developmental grade of PPS (poly(phenylene sulphide)), $\sim 100\text{ }\mu\text{m}$ thick. ICI PLC supplied all the samples, which were a light “straw” colour, bright yellow and dark brown respectively. All of these samples exhibit intense fluorescence under visible laser

excitation. We also studied powders, PEEK and trans-stilbene (ex Aldrich). The PEEK was used as supplied, and trans-stilbene was ground in a pestle and mortar. In each case the particles ranged from ca. 10-100 μm diameter; no attempt was made to accurately quantify the size distribution. Only the PEEK powder showed significant fluorescence; the trans-stilbene was only used to examine the temporal response of elastic and inelastic light scattering in powders.

The films were held as self-supporting samples in the probe laser beam, which was incident at ca. 45° to the film normal. The Fresnel ('specular') reflection from the sample interfaces was blocked before the collection lens by a small beamstop. The powders were lightly pressed into a small cup (ca. 3 mm diameter and 5 mm deep) and the laser beam was directed onto its surface, again at about 45° incidence.

Results and Analysis

Fluorescence rejection from film samples

Figure 1 shows (a) the 400 nm ungated, (b) the 1064 nm FT Raman and (c) the 400 nm Kerr gated Raman spectra of the PPS film. The fluorescence ($\tau_f \sim 600$ ps) was overwhelming with ungated 400 nm excitation, and even the FT Raman spectrum was heavily distorted by the intense fluorescence background. FT Raman spectroscopy is usually the method of choice with such highly fluorescent samples, but in this case the Kerr-gate approach was superior. With Kerr-gating, we obtained an improvement of ~ 200 in signal/background. Obviously, this approach cannot always succeed; with some samples the fluorescence intensity will be so overwhelming, or the lifetime so short, that even a background suppression of some 2 or 3 orders of magnitude will not yield a useable spectrum, and there remains the possibility of sample damage. Some materials will always exist for which no Raman spectrum can be obtained, irrespective of gating technology or laser wavelength. Good Raman spectra were also obtained from both the PEEK film Upilex SGA film.

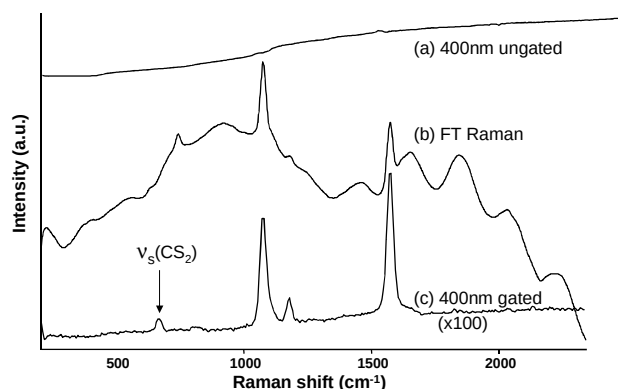


Figure 1. Fluorescence rejection from PPS film. Fluorescence rejection from poly(phenylene sulphide) film. Both of the visible spectra were averaged over twenty 20 scans, the FT Raman spectrum was averaged over 100 scans (~ 130 s total acquisition time). Excellent rejection was achieved, and the gated spectrum is superior to the FT-Raman spectrum in this instance. The band near 650 cm^{-1} is due to the CS_2 symmetric stretch in the Kerr cell. Spectra are offset for clarity.

The temporal response of scattering in powders

With powders or heterogeneous materials, both the laser beam and the scattered light will suffer refraction and reflection at particle/air interfaces, or any other refractive index discontinuities, and so will undergo diffuse reflection. Some will re-emerge from the sample and be collected, while a significant amount will be scattered and lost. Therefore, depending on particle refractive index, absorption coefficient and size/shape, it is possible that after incidence of the laser

pulse, light will re-emerge at times that are significantly longer than the laser pulse duration. This will induce temporal broadening of both the Raman and the fluorescence fluxes, and could potentially reduce the discrimination of these signals. Therefore it was decided to study the temporal response of the diffusely reflected Rayleigh and Raman scatter from powdered samples. As far as we are aware, this type of study has not been previously reported.

To study this effect, we obtained spectra of trans-stilbene as a function of the temporal position of the Kerr gate (see Figure 2). This particular material was used since it produces very strong Raman signals and good S/N spectra in a short time. In these spectra the notch filter in front of the spectrometer was tilted to allow a small fraction of the elastically-scattered light to reach the detector, so that we could monitor simultaneously both Rayleigh and Raman signals (at $\Delta\nu = 0$ and $\Delta\nu \sim 1600\text{ cm}^{-1}$) respectively. The gate was moved incrementally to later times relative to the position that maximised the Rayleigh signal ($t = 0$). The selection of spectra shown in Figure 2 were taken at 5, 10, 15, 20, 30, 40, 70, 100 and 150 ps respectively. The spectrum at $t = 0$ was not shown since it cannot easily be displayed on the same scale. However, it should be noted that while the Rayleigh signal was typically four times more intense at 0 ps than at 5 ps, the Raman signal was of similar intensity in each case. The inset to Figure 2 shows how the Rayleigh intensity falls more rapidly than the Raman signal. After 100 ps the Rayleigh band was about 1 % of its intensity at $t = 5$ ps, whereas the residual Raman signal was still about 30 % of that at 5 ps (see inset) and is easily detected even after 300 ps. This proves that the scattered light from this powder is no longer confined to the 1 ps laser duration, but also demonstrates that the Rayleigh and Raman bands obey different "decay kinetics".

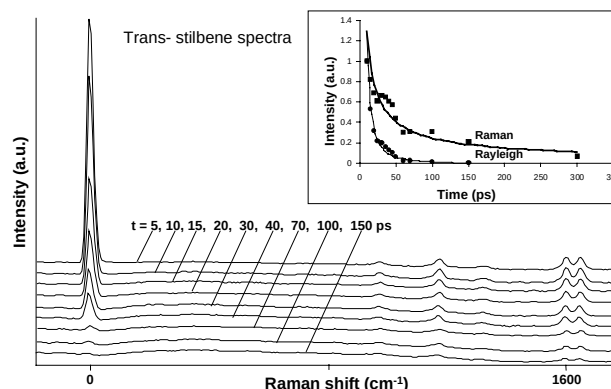


Figure 2. Time resolved spectra of trans-stilbene powder, each the average of fourteen 2 s acquisitions. Both the Rayleigh and Raman signals are significantly broadened compared to the incident 1 ps laser pulse, and the Raman signal decays more slowly than the Rayleigh line.

Implications for time-resolved Raman spectroscopy of powders

At first sight these findings might imply that the S/N of time-resolved data from powders could be reduced. Because the broadening is asymmetric in time, good fluorescence rejection can always be obtained by positioning the gate at $t = 0$, but if the Raman signal is dramatically broadened, a short gate cannot efficiently capture it and will reject both fluorescence and Raman bands. To test this hypothesis we recorded the spectrum of a sample of highly fluorescent PEEK powder. This material was not chemically identical to the PEEK film, in that it had a much shorter fluorescent lifetime (ca. 50 ps as opposed to 300 ps). Figure 3 compares the ungated and gated spectra of the powder; we observed a ~ 40 -fold improvement. Clearly, in this case any temporal broadening that occurred did not seriously degrade the Raman signal.

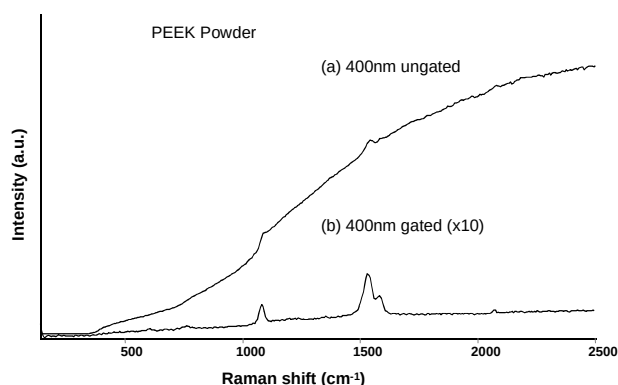


Figure 3. Fluorescence rejection with PEEK powder. Each spectrum was averaged over twenty 3 s scans. Again, the fluorescence background was efficiently rejected.

Future Work

To our knowledge, the possibility of utilizing time-resolved Rayleigh and Raman spectroscopy to study diffuse reflection has not been previously explored, and this study represents merely a preliminary investigation. The following questions immediately arise. Can the temporal response of the scattering be related to particle properties such as size, shape, packing, and optical absorption? How reproducible are the temporal curves? Can the effect provide insight into the optics of diffuse scattering or the nature of dense powders or dispersions? Can the particle size be reduced sufficiently to eliminate the effect? Can the shape of the Raman response be understood on a quantitative physical basis?

Probably the most immediately fruitful future work would be

- i) to compare the Raman and Rayleigh profiles from samples prepared with well-defined particle size distributions, to thoroughly investigate the effect of particle size,
- ii) to investigate the effect of optical absorption and
- iii) to analyse very thin powder samples, in order to minimise the possibility for diffuse reflectance.

Of course, further studies are also needed to assess to what extent temporal blurring prevents effective time-resolved fluorescence rejection with powders; our present work is inconclusive in this respect.

We hope to report these studies in future publications. A full account of the presented work has been submitted for publication⁴⁾.

Conclusions

Kerr-gated picosecond time resolved Raman spectroscopy dramatically reduces the fluorescent background from solid materials. With powdered materials, the Raman and Rayleigh temporal response following irradiation with a 1 ps laser pulse can be significantly broadened, due to the long intra-sample path-lengths that arise when photons are diffusely reflected. Photons can re-emerge from a powder hundreds of picoseconds after termination of the irradiating pulse, blurring the temporal distinction between Raman and fluorescence photons. It remains to be seen whether this temporal blurring will limit the general applicability of time resolved fluorescence rejection with powders.

As an aside, these effects could also have implications for pump-probe studies of powders. In the presence of diffuse reflectance it becomes difficult to define precisely the time between the pump and probe pulses, since the pump photons could persist for significant time periods.

Acknowledgements

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Ion-dip Spectroscopy of Ephedrine and its diastereoisomer pseudoephedrine

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Introduction

Chirality plays a vital role in the action of pharmaceuticals on the human body. The interactions between such molecules and an enzyme binding site (itself formed from chiral sub-units) depend on the shape adopted by the molecule which is itself a complex balance between bonded and non-bonded forces. Hydrogen bonding is ubiquitous, both externally with the binding site and with water molecules, and internally between the functional groups of the molecule itself.

The ephedra series of pharmaceuticals (see Figure 1) share a number of structural characteristics with the natural neurotransmitter adrenaline and have similar pharmacological effects, principally on the cardiovascular system. Ephedrine differs from its diastereoisomer pseudoephedrine by the change of one chiral centre. This seemingly minor change increases the melting point from 36°C in ephedrine to 120°C in the case of pseudoephedrine. Such dramatic changes indicate differences in *inter-molecular* interactions in the crystal phase. To examine similar effects in an isolated system we have studied ephedrine and pseudoephedrine in the environment of a jet-cooled supersonic expansion¹.

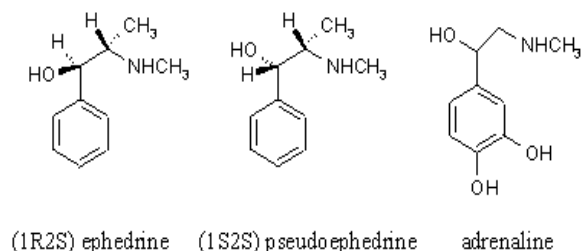


Figure 1. Molecules of interest.

In recent years, there has been a determined effort by a number of groups to explore the conformational preferences of small biomolecules^{2,3}. Powerful techniques such as infra-red ion-dip spectroscopy have been used to probe the hydrogen bonding nature of OH, NH and CH functional groups. The extraordinary sensitivity of such groups to the local hydrogen bonding network provides an ideal means to probe the conformational landscape. The technique is even more powerful when combined with time-of-flight mass spectrometry with its ability to mass separate ions. Such a combination allows an infra-red spectrum to be obtained which is both *mass* and *energy* selected; a situation which is crucial for the study of weakly bound clusters. Two distinct experiments were carried out; firstly the UV laser was tuned onto a resonant band and the IR scanned over the region of interest (3100-3800 cm⁻¹) to obtain a resonant ion-dip infra-red spectrum (RIDIRS). The second configuration consisted of a fixed IR frequency and the scanning of the UV laser allowing the identification of features in the UV spectrum originating from the same conformer.

The combination of such techniques with high-level quantum-chemical calculations allows the assignment of discrete conformational structures to experimental features with a *high degree of confidence*. Advances in computer technology mean that calculations on small biomolecules (containing up to twenty or thirty atoms) with methods that include electron correlation (e.g. second order Moller-Plesset perturbation theory) and with large basis sets which include polarisation and diffuse functions are now routine.

Ephedrine

The Resonant 2-Photon Ionisation (R2PI) spectrum of ephedrine is shown in Figure 2. It consists of one dominant feature (A) and a considerably weaker band (X) which was identified by spectral hole-burning. Also shown in Figure 2 are the RIDIRS spectra of both features which consist of an intense peak around 3500 cm⁻¹ assigned to an OH vibrational mode (A: 3493 cm⁻¹ and X: 3540 cm⁻¹) and a much weaker feature at 3378 cm⁻¹ in A due to the NH stretching mode. The red-shift of the OH band relative to a free alcohol (~3660-3680 cm⁻¹) indicates the presence of a hydrogen bond in which the OH groups acts as the proton donor. The two features to the *blue* of the OH mode for feature A are assigned to combination bands of the OH stretch with low-frequency torsional motions of the side-chain.

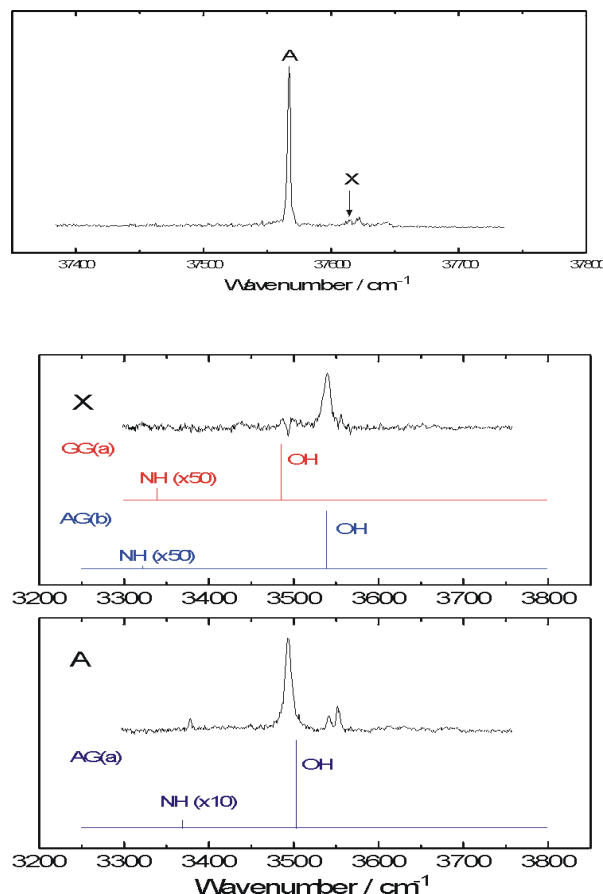


Figure 2. Resonant 2-Photon Ionisation (R2PI) spectrum of ephedrine (top panel). The lower panel shows experimental IR spectra of features A and X. Also shown are calculated infra-red spectra for the three low-lying conformers from B3LYP/6-31+G* calculation. Scaling factors of 0.9734 for OH modes and 0.956 for NH modes were derived from previous work on related molecules.

Ab-initio calculations, performed at a variety of levels, indicate that the lowest lying conformers of ephedrine consist of those with an intramolecular hydrogen bond between the functional groups of the side-chain in which the OH acts as proton donor and the NH group as acceptor. Structures with the opposing geometry are found to lie considerably higher in energy (ca. 10 kJmol⁻¹). The four low-lying structures are shown in Figure 3 with the relative energies from MP2/6-311G**

calculations. The notation (AG(a)) refers to the arrangement (anti or gauche) of the CCCN and OCCN atom chains while the term in brackets (a or b) refers to the configuration of the amino group. At all levels of theory the extended AG(a) conformer is found to be the global minimum followed by the GG(a) and AG(b) structures. The remaining conformer (GG(b)) is found to be much higher energy and would not be expected to appear in our experiments.

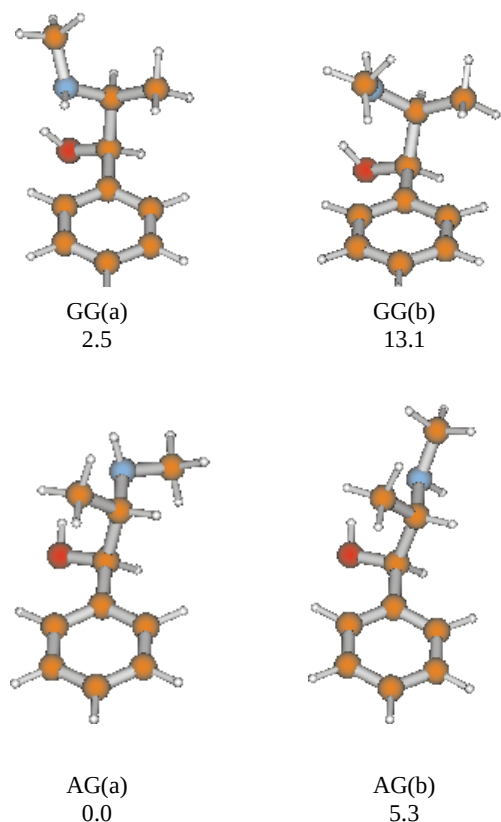


Figure 3. The four low-lying conformers of ephedrine. Relative energies (kJ mol^{-1}) are from MP2/6-311G** calculations and include a zero-point correction.

Vibrational frequencies were calculated using hybrid density functional theory (B3LYP/6-31+G*). These are shown for the three low-lying conformers in Figure 2 and are scaled by factors of 0.9734 for OH and 0.956 for NH. These empirical factors have been derived from previous work on related systems^{1,4,5}.

The assignment of feature A in the R2PI spectrum to the global minimum structure (AG(a)) is straightforward; agreement between experimental and calculated infra-red spectra is excellent. However, a problem arises when we try to apply the same criteria to feature X. Good agreement between experiment and theory is found, not for structure GG(a) which is the most stable conformer after AG(a), but for structure AG(b). Previous work on rotational band contours of the UV spectrum of ephedrine is also in agreement with this conclusion¹. Therefore we assign feature X to conformer AG(b). The apparent absence of the GG(a) structure will be discussed later.

Pseudoephedrine

The R2PI spectrum of pseudoephedrine is shown in Figure 4. Clearly, it is very different from that found for ephedrine. Spectral hole-burning allows us to identify four distinct conformational structures (A, B, C and X in Figure 4). The IR spectra of all four features are also shown in Figure 4. These are similar to those of ephedrine in that they all have a feature in the region of 3500 cm^{-1} due to OH (A: 3437 cm^{-1} , B: 3477 cm^{-1} ,

C: 3515 cm^{-1} and X: 3454 cm^{-1}) with the considerably weaker NH mode around 3350 cm^{-1} (A: 3378 cm^{-1} , C: 3328 cm^{-1} and X: 3383 cm^{-1}).

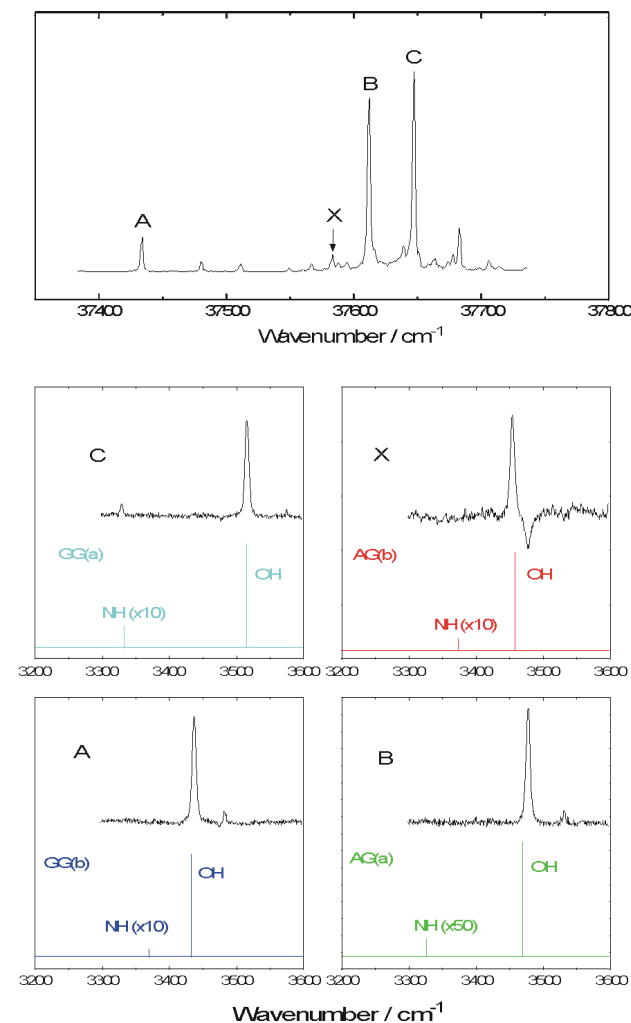


Figure 4. R2PI spectrum of pseudoephedrine (top panel). The lower panel shows the infra-red ion-dip spectra of features A, B, C and X. Calculated IR spectra are from B3LYP/6-31+G* calculations using scaling factors of 0.9734 for OH and 0.956 for NH modes.

Ab-initio calculations on pseudoephedrine reveal that the same four conformers as in the case of ephedrine are the lowest-lying structures. These are shown in Figure 5 with relative energies from MP2/6-311G** calculations. In contrast to ephedrine all four such conformers are relatively low-lying with the AG(a) structure again the global minimum. Calculated vibrational spectra (B3LYP/6-31+G*) are shown in Figure 4 and, in comparison with the experimental IR spectra, allow the assignment of all four experimental features to discrete conformational structures (A: GG(b), B: AG(a), C: GG(a) and X: AG(b)). Such assignments are in good agreement with previous work on the partially resolved rotational contours obtained using laser-induced fluorescence spectroscopy¹.

Discussion

The conformational landscapes of ephedrine and pseudoephedrine are a subtle and complex balance between a number of interactions. Dominant among these is the intramolecular hydrogen bond between the functional groups of the side chain. The geometry of the chain constrains the bond to

a non-optimum configuration with OH...N distances in the region of 220 pm and OHN angles around 120°.

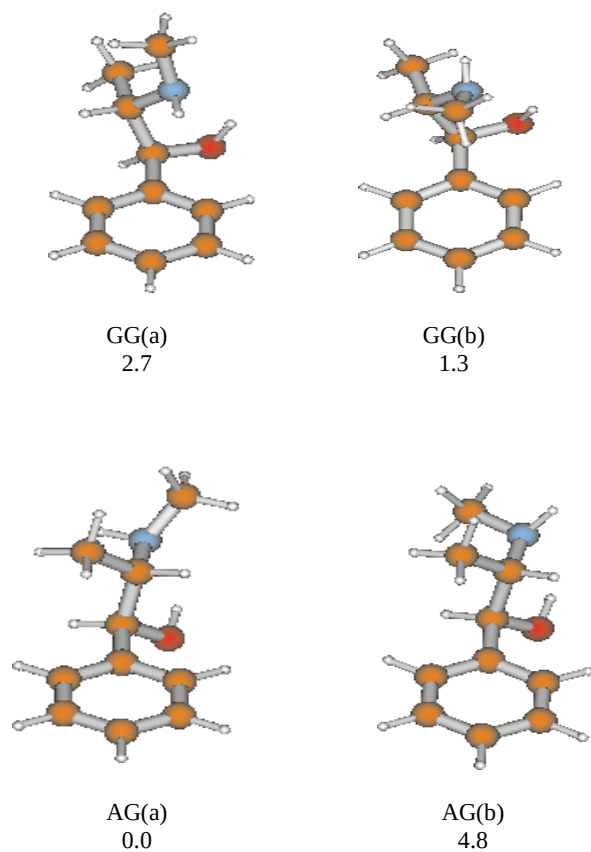


Figure 5. Calculated structures of pseudoephedrine. Relative energies (kJmol⁻¹) from MP2/6-311G** and include a zero-point correction.

These compare with the values from the phenol-ammonia cluster⁷⁾ (OH...N: 199 pm and ∠OHN: 170°). However, the range of the vibrational frequency of the OH mode for all six structures is of the order of 100 cm⁻¹ indicating the presence of other interactions that influence the strength of the hydrogen bond (and hence the resulting red-shift) through co-operative effects. Examination of the structures presented in Figures 3 and 5 provides some clues to the identity of these interactions; in particular structures GG(a) and GG(b) of pseudoephedrine. These two conformers (assigned to features C and A respectively) differ only in the configuration of the amino group. However, the OH stretching frequency of GG(b) is red-shifted by approximately 80 cm⁻¹ relative to that of GG(a). The secret lies in the orientation of the two methyl groups of the side-chain relative to each other and to the aromatic ring. In structure GG(a) the two are arranged in a *gauche* fashion reminiscent of that of butane and the N-methyl group points away from the ring. A further stabilising influence is provided by a hydrogen bond between the NH group and the π -system of the aromatic ring. This is manifested in the red-shift (and greater intensity) of the NH stretch (see Figure 4). The inversion of the amino-group (equivalent to exchanging the methyl group and the proton) results in a structure (GG(b)) in which such an interaction is no longer possible; instead the N-methyl group points directly towards the aromatic ring. To alleviate this destabilising influence there is a significant distortion of the side-chain which has the (beneficial) side-effect of improving the geometry of the intramolecular hydrogen bond. Furthermore, the two methyl groups are

orientated in the most energetically favourable staggered configuration. This combination of factors greatly depends on the local structure of the side-chain and is highly dependent on the absolute configuration of the chiral centres.

The combination of experiment and theory has allowed us to discern the conformational landscapes of ephedrine and pseudoephedrine. In the case of the former the assignments of discrete structures to experimental features provides a surprising result. Two conformers were observed corresponding to the AG(a) and AG(b) structures. The conformer GG(a), intermediate in energy between these structures was *not* observed. Calculations using a number of methods and basis sets failed to resolve the situation; indeed, the relative energies of AG(b) and GG(a) remained remarkably stable at all levels of theory. Calculations on the relaxation of GG(a) to the global minimum (AG(a)) yield a barrier greater than 1000 cm⁻¹, far greater than that found for systems in which conformer relaxation is significant⁷⁾ and we do not expect such a pathway to be viable in this case. We can only speculate on the absence of this structure from the experimental spectra; a weak transition moment and the lack of facile relaxation pathways from *higher* conformers to GG(a) may both play a role.

Ephedrine-Water complexes

The R2PI spectra of ephedrine-water recorded in the monomer (M⁺), monomer-water₁ (MW₁⁺) and monomer-water₂ (MW₂⁺) mass channels are shown in Figure 6. A number of features due to water clusters are observed (B, C, C*, D and E). Fragmentation of the cluster after ionisation with the resulting loss of at least one water molecule is common and we tentatively assign features C and E to a water₁ cluster, B and D to water₂ and C* to water₃. Currently we are attempting to confirm these assignments by ion-dip experiments.

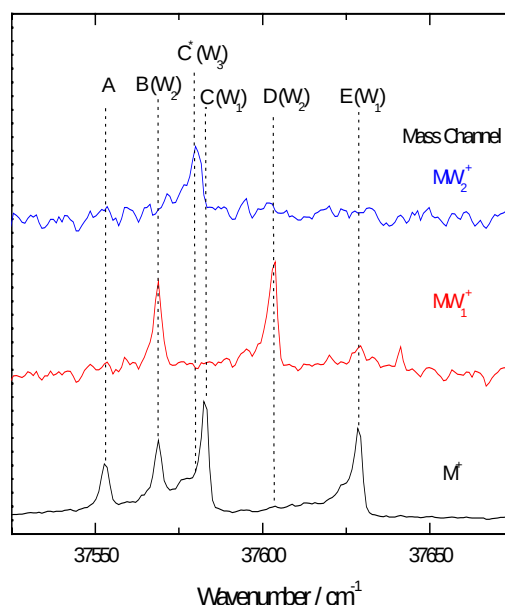


Figure 6. R2PI spectra of ephedrine-water clusters recorded in the monomer (M⁺), monomer-water₁ (MW₁⁺) and monomer-water₂ (MW₂⁺) mass channels.

Infra-red ion-dip spectra of the water₁ clusters (peaks C and E) are shown in Figure 7 along with calculated vibrational spectra for the three lowest-lying structures. At present, the experimental spectra do not extend to the region where the OH...N mode is expected. Relative energies and structures of the three low-lying water₁ conformers are shown in Figure 8. On the basis of comparison between (the incomplete) experiment and calculation we tentatively assign feature C to the AG(a)-W₁ structure and peak E to the GG(a)-W₁ cluster.

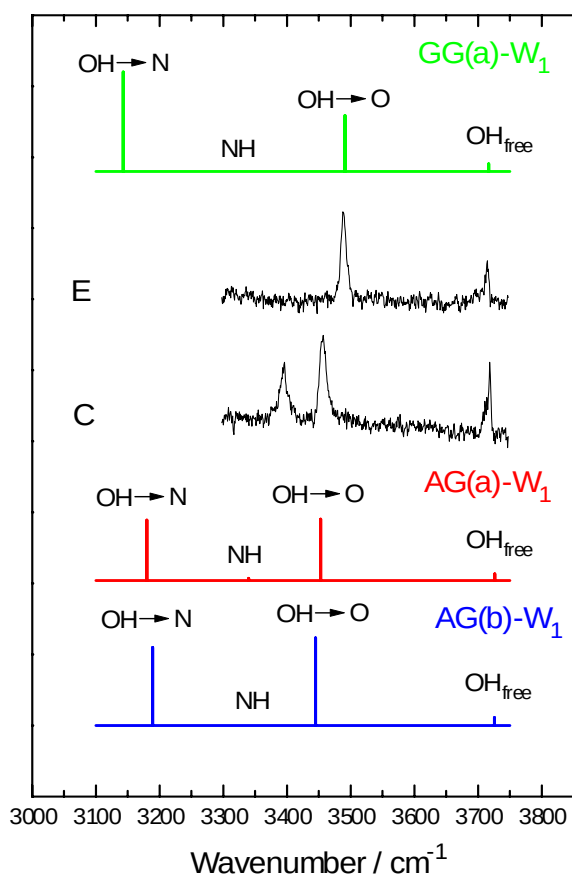


Figure 7. Infra-red ion-dip spectra of ephedrine-water₁ (features C and E). Also shown are calculated spectra for the three low-lying conformers (GG(a)-W₁, AG(a)-W₁ and AG(b)-W₁) calculated at the B3LYP/6-31+G* level with a scaling factors of 0.976 and 0.956 for OH and NH modes respectively.

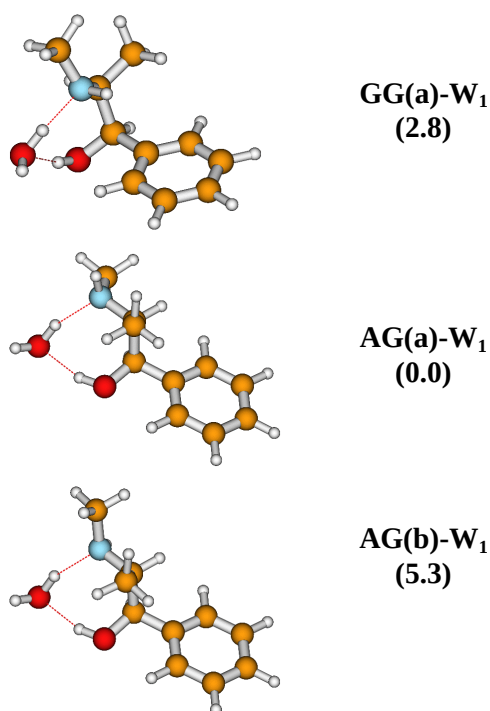


Figure 8. Structures of the three lowest-lying water clusters of ephedrine. Calculated energies are from MP2/6-311G** and include a zero-point correction.

Discussion

Hydration of ephedrine occurs across the intramolecular hydrogen bond; one strained H-bond is replaced with two more conventional bonds (OH(eph) → O and OH(wat) → N). To accommodate this, the side-chain is significantly distorted from the monomer geometry (the OCCN dihedral angle opens by approximately 20°); interactions between the methyl groups and between the NH and the aromatic ring are altered which, in turn, influences the relative stability of the individual conformers.

However, in the case of ephedrine hydration has only a minor effect on the relative energies of the conformers. It is interesting to note that, contrary to the case for the monomer, the singly hydrated cluster of structure GG(a) is observed. Such a situation has been noted for a number of small biomolecules⁸⁾ and is usually attributed to the inhibition of non-radiative decay of the excited electronic state by cluster formation. In the case of ephedrine we can only speculate about the behavior of structure GG(a) and its hydrate. Future work, currently in progress, will extend the infra-red spectra to cover the remaining OH band.

Conclusion

The conformational landscapes of the diastereoisomers ephedrine and pseudoephedrine have been examined using a combination of *ab-initio* calculations with a variety of experimental techniques. Assignments of experimental features to discrete structures have been made by comparison of experimental infra-red spectra with calculated vibrational spectra; two conformers were assigned in ephedrine and four in pseudoephedrine. In all six structures the principal stabilising factor was an *intramolecular* hydrogen bond between the functional groups of the side-chain with the OH group acting as proton donor. Secondary interactions, including methyl-methyl and NH- π , modified both the relative energy of the conformers and the strength of the principal hydrogen bond through co-operative effects. In the case of ephedrine the assignment of the weaker conformer was contrary to the calculated relative energies. The absence of the GG(a) conformer was tentatively explained by a weak transition dipole-moment and the lack of facile relaxation pathways to this structure from higher conformers. However, the 1:1 hydrate of this structure could be observed experimentally. Little or no change in the relative energy of the conformers was found on hydration.

Acknowledgements

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Excited State Dynamics of Organo-Lanthanide Electroluminescent Phosphors: The Properties of Tb(tb-pmp)₃ and Gd(tb-pmp)₃

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Introduction

Molecular lanthanide complexes show promising properties as phosphors in thin film organic electroluminescent displays. The narrow lanthanide emission bands offer superior spectral purity, while the chemical flexibility of the complexes provides a platform for manipulating the physical properties of the emitter. Up to now, complexes containing β -diketonate ligands have attracted much attention. Recently a high efficiency green electro-luminescent device based on an organo-terbium complex has been reported¹. This complex contains three 1-phenyl-3-methyl-4-(trimethylacetyl)pyrazol-4-one (tb-pmp) ligands. Since the performance of an organolanthanide-based light emitting diode (OLED) depends on the efficiency of the transfer of excitation energy to the lanthanide ion, we have sought to understand the relevant photophysical properties of these tb-pmp based OLED materials. Here we present the results of a study of the Gd(tb-pmp)₃ and Tb(tb-pmp)₃ complexes.

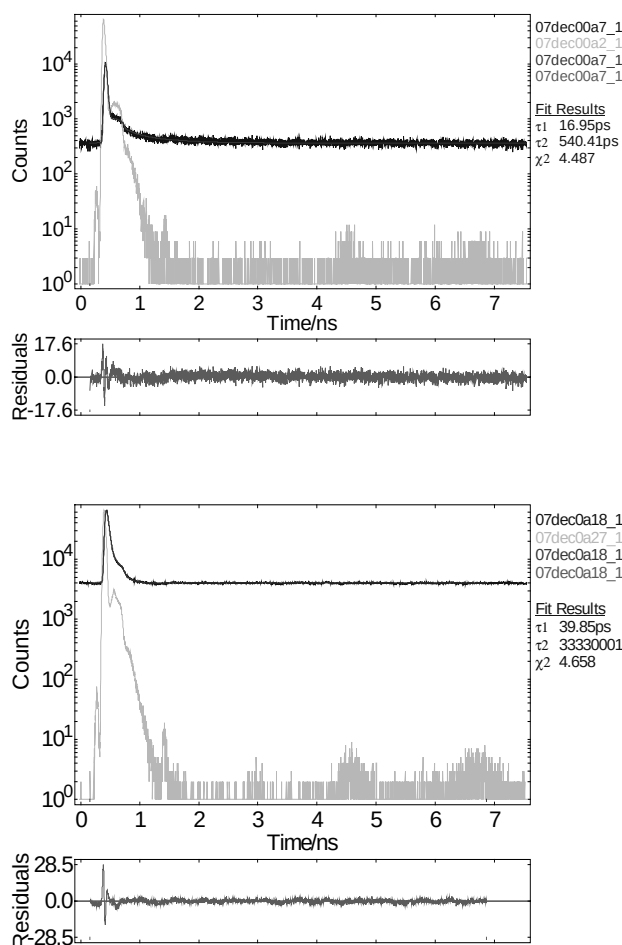


Figure 1. TCSPC 360nm excitation, 470nm detection, 38 ps instrument function (grey) upper: Tb(tb-pmp)₃ 17ps decay lower: Gd(tb-pmp)₃ 40 ps decay.

Experimental

Fluorescence decays were obtained by time-correlated single-photon counting (TCSPC), following excitation by a frequency-doubled mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics 150fs) operating at 360nm with a pulse repetition rate of 80MHz. The detection system consisted of a monochromator (H10, Jobin-Yvon) followed by a micro-channel-plate (R3809U, Hamamatsu). A combination of colour and interference filters were used to remove scattered laser light. Samples used were in powdered form in e.p.r. tubes. The instrument response function, obtained from the sample scattering detected at the laser wavelength, had FWHM of 38ps.

Conclusions

TCSPC and related results have enabled us to determine an energetic and kinetic scheme for the intramolecular transfer of energy from the ligand to the Tb(III) ⁵D₄ emissive state:

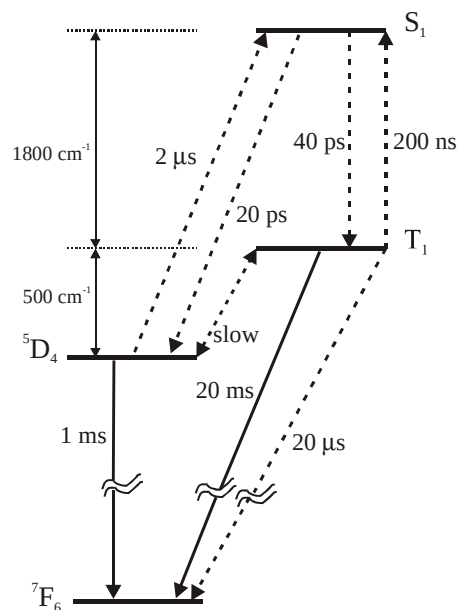


Figure 2. Intramolecular energy transfer scheme.

Although ISC is fast in these materials, we have demonstrated that ligand-to-metal energy transfer proceeds almost entirely through the singlet (S₁) state of the ligand, rather than from the triplet (T₁) as concluded in many previous OLED studies². Any population of the triplet state in Tb(tb-pmp)₃ leads to decreased quantum efficiency. The importance of this work for OLED design, is the subject of a recently submitted paper³.

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Two-Photon Spectroscopy of Thulium(III) in the Elpasolite $\text{Cs}_2\text{NaYCl}_6\text{:Tm}$

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Introduction

Two-photon fluorescence excitation (TPE) spectroscopy, using a tuneable nanosecond pulsed laser, provides a good probe of parity-conserving transitions in the solid state that are inaccessible to one-photon spectroscopy. We have used this technique previously to obtain polarised f - f spectra of Tb(III), Eu(III) and Sm(III) ions free of phonon structure, that conclusively identify large numbers of crystal-field levels¹. Although some 100 or so electronic states can be identified in each of these ions, these constitute a small fraction of the full manifold of the f^N states. As such, they provide only limited scope for testing an empirical Hamiltonian. We have now reported the energies of almost all the forty f -electron states expected for the much simpler case of the f^{12} Tm(III) ion in a cubic site², with the aim of identifying more clearly the limitations of a conventional crystal field (CF) Hamiltonian.

The crystal field is expressed as the sum of 1-electron operators:

$$H_{CF} = \sum_{i,k,q} B_q^{(k)} u_q^{(k)}(i) \quad (1)$$

where $u_q^{(k)}(i)$ is a unit tensor operator for the i^{th} f -electron, of rank k where $k = 2, 4, 6$, and q is restricted by symmetry. A rigorous test of the validity of this simple model needs a large energy level data set, and a small number of CF parameters. The cubic environment provided by the elpasolite lattice requires only two such parameters, $B_0^{(4)}$ and $B_0^{(6)}$, and is ideal for this purpose.

A more realistic Hamiltonian introduces the influence of electron-correlation on the CF³, and includes a spin-correlated part, the SCCF, described by the additional perturbation:

$$H_{SCCF} = \sum_{i,k,q} b_q^{(k)} \mathbf{S} \cdot \mathbf{s}_i u_q^{(k)}(i) \quad (2)$$

The parameters $b_q^{(k)}$ are a measure of the modification to the CF arising from the dependence of the radial part of the wavefunction of the i^{th} $4f$ electron on its spin orientation $\mathbf{s}_i$ relative to the total spin $\mathbf{S}$, in response to exchange interactions. The relative importance of these SCCF corrections is measured by the parameters $c_q^{(k)} = b_q^{(k)} / B_q^{(k)}$ such that:

$$H_{TOTAL} = \sum_{i,k,q} B_q^{(k)} u_q^{(k)}(i) \{1 + \mathbf{S} \cdot \mathbf{s}_i c_q^{(k)}\} \quad (3)$$

However, alternative physical mechanisms can also be described by this form of parameterisation. One such applies particularly to those lanthanides (e.g. Sm(III), Eu(III), Tm(III), Yb(III)) that have low-energy ligand-to-metal- f charge-transfer (CT) states. Configuration interactions between these CT states and the f^N manifold provides a description of f -orbital covalency that can incorporate a degree of spin-polarisation. Tm(III) ought to provide the simplest and most clear-cut demonstration of this effect, because CT transitions occur at particularly low energy.

Experimental

We chose broadband emission in the range 300-400 nm as a probe of the 2-photon absorption in Tm(III) crystals. This wavelength region is far from the exciting wavelengths (550-600 nm) and eliminates the detection of scattered laser light. It encompasses emissions $^3\text{H}_6 \leftarrow ^1\text{D}_2$ at 355 nm (should internal cross-relaxation processes depopulate $^1\text{I}_6$) together with the transition $^3\text{F}_4 \leftarrow ^1\text{I}_6$ at 345 nm. Photons were counted for a period of 1 ms following a 100 microsecond delay after the laser pulse. The emission lifetimes at 350 nm and 450 nm for 5% doped Tm(III) crystals was ~250 microseconds at 77 K.

In lanthanide 2-photon absorption, it is essential that there be a window at the laser wavelength free of 1-photon absorption, in order to avoid resonant excited state absorption (sequential 2-photon absorption or upconversion). In Tm(III) the sparseness of excited states makes the likelihood of 1- and 2-photon coincidence improbable. No up-conversion fluorescence was detected in the regions used for the excitation.

The most significant region of the excitation spectrum, in the region of the $^1\text{I}_6$ origin, for which no data had previously been available from single photon studies, is shown in Figure 1 at two different temperatures. The energy axis (wavenumber) represents the single-photon excitation energy or twice the energy of the exciting laser beam. The symmetries of the states are identified from their polarization: knowledge of hot band (56 and 148 cm^{-1}) structure² allows identification of forbidden transitions. The line designations (30-37), in the Figure, label some of the 40 crystal field electronic states.

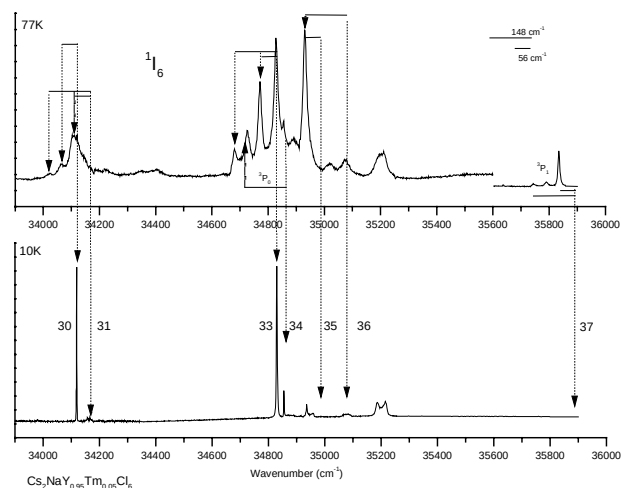


Figure 1. TPE spectra for $\text{Cs}_2\text{NaTm}_{0.05}\text{Y}_{0.95}\text{Cl}_6$ $^1\text{I}_6$, $^3\text{P}_{0,1}$.

Results

Due to the small number of electronic states, assignment of the spectrum is relatively straightforward on the basis of a 1-electron crystal field operator, using the F-shell program of M.F.Reid. The crystal field parameters are given in column 2 of Table 1.

Table 1 illustrates the very large deviations from 1-electron theory. Best fit effective crystal field parameters for the subset of energetically high-lying singlet states of the Tm(III) ion exceed those of the subset of low-lying triplet states by ~60%.

Levels	All	"Triplets"	"Singlets"
No. Levels	36	14	10
$B_0^{(4)}/\text{cm}^{-1}$	1919	1483	2396
$B_0^{(6)}/\text{cm}^{-1}$	214	189	250

Table 1. Crystal field parameters, B, for Tm(III).

From Equation (3) we also derive SCCF parameters ($c_0^{(4)} = +0.41$, $c_0^{(6)} = +0.24$). These values are some of the largest ever reported, values of $|c| \approx 0.1$ being more common for the lanthanides, and express mathematically the breakdown of 1-electron crystal field theory.

A comparison with other lanthanide hexa-halide complexes predicts CT transitions in TmCl_6^{3-} near 210 nm (48000 cm^{-1}). Transfer of an electron to Tm(III) f^{12} , of either spin, generates CT states derived from the same f^{13} doublet configuration of the thulium(II) ion. However CT states at 48000 cm^{-1} generated in this way, should mix much more effectively with the singlet states of Tm(III) near 35000 cm^{-1} , than with the energetically distant triplets. We believe that the much increased CF in the singlet states of Tm(III) in a chloride environment, as expressed in large positive SCCF coefficients, is therefore dominated by the influence of differential CT mixing and covalency.

Conclusions

We have obtained two-photon excitation spectra for thulium(III) in the elpasolite $\text{Cs}_2\text{NaYCl}_6\text{:Tm}$. 37 out of the total of 40 crystal field levels have been assigned, with the aid of a one-electron crystal field Hamiltonian, representing the most extensive data set so far reported for Tm(III) at a cubic site.

Deviations from 1-body crystal field theory have been shown to be very large ($\sim 60\%$) for Tm(III) in $\text{Cs}_2\text{NaYCl}_6\text{:Tm}$. This result is underpinned by two-photon selection rules and polarisations that provide a secure assignment of the majority of the CF components of the characteristic $^1\text{I}_6$ multiplet. These deviations are well described by the use of spin-correlated CF parameters. We believe the clear failure of the 1-body model in the Tm(III) ion is a consequence of the preferential admixture of low-lying ligand-to-metal charge-transfer states into the singlet states of the ion, leading to a large increase in the effective one-body crystal field parameters, relative to those in the triplet states.

Acknowledgments

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Crystallographic Studies on Excited-State Molecular Complexes

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Introduction

The photophysics of organometallic complexes has attracted a wide level of interest over recent years on account of the very applied nature of their emissive properties: e.g. for semiconductor devices, non-linear optical components and light-emitting diodes. The origin of these properties lies in the nature of the excited-states of these materials^{1,2}. The effects are prevalent in organometallic species due to their low-valent metal centre and the high degree of covalency between the metal and its ligands which results in the presence of various types of low energy excited states. The accessibility of these various states and thus the energy, intensity and lifetime of the associated emission depends inherently on the metal type and the nature of the ligands. In principle, one can therefore tune materials to exhibit specific emissive properties by judiciously varying the metal and ligand type. However, this requires a thorough knowledge of the exact nature of excited state that is responsible for the emission. This is no trivial matter, since this emissive state is usually a mixture of various types of low-lying excited states. One can infer a certain level of information *indirectly* through UV/vis spectroscopic measurements by comparing the different emission wavelengths, lifetimes and quantum yields for a given series of complexes e.g. ^{3,4}. Such inferences can be supported by theoretical molecular orbital-based calculations e.g. ⁵. Such work undoubtedly provides invaluable preliminary information. However, in Cambridge and Bath we are developing a new crystallographic technique that will enable us to see the nature of the excited state *directly*⁶. This technique exploits the recent advances in single-crystal X-ray diffraction instrumentation and pump-probe technology such that the crystal structure of a compound, whilst in its excited-state, can be realised.

Structural manifestations of excited-states

There are essentially seven possible types of excited states present in organometallic complexes: (i) metal-centred (MC) states, (ii) intraligand (IL) states, (iii) metal-to-ligand charge-transfer (MLCT) states, (iv) ligand-to-metal charge-transfer (LMCT), (v) metal-to-metal charge transfer (MMCT), (vi) metal-to-solvent charge transfer (MSCT) and (vii) solvent-to-metal charge transfer (SMCT).

MC or IL excited states correspond to electronic transitions between two orbitals on the same metal or ligand respectively. Low energy MC states are present in compounds where the M-M interatomic distance in the ground state is shorter than twice the sum of van der Waals radius of the metal and the shorter the distance the lower the energy of the excited state¹. This distance is perturbed in the excited state, either contracting or expanding depending on the nature of the orbitals involved. Low energy IL excited states occur in complexes where its binding to a metal does not alter significantly its electronic nature from that in its unbound state. Its involvement in emissive properties will also alter the relevant distances within the ligand but these are less detectable than the aforementioned M-M perturbations since the initial distances in ligands are markedly smaller and thus also are the changes in them.

MLCT and LMCT states originate from electronic transitions from a metal-centred orbital to a ligand-localised orbital and vice versa respectively. MLCT type transitions are commonly involved in the photophysics of organometallic complexes since

the metal is low-valent and the ligand acceptor orbitals are low in energy. In contrast, the contribution of a LMCT state to emissive phenomena in organometallic complexes is rare⁴. This is because the carbon based ligand donors are high in the spectrochemical series which results in ligand field energies that are much larger than excited states arising from other types of transitions. Indeed, LMCT states are generally observed only in organometallic complexes that contain metals in high oxidation states. The contribution of either MLCT or LMCT states to the character of the emissive state will perturb markedly the electron density between the metal and the ligand concerned, compared to that in the ground state.

MMCT states involve electronic transitions between orbitals on two metal centres. In the majority of cases, these states are the result of sigma-bonding to sigma-antibonding transitions and thus lead to efficient M-M bond breaking². Such states are poorly characterised but those of low energy are likely to be most prevalent in cluster complexes where the MMCT states are more delocalised over the core of the metals. In contrast, MSCT and SMCT states that arise from electronic transitions from a metal-centred orbital to a solvent-localised orbital and vice versa respectively, involve a bond making process. In common with MMCT states, only a handful of MSCT and SMCT states have been characterised for organometallic complexes despite the fact that emission wavelengths and lifetimes of such materials are commonly altered significantly by the presence of different solvent media and in comparison to solid-state measurements.

The character of the emissive state can also change significantly with temperature since the different types of electronic transitions are affected to various degrees by thermal effects, thus rendering different levels of mixing of excited states in differing thermal conditions⁷. Such temperature effects tend to be most stark in cases where metal-based electronic transitions show strong spin-orbit coupling on cooling, thus increasing their excited state energies to the extent that an energy cross-over with an unaffected IL state is incurred. This renders the formerly preponderant metal-based character absent and the IL state dominant in the emissive state. This will evidently affect the wavelength of the emissive state. Furthermore, IL states often occur via a spin-forbidden transition and thus emission lifetimes can increase dramatically with temperature in such cases. In more general terms, an increase in emission lifetime is usually concurrent with a reduction in temperature to some extent anyway due to the increase in quantum yield (population) of the emissive state. Given that our ultimate goal is to be able to tune organometallic materials to tailor specific physical properties, it is crucial that we obtain a comprehensive understanding of the true character of their emissive states, both at ambient and low temperatures.

Experimental methodology and results

In order to identify and quantify the type of excited-state in hand, one needs to be able to assess the nature of the associated electronic perturbations ensuing. The determination of an excited-state crystal structure via single-crystal X-ray diffraction is an ideal way to realise such information since the change in the electron-density distribution between the ground and emissive state, in affected areas of the molecule, can be mapped out using this technique. Moreover, where the changes are sufficiently distinct, differences owing to excited-state

perturbations can be detected simply by analysing changes in certain bond-geometries.

Practically, however, the development of pump-probe single-crystal X-ray diffraction is non-trivial, especially given the typically ephemeral nature of excited-states, and the struggle to achieve a sufficiently high percentage of molecules in their excited-state within a crystal, without destroying it (maximum possible conversion appears to be ~20-30%). In all of the experiments reported herein, the careful optimisation of the lasing power density was therefore an important consideration, the laser used in this case being the NSL-4 10Hz Nd:YAG laser. Another major consideration was to collect data as fast as possible and, in this respect, we have exploited the recent advances in single-crystal area-detector technology, all experiments being conducted using an Enraf Nonius Kappa-CCD diffractometer (Figure 1). Such an instrument enables one to collect a full data-set in minutes to several hours, thereby allowing excited-state structure determinations on compounds with long-lived excited-states (>30 minutes) using basic steady-state methods. In this respect, experiments were performed on the compound, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$, since it has an anomalously long-lived excited-state lifetime, $\tau = 10^7\text{s}$. This excited-state structure has already been determined using similar X-ray diffraction methods by Coppens et al⁶, who is a pioneer in this new field, and thus, these experiments served as an ideal means to test the technique with our experimental set-up. Two conventional data collections were performed on the compound, one with the laser (at $\lambda=488\text{nm}$) optically pumping the crystal for ~2 hours between the two experiments. The first-order difference obtained yielded the perturbation with respect to the excited-state as realised by Coppens et al⁶.

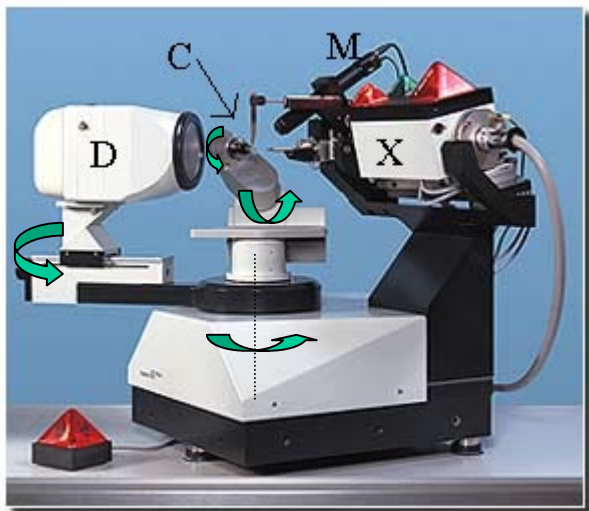


Figure 1. An annotated photo of a basic Enraf Nonius Kappa-CCD diffractometer. C = crystal position, D = detector, M = microscope, X = X-ray housing, source and shutter. The four degrees of angular freedom of the sample are marked with green arrows. In the experiments described herein, the cooling apparatus is not shown but comes in from above and the laser beam comes in from the back right, near the X-ray collimator (the pencil-shaped object to the right of the crystal).

Many components of the experimental set-up were optimised during this period, before turning our efforts to the more demanding continuous optical-pumping methodology, the target compound here being the 4,4'-dihydrobenzophenone:4,13-diaza-18-crown-6 complex. Here, an XRD experiment was performed in tandem with continuous optical pumping ($\lambda=488\text{nm}$), and the difference between these results and that of the ground-state structure determined, prior to pumping, was ascertained. This compound has an emissive lifetime of 50 ms

at 50K and we estimate that this continuous pumping methodology can be used with our set-up for compounds with lifetimes > 20ms, under optimum conditions. Results showed a perturbation in the hydrogen-bonding geometry: for the contact, O-H...N (labelled 'A' in Figure 2), the H...N distance in the ground/excited state structure was found to be 1.71(2)/1.78(2)Å respectively.

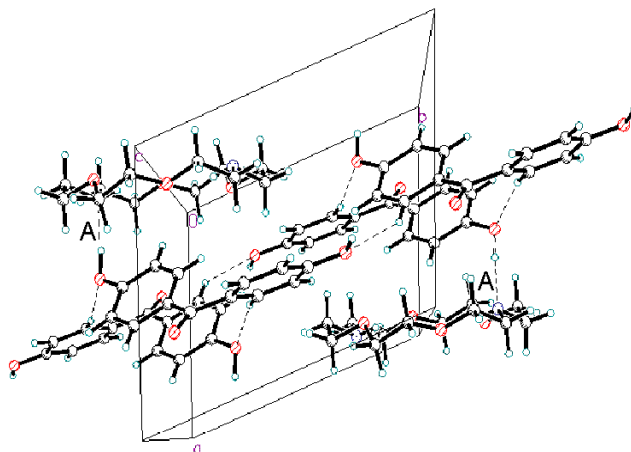


Figure 2. The hydrogen-bonding network of 4,4'-dihydrobenzophenone: 4,13-diaza-18-crown-6.

Whilst we are currently restricted to studies of compounds with excited-state lifetimes of > 20 ms, further work is in progress to enable the study of compounds with notably shorter emissive lifetimes (of the order of μs).

Concurrently, we have also been carrying out similar work using synchrotron radiation, where the pulsed X-ray source, inherent to a synchrotron, can be time-gated with respect to the laser pulse, such that a nanosecond time-structure can be realised. In this regard, the laboratory set-up described above was also very useful for the preliminary checking stages of a nanosecond time-resolved synchrotron X-ray diffraction experiment that we performed at the ESRF, France, on a Re carbene complex⁸ (Figure 3) in November 2000. The data from this experiment are still being processed, owing to the concomitant modifications required to adapt standard XRD data-processing software routines for this developmental work. However, what is expected is a perturbation of the Re-C bond and immediate surrounding geometry since the accompanying time-resolved UV/vis measurements on this compound predict that $^3\text{MLCT}$, $d(\text{Re}) \rightarrow \pi^*(\text{diimine})$ transitions dominate the emissive state character of the compound. Data pre-processing indicates a perturbation of ~0.6Å in the cell parameter, b, and during the experiment the crystal colour changed from yellow to red upon optical pumping ($\lambda = 400\text{ nm}$, using a femtosecond laser provided by the ESRF).

Further work is also in progress regarding the determination of excited-state structures as a function of temperature. As mentioned earlier, the lifetime and/or the character of the emissive-state of a compound can change dramatically with temperature. All of the experiments described above were carried out using an Oxford Cryosystems Cryostream that operates down to a temperature of 100K. However, by lowering the sample temperature further, one can often increase (by up to several orders of magnitude) the excited-state lifetime of a given compound, such that steady-state or continuous optical pumping methodologies become viable for the determination of their excited-state crystal structure. In order to exploit this temperature effect, at the close of the Laser Loan Pool period, we took receipt of the newly-developed Helix[®] open-flow helium cryostat cooling system ($T_{\text{min}} = 28\text{K}$) and conducted preliminary tests with this as a part of the experimental set-up,

as an alternative to the Oxford Cryosystems Cryostream. Such feasibility tests have proved very positive, such that we should be able to capitalise on the benefits of this additional ancillary equipment in subsequent development work.

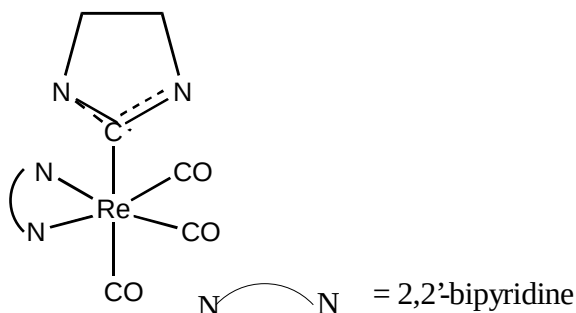


Figure 3. A schematic chemical diagram of the Re carbene complex studied at the ESRF.

Conclusions

Given the highly challenging experimental nature of this project, the bulk of the work in these initial stages of our developmental programme has comprised the testing and optimising of several test-case compounds. This has led to several promising results alone, and has afforded a firm basis of a good initial experimental set-up for further work. It has also enabled us to perform important preliminary work on our first very short-lived (nanosecond time-resolution) target compound which has potential as a building block for light-emitting-diodes. These results are being analysed at present but show promise at these early stages. Plans for further experiments and instrument development are now in place, including aims to realise microsecond lifetime experiments and to explore the temperature effects of the excited-state through the greater exploitation of the new Helix[®] cooling system ($T_{\min}=28\text{K}$) to the experimental set-up.

Acknowledgements

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Laser tweezers – Lattice forces in 2-D crystalline monolayers

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Introduction

Colloidal particles with radii in the nm to μm range may, depending on their wettability, adsorb very strongly at the oil-water interface¹. Oil-in-water, water-in-oil and multiple emulsions can be stabilized by particles alone for a wide range of applications including agrochemical, cosmetic and pharmaceutical formulations². The aim of the study described here was to use the laser tweezer apparatus developed at the Central Laser Facility, RAL to probe the lattice forces present within 2-D monolayers of spherical particles at an oil-water interface.

The particle monolayers

The system examined consisted of monodisperse, polystyrene spheres of 2.6 μm diameter which were spread at the interface between water and a mixture of decane/undecane. The upper oil phase composition was adjusted so as to have the same viscosity as the lower water phase. The polymer particles were spread by injecting a dispersion of the particles in *iso*-propanol directly onto the oil-water interface using a microsyringe. Following this procedure, all particles injected end up at the interface (i.e. none are in the bulk liquids) and the particle concentration within the interface is easily adjusted by variation of the amount injected. The small amount of *iso*-propanol spreading solvent is almost entirely lost by dissolution in the bulk liquids; surface tension measurements have shown that only minor traces are adsorbed at the oil-water interface.

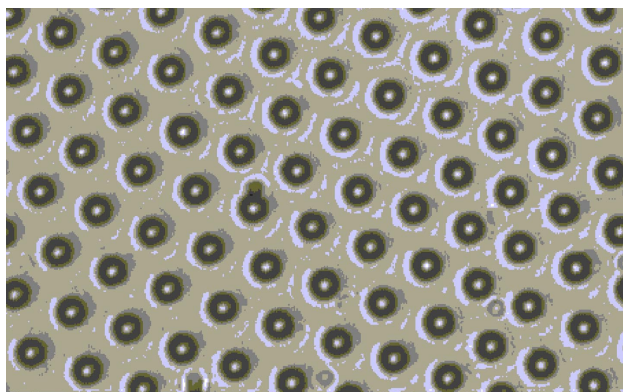


Figure 1. Optical micrograph of 2.6 μm diameter polystyrene spheres adsorbed at the oil-water interface. The particle centre-to-centre separation is 5.8 μm .

Figure 1 shows a micrograph image of a particle monolayer prepared as described above. Owing to the presence of very long range lateral repulsive forces between the particles (acting over many μm), the particle monolayers spontaneously form ordered 2-D hexagonal lattices. Adjustment of the particle surface concentration enables the particle centre-to-centre distance L to be varied over the range 4 to 15 μm . Based on monolayer surface pressure studies, the origin of the long-range repulsion between particles is thought to be electrostatic repulsion acting through the oil phase and resulting from a small fractional ionization of dissociable surface groups present on the particle surfaces¹. Capillary forces, resulting from

distortion of the oil-water interface caused by particle buoyancy effects, are estimated to be insignificant here, i.e. the oil-water interface is estimated to be virtually planar.

For this particle/solvent system, the contact angle formed between the oil-water interface and the particle surface is estimated to be 70 - 80°, measured through the lower water phase¹. Hence, the particles are slightly more immersed in the lower water phase than the upper oil phase. Equal immersion in both phases would correspond to a contact angle of 90°.

The laser tweezer apparatus

The laser tweezer setup is fully described in Reference 3. Briefly, the sample is mounted on the stage of an inverted microscope. The trap laser (continuous wave, variable power Nd:YAG) enters the sample from below and is focused by the microscope objective. In the configuration used here, the trap is formed at the waist of the beam focus which is located in the plane of the oil-water interface. Figure 2 shows a schematic side view of the sample cell, particle monolayer and laser beam light path. Key features of the apparatus include: (i) the ability to steer a single trap and the creation of multiple, steerable traps using fast-response acousto-optic deflection of the trap laser, (ii) sensing of the particle deflection within the trap using a position sensitive detector, (iii) the trapping force experienced by a single particle can be varied (in the pN range) by adjustment of the incident power of the trap laser, (iv) the microscope stage can be moved laterally under computer control using piezoelectric translators and (v) fast frame microscope image acquisition for subsequent image analysis. For the experiments described here, the acousto-optic deflector and position sensitive detector were still under development and were not used.

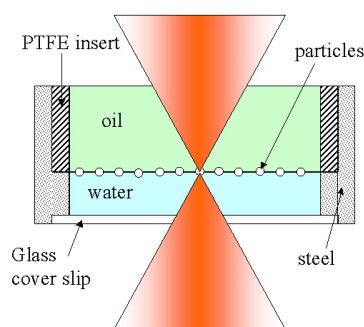


Figure 2. Schematic side view of the sample cell showing the particle array adsorbed at the oil-water interface and the trap laser light path.

Determination of lattice forces within the particle monolayers

A single particle, either isolated or within a 2-D crystalline array of particles, was trapped using a set laser power. We then applied an oscillatory lateral movement to the microscope stage. The lateral position profile was a smoothed triangular waveform of amplitude larger than the centre-to-centre particle separation L . The maximum stage velocity, and hence that of the liquid plus particle array surrounding the trapped particle, was v_{max} .

The trapping laser power was then decreased to determine the critical power P^* which was just sufficient to hold the particle within the trap against the forces associated with the fluid plus particle array motion as a function of the velocity $v_{\max}$.

The variation of P^* versus $v_{\max}$ for a single isolated particle in the absence of a particle array was used to obtain the calibration conversion of P^* into force values. The hydrodynamic drag force f_{drag} experienced by a sphere, of radius a , with a liquid of viscosity η , and moving with a velocity $v_{\max}$ is given by

$$f_{\text{drag}} = 6\pi\eta a v_{\max} \quad (1)$$

Equation (1) is strictly applicable only in isotropic, homogeneous fluids. For the case of a particle located in the oil-water interface, Equation (1) remains true when the viscosities of the two liquids are equal and the particle is equally immersed in both liquids (corresponding to the contact angle being 90°). However, for the system considered here, the contact angle is not exactly 90° and hence the use of equation (1) to convert values of P^* to f_{drag} introduces a small systematic error.

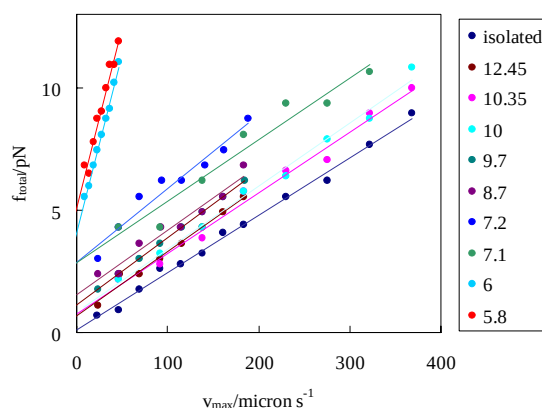


Figure 3. Variation of f_{total} with $v_{\max}$ for an isolated particle and arrays with lattice spacings L (in μm units) as indicated in the legend.

Figure 3 shows plots of the measured force f_{total} versus $v_{\max}$ for an isolated particle and for a series of 2-D crystalline arrays of different particle centre-to-centre separations L . For the isolated particle, the plot is linear with zero intercept, indicating that the critical hydrodynamic drag force required to free the particle from the laser trap is proportional to $v_{\max}$, as expected from Equation (1). For particle arrays with $L > 6 \mu\text{m}$, the plots are approximately parallel to the isolated particle case but the intercepts increase with decreasing L . This observation indicates that the measured total force f_{total} is the sum of two terms as follows.

$$f_{\text{total}} = f_{\text{drag}}(v_{\max}) + f_{\text{lattice}}(L) \quad (2)$$

The first term, f_{drag} , is the velocity dependent hydrodynamic drag force, equal to that seen for the isolated particle. The second term, f_{lattice} , is a velocity independent (at least approximately) force associated with the flow of the lattice around the laser trapped particle. The force f_{lattice} is a function of the lattice spacing parameter L .

For lattice spacings $L < 6 \mu\text{m}$, the slope $df_{\text{total}}/dv_{\max}$ increases sharply. When the particle surface concentration is high, the force associated with the lattice flow around the trapped particle becomes dependent on the velocity. The crossover in behaviour at which f_{lattice} switches from being velocity independent to being velocity dependent appears to occur at a fairly sharply defined value of lattice spacing L of about $6.5 \mu\text{m}$.

The variation of f_{lattice} with lattice spacing (expressed as $L/2a$, i.e. normalized relative to the particle diameter) is shown in Figure 4. The plot of f_{lattice} with lattice spacing has a similar shape to that of the plot of monolayer surface pressure versus lattice spacing, as described in Reference 1.

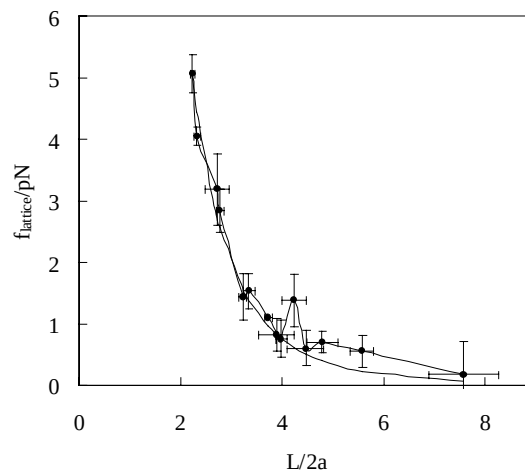


Figure 4. Variation of f_{lattice} with normalized lattice spacing $L/2a$.

Conclusions and future outlook

We have successfully determined the force exerted on a particle adsorbed at the oil-water interface as 2-D crystalline arrays of adsorbed particles flow around it. This force, f_{lattice} , is approximately velocity independent for $L/2a > 2.3$. For smaller lattice spacings, there is a crossover in behaviour and f_{lattice} becomes velocity dependent. The force f_{lattice} decreases with increasing lattice spacing, similar to the variation of monolayer surface pressure.

Following these first laser tweezer experiments with 2-D particle arrays at the oil-water interface, a number of interesting questions remain unanswered and are currently being pursued. The force f_{lattice} is expected to be related to the equilibrium particle-particle force versus separation relationship. We plan to measure this equilibrium force law directly using the acousto-optic deflector to create two traps with controlled separation. The position sensitive detector will allow measurement of the force on one trapped particle as a function of the distance to the second. Secondly, we are currently using molecular dynamics simulations to model the dynamic force f_{lattice} for different velocities using an assumed equilibrium force law. Lastly, we are planning experiments with a range of different particle types, oils and aqueous phases in order to elucidate the origins of the very long range inter-particle repulsion.

The laser tweezer facility at RAL offers a powerful, user-friendly tool to probe colloidal interactions in a very wide range of synthetic and biological systems, both at interfaces (as in this study) and in bulk phases.

Acknowledgements

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Ultrafast Spectroscopic Investigations of Metal Complexes Containing the DNA-Intercalating Dipyridophenazine (dppz) Ligand

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Introduction

Metal complexes which bind to DNA have been studied extensively by a number of research groups over recent years, with emphasis on understanding the photophysical and redox perturbations that are imposed through interaction with the DNA strand¹⁻⁴. The implications for clinical/diagnostic utility and for enhancing the understanding of natural DNA-mediated biological mechanisms are considerable.

Previous picosecond time-resolved resonance Raman (ps-TR³) experiments performed at the CLF by the Queen's group focused on providing definitive ultrafast dynamic and electronic characterisation of the key lowest excited states involved in the biologically relevant 'light-switch' photophysical effect, exhibited by the complex $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ (**1**) (phen = 1,10 phenanthroline; dppz = dipyridophenazine)¹. This effect manifests as a marked enhancement of luminescence of the complex when intercalated through the dppz ligand to DNA, or in non-aqueous solvent. The ultrafast studies proved to be confirmatory of the presence of two key dppz-based ³MLCT states, the relative energy ordering of which is tunable through local solvent environment of the dppz ligand. Interestingly ps-TR³ studies also appeared to point to the existence of a third, solvent sensitive 'precursor' state through which the excited complex progresses, prior to arriving at the lowest MLCT states².

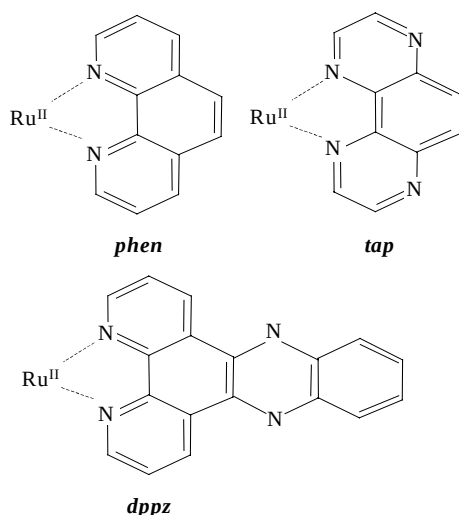


Figure 1. Diagram of Ligand Structures.

Recent ultrafast studies at CLF have been centred on other metal complexes containing the intercalating dppz ligand. One complex, $[\text{Ru}(\text{tap})_2\text{dppz}]^{2+}$ (**2**) (tap = 1,4,5,8 tetraazaphenanthrene), is structurally analogous to (**1**). The tap ligand is a structural analogue of phenanthroline, with extra nitrogens at the 5 and 8 positions. Binding to DNA persists through the dppz ligand. However, preliminary nanosecond transient Raman investigations on this system have suggested that the lowest excited MLCT state is based on one of the tap ligands(**3**). Further, preliminary photophysical evidence has been acquired describing photooxidation of guanine base by the excited state of (**2**), when bound to DNA, resulting in formation

of the electron transfer species $[\text{Ru}^{\text{II}}(\text{tap})(\text{tap}^{\cdot-})(\text{dppz})]^+$ and $\text{G}^{\cdot+}$ ³. Preliminary ps-TR³ experiments have been carried out also on the complex $[\text{Re}(\text{CO})_3\text{dppz.py}]^+$ (**3**)⁴ for which initial nanosecond studies have suggested prominent involvement of a triplet $\pi-\pi^*$ lowest excited state centred on the dppz ligand.

Results and Discussion

(a) $[\text{Ru}(\text{tap})_2\text{dppz}]^{2+}$

Picosecond transient absorption (ps-TA) spectra of (**2**) in buffer are shown in Figure 2 (a). The wavelength range covered was sufficient to encompass both the regions of ground state depletion between ~ 400 - 500nm and of positive transient absorption beyond 500nm. The overall ΔA profile here is typical of that for a ³MLCT state of Ru-polypyridyl complexes.

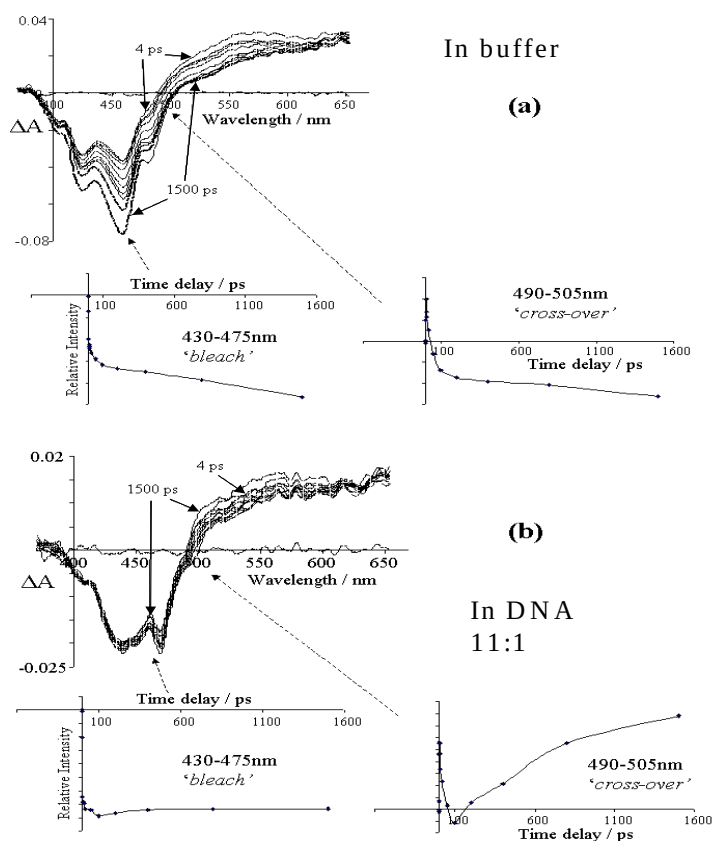


Figure 2. Picosecond transient absorption spectra of (**2**): (a) in buffer, (b) [DNA phosphate]:[Ru] ratio of 11:1. Recorded by multichannel detector at a range of time delays between -1 and 1500ps after excitation at $\lambda_{\text{ex}} = 400$ nm (ca. 1ps pulse duration). Shown for each kinetic series is a kinetic plot derived through integration of signal intensities at pixel values between 430 - 475nm and 490 - 505 nm for each trace within the series.

As mentioned above, the ³MLCT state in this case is 'tap-based'. Interestingly however, upon changing the time delay between pump pulse and interrogating continuum, the precise wavelength at which the absorption profile crosses the ΔA zero

line (at ca. 500nm) shifts gradually to longer wavelength as the time delay is increased. Also, in the region of excited state depletion, an unusual effect was observed, in that the bleach did not reach its maximum extent immediately following the excitation pulse but gradually increased over the time range interrogated. Further, the profile of the bleach region changed gradually with time, depleting more with time at longer wavelengths, than on the shorter wavelength side, indicating depletion of a transient absorption which had been countering the bleach more on the long wavelength side. These observations suggest progression through an absorbing intermediate excited state. Absorption due to this state, while it must overlap significantly with the absorption of the later $^3\text{MLCT}$ state in the region beyond 500 nm, also seems to extend further to the short wavelength side of 500nm. Parallel investigations of **(2)** in acetonitrile showed a very similar series of spectra, indicating little solvent dependence for the spectral changes, in contrast to the marked solvent-dependent photophysics of **(1)**^{1,2}.

Figure 2 (b) shows ps-TA spectra recorded of **(2)** in DNA at a [DNA phosphate]:[Ru] binding ratio of 11:1. Clearly, the kinetics are significantly perturbed upon DNA binding, observable through comparison of the integrated kinetic plots shown for the 'bleach' and 'zero-absorbance' regions with the respective plots for the complex in the absence of DNA. There are marked differences from Figure 2 (a) at the zero ΔA point, which appears not to shift to longer wavelength with increasing time delay. Indeed, the reverse tends to occur in this case (although the effect is smaller), the shortest wavelength 'zero absorbance' cross-over actually corresponding to the longest time-delay (1500 ps). Also, the profile of the ground state bleach no longer follows a pattern of delay steadily increasing with time, nor does the profile of this region change significantly with time delay as was observed in the absence of DNA. However, the main region of positive absorption does seem to follow a pattern similar to that seen for the complex in absence of DNA.

These spectral distinctions observed when **(2)** is bound to DNA are subtle but significant. The differences become especially evident upon comparison of the kinetic plots derived from both the regions of 'bleach' and 'zero' absorbance cross-over (Figure 2 (b)), with the corresponding kinetic plots for the complex in the absence of DNA (Figure 2 (a)). The overall perturbation to the spectra in the presence of DNA can be ascribed to the grow-in of a transient absorption. The fact that the main region of positive absorption does seem to follow a pattern similar to that seen for the complex in absence of DNA, suggests progression to a state characterised

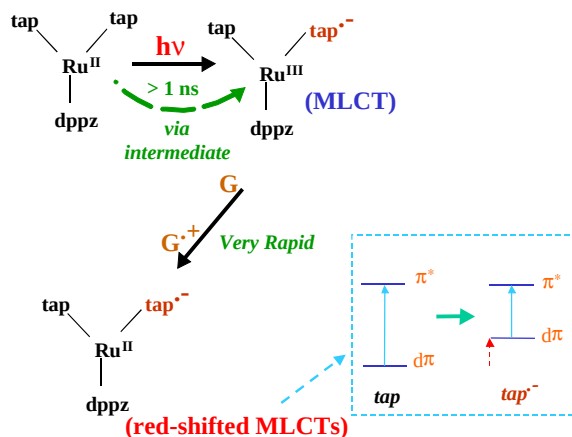
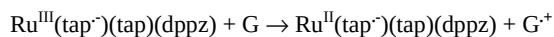


Figure 3. Scheme illustrating photophysical pathway of **(2)** in presence and absence of DNA.

by the same $\pi^*-\pi^*$ transitions, most likely of the anionic tap^{-•} species. A tap^{-•} moiety present in the species would account for the absorption in the wavelength region beyond 500nm.

Consideration of complementary evidence, from such studies as luminescent lifetime/steady-state measurements and nanosecond TR² spectroscopy, indicating that the excited state of **(2)** when bound to DNA is quenched³ suggests that the most likely conclusion from the ps-TA data is that photo-induced electron transfer from the DNA base, guanine, to the lowest $^3\text{MLCT}$ state of **(2)** is taking place:



The Ru^{II} species resulting from such an electron transfer to the Ru^{III} centre, would obviously bear considerable resemblance to the complex in its electronic ground state, with the obvious difference that one of the tap ligands would now be in anionic form. One effect of this extra electron density on a tap ligand might be to destabilise the $d\pi$ -orbitals of the Ru^{II} centre, thus causing a red-shift in the remaining MLCT transitions of the reduced complex (as illustrated in Figure 3 - inset). Given the original positions of the MLCT absorption bands of the ground state complex, the reduced transient species may reasonably be expected to exhibit MLCT absorption in the wavelength region around or below 500nm. What we see then in the picosecond transient absorption data for **(2)** bound to DNA, is this reduced species undergoing what can be described as a *dynamic perturbation* caused by the electron transfer from the guanine. An electrochemical 'model' for the guanine-reduced transient species has in effect been provided by the first reduced species of **(2)** generated in an optically transparent thin-layer electrochemical cell. The electronic absorption spectrum of this species shows depletion of MLCT absorption bands and a concomitant grow-in of absorption further to the red³.

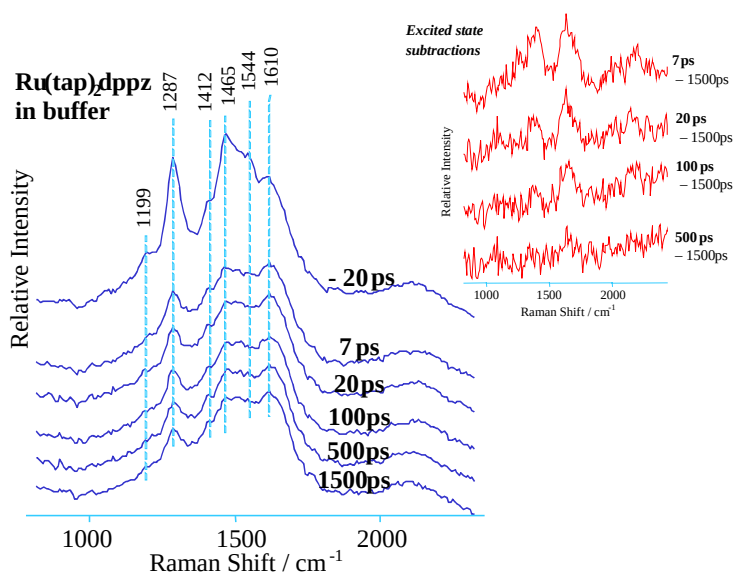


Figure 4. ps-TR³ spectra of **(2)** in buffer at 400/480 nm pump and probe at various delay times. Inset: Series of spectra generated through subtracting the pure excited state spectrum at 1500 ps from each excited state spectrum at early times.

Thus, as summarised in the scheme of Figure 3, a plausible photophysical picture which may now be associated with the ps-TA spectra of **(2)** in the absence and presence of DNA runs as follows:

Excitation and progression to a $^3\text{MLCT}$ state takes place via an intermediate state (as yet unspecified) over the time range studied (1.5ns). In the absence of DNA, the $^3\text{MLCT}$ state forms efficiently and is readily identifiable by the spectra discussed above. A similar process has been observed for the complex in acetonitrile.

When (**2**) is bound to DNA, an extremely rapid electron transfer from the guanine base to $^3\text{MLCT}$ takes place upon formation of the latter. The electron transfer is too fast to be resolved here on the timescale used. Thus, the spectra *appear* to represent transition from the intermediate state to the reduced species, occurring at a similar rate to the process above in absence of DNA. In actual fact, progression through the intermediate species represents the rate-determining step for forward electron transfer with DNA (a process which has never been monitored directly by spectroscopic means due to the almost instantaneous nature of the process in nucleic acids), the intermediate state itself being at too negative a potential to induce the electron transfer process. The reverse electron transfer process is expected to occur beyond the time range probed.

Preliminary ps-TR³ experiments have been performed on (**2**) in absence of DNA in an attempt to probe more extensively the photophysical processes in the sub-nanosecond time-regime. These initial spectra, recorded with 480 nm probe wavelength in order to attempt to establish resonance with the intermediate state, are shown in Figure 4. Spectral subtractions have been used to provide evidence of sub-picosecond dynamics in the TR³ series. Similar experiments are presently being carried out on (**2**) in presence and absence of DNA under more optimised conditions of spectral resolution and sample concentrations.

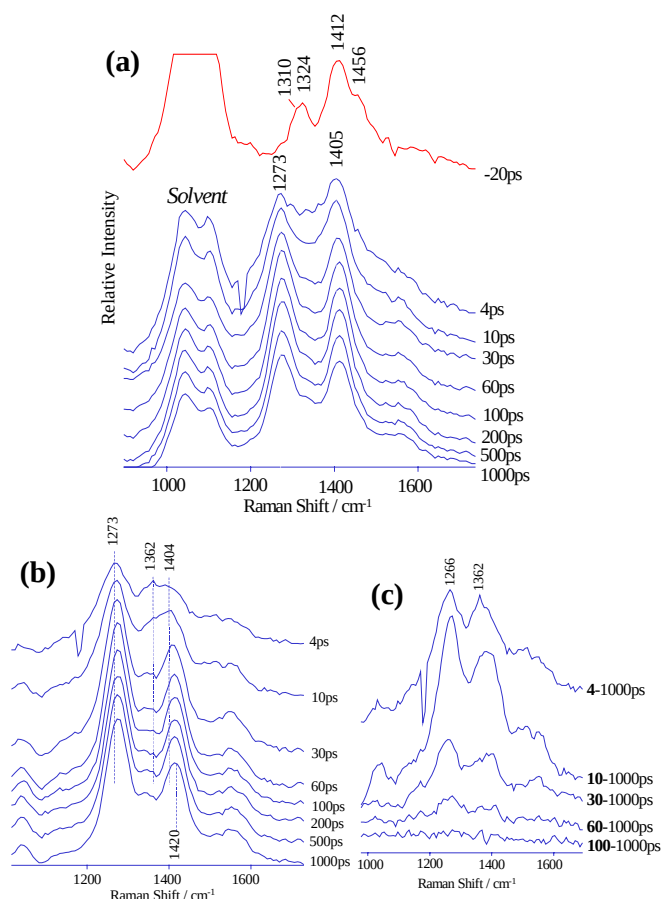


Figure 5. (a) ps-TR³ spectra of (**3**) in buffer at 400 / 480 nm pump and probe at various delay times; (b) Pure excited state spectra generated through subtraction of the -20 ps spectrum, cancelling on ground state features; (c) Series of spectra generated through subtracting the pure excited state spectrum at 1000 ps from each early delay pure excited state spectrum.

(b) $[\text{Re}(\text{CO})_3\text{dppz.py}]^+$

Picosecond-TR³ spectra recorded of (**3**) at 400nm pump / 480nm probe over time delays spanning 4 – 1000 ps are shown in Fig. 5 (a). Bands at later time delays are consistent with those observed in complementary nanosecond TR³ studies performed in Belfast, and are attributable to formation of the intraligand triplet $\pi-\pi^*$ state of dppz, from which it decays over several hundred nanoseconds. However, further manipulation of the ps-TR³ data, through subtraction of ground state (Figure 5 (b)) and subsequent subtraction of the 1000 ps pure excited state spectra from those at earlier time delays (Figure 5 (c)), reveals a process occurring over approx. 100 ps. Whilst 'long-lived' vibrational cooling cannot be ruled out due to the presence of the co-ordinated CO groups, it is conceivable that this dynamic event represents conversion from an earlier excited state. Furthermore, the bands distinct to the spectra at early times, as revealed through the subtractions in Figure 5 (c) are coincident with some known bands of the dppz⁻ radical anion. Thus, the 480nm probe wavelength may be in pre-resonance at early times with the long-wavelength transitions ($\sim 500\text{nm}$) of a state which is MLCT in nature. Further ultrafast experiments are planned in order to determine the precise photophysics of this complex in a variety of media. Preliminary evidence of photo-induced electron transfer between DNA and this complex⁴⁾ is presently being sought at experiments at the CLF.

Acknowledgements

We wish to thank Dr A. Kirsch-de Mesmaeker for a sample of $[\text{Ru}(\text{tap})_2\text{dppz}]^{2+}$ and Prof. J.M. Kelly for the sample of $[\text{Re}(\text{CO})_3\text{dppz.py}]^+$ and project input. We also thank Dr M. George for useful discussions.

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The Dynamics of a Single Tryptophan Residue in the Myosin Catalytic Domain

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Introduction

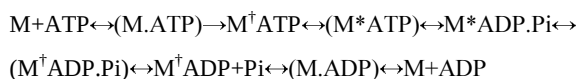
Myosin is a motor protein that converts the chemical energy of ATP into mechanical work. This enzyme exists in all eukaryotic cells. The most commonly known myosin type is myosin II located within muscle and is responsible for its contraction. Actin is the other essential component of muscle. Actin and myosin form a filamentous structure (the sarcomere) and contraction is the consequence of relative movement of a myosin filament and actin filaments.

Myosin alone has a relatively low ATPase activity, but this increases greatly in the presence of actin. ATP turnover (from binding to product release) is a multiple-step reaction. Based on the simplified Lymn-Taylor model¹⁾, myosin binds to actin strongly in the absence of ATP. Upon addition of ATP the two proteins dissociate and during ATP hydrolysis myosin goes through a large conformational change (pre-power stroke). During product release (inorganic phosphate and ADP) myosin rebinds to actin and in a reverse conformational step (power stroke) it pulls the actin filament thus causing contraction.

Recently, the most studied myosin II originates from *Dictyostelium discoideum*, because it offers a very efficient expression and molecular biology system, its catalytic fragment crystallizes relatively easily and it behaves similarly to myosin II-s from other sources. Myosin (*Dictyostelium*) has been crystallised in the presence of different nucleotide analogs that mimic certain conformational and kinetic states. The atomic structures show essentially two different conformations called open and closed states. In a theoretical approach they were assumed to be the post-power stroke and pre-power stroke states, respectively.

The kinetic mechanism of ATP hydrolysis by all myosin II appears similar. Although the absolute values of the rate constant of equivalent steps may differ, their ratios are such that a similar distribution of nucleotide states is obtained during the steady state. The mechanism has been studied mainly by following intrinsic fluorescence changes of myosin. In our studies we used a recombinant mutant *Dictyostelium* myosin catalytic domain (W501+ mutant) in which all of the tryptophan residues, except W501, were replaced with phenylalanine. These mutations do not affect the enzymic properties but give a very efficient experimental tool. W501 is the only native tryptophan in *Dictyostelium* myosin that responds to the addition of a nucleotide and so by eliminating the others non-responding background signal is reduced. W501 is located in the region where the main conformational change occurs during the open-closed transition coupled with the pre-power stroke and the power stroke.

By modifying the Bagshaw and Trentham scheme, we established an eight-step model²⁾ for the myosin ATPase reaction:



In this scheme “†” and “*” indicate a fluorescence decrease and enhancement, respectively. The fluorescence decrease is related to the conformational change coupled with nucleotide binding. The large increase indicates the open-closed transition followed by the hydrolysis step. States in parentheses are present at near negligible concentrations. Under the usual conditions of assay, the $M^* \text{ADP} \cdot \text{P}_i$ state predominates during the steady-state hydrolysis of ATP. By adding the P_i analog AlF_4 to the *D. discoideum* $M^{\dagger} \text{ADP}$ complex (open state), a stable $M^* \text{ADP} \cdot \text{AlF}_4$ complex (closed state) can be made which has an enhanced fluorescent state and provides a useful analog of the $M^* \text{ADP} \cdot \text{P}_i$ state for spectroscopic studies. Care is required, however, in relating a particular analog state to a particular ATPase intermediate because in many cases these complexes exist as a mixture of conformations.

We further investigated the W501 tryptophan fluorescence to find whether single states can be coupled directly to certain spectroscopic states³⁾.

Time-resolved Fluorescence Measurements

Time-resolved fluorescence measurements were carried out using the time-correlated single-photon counting method at the Rutherford Appleton Laboratory, Central Laser Facility. Samples (5–25 μM) were excited at 296 nm, achieved with a frequency-doubled, cavity-dumped, mode-locked synchronously pumped dye laser (Spectra-Physics model 3500) operating at 4 MHz with a pulse width of 10 ps. The fluorescence emission was collected via a WG335/UG11 filter combination (WG320 was used for tyrosine emission) using an MCP-PMT photomultiplier tube (Hamamatsu, R3809U) with response time of 85 ps. The WG335 filter was used in preference to the WG320 filter in these studies to minimize the potential scattering artifact and tyrosine contribution to the signal. Time-resolved anisotropy was measured through a film polarizer (Halbo Optics, DPUV-25) in the emission channel, and the vertical and horizontally polarized light was collected sequentially. The total emission intensity for lifetime measurements was calculated by summing $I_v + 2 \cdot I_h$. A wedge depolarizer was placed in front of the photomultiplier tube, and the G factor of the detector was confirmed as unity by excitation with horizontally polarized light. The data were collected in 1024 channels (width 40 ps) using the Becker and Hickl GmbH (Berlin) single time-correlated single photon counting pc card module (SPC-700). The standard functions of the single photon counting setup, such as time-to-amplitude converter and constant fraction discriminator, were computer-controlled with software supplied with the SPC-700 module.

Results

Time-resolved fluorescence measurements were carried out in the absence and presence of nucleotides and nucleotide analogs. We found that lifetime decay was well fitted by two components with τ values of the order of 1 and 5 ns. Interestingly on addition of nucleotides, these lifetimes did not change significantly; rather, the fractional amplitudes changed. The change in mean lifetime is in the direction expected from the observed emission intensity, ATP and ADP. AlF_4 causes a relative increase in the 5 ns component and an increase in the

State	Relative fluorescence emission	Relative absorbance	Quantum yield	Relative quantum yield	Fluorescence lifetime					Anisotropy		
					A ₁		A ₂		Relative normalized area	A _{ss}	A ₀	Φ
					τ ₁	τ ₂	τ ₁	τ ₂				
Apo	1.00	1.00	0.058	1.00	ns	ns	0.42	1.00	0.58	0.210	0.209	59 ± 4
ATP	1.85	1.13	0.095	1.64	0.25	1.11	0.75	4.78	1.18	0.216	0.191	59 ± 2
ADP	0.82	1.00	0.047	0.82	0.45	0.91	0.55	4.74	0.92	0.214	0.194	54 ± 2
ADP · AIF	1.88	1.14	0.095	1.64	0.27	1.37	0.73	4.82	1.19	0.216	0.203	68 ± 4

Table 1. W501 spectroscopic properties.

overall emission intensity, whereas ADP causes a smaller change in the opposite direction. So the nucleotide induced changes in emission intensity contain a dynamically quenched component. However, quantitative comparison shows that the change in lifetime is only a partial explanation of the change in emission intensity. In all of the three states (apo, ADP, ATP (or ADP·AIF4)) a significant statically quenched component exists. Thus, a large proportion ($\geq 60\%$) of the population W501 forms a ground state complex with a quenching centre that changes the absorption characteristics and causes the excited state to return to the ground state by a nonradiative mechanism.

Also we measured steady-state and time-resolved anisotropy of the W501+ mutant. In the steady-state measurement, we found no significant anisotropy change on addition of any nucleotide. The value observed of 0.21 at 20 °C was close to the limiting value of 0.23 measured in the presence of 90% glycerol at 9 °C. In contrast, anisotropy dropped to 0.1 in the presence of 7 M guanidium hydrochloride, a denaturing agent. These data suggest that W501 is very immobile in its native environment. The difference between the limiting anisotropy value and the theoretical maximum value of 0.4 is indicative of a difference in the angle between the absorption and emission dipoles and/or small amplitude, high frequency motions ($t \ll 1$ ns) that lead to partial depolarization.

These steady-state studies were complemented with time-resolved anisotropy measurements. As expected, a high limiting anisotropy value was observed (around 0.2) with only a slight decay over 40 ns in all records. The short lifetime of tryptophan results in a limited ability to follow the anisotropy decay beyond 10-20 ns. However, because a protein solution is randomly oriented, there should be no residual anisotropy at infinite time, and the data may be analyzed by force fitting to an exponential function that decays to zero. With such an analysis, single rotational correlation times, Φ , of the order of 50-70 ns, were obtained for all nucleotide states of the *D. discoideum* motor domain (Table I). We found no systematic difference in Φ for the different nucleotide states in three independent runs. This time scale is close to that expected for the whole protein molecule. Although we cannot rule out a second slower rotational correlation time, the calculated limit from the whole protein motion indicates that this would not be longer than about 150 ns. As a control sample we measured the anisotropy decay of human serum albumin (molecular weight 66,000 Da) under the same conditions and found the rotational correlation time, Φ , of the slow component to be 39.5 ns at 20 °C, in good agreement with 38.6 ns determined by phase fluorometry. Overall, the time-resolved anisotropy data corroborate the steady-state values and demonstrate that the W501 has little independent motion relative to the rotational correlation time of the whole protein in all nucleotide states examined.

Conclusions

In conclusion, the time-resolved fluorescence data presented here show that W501 experiences at least three different microenvironments. The coupling between the occupancy of the nucleotide site and the W501 environment does not correspond to a simple one-to-one relationship. Rather, nucleotide binding allows the W501 side chain to redistribute among different environments on a time scale of >5 ns and <20 μ s. It is therefore not possible to equate a particular nucleotide state or a particular gross conformation (open or closed state), to a unique set of

coordinates for W501 and its surrounding residues, as might be implied by some crystal structures. This behavior has been reported in other probe studies that reflect gross conformational rearrangements of the myosin motor domain. Nevertheless, the crystal structures are valuable in defining the potential environments that surround the W501 side chain.

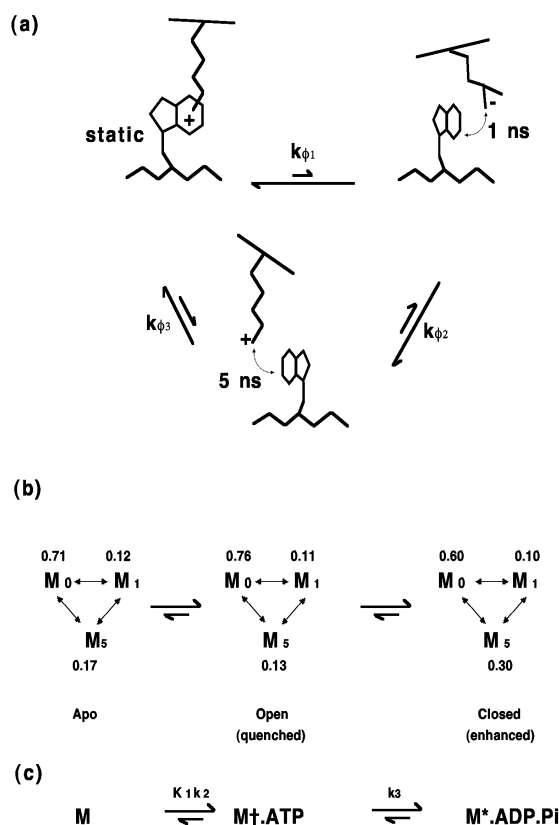


Figure 1. Schematic diagram to show the interconversion of W501 microstates and their relationship to nucleotide states. *Panel a*, the mechanism of W501 fluorescence quenching involves three microstates, one of which (M₀) is statically quenched (effective fluorescence lifetime = 0), whereas the other two (M₁ and M₅) have lifetimes of close to 1 or 5 ns. *Panel b*, microstates are in rapid equilibrium compared with chemical steps and gross conformational changes and are distributed according to the fractional occupancy. *Panel c*, corresponding transitions as applied to the first three chemical steps of the ATPase pathway.

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X-ray spectrum characterization for biological dosimetry

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Introduction

A high-flux biological irradiation facility has been designed for use with the RAL laser-plasma induced ultrasoft x-ray source. The high intensity and broad beam, together with the reduced x-ray source-to-sample distance has been used to overcome the high attenuation of low energy x-rays and produce high dose rates in the sample, enabling a range of biological and chemical endpoints to be measured. A polypropylene target is of particular interest emitting characteristic x-ray lines ranging from ~300 eV up to ~500 eV, with the main x-ray line (C VI L α) at 367eV.

Knowledge of the x-ray spectrum is important, not only to determine the average x-ray energy incident on the sample but also for accurate dosimetry.

Sample irradiation

Samples are irradiated in glass walled dishes (3cm internal dia.) with a 0.9 μ m mylar base. These samples typically include mammalian cells grown on the mylar base as an attached monolayer (~5 μ m thick). Alternatively, lymphocytes or plasmid DNA are spread evenly across the mylar base under a CR39 disc to form a uniform layer (typically 8 μ m thick). These samples are positioned directly above the source of x-rays, which were produced by focusing KrF excimer laser pulses onto a moving polypropylene tape. Between the x-ray source and the dish is helium gas at atmospheric pressure and a UV/light filter.

Dosimetry

Dosimetry is carried out by replacing the sample dish with a photodiode. This is then cross-calibrated before and after each exposure with a second monitor photodiode with identical filters, which is then used to monitor the dose during sample irradiations. The main dosimetry photodiode also has a 0.9 μ m mylar dish base filter to allow for attenuation in the sample dish base.

For monoenergetic x-rays of energy E , the photon fluence on the incident surface of the sample, Φ_s , is given by equation (1)

$$\Phi_s = \Phi_d k_{He} k_A \quad (1)$$

The photon fluence incident on the main dosimetry diode is given by equation (2)

$$\Phi_d = \frac{Q}{SAE} \quad (2)$$

where Q is the charge collected by this diode through an aperture, area A . The sensitivity of the x-ray diode is energy dependent and in the case of soft x-rays is given by equation (3)

$$S = (e/\epsilon) \exp[-(\mu/\rho)_{Si} \rho_{Si} d] \quad (3)$$

where e is the electronic charge, ϵ is the energy required to generate an electron hole pair in silicon, $(\mu/\rho)_{Si}$ the mass attenuation coefficient of the x-rays in silicon which has density ρ_{Si} and d is the dead layer thickness of the detector. The target to sample dish distance, t_s , is 53.9 mm compared with a target to

diode distance, t_d , of 74.7 mm. The correction factor, k_{He} , for the increased helium path is given by equation (4)

$$k_{He} = \frac{(t_d/t_s)^2}{\exp[-(\mu/\rho)_{He} \rho_{He} (t_d - t_s)]} \quad (4)$$

where $(\mu/\rho)_{He}$ and ρ_{He} respectively represent the mass attenuation coefficient and density of helium. The experimentally determined factor k_A , corrects for the variation in photon flux across the whole of the sample area compared to the smaller region, A , seen by the diode.

The absorbed dose at the entrance surface of the sample can be calculated by using the equation (5)

$$D_{surf} = \Phi_s (\mu_{en}/\rho)_s E \quad (5)$$

where $(\mu_{en}/\rho)_s$ is the mass energy absorption coefficient of the sample. These low energy x-rays are attenuated in the sample, therefore the mean absorbed dose in the sample can be calculated by using the equation (6)

$$D_{mean} = D_{surf} \frac{1 - \exp[-(\mu/\rho)_s \rho_s x_s]}{(\mu/\rho)_s \rho_s x_s} \quad (6)$$

where $(\mu/\rho)_s$ and ρ_s represent the mass attenuation coefficient and the density of the sample with thickness x_s .

The mass energy absorption coefficient of the sample and the mass attenuation coefficients of the sample, helium and silicon are all energy dependent. Therefore for a spectrum of x-ray energies, these equations would have to be integrated over the whole energy range. Attenuation through the sample will typically result in an increase in the mean x-ray energy with depth. For accurate dosimetry it is important not only to know the relative intensities of the main x-ray lines but also to determine the contribution of the continuous background x-ray spectrum, which extends to much higher energies. This may dominate if the main characteristic lines are heavily attenuated by the system.

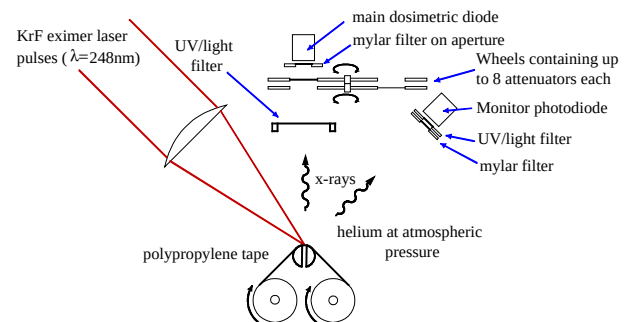


Figure 1. Schematic of experimental set-up used for attenuation measurements.

Attenuation measurements

To access the contribution of the background x-ray continuum, attenuation measurements were made. This was achieved by comparing the ratio of charge collected from two photodiodes

with various thicknesses of attenuating films positioned in front of the main dosimetry diode (now 141 mm from the target). This is shown schematically in Figure 1.

The results of initial experiments performed using mylar and aluminium attenuators, with and without a mylar dish base filter and using a 0.4 μm aluminium UV/light filter, are shown in Figure 2.

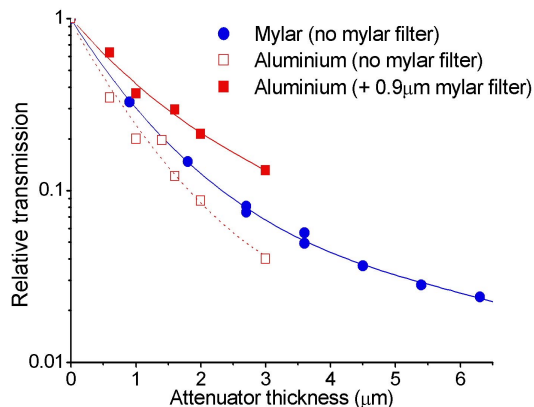


Figure 2. Attenuation data obtained with a 0.4 μm aluminium UV/light filter.

The gradients of these attenuation curves after traversing a 0.9 μm mylar dish base corresponds to that expected from x-rays with energies in the range 650 to 700 eV. This is much higher than the energy of the characteristic emission lines. The graphs also indicate a further increase in the average x-ray energy with increasing attenuation.

On-going experiments are testing the use of titanium UV/light filters, which have an absorption edge at ~ 450 eV, to help reduce the higher energy component.

Conclusions

The results indicate that the background x-ray continuum is critically important for these experiments. The x-ray spectra can also be determined by theoretical simulations. The intention is to compare these experimental data with those predicted by simulations in order to obtain realistic x-ray spectra for dosimetric calculations.

Multiphoton UV and X-ray micro-irradiation to track intra- and inter-cellular dynamics

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The molecular dynamics of DNA repair

Interactions between proteins and nucleic acids have traditionally been analysed by gel electrophoresis. These conventional molecular biology techniques require that bulk proteins and nucleic acids are isolated from many thousands or even millions of cells. A reasonable amount of product has to be present in order for it to be stained and visualised in a gel. Radio-labeling of the constituents of interest increases the sensitivity of detection, but the radioactive emission from the labeling isotopes is measured on a bulk population of molecules. Organic molecules can now be labeled with an array of fluorescent markers. Together with the recent developments in optical microscopy, this has made direct visualisation of the territory of a single molecule possible.

Using the traditional analytical gel methods, biologists relied on deriving models to describe the dynamics of molecular interactions which led to the final result. In many cases these models remain untested and some of the more challenging and thought provoking concepts were considered not to be testable. Technological advances, which have opened the way to examination of molecular biological machinery at work in the cell, provoke a robust challenge to this view.

Currently, one of the most intriguing questions which is stirring scientific activity is 'how is DNA synthesis (the duplication of genetic material) organised at the architectural level in the cell?' Considering that the DNA in each human cell would be 3 metres long if stretched out, the packaging and making of new DNA in a 10 micron nucleus must be very intricate. The disputed concept is whether the proteins which duplicate the DNA track along the DNA or the DNA moves through fixed protein complexes as it replicates.

It is known that chromatin (DNA + histones) is organised in loops around fixed sites at the nuclear matrix¹. These loops are pulled through these sites and loops with new DNA extruded during DNA replication. These loops are 200-300nm in size.

DNA may be damaged by UV-C light (ca. 260nm) which induces distortions in the DNA. The predominant distortions produced are cyclobutane pyrimidine dimers (CPDs) and 6-4 photoproducts (6-4pps). The cell can execute a repair system to remove these lesions. This is known as nucleotide excision repair where a piece of DNA containing the lesion is cut out and new DNA synthesised in its place. The polymerases which carry out the repair replication are the same enzymes that are responsible for DNA replication during cell division. It would seem, therefore, reasonable to suppose that this DNA repair activity may be organised in a similar manner to that of normal synthesis.

The DNA lesions can be tagged by fluorescent markers on antibodies or proteins which bind to the lesions. These will then form positional markers on the DNA, which if not repaired quickly, may reveal movement of the DNA in an interval following the induction of the lesions. This could only be revealed if the lesions are induced in a very small area, at best, as small as the 200-300nm chromatin loops. The probability of detecting such small changes will be increased if the induction of lesions is projected in a recognisable pattern in a cell nucleus. Distortion of the pattern as well as the time dependence of

disappearance of elements of the pattern will reveal the nature of the dynamics or the repair system. If the number of lesions is kept low, there will also be more chance of detecting repair at a site where proteins are fixed. Larger amounts of damage will place a greater demand and induce the cell to make new proteins. The diffusion of these proteins may obscure the fact that repair is taking place at fixed sites.

Putative model of movement of DNA damage sites

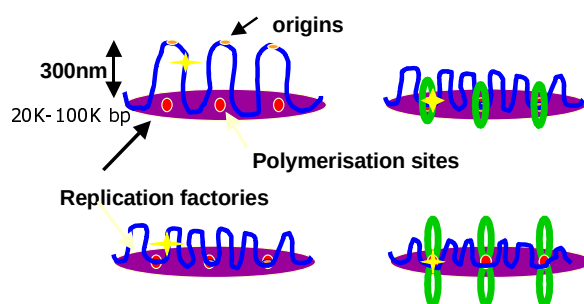


Figure 1. A site of DNA damage which is indicated by the yellow star is drawn closer to the replication factories as the DNA loops are drawn through the matrix attachment sites.

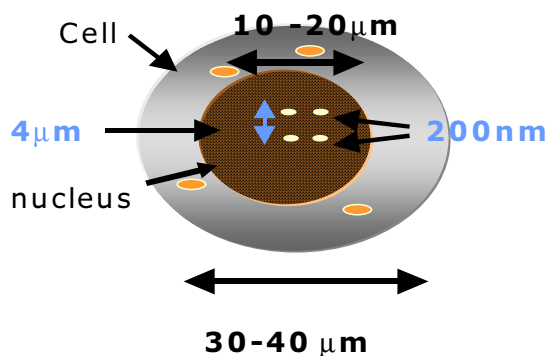


Figure 2. Diagram showing dimensions of the mammalian cell and the pattern of induced DNA damage.

An equally important reason for inducing the low levels of lesions in distinct patterns is to confirm the authenticity of the staining by fluorophore tagged proteins. If the distribution of fluorescent markers reflect the original pattern, it confirms that markers are binding to DNA lesions and not creating artifacts of fluorescent aggregates.

At least two approaches are being tried to create a microfocused pattern of DNA damage in a cell nucleus.

The first is using UV light of 248nm wavelength which is very near to the peak of absorption of DNA and the induction of CPDs. An attenuated 248nm UV laser beam is projected through a mask with a pattern of 10µm holes on a 400µm square. The filtered light is then passed through a 100x UV microscope objective. This should reduce the pattern of light from the objective to 100nm holes on a 4µm square, but because of the diffraction limitations of the light the hole size is likely to be, at best, 200nm. The cells are grown in a culture

dish with a base of fused silica which sits on a precision xyz stage. Glycerol is placed between the objective lens and the silica base of the cell dish in order to minimise the diffraction of the light.

A second approach uses multiphoton absorption processes to induce patterns of DNA damage in the cell nucleus. The ~250-260 nm pseudo UV focused light is generated from near infra-red laser pulses through multi-photon reactions.

An antibody to thymidine dimers has been used to stain DNA damage sites in cell nuclei. Recent results are very promising and indicate that we can induce submicron areas of DNA damage in a cell nucleus.

Intercellular gap junction communication

The survival of individual cells which have been exposed to radiation is determined by the effectiveness of the DNA repair mechanisms described above, but recent research has shown that cells in populations do not have to be directly irradiated in order to suffer damage. An important dynamic cellular process which controls the spread of the effects of damage through a cell population is gap junction intercellular communication (GJIC). It is not possible to study the mechanisms of GJIC in irradiated cells unless the radiation is carefully confined to single cells. The dispersal of tracks or the range of penetration of radiation of high photon energy will not ensure that direct radiation effects will be limited to the territory of one cell at a time. This is most important if GJIC is the focus of interest as cells will have to be in contact with each other.

The energy of Cu x-rays from the CLF laser plasma x-ray source are low enough (1.1KeV) that the interaction of the radiation with cellular components can only take place in cells on which the x-rays impinge. Thus it is one of the few sources in the world which can be used to study gap junction communication in irradiated cells with some reliability. The x-ray spectrum from the laser plasma source is sufficiently soft for long range scattering to be very weak.

Using the CLF x-ray source, we previously observed a situation where toxic effects were passed from irradiated to non-irradiated cells. A monolayer of cultured cells was partially shielded from the x-rays, but death of cells in the shielded areas also took place. Amplification of cell death took place only in confluent irradiated cell cultures, suggesting that the mechanism requires cell to cell contact. Since death of non-irradiated neighbour cells did not occur in non-contacting irradiated monolayers, the toxic effects were not spread by reactive oxygen species (ROS) or cytokines (death molecules) released into or generated in the culture medium.

We designated this amplified cell death in the irradiated confluent monolayers 'contagious cell death' since it appears to require inter-cellular contact in order to occur. A prime regulator of this effect is therefore likely to be the functioning of gap junction communication. Gap junctions act like valves between cells which are in contact and control the passage of stimulatory or inhibitory molecules between cells. They are not highly selective as to the molecules they allow to pass but can be 'open' or 'closed'. In this way, they control a social co-operation between cells of the multicellular organism and play a vital role in tissue development and function. They are comprised of a hexameric arrangement of connexin molecules which allow the inter-cell transfer of low molecular weight materials (<1kDa). Their role is thought to be important in maintaining tissue homeostasis and co-ordination and they are particularly important in the control of cell proliferation²⁾. Gap junctions may also be able to mediate the transfer of potentially damaging molecules such as ROS and Ca⁺⁺. Under conditions of extreme toxicity, gap junctions close, presumably to protect the tissue against the spread of toxic species which promote

necrosis. There are several implications regarding the spread of damage to neighbouring cells including:

- i) the amplification of damage to embryonic cells during development;
- ii) the amplification of radiation induced mutation;
- iii) the potential for 'bystander' (i.e remote) effects in radiotherapy;
- iv) significant amplification of effects of low doses of radiation such as may be received from environmental contamination.

The laser plasma x-ray source is a highly appropriate and necessary tool to use for the study of 'bystander' effects in radiation. It can produce x-rays which are spatially very well defined. This means that a single cell, lines of cells of only one cell width, groups of several cells or a number of single cells spatially separated may be exposed to radiation with no risk of the radiation at the shielded cells. The number and pattern of the cells irradiated can be dictated by the design of the mask through which the x-rays reach the cell monolayer. It is essential that the mask be machined to produce very well defined sharp edges when the x-rays travel through the micro-spaces. This technology provides a means whereby effects transmitted from irradiated cells to non-irradiated cells may be quantified as the number of cells and the geometry of an area of cells exposed can be determined with some reliability. Because of this spatial control of the x-rays, it is an especially suitable source to use to determine the role that GJIC plays in radiation bystander effects. A further advantage over most soft x-ray sources, is that because of the pulsed nature of the source, the dose of x-rays can be controlled and as the system is capable of delivering 3Gy s⁻¹, a substantial dose may be given in a very short time.

Sharp edged focused radiation from the laser plasma soft x-rays

A 25µm x 3mm slit was manufactured in a disc of stainless steel of 13µm thickness which was fitted into the wall of the chamber directly above the point of the laser plasma. Stainless steel is completely opaque to the 1.1KeV x-rays. An aluminium filter (3µm thick) placed between the x-ray source and the x-ray outlet excluded all visible and UV light. The 1µm Hostaphan base of the cell culture dish is also opaque to UV light. Film with a layer of radiochromic chemical a few microns thick on one surface (Gafchromic Film , ISP Technologies Inc.) was placed face down on Hostaphan over the micro-slit in the stainless steel. This was then exposed to the x-ray plasma for several minutes. A sharp edged image exactly 25µm wide and 3mm long was obtained on the film as shown in the micrograph below. This supports the idea that these x-rays will not spread to cells that are not directly above the slit in the mask.

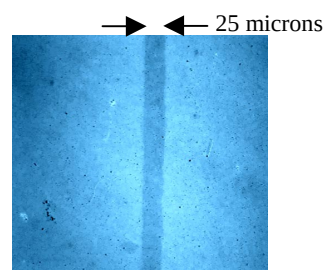


Figure 3. Image of 1.1KeV Cu x-Rays through the 25 micron slit.

Gap junction intercellular communication was studied in primary rat hepatocytes³⁾ and an immortalised cell line, MH₁C₁. The MH₁C₁ cell line originates from the epithelium of

rat liver hepatoma but despite its tumorigenic phenotype, was shown to express connexin 32 (Cx32)⁴⁾. This led to the expectation that these cells may have functioning gap junctions, but when tested by a scrape loading assay and compared to another cell line, WB F344 (non-transformed rat liver epithelial cells) there was virtually no migration of the lucifer yellow dye, a gap junction indicator, through the monolayer of contacting cells. WB F344 cells have been shown to express connexin 43 which may be a more reliable indicator of functioning gap junctions⁴⁾.

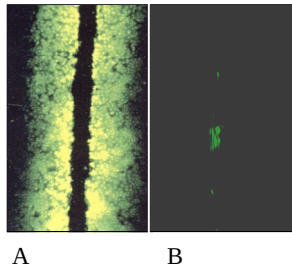


Figure 4. A. The migration of lucifer yellow dye through a confluent population of WB F344 cells can clearly be seen. The dye was loaded by scratching the cell monolayer as shown. B. MH1C1 cells subjected to the same procedure show no spread of the dye indicating cellular gap junctions process.

Partial irradiation of cell monolayers

In preliminary experiments, MH1C1 cells were grown to confluence and irradiated through a slit, 3mm in length and 200µm in width. The incident dose of radiation was 100Gy. The irradiated cells over the slit were stained with 10µM dihydroethidium which fluoresced at 488nm excitation. In contrast, contacting cells which were shielded from the radiation showed no staining. Dihydroethidium is oxidised by the superoxide anion to produce ethidium bromide which intercalates with DNA. No spread of the dye to non-irradiated cells was observed.

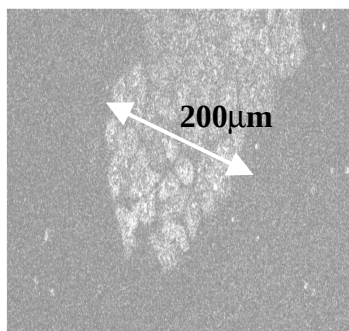


Figure 5. Partially irradiated (through slit 200 µm x 3mm) monolayer of MH1C1 cells stained by dihydroethidium.

Cells were also irradiated over a 25µm x 3mm slit with an incident dose of 100Gy. Helium in the interior of the target chamber was replaced with vacuum which ensured close contact of the hostaphan base of the cell dish with the micro-machined slit in the stainless steel mask. This time an area of cells greater than 25µm in width was stained with the dihydroethidium dye. Since the MH1C1 cells had been shown to lack GJIC, it was concluded that the downward pull created by the vacuum on the hostaphan membrane over the slit imposed a stress on adjoining cells which caused them to produce reactive oxygen species.

Caution must therefore be exercised when using markers such as dyes that identify reactive oxygen species or dyes which stain calcium ions. Changes in the cellular levels of these species can be produced by stress induced by the technical procedures themselves.

The spread of these changes amongst contacting cells may also reflect membrane potential effects as well as gap junction transport.

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Two-photon fluorescence correlation microscopy for pharmacokinetic studies

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Abstract

Two-photon fluorescence correlation microscopy of fluorescent biomolecules provides spatially resolved measurements of concentration and mobility, potentially allowing one to quantify the kinetics of drug distribution and action *in situ*. The use of two-photon fluorescence excitation offers substantially better performance when compared with conventional fluorescence methods. We present the basic features of an experimental set-up based on a relatively simple fibre-optic interface with our existing research microscope. Preliminary experimental results with two-photon excitation are presented for a suitable dye. Despite some technical problems the proposed design is simple, requires relatively low-cost optics and has a reasonably low dispersion on the optical elements.

Introduction

Fluorescence correlation spectroscopy (FCS) provides information about fluorescent particle concentration and mobility in a small volume illuminated by a focused laser beam. The method has been used extensively in recent years to probe various biochemical interactions between molecules. The method has even been used to measure binding at cell surfaces and to probe the internal microenvironment of individual cells. We are attempting to use the technique to gain insight into the dynamics of fluorescently labeled biopharmaceuticals in living tissue. The method is attractive because it is the only optical method that could potentially provide a measure of *absolute* concentration (i.e. particles per femtolitre) with μm -level spatial resolution. Moreover, by measuring the characteristic particle transit time within the illuminated volume, the method quantifies the rate of tissue penetration and processes such as hindered diffusion and binding. Hence the method is extremely attractive for the study of biopharmaceutical pharmacokinetics, where the microscopic disposition of large, complex biological molecules in living tissue is a prevalent problem.

The light absorbing and scattering properties of most tissues are a practical barrier to the use of FCS *in vivo*. The use of two photon fluorescence excitation could overcome these problems by providing a fluorescence excitation source that better penetrates tissue with less photo-damage. The advantages of two-photon fluorescence excitation in applications such as laser-scanning confocal fluorescence microscopy are well documented¹⁾. The advantages of two-photon excitation are deeper penetration of red and near-infrared light into the turbid tissue allowing excitation of specific biological molecules labelled with fluorescent dye in their native environment inside the cells, better background rejection of out-of-focus fluorescence, and a lower threshold for photobleaching and photo-damage of living cells. In combination with conventional microscopy, two-photon fluorescence correlation provides molecular dynamics measurements at high spatial resolution.

The principle of two-photon spectroscopy is that a fluorescent molecule absorbs two photons nearly simultaneously, instead of a single higher-energy photon, to cause the transition to the metastable excited state. As the probability or equivalently the cross-section of this process is significantly less than for single-photon absorption it is necessary to provide sufficient power density to achieve the two-photon event. The lifetime of usual fluorophores in the excited state is of the order of a few nanoseconds so the excitation pulse should be even shorter to attain a suitably high power density with a suitably low average flux. A traditional source providing ultra-short pulses is a

titanium-sapphire laser. It can generate femtosecond pulses with a repetition rate of 80-100 MHz. A high repetition rate is necessary to renew the population of the excited state each time after the fluorescence has decayed. Another important parameter is the peak power. It was estimated that a focused beam power of several tens of milliwatts is sufficient to reach the saturation level for maximum output fluorescence.

The aim of the present study was to provide a simple fibre optic interface for easily and safely adding a TPCM capability to an existing wide-field fluorescence microscope. It was desirable to use fibre optics because of the safety and practical considerations of operating in a biological laboratory. We wanted to avoid direct contact of the laser output with a biohazard environment whilst also limiting the possible exposure of biological scientists to a naked, high power, nearly invisible beam. We recognised that the transmission of pulses through fibres and the microscope optical elements would broaden pulses and limit the peak power. This article is focused mainly on the technical aspects and feasibility of a novel experimental set-up for TPCM.

Materials and Methods

The two-photon correlation set-up consists of a modified Nikon upright research microscope E800, femtosecond titanium-sapphire laser and computer-based correlator. The optical arrangement is shown schematically in Figure 1. The basic element of two-photon excitation is a laser source generating femtosecond pulses. It includes the pump laser, Spectra Physics Millennium, with an output of 5 W and Tsunami femtosecond Ti:Sapphire laser all mounted on an optical breadboard. The nominal pulse width in the wavelength range 790-850 nm is 80 fs with repetition rate 82 MHz and with average output power up to 1 W at optimal conditions.

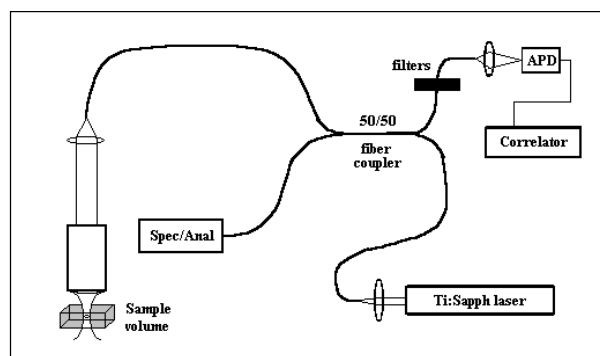


Figure 1. Schematic of optical arrangement for two-photon correlation experiment.

Laser output is launched into a fused gradient index coupler (50/125mm, Laser 2000) using a Gradium achromatic doublet (Newport). The effective lens NA matched to the NA of the fibre to ensure a stable light split and no modal noise due to environmental perturbations. To ensure a stable modal pattern the splitter legs were each 2m long. The unused splitter legs were index matched to reduce reflections. Typically a launch efficiency of 70% was achieved. Similar optics were used to refocus the light for collection.

We used the same fibre as both the source and detector aperture. In most cases a single mode fibre is preferred to serve as a source to allow a diffraction limited spot and minimum temporal spread of the pulse. However single mode fibres are

efficient only on a narrow wavelength range and have a low numerical aperture making them inefficient for combined emission and detection of different wavelengths. Whilst the multimode fibre can support a very large number of modes entering and emerging from the fibre under the different angles, these finally give rise to high pulse dispersion and enlargement of the effective illumination spot. The gradient index fibre reduces this by its parabolic index profile making it an optimum compromise. The incorporation of the excitation and emission light into single fibre path offers flexibility, stable alignment and safe operation of the whole optical scheme. We used a multimode fibre coupler to split the optical signal in ratio 50:50 onto two equivalent arms. One was coupled to the titanium-sapphire laser and the other delivered fluorescence to a photodetector. The last tip of the fibre was connected directly to a spectrum analyser which traced continuously the shape of pulses and effectiveness of coupling.

The fibre output was collimated into a parallel beam using a good quality achromatic lens so that the diameter matched the diameter of the back aperture of the microscope objective. The rear port of the microscope and the video port were used equivalently for coupling light into the Nikon microscope. The sample was viewed in epifluorescence mode, in most cases with a 40X/0.6 Plan Fluor objective.

In order to reject background laser illumination caused by multiple reflections inside the fibre coupler a fibre optics U-bracket assembly (OZ Optics Ltd.) was inserted into the path of the fluorescence. It was designed to transmit light from the optical fibre, across an air gap, and back into a second fibre with low losses. The assembly itself served as a spatial filter providing better conditions for focusing the fluorescence light at the average wavelength 530 nm and discriminating against other wavelengths, in particular and most importantly the laser wavelength. But, since a large amount of laser light could still propagate beyond this, low-pass and band-pass filters were inserted into the air gap to select a particular fluorescence band.

The detection system was the same as used previously for single-photon experiments²⁾. Fibre output was focused onto the face of a silicon avalanche photodiode (APD) which operates in single photon counting mode (SPCM-AQ-121, EG&G). Output of SPCM directly fed the computer-based correlator (ALV-5000/Fast, ALV-GmbH, Langen, Germany). Correlation data was analysed by ALV-software and SigmaPlot'2000 package by using a Marquardt nonlinear least-square fitting routine.

During femtosecond pulse propagation through the fibre optics and microscope glass, pulses are spread in time due to group velocity dispersion. It was estimated previously³⁾ that the final pulse width at the sample should be on the order of 150 fs. Most implementations avoid the use of fibre elements in their set-up design as introducing additional pulse dispersion. However this implies mounting quite bulky laser equipment on the same vibration isolated surface together with the microscope. This can sometimes be unacceptable. For example, when working with biological hazards the laser equipment should be well separated from chemical and biological hazards to avoid dangers of contamination. Fibre optics offers flexibility in design, safety, and stability in performance. We examined the spectral broadening introduced by the fibre. On the photographs below we present the undisturbed spectrum from the laser and the spectrum at the fibre output. The actual deterioration of pulse characteristics was less than 30%, which implies a broadening of the final pulse width to 100-110 fs. In the case of sufficient peak intensity this pulse broadening is tolerable.

A conventional step index fibre is often used in optical arrangements but this suffers from modal dispersion. Often fibre length is restricted to reduce this problem but this leads to

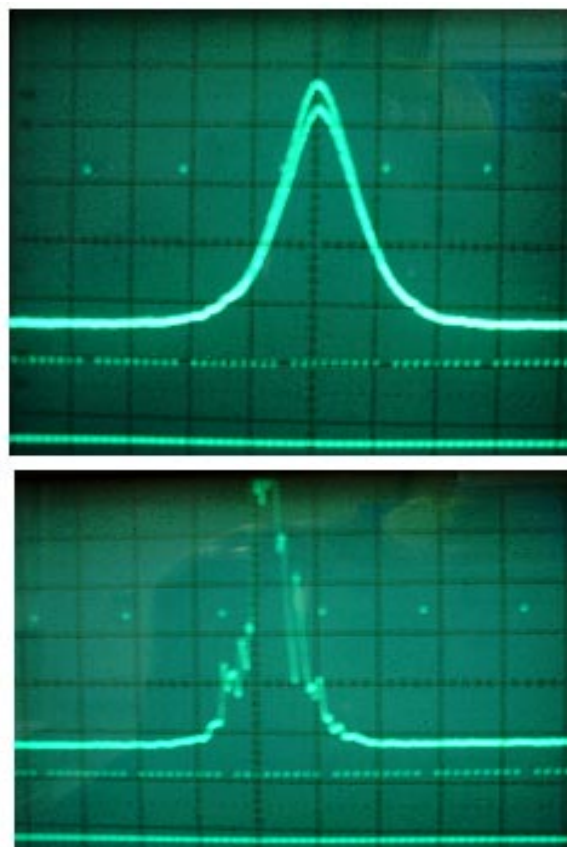


Figure 2. Laser emission spectra. Undisturbed (upper) and passed through multimode fibre (lower).

a second problem of unstable modal patterns which may be affected by environmental factors and give rise to false signals.

The gradient index fibre coupler allows a mere 30% (20-30 femtosecond) increase in pulse width whilst allowing a highly stable alignment even with a fibre length of 4m. Whilst monomode fibre is costly and requires a very high degree of cleanliness the GRIN fibre is highly economic (\$0.5/metre) and less prone to cleanliness issues making it more suited to many microscopy applications. Two-photon operation in the near IR region increasingly allows these standard communications fibres and components to be used.

The crucial element is the microscope objective, which should have excellent achromatic properties and near IR light transmission. Good achromatic performance is important because the focus point for both excitation and emission wavelengths, widely separated in two-photon spectroscopy, should coincide as two-photon excitation is a highly "confocal" event. The fluorescence can be excited uniquely within the focal plane and nowhere else.

The power at the sample is reported³⁾ to require a few tens mW well focused on the sample. Despite the 50% loss of power associated with the fibre coupler the major power loss occurred at the interface with the microscope optics.

Results and Discussion

Two-photon excitation spectra for traditional fluorophores are not widely available in the literature. Although the excitation wavelength for the two-photon process is roughly twice that of the single photon process, significant deviations have been reported. As the data about two-photon absorption cross sections is quite limited, we have compared the fluorescence intensity from different dyes on the different wavelengths within the tunable range of the Ti:Sapph laser. Rhodamine 6G absorbs single photons at 528 nm (green) peak and emits the

fluorescence photons at a peak of 551 nm in the yellow region. We observed a maximum in rhodamine 6G fluorescence when excited at a wavelength between 800 and 830 nm that is slightly less than reported previously⁴⁾ (850 nm). Another fluorophore we used was calcein, which can absorb single photons around 494 nm (blue) and emit in a bright green spectrum around 517 nm. We found that calcein had a bright emission yield with maximum excitation around 765 nm. Both fluorophores could be excited at the same wavelength, for example at 780 nm and had distinguishable emissions – one green and the other yellow, that may find further application in dual-colour fluorescence spectroscopy or cross-correlation spectroscopy.

We attempted to observe two-photon absorption by molecules of PicoGreen fluorophore in the presence of DNA. This fluorophore is an extremely sensitive marker of dsDNA for quantitative measurement of small amounts of DNA, with excitation at 502 nm for single photon absorption, and emission at 523 nm. Despite our expectations we were unable to observe any two-photon fluorescence. We hypothesise that this absence of fluorescence is due to the relatively low power density in our system.

Calibration

An autocorrelation function was recorded from the cell filled with an aqueous solution of calcein. The data were recorded with an average photon count rate of 2.5 kHz. The excitation wavelength was 780 nm. The autocorrelation decay time constant at 2 ms leads to an estimate of the detection volume diameter as 3 μ m. The theoretical equation for a single diffusing component²⁾ gives a good fit to experimental data shown by the solid line in Figure 3.

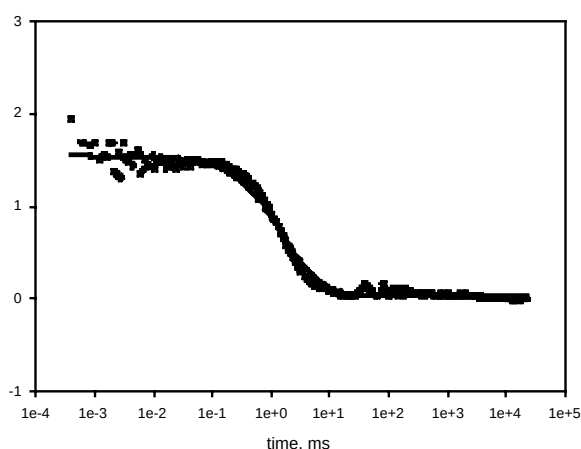


Figure 3. The experimental autocorrelation function for Calcein diffusion in water.

The triplet state is not apparent in the data. In contrast, an initial rapid decay in the autocorrelation function is observed in the equivalent single-photon correlation experiment. With two-photon excitation, it may be difficult to reach the power saturation at which transient non-emission states are induced. The same effect has been reported for Rhodamine 6G and Texas Red⁴⁾.

In conclusion we developed an experimental set-up for two-photon correlation spectroscopy with flexible design appropriate for biological applications in which it is desirable to isolate the laser system from the potentially hazardous environment. The optical scheme is based on the incorporation of excitation and emission light into the single fibre pathway allowing the automatic alignment of illumination and detection areas and good stability of the whole scheme. Although, due to femtosecond pulse propagation through the fibre, pulses were spread in time due to group velocity dispersion, the gradient

index fibre which we used allowed a mere 30% (20-30 femtosecond) increase in pulse width.

We were able to produce two-photon fluorescence with highly focused laser light on the microscope stage that could be observed even by the naked eye. Further optimisation of the optical parameters is needed to improve some performance characteristics such as the spot size, excitation pulse width and peak power.

We examined appropriate fluorescent dyes that can perform efficient two-photon excitation. We found that Rhodamine 6G and Calcein have comparable emission yield characteristics and overlapping excitation spectra. Both of them can be successfully excited at 780 nm whilst their fluorescence emissions lie in different spectral bands – around 517 nm for Calcein and 551 nm for Rh6G. The cross-correlation or dual-colour experiment can be developed on the basis of our design implementing the same fibre coupler that will split the fluorescent signal into two equivalent arms with additional spectral filtering of each component.

We calibrated our set-up by measuring the translational diffusion of Calcein molecules in water. The estimated size of spot was around 3 μ m.

Despite difficulties of good maintenance of expensive and bulky laser equipment, two-photon excitation microscopy is an extremely sensitive and precise technique for measuring molecular dynamics within femtoliter excitation volumes. This major advantage of two-photon technique can be exploited when imaging thick and turbid biological samples.

Acknowledgments

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Calibrated Diffraction Gratings for the Analysis of Laser-Plasma X-Ray Spectra

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Introduction

In the development of the laboratory x-ray microscope¹⁾ careful source characterisation is needed. This requires determination of the laser-plasma source size and spectral emission characteristics, both of which have been carried out previously using the original LSF target chamber and (reversed) audio tape targets^{2,3)}. However, in that work the diffraction grating used in the transmission grating spectrometer was not calibrated in terms of its efficiency. Although a degree of self-calibration was possible in the analysis, quantitative spectral intensities could not readily be obtained. Also, the measurements had not been performed using the target chamber built for the x-ray microscope or using a range of targets to identify materials suitable for elemental and chemical state mapping, which require a tunable source.

In this report a preliminary analysis of spectra recorded with calibrated transmission gratings is presented (although it should be noted that the calibration analysis is not complete). The spectra were recorded on Kodak DEF film using a range of tape targets. The x-ray microscope target drive was designed to use video tape, since this provides more "tracks" than audio tape does, allowing longer times between tape changes. In earlier microscopy experiments it had been observed that reversed BASF Vision video tape appeared to give higher emission in the C VI Ly α line at 3.37 nm than other types of video tape did, possibly due to a carbon coating on the tape. The characterisation was therefore carried out for several commercially available video tapes, reversed to present the plastic (Mylar) or carbon surface to the laser beam and unreversed to form a metallic plasma suitable for a tunable source. Uncoated Mylar was also used.

Unfortunately the lasers in the LSF x-ray laboratory performed inconsistently during the experiments, making quantitative comparisons between the different types of tape difficult.

The gratings

The gratings were made by electron-beam lithography followed by nickel electroplating. The nominal period was 300 nm, with a mark to period ratio of approximately 0.5. The spectral resolution is determined by two instrumental effects, the number of grating lines illuminated and the variation in incidence angle across the grating³⁾. The former gives better spectral resolution as the grating aperture increases while the latter gives worse and thus there is an optimum aperture size, of $\approx 20 \mu\text{m}$ for the experimental parameters in use. Gratings were therefore made with square aperture sizes of $15 \mu\text{m}$, $20 \mu\text{m}$ and $30 \mu\text{m}$ (Figure 1a). They are supported by $500 \times 500 \mu\text{m}$ silicon nitride (Si₃N₄) membranes on $5 \times 5 \text{mm}$ silicon chips, and the Si₃N₄ around the gratings is coated with thick nickel so that it is reasonably opaque to soft x-rays. Each chip contains two gratings, as shown in Figure 1b. The lines of each grating are perpendicular to those of the other so that, with a horizontal x-ray beam, one will diffract horizontally and one vertically, eliminating alignment problems.

The incident and diffracted intensities of the gratings have been measured over a range of wavelengths at the Beijing Synchrotron Radiation Facility. An example of a diffraction pattern, recorded at a wavelength of 4.43 nm, is shown in Figure 2a; the zero-orders of both gratings can clearly be seen, as can the two first-order peaks of one of the gratings. Higher orders of the monochromator are also visible. The first-order peaks are asymmetrical due to the spectral resolution of the

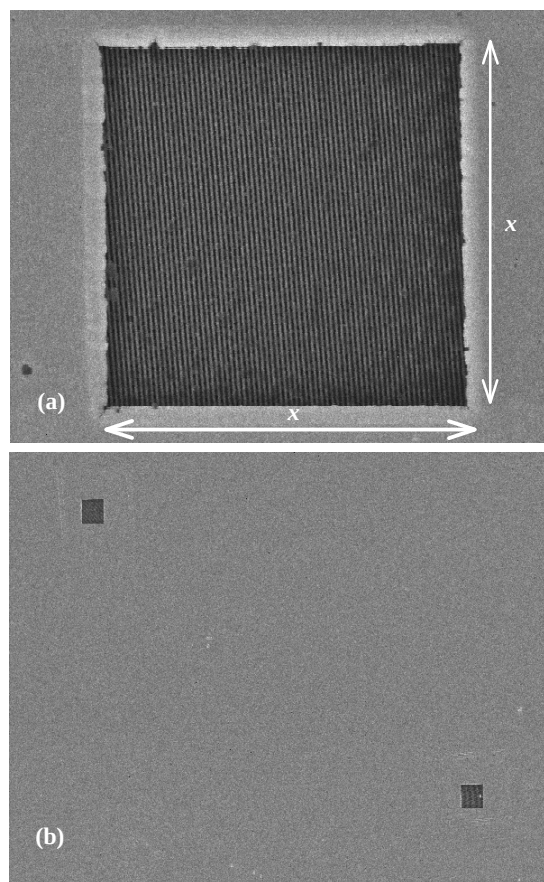


Figure 1. (a) An electron micrograph of one of the gratings. The distances x are either $15 \mu\text{m}$, $20 \mu\text{m}$ or $30 \mu\text{m}$. (b) The orientation of the two gratings on each chip.

monochromator. To allow the most accurate determination of the diffraction efficiencies the peaks have been fitted to two-dimensional Pearson IV distributions³⁾, which take account of the asymmetries, and an example of a fit is shown in Figure 2b. The fits show that the actual grating periods are $\approx 260 \text{ nm}$, indicating a possible mis-calibration during the lithography stage, while the shorter wavelength data contains components due to second-order diffraction from the grating, indicating that the mark/period ratio is not quite 0.5. The quantitative analysis of these results is continuing.

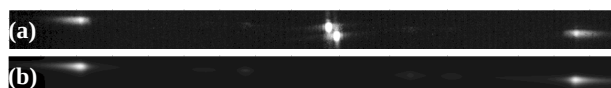


Figure 2. (a) Diffraction from the grating recorded at $\lambda = 4.43 \text{ nm}$ using the Beijing synchrotron. The intensity scale is logarithmic, and the zero orders are saturated. (b) Fit to the diffraction spectrum (except the zero orders) using the Pearson IV function.

Laser-plasma spectra

For each tape/grating combination spectra were recorded for a range of laser shots, typically several hundred to several thousand. This was to allow self-calibration of the film, but since so many shots were needed, the variable laser performance may mean that this will not be possible. In the preliminary analysis, the spectra for each combination have

been summed, after the film densities were measured on a calibrated microdensitometer at King's College (see Table 1).

Tape	Grating			Total no. of shots*
	15 μm	20 μm	30 μm	
BASF Vision, r [†]	✗	(a) ✓	(b) ✓	(a)22000 (b)5250
BASF Vision, u [‡]			✗	
Fuji SD, r	✓	✗	✗	70000
Fuji SD, u			✓	5900
Fuji Super, r			✗	
Fuji Super, u			✗	
TDK, r			✗	
Mylar	✗	✗	✓	11000

Table 1. Summary of data taken and analysis state

✓ Spectrum recorded, densitometered and partially analysed

✗ Spectrum recorded and densitometered but not yet analysed

[†] tape reversed, carbon or Mylar plasma

[‡] tape unreversed, metal plasma

*for (partially) analysed spectra only.

Examples of the summed spectra are shown in Figure 3. Although these have not yet been analysed in detail, some comments can be made. First, for the unreversed video tapes and Mylar, any spectral features at wavelengths longer than that of the C V He α at 4.02nm are due to higher orders of the diffraction grating. Second, the BASF reversed and Mylar spectra taken with the 30 μm aperture grating are similar, as would be expected. The spectral features of the BASF spectrum appear to be sharper; this is probably because more shots were needed to record the Mylar spectrum since the lasers were not performing so well then, and thus accumulated noise is larger. The unreversed Fuji SD spectrum, which should result from a metal plasma, does show some carbon and oxygen lines, from the Mylar substrate, indicating that the coating was thin enough to be fully removed and allow some Mylar plasma formation. The BASF reversed spectrum taken with the 20 μm aperture grating appears to be less well resolved than that taken with the 30 μm grating, again probably resulting from the larger number of shots necessary due to the smaller aperture; the minimum in the spectral broadening versus grating aperture curve is rather broad and there should be little difference between the two spectra. The FUJI SD reversed spectrum taken with the 15 μm grating shows little except for the C V Ly α , due to the small aperture and the resulting large number of shots.

The further analysis of the spectra will involve fitting the lines to the Pearson VII function³⁾ and the recombination edges to the Pearson IV function. Combined with the calibrated diffraction grating efficiencies this will allow absolute line intensities to be determined.

Acknowledgements

We are indebted to Dr V Kudryashov of the Institute of Microelectronics, RAS, Chernogolovka, Russia for the manufacture of the gratings. The synchrotron measurements were carried out by Prof M Cui and Dr P Zhu of the Beijing Synchrotron Radiation Facility, and we are grateful to them and to the staff of the x-ray laboratory at the LSF, Dr G Hirst and W Shaikh, for their assistance. This work was supported in part by EPSRC grant GR/N28061/01.

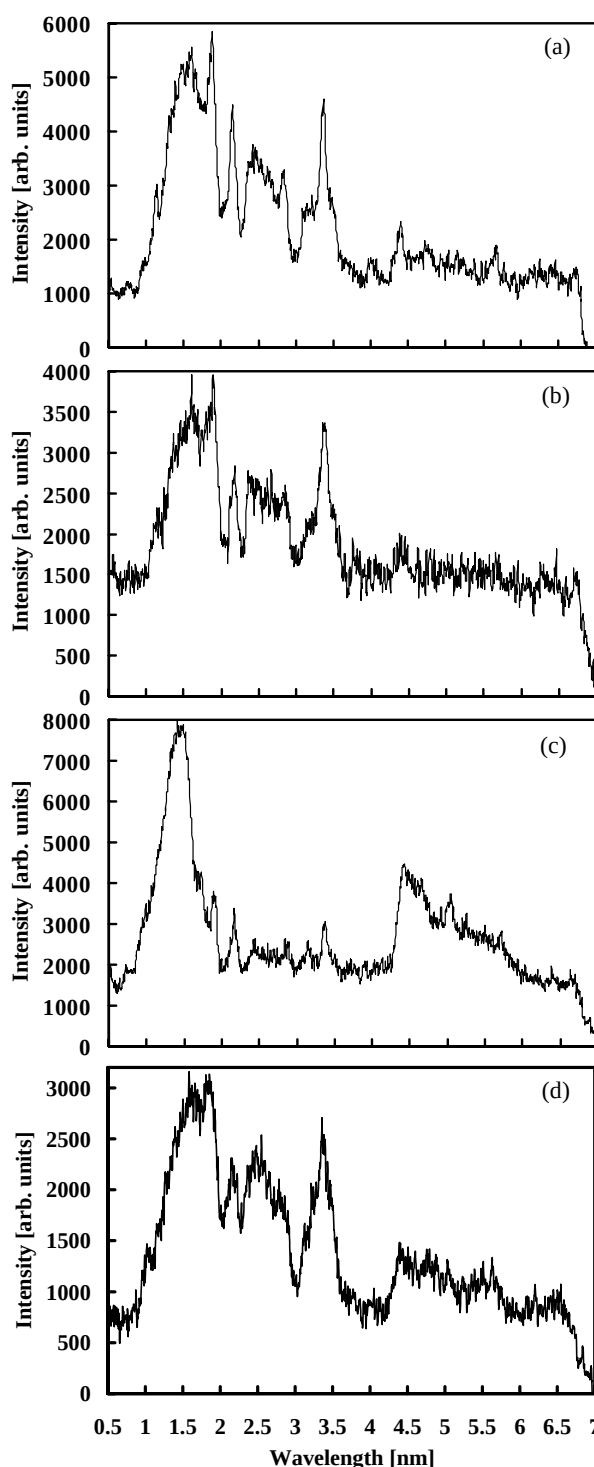


Figure 3. Spectra obtained using different tapes and grating apertures. (a) BASF reversed, 30 μm aperture. (b) Uncoated Mylar, 30 μm . (c) Fuji SD unreversed, 30 μm . (d) BASF reversed, 20 μm .

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X-ray Masks and Metal Patterns

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Introduction

For the past 20 years lithography has been one of the key technologies in the semiconductor industry. As the relentless decrease in minimum feature size continues in line with Moore's Law, radiation with ever shorter wavelength is being used in lithography systems. No less than four possible alternative technologies are being investigated for the replacement of deep UV. These are proximity X-ray lithography, extreme-UV projection, electron projection lithography and ion projection lithography.

Proximity X-ray lithography (PXL) has been under development since the early 1970s. Drawbacks of PXL include the requirement for a 1:1 mask and the small 10-20 μ m gap between mask and substrate. The X-ray source for PXL can be either a synchrotron or point source. The synchrotron is expensive and bulky but has higher throughput than the alternative. These can have an exposure intensity of around 45mW/cm² across a 30 $\times$ 30mm field, corresponding to an exposure time of about 2s per field. The alternatives to synchrotron are point source systems. These are usually of the laser-driven plasma type and are cheaper and smaller than synchrotron sources. One such source exists at the CLF and has been described elsewhere¹⁾. This is being used in conjunction with a novel method of X-ray mask production being developed at the University of Dundee²⁾.

Laser direct writing is another technology which has been the subject of much interest in recent years. Here a film of a metal-containing compound is exposed to a laser beam to directly produce high-resolution patterns. Such a technique offers the advantages of a greatly simplified manufacturing method in addition to the flexibility of 'mask-free' processing. We have been studying both the composition and surface morphology of laser irradiated organometallic films³⁻⁵⁾.

This report describes two main areas of research: X-ray lithography mask manufacturing and the production of interconnects.

Experimental Details

X-Ray Lithography

We have developed a novel method for the fabrication of X-ray masks at the University of Dundee. To provide good pattern transfer with a reasonable absorber film thickness, elements with high atomic number such as gold or platinum are used. The metal-containing organic compound is deposited onto an X-ray transparent silicon nitride membrane by vacuum evaporation. The thickness of this precursor film is typically of the order of 1 μ m. Precursor materials include dichloro(1,5-cyclooctadiene)platinum(II) and chlorotriphenylphosphine gold(I). The thickness of the deposit produced by the electron beam patterning of the organometallic film is dependent on the initial film thickness, the density and metal content of the organometallic. The relative thickness of metal remaining after complete decomposition of the organometallic film can be between 2 and 13% of its original thickness depending on the particular compound. A film of dichloro(1,5-cyclooctadiene)platinum(II), reduces in thickness by around 87% when completely decomposed i.e. if a 1 μ m film of organometallic was completely disassociated it would leave

behind a 130nm layer of pure platinum. Figure 1 shows the relative transmission of films of pure platinum of various thickness. It can be seen that at the X-ray energy of interest, 1.2keV, a 100nm film of platinum reduces the intensity of the transmitted X-ray signal by up to 50%. Obviously, thicker metal films would offer greater contrast and therefore potentially better X-ray transfers but a trade-off must be met between contrast and resolution. The limiting factor is the thickness of the precursor film, i.e. forward scattering of the electron beam during the writing of the mask limits the attainable lateral resolution to around that of the initial film thickness (i.e. 1:1 aspect ratio).

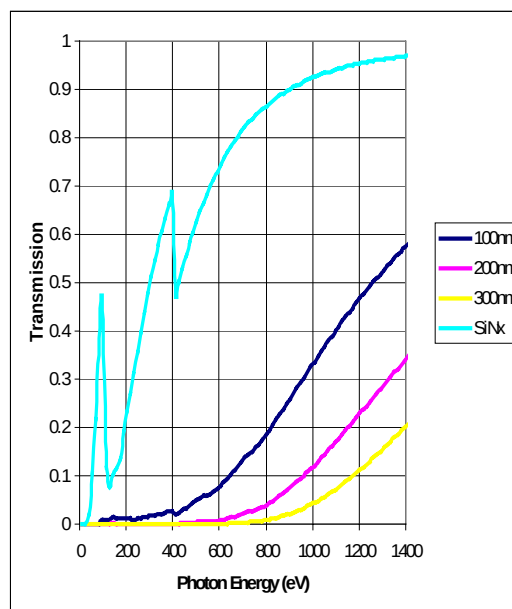


Figure 1. Relative transmission of various platinum films.

The electron beam exposures were performed in a modified scanning electron microscope (JEOL T220). Several additions and alterations were made in order to make the SEM operate as an effective pattern generator. An electromagnetic beam blank was added to allow rapid control of the electron beam which is necessary to prevent the unwanted exposure of the film. A liquid nitrogen-cooled aperture was placed close to the sample in order to condense any volatile decomposition products to prevent the contamination of the column and to enhance the filament lifetime. The sample was mounted on an aluminium stage equipped with a calibration grid for beam alignment and Faraday cup for beam current determination. The position of the electron beam was controlled using the microprocessor-based ELPHY Quantum software. The voltage applied to the beam deflection coils is controlled by a 16 bit digital-to-analogue converter allowing 2¹⁶ or 65536 beam steps. In practice, the beam diameter is much greater than the smallest step allowed by the hardware and the step size used is typically around 25nm. The dwell time (i.e. the length of time that the beam is held stationary) determines the dose given to each pixel. Following exposure the unexposed material is simply removed by rinsing in acetone followed by isopropyl alcohol. The organometallic film is behaving in an analogous manner to a negative-tone electron beam resist. Exposure to the electron

beam causes the irradiated material to become less soluble in the rinsing solvent. Figure 2 shows a contrast curve for dichloro(1,5-cyclooctadiene)platinum(II). This sample was irradiated with 30keV electrons. The thickness of the film after exposure was measured by atomic force microscopy.

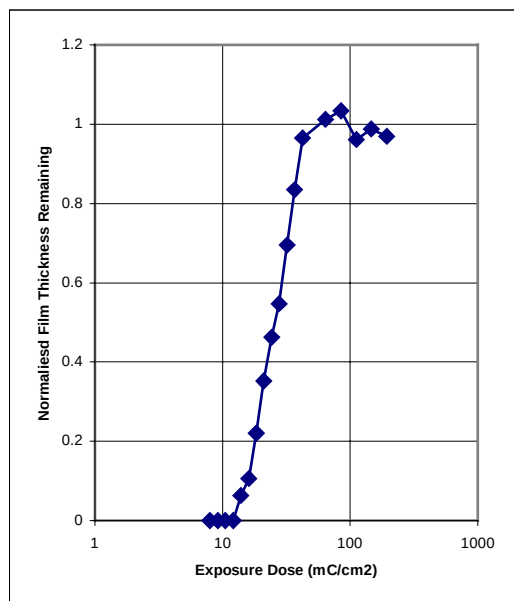


Figure 2. Contrast curve for dichloro(1,5-cyclooctadiene)platinum(II).

From Figure 2 it can be seen that the sensitivity of this particular organometallic is approximately 50mC/cm². At this dose the thickness of the electron beam written deposit is approximately the same thickness as the precursor film. Absorber patterns with dimensions of 200nm can routinely be produced using this technique. When thinner organometallic films are used, even narrower line widths down to 60nm can be produced. Figure 3 shows an example of a high-resolution metal pattern produced by electron beam irradiation of dichloro(1,5-cyclooctadiene)platinum(II).

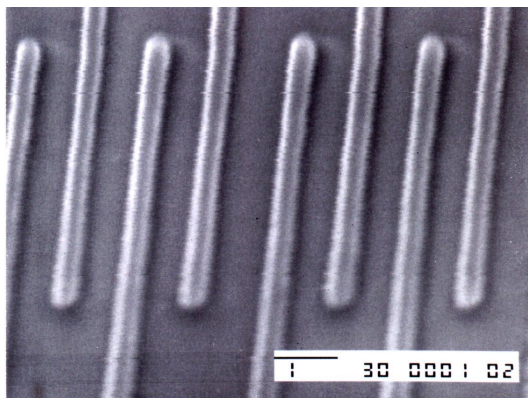


Figure 3. Scanning electron micrograph of high-resolution absorber pattern.

X-Ray exposures were performed using a copper L α source with photon energies of around 1.2keV. A beryllium filter was used to prevent the UV-exposure of the resist and also to prevent target debris from contaminating the mask assembly. The resist used in the recent experiments (Shipley DUV3) was specifically manufactured for deep-UV lithography and consequently was not very sensitive to the soft X-ray radiation used here. At around 80mJ/cm², the sensitivity to copper X-rays was around four times less than the resist used in our previous experiments and it also had poorer contrast properties.

Laser Processing of Organometallic Films

The second series of experiments performed in the UV X-ray lab were to investigate the effect of deep UV irradiation on the organometallic films. These experiments aim to investigate the possible application of organometallic materials in the production of interconnects. For use as interconnects it is essential that the electrical conductivity of the deposited material is close to the value for the bulk metal. A consequence of using organometallic materials is that the laser-irradiated films invariably contain impurities, which are predominantly carbonaceous. The simplest method to remove these is to anneal the films. This not only purifies the deposit but also results in a marked improvement in its electrical properties. Figure 4 shows the improvement in resistivity as a function of annealing temperature for a film of laser irradiated cis-dichlorobis(triphenyl-phosphine)platinum(II).

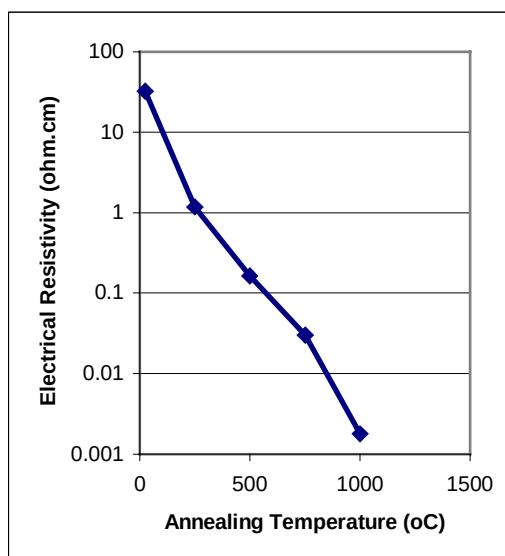


Figure 4. Effect of Annealing on resistivity of laser irradiated organometallic films.

Annealing to 1000°C improves the conductivity of the films by over four orders of magnitude.

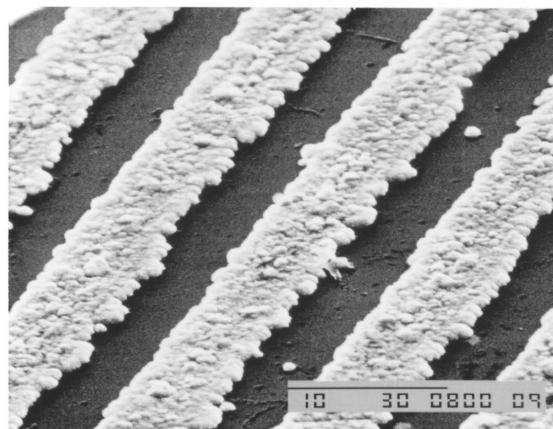


Figure 5. Scanning electron micrograph of 5µm wide copper plated tracks.

An alternative approach to the formation of interconnects is to produce a pattern of platinum containing material which can then be copper plated to produce a highly conductive copper film. In this case a film of a platinum-containing organometallic is irradiated to produce a seed layer. This is then coated with copper in an electroless plating bath. This is a catalytic process and only takes place in the presence of a metal such as platinum

or palladium. The key advantage of this process is that the metal layer does not need to be pure and can also be very thin (<10nm). This is ideally suited to these materials and we have demonstrated the ability to produce good quality 5µm metal tracks with conductivities close to that of the bulk metal. Figure 5 shows an example of copper tracks produced using this technique.

Conclusions

We have demonstrated the fabrication of X-ray masks by the electron beam irradiation of organometallic films. Platinum lines of widths down to 60nm can be produced although the thickness of these deposits would require a resist of higher contrast than that currently available for successful X-ray lithography.

The production of metal tracks for interconnect applications has also been demonstrated. Two main methods of fabrication have been used: 1) irradiation of the organometallic film followed by a thermal processing step and 2) laser irradiation followed by electroless copper plating.

Acknowledgements

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Acoustic Instability of Fully Premixed Flames

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Introduction

As a result of the widespread introduction of stringent emissions standards in European countries there is considerable interest in the development of fully premixing burners for use in gas-fired domestic water heaters¹⁾. Burners which mix the whole of the combustion air with the fuel before combustion commences offer a number of potential advantages over conventional partially premixing designs in terms of reduced emissions of NO_x and CO₂ and increased thermal efficiency, compactness and flexibility. They also possess one very undesirable characteristic, however, viz. their propensity to excite unacceptable vibrations when incorporated within sealed heating systems. This vibration problem is the principal obstacle to the successful utilisation of fully premixing burners in these systems at the present time.

It is known that the vibration problem is caused by the establishment of a resonance between a fluctuation in the rate of the heat release in the premixed flame and one or more of the natural acoustic modes of the burner enclosure and flue. Fluctuations in the rate of heat release are accompanied by movements of the flame front which generate sound, a proportion of which is reflected back towards the burner by the containing enclosure. If the reflected sound has the effect of amplifying a particular flame fluctuation then it closes a positive feedback loop with the amplification of the original fluctuation as the system gain. The oscillation is thus self-amplifying until non-linear effects cancel any further gain and a limit cycle is established which repeats itself indefinitely.

Whilst the general dynamic character of such unstable couplings is well understood, the analysis and prediction of resonant behaviour in any given circumstances remains problematical because little is known about the mechanisms by which the flame responds to the acoustic feedback. A programme of fundamental research has therefore been carried out at Leicester in which fully premixed flames, stabilised on practical designs of burner, have been subjected to simulated acoustic feedback of various frequencies and amplitudes. By imaging the flames at different phases of the incoming sound waves qualitative and quantitative information has been provided about both the mechanism of the flame response and the resultant system gain. The work was carried out during the year under review using equipment made available from the Loan Pool under Loans LP7 E1/2000 and LP14 E3/2000.

Experimental details

The flames visualised in the experiments were laminar fully premixed methane-air flames, in most cases supplied with a quantity of air which was 30% in excess of the stoichiometric requirement. They were stabilised on a range of specially made test burners which replicated the essential features of practical designs. These were fabricated from plaques of refractory ceramic and contained parallel arrays of slots, each approximately 1.2 mm in width. They differed from each other in the spacing of the slots, the topography of the firing surface and certain other key details. The reactant mixture issued from the slots with a velocity of up to about 4 m/s, each slot supporting a separate flame a few mm in height and shaped, in cross section, like an inverted vee (Figure 1).

The acoustic feedback was simulated by means of a very large horn loudspeaker and the experiments were carried out in a semi-anechoic chamber.

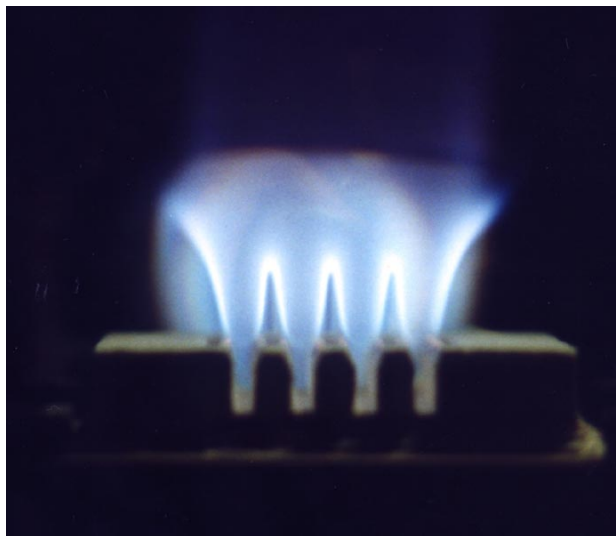


Figure 1. Unperturbed flames on typical test burner.

The part of the flame it was required to image was the flame front - a region less than 1 mm in thickness in which essentially all of the parent fuel is consumed and the bulk of the heat release takes place. The use of a planar laser-induced fluorescence (PLIF) technique was essential for this purpose but there was concern that images of the flame front formed in the established way²⁾ using fluorescence from OH would be seriously degraded by persistence of this dissociated specie into the burned gas. An alternative technique which had been developed during a previous laser loan and which used fluorescence from CH was therefore employed instead.

To implement the technique the third harmonic of a Spectron SL805G Nd:YAG laser was used to pump an Exalite 392A dye solution in a Sirah PrecisionScan dye laser, the output from the latter being tuned to one of the lines in the Q branch of the B²Σ⁺←X²Π(0,0) absorption band of CH at a wavelength close to 390 nm. The beam was formed into a thin sheet and used to illuminate a cross section of the region immediately above the top of the burner. Rapid electronic energy transfer in the flame from the excited v=0 vibrational level of the B state of the CH to the v=1 vibrational level of the A state then produced fluorescence from the transition A²Δ→X²Π(1,1) which could be detected at wavelengths near 430 nm. The fluorescence in this band was collected with an f/2 lens, separated from scattered laser light with a narrow band-pass filter and focussed onto an intensified CCD array. Because of the weakness of the fluorescence at the detection wavelength it was necessary to integrate the fluorescence generated by several hundred identically phased pulses of the laser to produce a clear image of the flame front. The image intensifier was gated off between pulses to reject background emissions at the detection wavelength from the flame and burner.

More than twenty complete sets of images were produced in total, the matrix of test conditions involving six different sound frequencies, four sound pressure levels, three mixture equivalence ratios, four mixture velocities and seven variations of burner design.

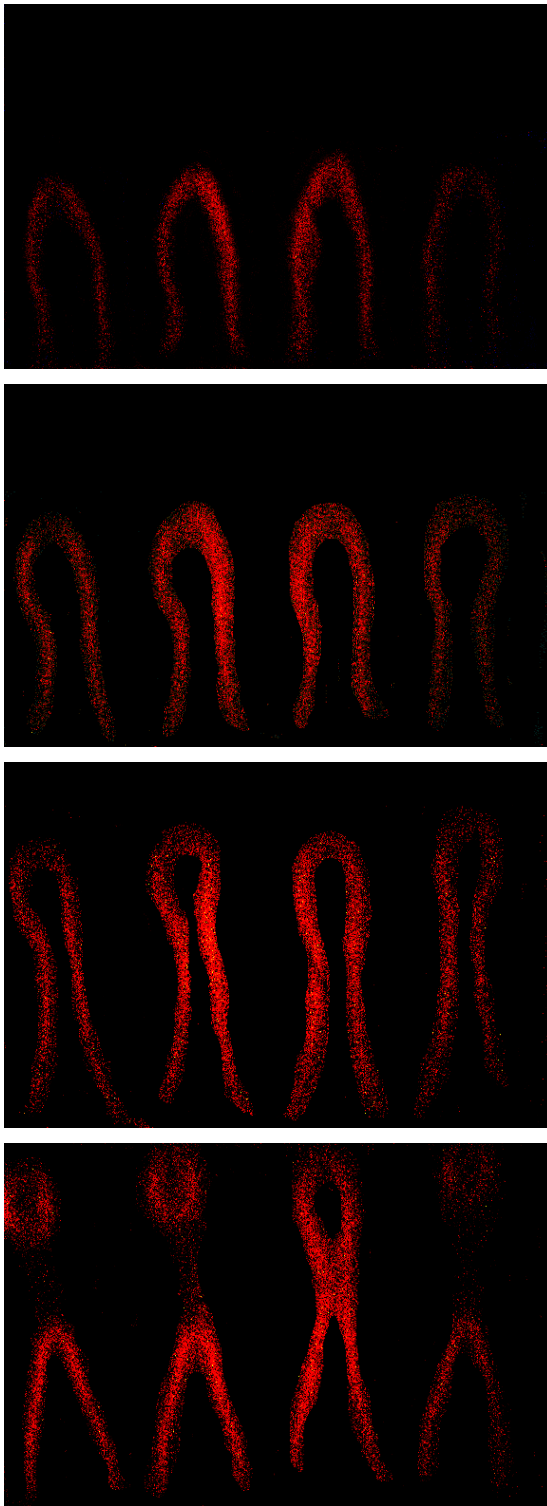


Figure 2. Oscillating flames imaged at 90° increments of phase.

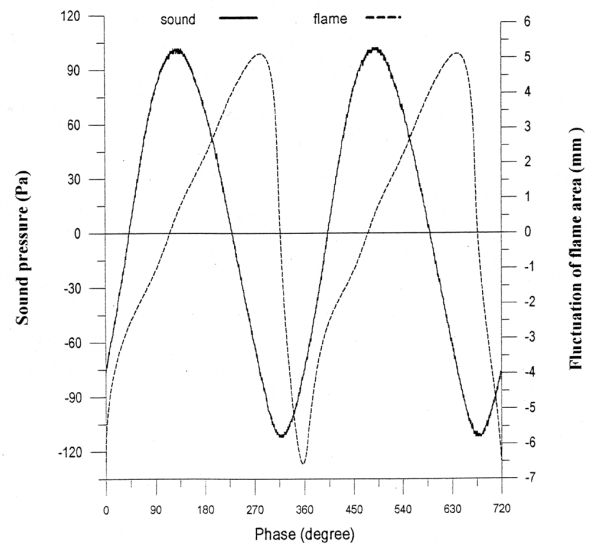


Figure 3. Correlation between heat release rate and acoustic pressure for case of Figure 2.

Results

Four representative flame images, taken from one of the test sequences, are presented in Figure 2. The flames are here oscillating at a frequency of 600 Hz and the pressure level of the sound waves incident on the burner is slightly in excess of 130 dB. It can be seen that each flame responds to the acoustic forcing in a strictly periodic manner, growing in length and forming a swollen head which, if the disturbance grows to a sufficiently large amplitude, detaches itself from the main body of the flame. Similar patterns of oscillation were seen in most of the test cases although the amplitude of the oscillation and its phase relationship to the acoustic field varied from case to case.

Qualitative and quantitative information extracted from the image sequences is being used to improve our understanding of the very complex aeroacoustic mechanisms by which the flames respond to acoustic feedback in practical situations and also to determine the extent to which the sound waves are amplified or damped by the flame oscillation. The critical parameters in the latter context are the instantaneous rate of the heat release in the flame (which can be estimated quite accurately from detailed examination of the individual images) and its phase relation to the acoustic pressure. Figure 3 shows the correlation between these two parameters for the flame oscillation of Figure 2. In this particular case the heat release rate and the acoustic pressure are in phase with each other only for part of the cycle and so, by Rayleigh's criterion³⁾, the amplification of the sound waves by the flame oscillation will have been relatively weak.

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Poling of Optical Fibres using a Frequency Doubled Argon Laser

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Introduction

It has previously been shown to be possible to pole the cores of optical fibres by exposing them to guided, coherent, fundamental and second harmonic radiation from a Q-switched and mode-locked infrared laser¹⁾. The cores of fibres usually consist of germanosilicate glass which is photosensitive to light of wavelength 240 nm²⁾ due to a germanium defect absorption band situated near 5 eV. This means that, when a Nd-YAG laser is used as the source, the poling phenomenon must depend on multiphoton processes. Interfering processes involving two second harmonic photons and two fundamental and one second harmonic photon produce polarization in the fibre core of the correct spatial period for quasi-phase matching of fundamental to second harmonic waves.

In earlier experiments³⁾ two-photon interference between forward and backward waves, launched into fibres from a single frequency argon laser, produced Bragg reflection gratings. The presence of these gratings, now known as Hill gratings after their discoverer, was revealed by two-wave mixing.

In the experiments described below an attempt has been made to use novel processing and interrogation geometries to extend the scope of photosensitive phenomena in germanosilicate fibres. The next section describes the processing of fibres with visible and UV radiation from a frequency doubled argon laser while the following one shows how two-wave mixing might be used to detect the presence of any axial polarization produced.

Finally, in a concluding section, the motive for the search for axial, rather than transverse, core polarization is discussed.

Visible/UV laser processing of fibres

Some specimens of single mode optical fibre having a high core germanium content were first shown to be sensitive to pulsed infrared radiation by repeating the experiment⁴⁾ in which processing with IR and second harmonic radiation produced a grating and made the fibre into a quasi-phase matched second harmonic converter. On the assumption that interference of odd and even photon absorption is the basis for the phenomenon observed, an attempt was made to axially pole specimens of the same type of fibre by exposing them simultaneously to fundamental and second harmonic radiation from the LSF loan pool frequency doubled argon laser. The intra-cavity doubled laser provided 100 mW of UV output (244 nm) and, with the visible filter removed, about 40 mW visible output (488 nm) coherent with the UV. Since the attenuation coefficient of the UV radiation in germanosilicate glass is known⁵⁾ to be about 0.1 mm⁻¹, it was necessary to use transverse rather than guided wave illumination of the fibre core. The orthogonal polarizations of the UV and visible outputs were not altered but the fibre specimens were oriented in such a way that each frequency component of the field had a Cartesian component parallel to the fibre axis. Each fibre was drawn through the overlapping blue and UV beams on a stepper motor driven stage.

Thus, the fibre processing conditions were different in most respects from those used in processing fibres for conditioned second harmonic generation. Each section of fibre was exposed for only a fraction of the total exposure time; the processing wavelengths were different and a cw rather than a pulsed source was employed. In these circumstances it was quite difficult to estimate equivalent exposures. However, one-photon and two-photon absorption cross sections being much larger than the two-photon and three-photon cross sections in the same

absorption band when the IR source was used, exposure times for each section of fibre of the same order as those in guided wave experiments were considered appropriate.

In experiments on induced second harmonic generation the production of visible light from infrared is a sensitive indicator of success in the poling process. However, direct evidence of periodic poling of the fibre core has now been reported⁶⁾. Unfortunately, in the present experiment, the test of whether axial poling has been achieved is once again indirect and is less straightforward than is the detection of visible output that would not otherwise be present. In the next section a method of interrogation suitable for detection of any axial polarization that may have been produced in a fibre is described.

Interrogation of fibres using red laser light

The arrangement shown in Figure 1 has been designed to test whether axial poling and consequent photovoltaic and electro-optic properties have been developed in the fibre core. The beam paths can be blocked at points A and B. In an idealised situation, with each of the beam splitters splitting in the ratio 1:1 and either one of the beam paths blocked, one quarter of the laser power will arrive at photodiode 1 and none at photodiode 2. This is because light travelling from left to right along the fibre will create a Bragg grating with a reflectance that tends eventually to unity. Light travelling from right to left erases any grating that may initially exist. This behaviour is clearly non-reciprocal though unblocking one beam path at any instant and simultaneously blocking the other path should give, at that instant, reciprocal reflection⁷⁾.

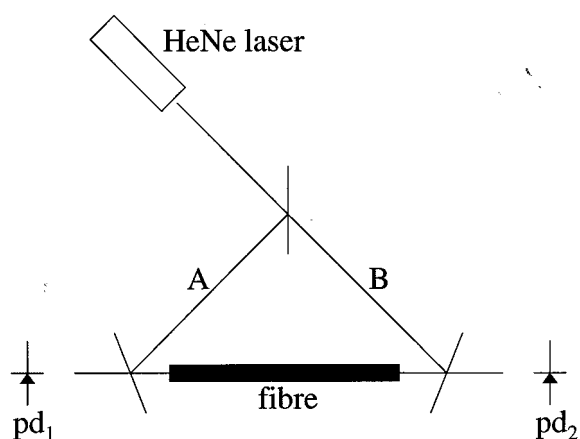


Figure 1. Method of interrogating processed fibres to find evidence of axial poling. pd_1 and pd_2 are photodiodes.

Procedures similar to those described in the last paragraph were used to interrogate 0.5 m lengths of photosensitive fibre of which 5 cm sections had been exposed to blue and UV laser light. Some relatively small changes in transmission and reflection were observed but the consistent pattern described above was not evident, largely for reasons of weak photorefractive response. There was no opportunity in the time available to pursue the sort of material optimization techniques

that are known to be effective in experiments with conventional photorefractive crystals.

Conclusions

Attempts at poling optical fibres that have been reported up to now⁸⁾ have been directed toward producing transverse core polarization for electro-optic modulators and parametric frequency converters and amplifiers. In an axially poled fibre the formation of Hill gratings by guided visible light may be expected to be a very efficient process. This is because two-wave mixing by the classical photorefractive mechanism⁹⁾ of photovoltaic, electro-optic, response is allowed in the lowered symmetry of the poled medium. Axial poling endows the fibre with a preferred guiding direction and opens the way to non-reciprocal fibre devices of a new type¹⁰⁾.

It has not yet been possible to demonstrate such effects convincingly but there seems to be no reason why, in principle, they should not be achievable.

Acknowledgement

I am very grateful for the loan of the CLF laser loan pool frequency doubled argon laser that has allowed this investigation to be carried out.

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Use of diffractive optical elements in laser micro-machining

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Introduction

The increased availability and reduced price of high-power laser sources have made laser material processing one of the current mainstream techniques. Laser systems are now routinely used for annealing, cutting of sheet materials and for welding complex structures. Micro-machining of materials by direct laser ablation is now used by an increasing number of companies to create new products and fabricate existing ones more efficiently.

Present state of the art systems use conventional optics and do not have dynamic control over the optical parameters of the system. In these systems a single diffraction limited focussed spot is used, and generally the laser power and workpiece position relative to the laser beam (focus position) are the only free parameters. Due to the finite depth of focus of such conventional optics the performance of current systems is severely limited outside the focal plane¹⁾.

We have used diffractive optics to modify the pupil function of the focusing lens in a laser micro-machining system in order to correct for aberrations initially present in the system, and to enhance the 3-D machining performance.

Experimental

The test optical system was based on a 4-f configuration (see Figure 1): a collimated 532 nm wavelength 6.5 mm diameter light beam from a Spectra Physics GCR11 Q-switched frequency doubled YAG laser (S) was incident, after passing through a polarizing beam splitter cube (PBS), on a 256x256 pixel ferro-electric liquid crystal spatial light modulator (SLM, Displaytech SLM256P). This combination of the SLM and PBS provides a complex amplitude transmissivity with uniform magnitude and 0 or π phase shift. The spatial light modulator was positioned in the back focal plane of an $f=250$ mm plano-convex singlet (L1), which produced the optical Fourier transform of the spatial light modulator pattern. The spatial light modulator patterns were designed to incorporate a carrier grating, which produced distinct diffraction orders in the Fourier plane. From the optical Fourier transform the +1 diffraction order was selected by a 2.5 mm diameter aperture (A). The aperture size was selected such that the zero order was just excluded when the +1 diffraction order was placed at normalized optical co-ordinates $v_x=v_y=32\pi$ with the aperture centred on it. The transmitted diffraction order was then inverse Fourier transformed by a second plano-convex singlet (L2, $f=300$ mm) to generate the wavefront that was used to illuminate the pupil of a NA=0.2 objective lens (O). The objective lens pupil was under-filled resulting in an effective NA of 0.083. The specimen (W) was mounted on a 3-D positioning stage assembly (P) in the focus of the objective lens. The positioning stages and the laser were operating under full computer control.

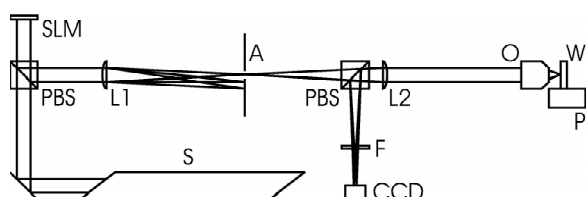


Figure 1. Schematic diagram of optical system.

A CCD camera and colour filter (F) were also added to enable direct viewing of the specimen during machining and alignment.

Diffractive optics design procedures

For the design of the diffractive optical elements, 'filters' in the following, a direct binary search algorithm was used²⁾. First the filter is divided into 256x256 square pixels corresponding to the resolution of the spatial light modulator, and a random 0 or π initial phase is assumed for each pixel. The algorithm operates by toggling the phase shift value between 0 and π for randomly selected filter pixels, calculating the least-squares error between the intensities that would be generated by the modified filter at given 3-D positions and a set of intensity values that were prescribed for those positions, and then accepting or rejecting the pixel change depending on whether the error decreased or increased. Using the above procedure two-level filters were designed with the peak target intensity positions displaced from the origin, i.e. with a carrier grating having a spatial frequency that placed the +1 diffraction order at $v_x=v_y=32\pi$ (normalized optical co-ordinates) in the plane of aperture A. The actual design process for the filters consisted of two steps.

First, filters were designed to compensate for increasing amounts of primary Zernike aberrations by specifying a single target point for which the intensity was maximized. These filters were then loaded onto the SLM, and the intensity profile in the focussed spot of the experimental setup was measured. The aberration coefficients were then repeatedly adjusted and the filters re-designed until a practically diffraction limited focussed spot was obtained ('corrected system'). The system was found to have significant astigmatism and a small amount of spherical aberration. Figure 2 shows calculated estimates of the original un-corrected intensity point spread function (PSF) for the system, the SLM pattern and corresponding pupil phase distribution, and the corrected intensity PSF.

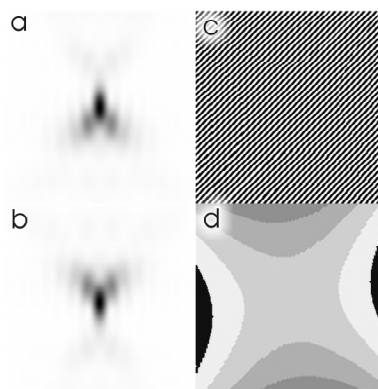


Figure 2. XZ (a) and YZ (b) sections from the calculated estimate of the intensity PSF for the original un-corrected system. Binary two level SLM pattern (c) used to create pupil phase distribution (d) for aberration correction. XZ (e) and YZ (f) sections from the calculated estimate of the intensity PSF for the corrected system.

During the second stage of the design process the aberration coefficients were kept constant and intensity values were specified for additional points. The positions and required intensities for these additional points were selected in such a way so as to obtain an axially extended focussed spot while the lateral extent of the spot was forced to stay constant at the

diffraction limited spot diameter. The axial intensity within the extended spot was also forced to be uniform. The intensity profile produced by the finished filter design ('corrected + enhanced system') is shown in Figures 3c and 3d. To further illustrate the effect of the filters shown in Figures 2 and 3, axial line traces extracted from the intensity PSF estimates for the two filters are presented in Figure 4. The dashed line corresponds to the corrected system and is the same as the sinc line trace that would be obtained for a diffraction limited system. The continuous line corresponds to the corrected + enhanced system and shows the uniform intensity distribution produced within an extended axial region compared to the diffraction limited case.

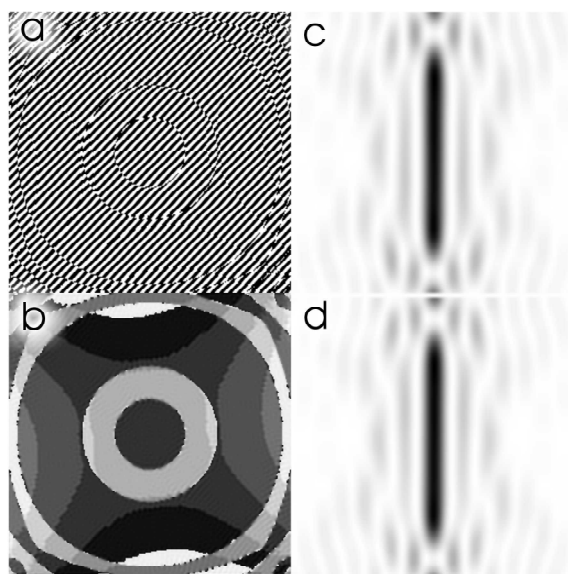


Figure 3. a) Binary two level SLM pattern, b) pupil phase profile corresponding to the SLM pattern, c) and d) XZ and YZ sections respectively from the calculated estimate of the intensity PSF for the aberration corrected + enhanced system realised using the SLM pattern shown in a). The sections correspond to 16π lateral (horizontal direction in the image) and 50 axial (vertical in image) normalized optical co-ordinate units.

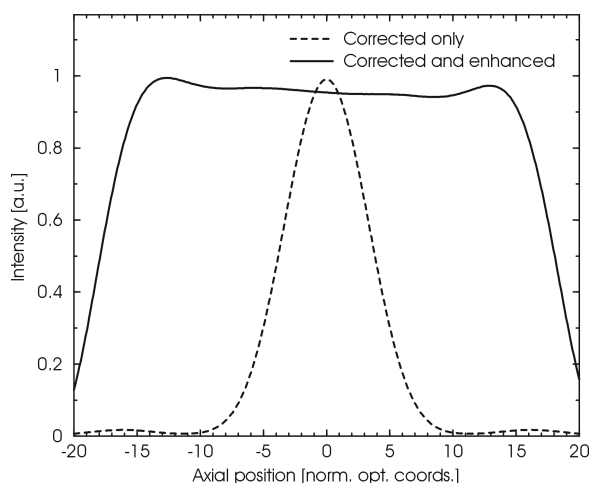


Figure 4. Axial line traces extracted from the calculated intensity PSF estimates for the corrected (dashed line) and corrected+enhanced (continuous line) systems.

Results

The performance of the filters was tested by attempting line cuts through an $\sim 50 \mu\text{m}$ thick Al foil using a range of focus positions and laser pulse energies. The range of focus and pulse energy values that resulted in a complete cut through the foil without any cut-line widening is shown in Figure 3. The light grey area represents the system where the filter was used only for aberration correction, and the dark grey area represents the corrected and enhanced system. The results clearly demonstrate that the *process latitude for producing good quality cuts is increased by approximately an order of magnitude*. This improved performance can be achieved without significant penalties, the only drawback of the technique being the $\sim 5\times$ increase in the minimum ablation threshold. It is also important to point out that the technique can be used to create almost arbitrary 3-D intensity distributions enabling significantly improved process control, and can be used to achieve, e.g. better side wall profiles and deeper aspect ratios for laser drilling, or the elimination of 'hot cracking' during laser welding.

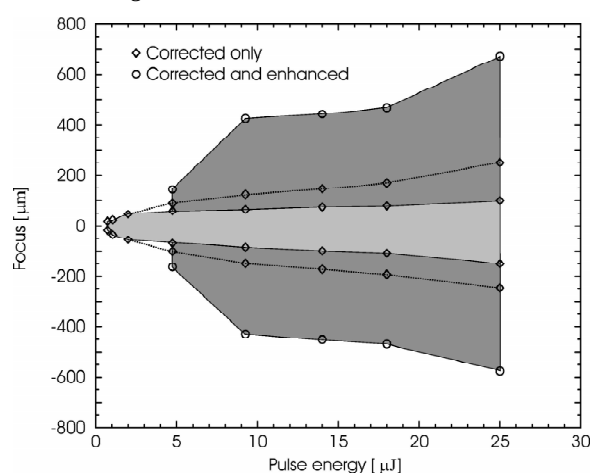


Figure 5. Measured ablation threshold – focus latitude plot for the 'corrected' and 'corrected + enhanced' systems.

Acknowledgements

Support for this work by The Royal Society, London and by the CLRC Laser for Science Facility, UK is gratefully acknowledged.

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Photoluminescence from Silicon Nanostructures

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Introduction

The discovery of visible photoluminescence from porous silicon by Canham¹⁾ has created extensive studies of silicon nanostructures²⁾. Light emitting silicon nanostructures have since been produced by using a wide range of different techniques. Initial excitement surrounded porous silicon (por-Si) because it represents an inexpensive and easily prepared form of nanostructured silicon. Quantum confinement effects are prominent in por-Si, which has led to a wide range of studies into its optoelectronic properties. While an explanation of Canham's observation of visible light emission¹⁾ has motivated most of the work on por-Si, increasingly interest has developed in por-Si as a bio-compatible material and as a component of chemical and biochemical sensors. Thus, we have undertaken studies of por-Si both clean and in the presence of deposits.

The origin of visible photoluminescence (PL) from nanoscale Si is still the subject of much debate. Views are polarized between quantum confinement and other mechanisms^{3,4)}. An explanation based on quantum size effects alone does not explain all observations. Surface species, surface states, fabrication wavelength and pore structure also play a role; as reflected in recent discussions^{2, 5-8)}.

Another possible route to nanometre-scale Si structures is the exploitation of sputtered metal nanoparticles as masks for reactive ion etching (RIE). Seeger and Palmer created Si pillars and cones by utilising rough metal films⁹⁾ as masks for reactive ion etching. Building on their work, we fabricated silicon nanocones in a silicon-on-insulator (SOI) film and here we report for the first time strong visible photoluminescence from such cones.

Photoluminescence of porous silicon thin films

In this study por-Si is prepared by a photoelectrochemical technique, previously described^{10,11)}, without external bias. The holes necessary for etching are created on excitation of an electron from the valence band to the conduction band by a HeNe laser. We have observed¹²⁾ a deposit on the external surface when potassium ions are present in the etchant. In subsequent studies¹³⁾ we determined whether the deposit is present on the internal surface, its chemical composition and its effect on PL.

Laser assisted etching of n-type silicon, without an applied potential, in a variety of etchants produces photoluminescent porous silicon. Porous silicon produced from etchants containing K⁺, Cs⁺ or Rb⁺ can have cubic crystallites of hexafluorosilicate on top of, and embedded in, the porous silicon film. These are formed during etching from the metal ion and the etch product, SiF₆²⁻, via heterogeneous nucleation and growth. The photoluminescence of the hexafluorosilicate-coated por-Si on excitation with UV light is blue-shifted (590–610 nm), as compared to porous silicon which shows red photoluminescence (~640 nm), even though the pure hexafluorosilicates exhibit no photoluminescence of their own.

One of the motivating factors for this investigation was to produce por-Si with modified PL by deposition of a material within the porous layer. The deposited material can modify the PL signal either because it is itself luminescent or through

changes induced by deposition in the properties of the film. Air-dried thin films of por-Si prepared in 3–6 molal HF(aq), NaF/HF, NaF/HCl, HCl/HF and NH₄HF₂ photoluminesce in a broad peak centred at 642±13 nm. The peak is roughly Gaussian but is broadened on the low-energy side. The FWHM is roughly 110–120 nm. Films produced in KHF₂ that are not covered with a deposit also exhibit a similar PL spectrum, Figure 1. The PL spectra from these films are slightly blue-shifted compared to films produced in 48% (w/w) HF(aq), which luminesce at 677±18 nm⁷⁾. The peak shape and width is similar in all instances.

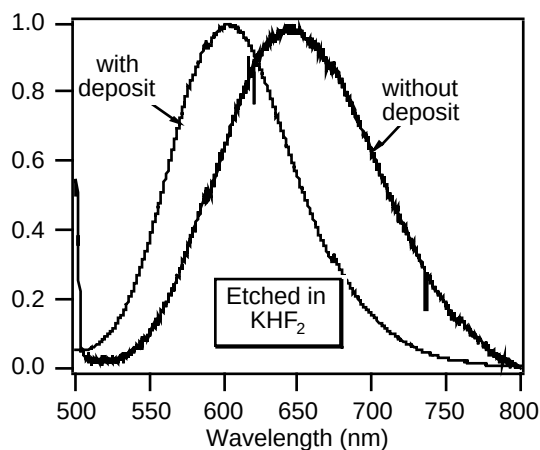


Figure 1. Photoluminescence spectrum from porous silicon produced by etching in aqueous KHF₂. A significant blueshift and intensity enhancement is observed in the presence of a deposit of K₂SiF₆.

When crystallites are visible on the surface of the por-Si the PL has a peak at 611±12 nm or 593±18 nm for films produced in KHF₂ or KHF₂/HCl, respectively, as shown in Figure 1. The peak PL wavelength for Rb and Cs hexafluorosilicate deposits fall within the range of samples with deposits produced in KHF₂. The question is now whether the deposit leads to the PL shift directly, as a result of its own photoluminescence, or indirectly, from some effect on film properties (structure, dielectric constant, etc.). We find that pure K₂SiF₆ does not luminesce significantly in the visible under UV excitation. Therefore, it cannot be the source of the PL spectrum from films with a deposit and the blueshifted PL results either from a modification of the por-Si in the presence of K₂SiF₆ or from newly formed interface states.

Photoluminescence from Nanoscale Silicon Cones

Nanoscale silicon cones, Figure 2, have been fabricated by reactive ion etching on silicon-on-insulator (SOI) substrates utilizing rough silver films as a mask. Photoluminescence visible to the eye was observed after oxidation and annealing¹⁴⁾. Samples oxidised at 900°C exhibit intense photoluminescence centred at about 530 nm, Figure 3, whereas samples oxidised at 1000°C luminesce weakly in the red to infrared region with peak positions between 650 and 760 nm (Figure 4).

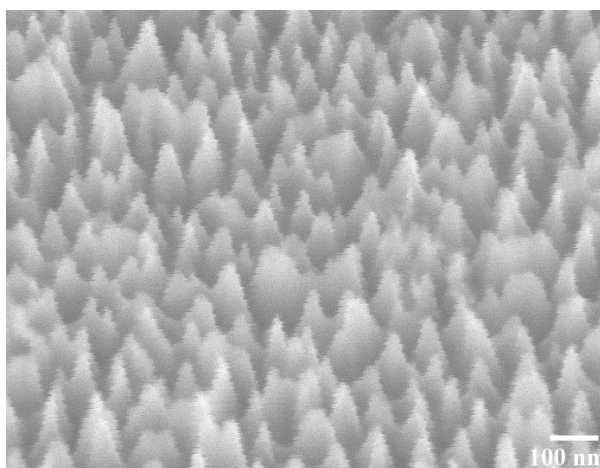


Figure 2. Scanning electron micrograph of silicon cones on an insulating oxide layer (tilted 30°) after etching and cleaning.

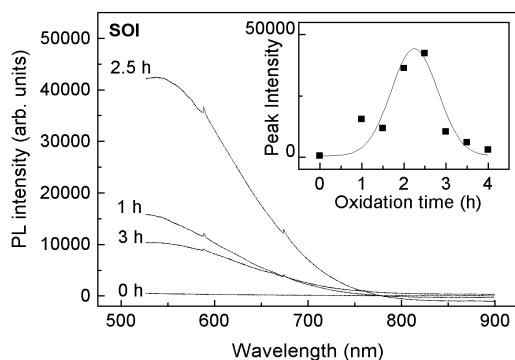


Figure 3. Typical PL spectra of silicon cones oxidised at 900°C etched in silicon-on-insulator substrates. The inset shows the evolution of the peak intensity with oxidation time; the lines are drawn to guide the eye.

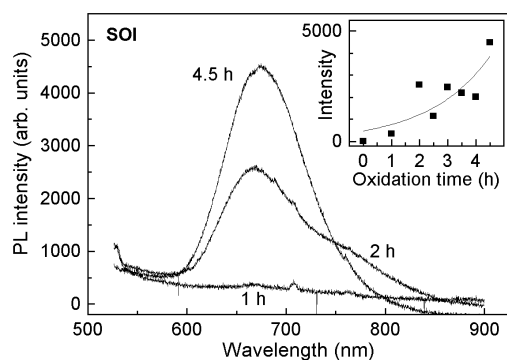


Figure 4. Typical PL spectra of silicon cones oxidised at 1000°C etched in silicon-on-insulator substrates. The inset shows the evolution of the peak intensity with oxidation time; the lines are drawn to guide the eye.

Silicon nanocones fabricated on Si(111) substrates acted as a reference system since the cones are not isolated from the substrate by a wide band gap layer. The samples also showed visible photoluminescence after repeated oxidation in a dry oxygen atmosphere and annealing in nitrogen. Samples oxidised at 900°C were found to emit light in the yellow region similar to cones etched on silicon-on-insulator. This photoluminescence and its intensity evolution can be

understood in terms of defect creation and annealing. Cones etched on Si(111) substrates oxidised at 1000°C exhibit weak red photoluminescence centred at 650 to 670 nm. This type of photoluminescence most likely arises from a defect in the oxide whereas photoluminescence signals centred at higher wavelengths were attributed to a quantum confinement effect in silicon clusters, or a combination of a quantum confinement effect and Si/SiO₂ interface states.

Conclusions

Diverse silicon nanostructures exhibit efficient visible photoluminescence. The radiative mechanisms remain complex and difficult to elucidate; however, it is becoming increasingly certain that various mechanisms are responsible for light emission depending on the conditions under which the silicon nanostructures are formed.

The results demonstrate to our knowledge the first silicon nanocones fabricated by reactive ion etching in silicon-on-insulator which exhibit photoluminescence. In the future it would be interesting to explore the photoluminescence properties of ordered arrays of silicon cones or pillars because of their narrower size distribution and since such structures should also display a photonic band gap.

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Laser Science and Development

- 1) Vulcan Petawatt**
- 2) Vulcan**
- 3) Astra**
- 4) Lasers *for* Science Facility**
- 5) Laser Optics and Laser Design**

Vulcan Petawatt Upgrade Overview

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On the 1st April 2001 the Vulcan Petawatt upgrade was 2 years in to a 3.3 year project to enhance the ultra-short pulse capabilities of Vulcan to the Petawatt level. The upgrade is funded through an EPSRC grant and a collaboration arrangement with Lawrence Livermore National Laboratories (LLNL) US which provides ex-NOVA laser components in exchange for beam time on Vulcan. The upgrade will deliver Petawatt power to target with the capability of adding additional beams in the future for plasma probing and heating. A brief summary of the main areas of activity is given below with further details described in the following articles.

Target area building

A major milestone of the project was the construction of a large, new target area adjacent to the existing laser facilities to house the Petawatt beam compression gratings and interaction chamber. The building was completed ahead of schedule and officially handed over to RAL at the end of December 2000. The completion of the new Petawatt target area building was marked with a small celebration for staff and contractors on 24 January 2001. The photograph below, Figure 1, shows Prof. Henry Hutchinson, Director of the Central Laser Facility, explaining how the new laser will enhance the current capabilities of the CLF's Vulcan laser and stimulate the scientific programme of its users.

Pulsed power upgrade

The reconstruction of the Vulcan capacitor bank using high energy density capacitors from NOVA was critical to the upgrade. All major components including capacitors, triggers and charging units were pre-assembled and tested off-line throughout the year. Vulcan was taken off-line to users in January 2001 for three months to enable the work to proceed. The installation went according to schedule, helped considerably by meticulous planning of every stage. After some minor problems with electrical noise were solved, Vulcan was back on-line to users in April 2001.

Design of the compression and interaction chambers

The design of the two large vacuum vessels in the Petawatt target area has been a major activity for the CLF's Engineering Group during the year. The 71 ton compressor chamber is composed of three main sections. Two cylindrical vessels at either end hold the 1m aperture pulse compression gratings. They are connected by a 13m long centre section which transports the beam under vacuum between the gratings.

The interaction vessel is box-like in construction, 5m x 3m x 2m, and weighing 60 tons. In use it will be surrounded by 70 tons of lead, aluminium and polythene radiation shielding. The chamber supports all major geometries for user experiments as detailed in last year's Report and retains versatility for future enhancements. The chambers are under manufacture and scheduled to be installed in mid-2001.

Clean Room Infrastructure

In support of the Vulcan Upgrade project, a new cleanroom facility has been established in R2 for the purposes of handling and testing large aperture optics up to 1 m in diameter and for servicing disc amplifiers. The facility is in close proximity to the capacitor test bank which is used to test the halfshells and completed amplifiers off-line. The location of the whole cleanroom complex in one contiguous unit improves the cleanliness achievable, minimises component handling and transportation and makes amplifier servicing more efficient.

Project Management

The Vulcan Upgrade Project is managed according to the processes defined by the CLRC's Corporate Project Management (CPM). The project is controlled by the Project Management Committee under the chairmanship of Dr TG Walker, CE of CCLRC. The PMC membership includes Profs O Willi and J Wark (Principle users of Vulcan), Dr D Watson and Mr. D Harman (EPSRC), Prof. MHR Hutchinson (Director, CLF) and Dr C Edwards (Vulcan Petawatt Project Manager).



Figure 1. Henry Hutchinson describes the Petawatt upgrade and explains its future impact on the user community.

Construction of the Buildings and Services for the Vulcan Petawatt Upgrade

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Introduction

Last year we reported on the design of the building for the Vulcan Petawatt Upgrade ¹⁾. This article sets out the progress made on construction during the past year.

The building plan is shown in Figure 1 for reference.

Modifications to existing buildings

Target Area 2 ceased to be operational in April 2000 and work commenced to join it with the Users Area. This involved the removal of all the equipment from the areas, the removal of the interconnecting wall, the re-routing of the stairs and corridor over to the South Control Room, and the installation of a new corridor to the new Target Area Petawatt (TAP) building.

Early in 2001 the wall between Laser Area 3 and Target Area 2 was removed and it was decided to remove the YLF Oscillator Room completely as well as re-siting air conditioning plant. This gap has been temporarily filled to enable Vulcan Operations to continue whilst the new Petawatt amplifier chain and diagnostics area (Laser Area 4) is established and equipment commissioned. This wall will eventually be removed.

New building and services

The specification for the new building was outlined in last year's article ¹⁾. The following describes the building progress through the year.

The contract for the new building was placed with Knowles and Son and construction work started on the 14th February 2000.

Upon digging the foundations, electrical supply cables to R1 were discovered to run directly under the proposed wall. Bridging foundations then had to be laid over these.

The foundations for the walls were completed at the beginning of April.

By the middle of April the main steel frame for the entire building was erected.

As part of the building two large 1 metre thick reinforced concrete plinths were constructed by mid May, one to support the compressor chamber and one to support the interaction chamber. The plinths are necessary to ensure stability of the optics that make up the pulse compressor. Photo 1 shows the situation at this stage.

The floor of the target area, with in-built ducts, was completed in June. Construction of the concrete shielding inner wall and the brick outer wall progressed significantly. Photo 2 shows the situation at this stage.

During July the building work advanced rapidly with both the internal concrete shielding wall and the external brick wall rising to the upper levels.

Building work continued through August. The installation of the 5 T crane was the first sign of internal work on the building.

The fitting of the aluminium roof in September saw the building looking externally complete whilst the inside walls were finished with plasterboard. Installation of plant for the building's air conditioning services also began. Photo 3 shows the situation at this stage.

The completion of lighting, suspended ceiling and other services saw the building nearing completion in November.

The building was completed ahead of schedule and officially handed over to RAL by the end of December 2000.

Photo 4 shows the completed building following the tarmacing of the perimeter road. This should be compared with the impression of the building published last year ¹⁾, Figure 3.

Services

Following completion of the building, work has been progressing on the installation of the basic infrastructure services required to operate the Petawatt laser.

Photo 5 shows the building air conditioning plant installed on the 1st floor of the new plant room.

Additional power distribution has been installed for plant ready for commissioning the facility. The CLF's N₂ distribution pipe-work has been extended to provide N₂ for cooling amplifiers and pneumatically operated equipment. A computer network and telephone backbone has been extended to the new areas. A comprehensive trigger/signal network has been installed between TAP, its Control Room and the existing Vulcan.

On the ground floor of the plant room the large roots/rotary vacuum pumpsets, the twin air compressors and receiver for the compressor and interaction chambers pump down and let up have been sited ready for final installation and commissioning (see Photo 6).

Future work

The vinyl floor will be laid after the large compression and interaction chambers have been delivered and the large temporary opening in the south wall will then be sealed up when the large equipment has been commissioned.

The laser interlocks will be installed soon during a convenient slot in the Vulcan operations program.

The temporary walls between LA3, LA4 and TAP will be removed and additional lead shielding doors and concrete shielding walls added at a convenient time.

Conclusions

The construction of the Petawatt Target Area building and modifications to the existing Vulcan laser building have been completed on schedule thanks to the efforts of many members of CLRC staff and contractors and await the installation and commissioning of the Petawatt laser itself.

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Photo 1. Building as at May 2000 - Foundations complete, steel framework erected, reinforced concrete plinths cast.



Photo 2. Building as at June 2000 – Floor complete, internal concrete shielding and external brick wall being erected.



Photo 3. Building as at September 2000 – Internal concrete shielding and external brick wall nearly complete, crane installed, aluminium roof installed, building services plant being installed internally.



Photo 4. Building as at December 2000 – Building and road complete.



Photo 5. Air Conditioning Plant on 1st Floor of new Plant Room.



Photo 6. Vacuum pumpsets and Let up compressors and receiver on Ground Floor of new Plant Room.

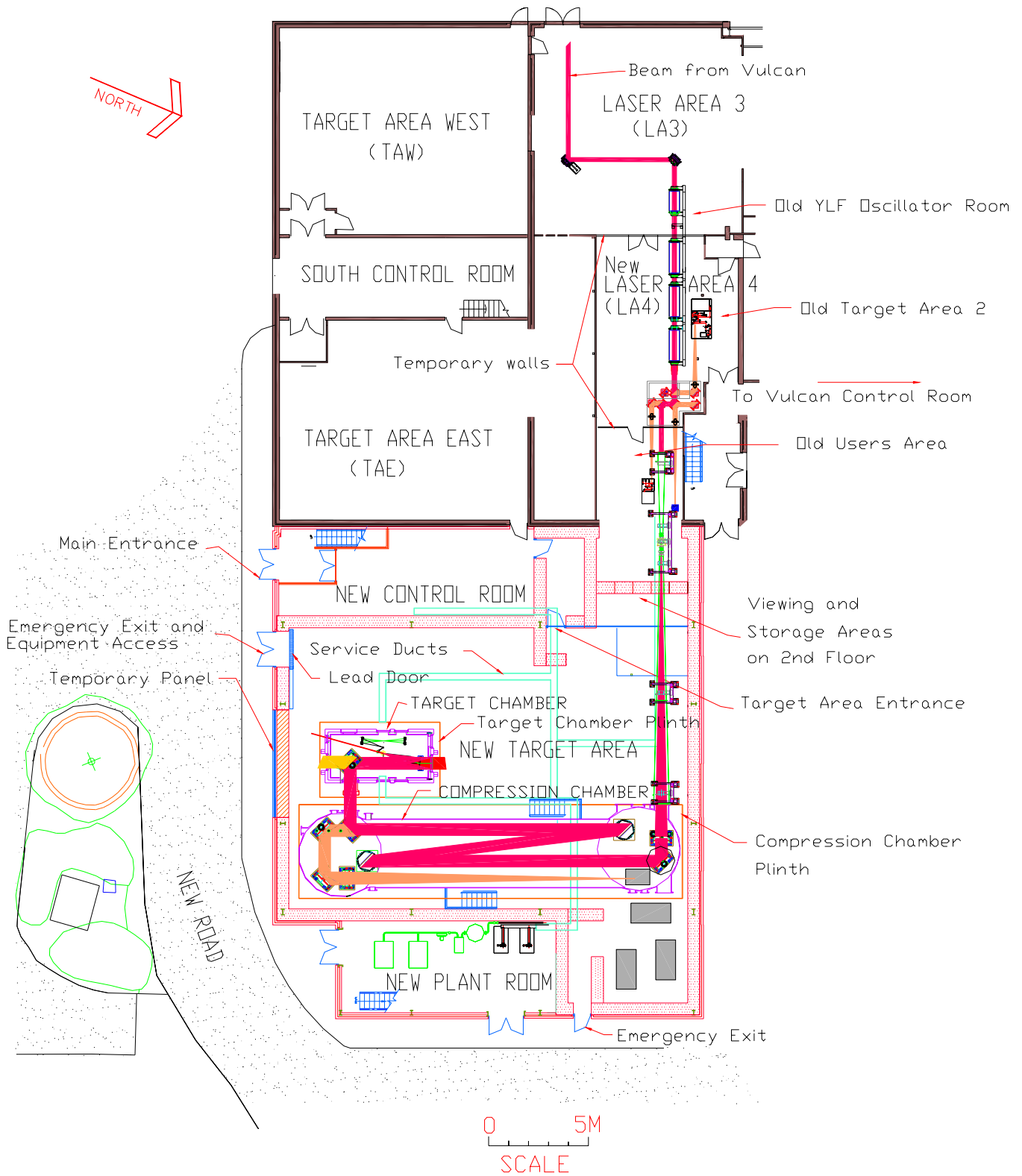


Figure 1. Plan of Vulcan Petawatt Building.

Vacuum System Design for Vulcan Petawatt Interaction and Compression Chambers

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Introduction

A suitable vacuum environment is required in the interaction and compression chambers for the propagation of the Petawatt beam, the use of certain targets and diagnostics and to ensure the efficient transmission from the interaction region of various forms of radiation in particular harmonics and soft x-rays. The chambers are relatively large with volumes of 28 and 120 cubic metres respectively. This report describes some of the details of the design of the vacuum system to be used to achieve the pumping timescales for the interaction chamber of: 10^{-3} mbar in 15 minutes; 10^{-4} mbar in 1 hour; 10^{-5} mbar in 24 hours; and with a let up time to atmospheric pressure of 15 minutes. Only the interaction chamber will be routinely vacuum cycled and hence is critical in the specification. The compressor chamber will be isolated from the interaction chamber via a large aperture, 630mm, gate valve and will only be let up to atmosphere for maintenance purposes. The vacuum system for the compressor chamber is therefore only required to have a pump down time to 10^{-3} mbar in 24 hours and 10^{-5} mbar in 72 hours.

Vacuum pump selection

In order to select the most cost effective vacuum pumping system that would meet the timescale requirements, a feasibility study was carried out on a number of possible design options.

From this study the most favourable systems were theoretically modelled in both the rough to medium vacuum range and the medium to high vacuum range to establish the optimum vacuum pumping system. It was an important requirement to ensure that the vacuum system selected would have:

- high reliability
- present a low risk of hydrocarbon contamination
- possess an inherently low vibration signal
- be able to withstand high electro-magnetic radiation fields.

These criteria led to the system illustrated in Figure 1. The vacuum system is comprised of rotary pumps, roots boosters and turbo-molecular pumps. The let-up system is comprised of oil free compressors delivering clean dry air through a gas reservoir.

The roughing system¹⁾ comprises duplex pump packages using a combination of $1000 \text{ m}^3 \text{ h}^{-1}$ roots pump and a single stage $280 \text{ m}^3 \text{ h}^{-1}$ rotary vane pump to give a total nominal roughing pump package performance figure of $1460 \text{ m}^3 \text{ h}^{-1}$ at the pump inlet port. An inherent part of the roughing pump package selection process was the performance losses caused by the remote location of the roughing pump packages in the plant room. These losses were also theoretically modelled and an

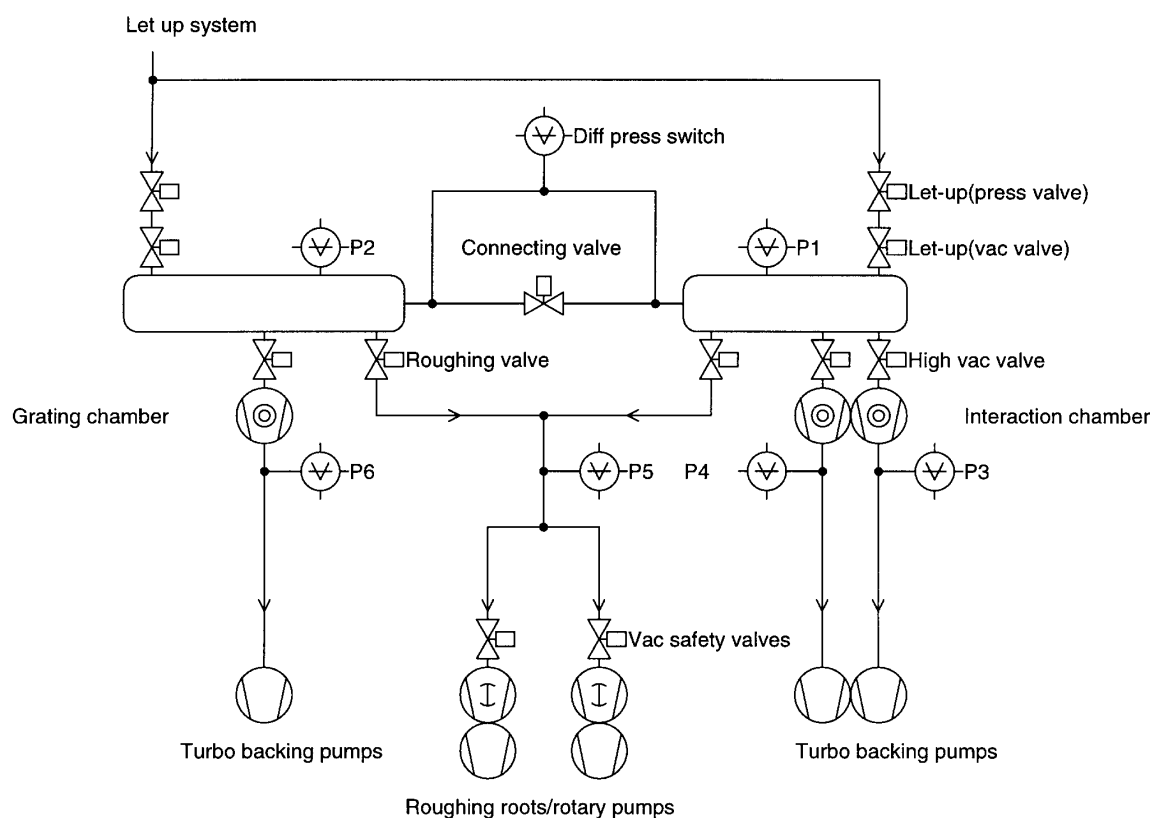


Figure 1. Schematic design of the vacuum and let-up system for the Vulcan Petawatt Compressor and Interaction Chambers.

optimum roughing pipeline diameter of 160 mm was selected. The roughing pump package location was chosen because of the considerable heat and noise generated by the vacuum pumps when operating under full load conditions. Additionally as the surface areas are very large within both vacuum chambers the surface outgassing from the pumped volumes has been minimised by the use of low outgassing materials where possible and electrodeless nickel plating of the vacuum chamber interiors.

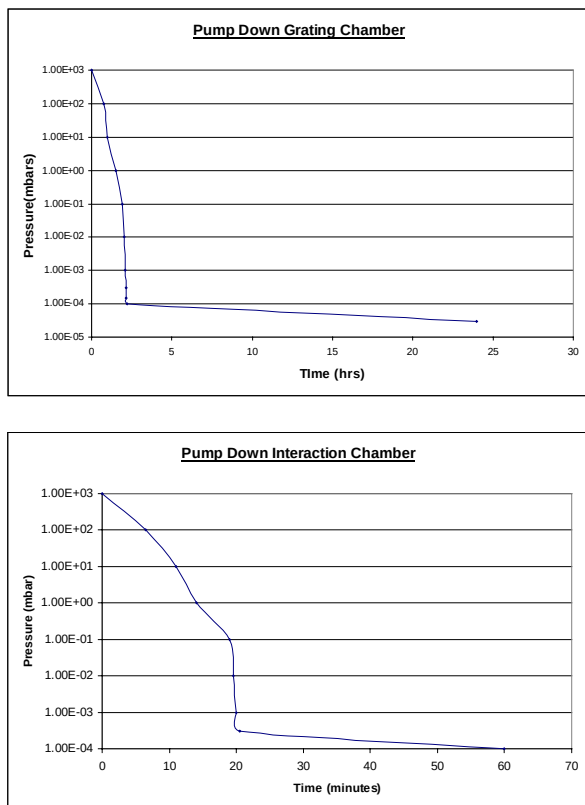


Figure 2. Theoretical pump down curve of (a) The Compressor Chamber. (b) The Interaction Chamber.

The roughing pump packages are capable of an ultimate pressure of $< 6 \times 10^{-3}$ mbar, which provides for a wide margin of ultimate pressure performance at maximum pumping speed to complement the performance characteristics of the 2000 l s^{-1} high throughput Turbomolecular vacuum pumps²⁾. These pumps were selected as they meet all the performance criteria with the additional benefits of the ability to handle high gas loads at high fore-vacuum pressures and require minimal low cost maintenance. From the theoretical modeling process it was again established that duplex pumps would be required to meet the specification requirements on the interaction chamber and that one pump would be capable of maintaining the vacuum to specification within the compression chamber. The Turbomolecular pumps are all close coupled through a gate valve to each chamber for increased pumping speed and flexibility. The backing pumps for each Turbomolecular pump are also close coupled to maximise performance and minimise cost.

The theoretical performance of the complete system is shown in Figure 2 (a) and (b). The Compressor Chamber is calculated to pump down to 10^{-3} mbar in 2 hours and 10^{-4} mbar in 24 hours. The Interaction Chamber is calculated to pump down to 10^{-3} mbar in 20 minutes and 10^{-4} mbar in 1 hour. These times are largely within the specification highlighted in the introduction with the exception of the pump down to 10^{-3} mbar in 20 minutes for the interaction chamber which was cost

constrained. It should be noted that these estimates are based on a clean environment and could be lengthened dependent on user diagnostic and target requirements.

Let-Up System

With large volume vacuum chambers housing delicate optical components such as those used in the Petawatt upgrade the re-pressurisation process requires a let-up system that will not damage or contaminate the optics and chamber interior. Any contamination of the chamber interior also compromises subsequent re-evacuation cycles, as contamination products such as water vapour can greatly extend the chamber cycle times. The Petawatt let-up system consists of duplex oil free compressors capable of delivering 30 l/s at 7 bar with forced air aftercooling, refrigerant dryer and 0.01 micron filtration stages to produce oil free, clean dry air at high pressure, which by the incorporation of a pressurised reservoir will meet the required re-pressurisation timescale specification.

Control system

The system designed to control the vacuum and let-up components and their sequence of operation consists of a modular Programmable Logic Controller (PLC) system³⁾, with a user terminal including a colour graphics screen. The modules consist of digital I/O, relay outputs and analogue inputs. The digital I/O is used to operate solenoid valves and return the valve status, and the relay outputs are used to engage the contactors that supply the vacuum pumps. An analogue signal is taken from the vacuum gauge controller which allows the chamber pressure to be displayed on the graphics screen. A schematic diagram is also displayed, showing pump operation and valve position, with various pump down and let-up options available.

Conclusion

A vacuum and let-up system has been designed to fully meet or exceed the operational performance requirements of the Vulcan Petawatt Compressor and Interaction Chambers.

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Vulcan Pulsed Power Installation and Commissioning

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Overview

Before the Petawatt upgrade was financed for the Vulcan laser it was recognised that the disc amplifier pulsed power equipment was vulnerable to total failure through component obsolescence. One power supply unit was a remnant of the initial 1976-77 installation, and was at this time supporting the six main output amplifiers. In light of the serious implications for the facility, funding to replace the pulsed power equipment was sought, and agreed by the EPSRC.

The proposal presented costing for a multi-channelled, modular disc amplifier system utilising switched mode units to charge each capacitor bank, to be further enhanced by new Ignitron trigger modules to provide a reliable amplifier cascade triggering option. The cascade firing of amplifiers provides a convenient and accurate mechanism for balancing the relative individual beam intensities, or otherwise as required.

At this time a proposal to upgrade the Vulcan laser to Petawatt capability was under discussion which concluded with funding being provided by EPSRC and hardware made available from the closure of the Nova laser at Lawrence Livermore National Laboratories (LLNL) in the US. This hardware included

capacitors, ignitrons, racks, resistors and fuses all of which would be used in the Vulcan pulsed power system. As a result of this development, the pulsed power upgrade project was incorporated into the Vulcan laser upgrade project.

The Upgrade Requirement

The proposed laser upgrade involved boosting the output with the addition of three Nova 208mm amplifiers, and to provide isolation with a 208mm Faraday Rotator. To accommodate this hardware one target area, a user computer room and an oscillator room would be converted into an extension of the laser (LA4). A new building would provide for a sixteen-metre beam compression chamber, and a new interaction chamber. Space would be generated to accommodate the extra pulsed power requirement by replacing the existing capacitor banks with a reconfigured installation utilizing higher density capacitors from Nova powered from switched mode power units.

Pulsed Power Project

It was clear that successful completion of the installation within the allotted period from January to April 2001 would require



Figure 1. Paul Holligan of the CLF Electrical Engineering Section adjusting a PFN following installation of the new Vulcan pulsed power area.

pre-construction and testing of all equipment to be installed. Although there were practical limits to the amount of pre-construction possible, all equipment was procured and tested in some form during the preceding year.

To accomplish this goal it was essential to provide a suitable test facility with capability for testing at least one complete modularized amplifier channel. With future test requirements in mind an independent off-line amplifier test facility was designed and built to accommodate all sizes of amplifier used in Vulcan. Until this time amplifier testing had been slotted into the experimental programme utilizing on line equipment. The off line facility adjacent to the amplifier construction room has greatly improved the overall efficiency of the construct and test procedure.

Testing and Commissioning

It took several months to procure equipment, construct and commission the test facility which provided a capacitor bank blockhouse and amplifier test bay, driven from, and monitored through power units coupled to a Camac system controlled from a PC linked by Ethernet. The test facility was commissioned in April 2000 and a long test programme that would take us through to the commencement of the upgrade proper was started.

All 360 plus capacitors had been received from LLNL by the start of the testing and were being built into units of four and five capacitors on standard reinforced plastic palettes. This method of construction proved to be a cost-effective solution to the logistical and geometrical problems of bank building, storage and safe maneuverability. Each capacitor was inspected for damage and capacity before being numbered and mounted onto a palette for unit testing. The capacitor unit support frame was built complete with Pulse Forming Network units [PFNs] attached, thereby making the capacitor unit change-round a fairly innocuous task, which took only a few minutes. A fork-lift unit was used to maneuver the capacitor units into position, and the connection of bus bars to the PFNs completed the task. Testing amounted to charging the capacitor units from 5 to 20 kV in 5kV steps and finally 22kV. The stored energy was discharged into dummy loads at each level with the control computer recording each event to disc. A hard copy of all related data showing all charge details including a linear plot of the constant current charge, and the discharge waveforms was recorded through a Camac based Transient Recorder module.

The test facility proved very successful allowing parallel testing of power units and the control interface, Ignitron cabinets, Ignitron trigger units, and Camac based trigger pulse delay units with fibre optically coupled outputs developed for this purpose. Upon completion of power unit tests there was sufficient space available to build them into cabinets ready for installation as complete units of four supplies, a control interface, and individual three phase input breakers.

Procurement of industrial storage racking for the new capacitor bank construction provided opportunity for engineering personnel to get a feel for constructing the support frames. This again proved to be a cost-effective, efficient acquisition that required the minimum of effort to construct and provided temporary storage for tested capacitor units.

Installation

Installation of the pulsed power equipment started in earnest on January 8th 2001. There was much to be accomplished in a relatively short time, and the schedule was precise.

The Vulcan pulsed power equipment was removed in a few days with just two items of the old installation retained, the Faraday Rotator Capacitor bank, and all existing amplifier cables which were supported out of harms way. Vulcan was now truly out of operation, and the pulsed power room became

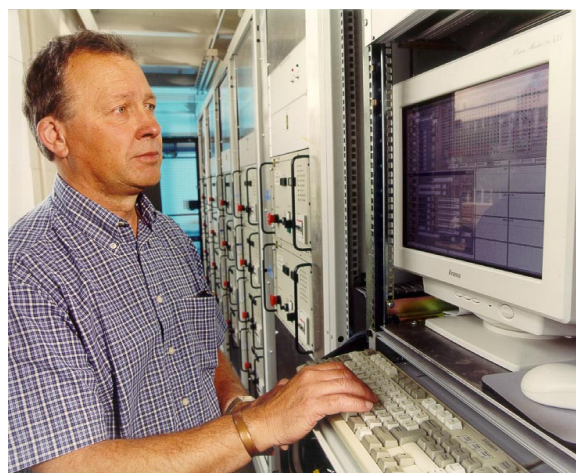


Figure 2. Ray Wyatt, Section Leader, CLF Electrical Engineering monitoring the pulsed power performance through the dedicated PC control.

a centre of concentrated effort for the entire complement of the department's engineering group. Everyone working on the project was aware of the importance for the installation being completed on time, and was resolutely committed to achieving this goal.

Installation of the hardware was effectively completed by mid-March, with no major hold up, and the test programme began by checking the high voltage integrity of each circuit to 24kV. This was followed with each individual controlled item being checked for correct operation. Once this important preliminary stage of testing was satisfactorily completed it was possible to move on to testing local computer control, and iron out any software problems. At this stage it was of paramount importance that we had confidence in control, and were able to cope with all foreseeable eventualities during the capacitor bank charge and discharge tests which followed.

The capacitor banks were charged individually in stages to full charge status with the stored energy being discharged into dummy loads. These tests were conducted under local control, and were an essential precursor to amalgamation with the main control system, and the eventual commissioning of the laser as a working unit.

Integration of the pulsed power system with the main control was not accomplished easily, and many problems were resolved throughout the commissioning process. This was the only part of the installation project that it had not been possible to pre-test. As a consequence the commissioning programme overran by two weeks, during which many lines of software were added or amended. During this time the amplifier monitoring and data acquisition equipment was tested, providing on screen detailed analysis of amplifier performance. Amplifiers and Faraday Rotators were fired individually and eventually in combinations, with the relative timing to the front end being tuned for optimum performance. In only three and a half months the Vulcan laser was brought back on line, with experiments running in target areas East and West.

Vulcan Petawatt Compressor Chamber Design

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Introduction

The compressor chamber houses the two large aperture (940 mm) diffraction gratings under vacuum to preserve pulse fidelity to target. The beam configuration, the beam size and the footprint of the optical mounts largely governed the size and design of the chamber. The chamber will be manufactured in three main parts: two cylindrical vessels that house the optics, and a rectangular transport section between the two. The chamber will be manufactured from nickel plated mild steel. It will weigh 71 tons and has a volume of 120 cubic metres. It will have a turbo-molecular vacuum system capable of pumping down to 10^{-3} mBar in 24 hours or 10^{-5} mBar in 3 days.

An artist's impression of the inside of the chamber is shown in Figure 1. The beam enters the chamber via an expanding vacuum spatial filter (shown in green below) which is part of the same vacuum system to minimise the number of optics in the beam. The beam is collimated with a 14m focal length lens then turned using one of the reworked LLNL large aperture mirrors onto the first of the grating pair. After compression the beam is turned into the main interaction chamber using a partially transmissive mirror. The 0.2% leakage through the back of the mirror is used for compressed beam diagnosis and is represented as the red focusing beam at the top of Figure 1.

Foundations

In order to achieve optimum compression the grating stability is of critical importance. The angular mismatch that can be tolerated between the two gratings is 18 micro radians and the sensitivity to the pointing accuracy of the incoming beam is 2 milliradians. In order to achieve these criteria the building was designed with an independent plinth (foundation) for the compressor chamber. This measured 19m x 4.7m and was 1m deep made up of reinforced concrete. It is designed in this way so that the compressor chamber will be supported on a stiff 'raft' and that this will allow some independent movement of the foundations within the target area. This could be

particularly important when the 70 tons of shielding is installed around the interaction chamber.

Chamber design

The chamber was designed in-house with detailed drawings provided by an external contractor ¹⁾. Its cost and the requirement for vacuum and laser cleanliness drove the material specification, with the whole chamber manufactured from Nickel-plated mild steel.

The first of the tanks contains the collimating lens from the expanding Vacuum Spatial Filter, a 940 mm diameter turning mirror and the second of the compressor gratings. The second tank contains the first grating, diagnostic mirrors and the final turning mirror in to the interaction chamber. The tanks are made from 25 mm thick rolled mild steel, are 4.5 m in diameter and 2.0 m high. Ports are made available for beam access and to diagnose the beam. A set of six ports in each chamber will allow feed-throughs for electrical cables for the mirror drives.

The floors of the compressor tanks are 85 mm thick and will be secured directly to the plinth via a 600 x 600 mm array of pre-tensioned vacuum sealed bolts. This will reduce the deflection of the floor under vacuum thus giving a stable surface for the mounting of the lenses and diagnostic mirrors. The gratings and the first turning mirror, which require additional stability, are supported through the tank floor directly on to the concrete plinth and vacuum isolated via bellows assemblies.

The lids of the two tanks are each spun from a single sheet of 25 mm thick mild steel. Each lid weighs 4 tons and for mirror installation and removal will have to be taken off the tank completely with the internal crane, which has a capacity of 5 tons. For more routine personnel access a 600 mm port is provided in the lid. A smaller port is provided centrally in order to illuminate the tanks.

The beam transport tube between the two tanks is of 3.5m x 0.85m rectangular section. To resist buckling under

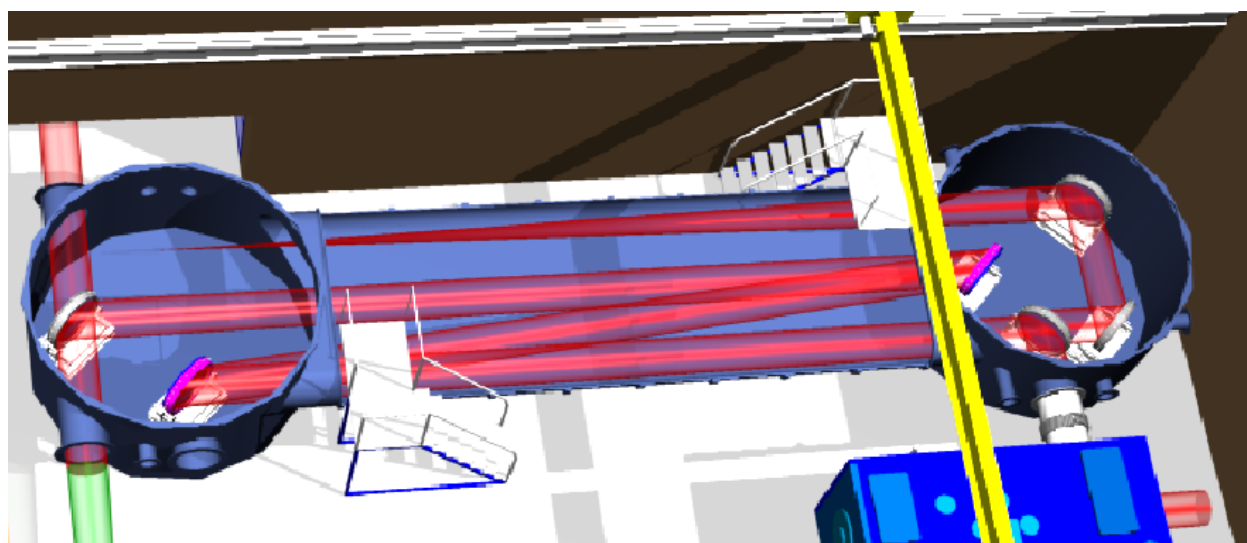


Figure 1. Artist's impression of the inside of the compressor chamber showing the incoming beam in green (bottom left), the diagnostic beam as a focusing red beam (top) and the interaction chamber (bottom right).

vacuum a series of ribs of 1m spacing are welded externally to the tube. The design was optimised using finite element analysis. Five vacuum ports for the entire compressor chamber are provided beneath the rectangular transport tube. Due to the complexity of the beam transport tube and to ease Nickel plating it will be manufactured in three sections and welded together at RAL. An artist's impression of the compressor chamber when fully installed in the Petawatt target area is shown in Figure 2.

Gate Valve

A gate valve will be available to provide isolation between the compressor chamber and the interaction chamber. This is required as it will be necessary to vacuum cycle the interaction chamber during experiments. The gate valve will have an aperture of 630mm. A picture of the valve following final testing is shown in Figure 3. In order that alignment within the interaction chamber can continue whilst the gate valve is closed it is designed with five windowed ports. One is of 90 mm clear aperture, centrally mounted, and 4 are of 40 mm clear aperture which define the 73% points of the beam aperture in the horizontal and vertical planes.

Diagnostic capability

The compressor chamber has been designed to allow comprehensive diagnosis of the laser beam:

- The stretched pulse, which is injected into the vessel from the laser, can be diagnosed via leakage through the first mirror and through a full aperture port, although initially this will not be catered for.
- The diagnosis of the compressed pulse is via leakage through the final turning mirror in the compressor chamber.

This beam is then turned through 180 degrees using two turning mirrors and then focused using a lens identical to the collimating lens for the incoming beam. It is appropriate to focus the beam inside the compressor chamber, as it is easier to control the B-integral of the down collimated beam and does

away with the need to provide a full aperture window to extract the beam from the chamber. Two small ports are provided through which the diagnostic beam can be directed where an array of short pulse diagnostics are provided.

Conclusion

A large and complex vacuum vessel has been designed to incorporate the optics associated with the compression of the Vulcan Petawatt laser facility. The chamber is currently in manufacture and will be installed within the target area at the end of 2001.

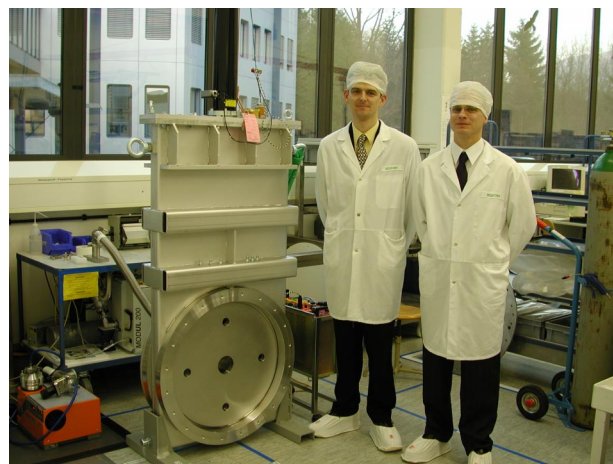


Figure 3. Dave Rodkiss (right), CLF Mechanical Engineering, inspects the large aperture gate valve at the manufacturers, Messrs VAT²⁾, prior to delivery.

References

1. Fernley Engineering, Crystal Haven House, Chertsey, Surrey
2. VAT Vakuumventile AG, CH-9469 Haag, Switzerland.

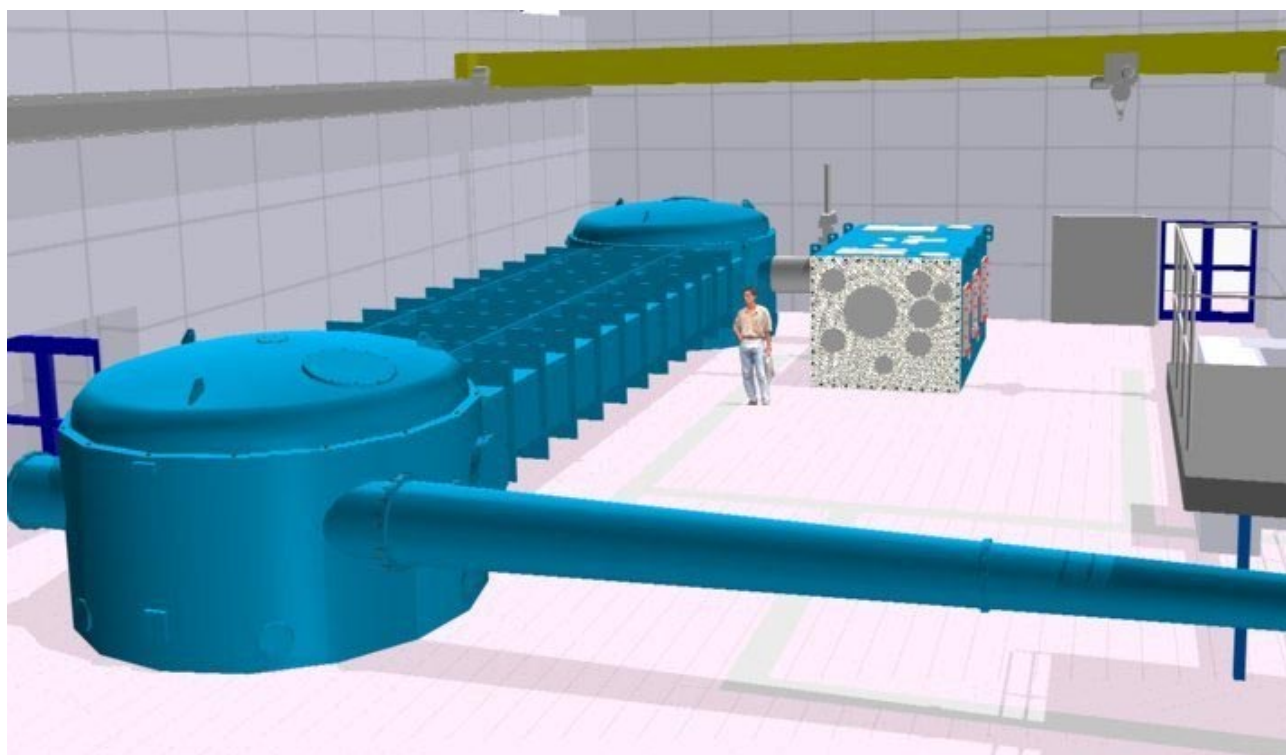


Figure 2. Artist's impression of the compressor chamber when fully installed in the Petawatt target area.

Interaction Chamber for the Vulcan Petawatt Upgrade

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Introduction

The Vulcan Petawatt Upgrade will deliver 1 Petawatt of power (500 J in a 500 fs long laser pulse) on target. The beam diameter will be 600 mm and the beam will be nearly diffraction limited.

The design of the interaction chamber has to fulfill various requirements¹⁾. It has to be stable enough for focusing the beam with an F/3.1 off-axis parabolic mirror. Access for a large number of different diagnostics to the interaction point is necessary. The vacuum system has to be capable of pumping down the chamber in the time between two shots of the Vulcan laser. Because of the large amount of radiation (γ , p, e, n, X-rays) the chamber also must accommodate sufficient radiation shielding²⁾.

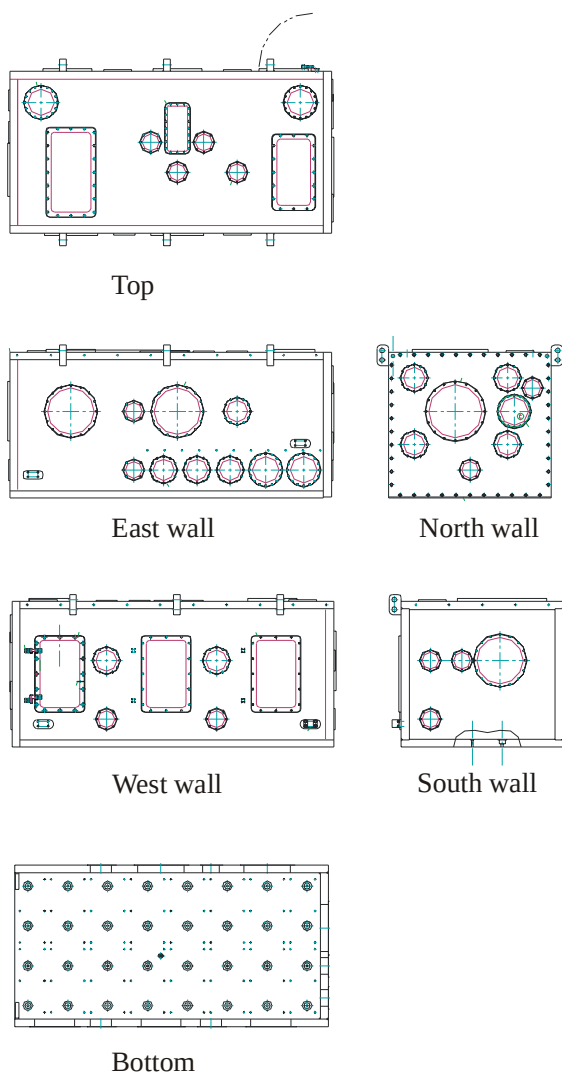


Figure 1. Drawings of the chamber walls.

General design

The design of the interaction chamber is shown in Figure 1. It is a rectangular tank made of 125 mm thick mild steel. This design was chosen because of the lower cost compared to a chamber made from thinner plates with welded stiffeners. The 125 mm steel also provides an additional radiation shield. The size of the interaction chamber is 2m x 2.2m x 5m.

The north wall of the chamber (Figure 1) can be removed in one piece by means of the crane installed in the target area. This enables access to the chamber to install unwieldy equipment inside the chamber.

The inside of the interaction chamber will be nickel plated to reduce outgassing and meet clean vacuum and laser requirements.

Foundations

Finite element calculations showed that the biggest deflection of the chamber floor during evacuation would be about 1 mm. It was therefore decided to put a single block of concrete, which is 1 m thick, underneath the chamber. The chamber will then be bolted down to this concrete block by thirty two M24 bolts. This will reduce the movement of the chamber floor to less than 4 μ m between atmospheric pressure and vacuum. It will enable us to mount all the mirror and target mounts directly to the floor of the chamber, thus providing us with a maximum of flexibility in future experimental setups.

Ports

An overview of all the ports is shown in Figure 1. The chamber was designed not only to meet the requirements of experiments with a single Petawatt beam of 600 mm diameter but is also capable of providing additional long pulse high energy beams to the target. These long pulse beams are necessary for a whole range of future experiments. Ports for the long pulse beams are mainly on the west and the north side of the chamber.

The west side of the chamber also has three large rectangular ports. Access to the chamber will be provided by one door which can be mounted at either one of these ports, depending on the particular experimental setup. The other ports can be used as access ports for diagnostics.

The large beam port on the north side of the chamber can be extended by a tube, making it possible to install focusing optics, e.g. an off-axis parabolic mirror with a large F-number. This would be necessary for a large number of experiments aiming at new particle acceleration schemes. The big rectangular ports on top of the chamber will give direct access to the mirrors or mirror mounts.

Shielding

In order to avoid activation of the chamber walls by radiation produced by fast particles during experiments, there will be a 20 mm thick Al lining inside the interaction chamber. The activation of the Al will be routinely monitored, and it will be replaced if necessary. To meet the environmental regulations, the complete interaction chamber will be housed in 150 mm of Lead backed up by 100 mm of high density polythene. This shielding together with the 60 cm concrete walls of the target area will be sufficient to decrease the amount of radiation to the level of the natural background outside the Petawatt Target Area.

References

1. D Neely *et al.*, CLF Annual Report, (2000).
2. R. Allott *et al.*, CLF Annual Report, (2000).

940 mm mirror and grating mount design

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The large optics used within the compressor and interaction chambers of the Vulcan Petawatt target area required mounts to be designed to provide adequate stability and resolution of adjustment. The compressor system was designed using two main turning mirrors, two diagnostic mirrors, two lenses and two gratings. In addition the interaction chamber houses a turning mirror and the focussing parabola. All these optics could be mounted using a similar system with specific requirements individually catered for, i.e. translations and rotations. Nine mounts were acquired of the LLNL design which were originally used to support mirrors off the Nova space-frame. This did not lead to a compact or vacuum compatible design but with significant modification it will be possible to use these mounts for the upgrade.

The Petawatt upgrade required the mounts to be housed within the vacuum chambers, plus occupying as small a footprint as possible to minimise the size of the chambers. This was achieved by utilising the main body of the LLNL mounts by cutting and re-welding the framework to enable the x-y positioning slides to be used. The mirror bezel was also retained by mounting it vertically on existing mounting flats as shown in Figure 1. With the addition of radial slides to give the mirror tip and tilt about its front face a fully gimbaled design was achieved. This design was then used to house both the lens assemblies with the extra design feature of rotation about the centre axis mounts for the gratings, and the off-axis parabola. The specification of the adjustment range and degree is given in the table below.

Adjustment Range	Horizontal Axis	Vertical Axis	Longitudinal Axis
Angular Adjustment Range	$\pm 5^\circ$ fine	$\pm 5^\circ$ fine variable + 45° coarse variable mirrors $\pm 180^\circ$ coarse variable gratings	$\pm 5^\circ$ fine
Linear Adjustment Range	± 50 mm (+300 mm final turning mirror)	No adjustment	± 50 mm

Fine Adjustment	Resolution	Reproducibility
Vertical Axis Rotation (Tilt)	$< 5 \mu\text{rad}$	$< 5 \mu\text{rad}$
Horizontal Axis Rotation (Tip)	$< 300 \mu\text{rad}$	$< 300 \mu\text{rad}$
Longitudinal Axis Rotation (Rot)	$< 30 \mu\text{rad}$	$< 30 \mu\text{rad}$
Longitudinal Translation	0.1 mm	0.1 mm
Horizontal Translation	0.1 mm	0.1 mm

A common mirror adjuster was designed in order to achieve the required degree of accuracy in a cost-effective manner. This mechanism consists of a floating ball nut and screw unit housed within pivot bearing assemblies. This allows the linear movement to be transmitted to the angular rotation required for tip, tilt, and rotation. For the x-y movement the pivots allow the units to be mounted at any angle therefore allowing for any misalignment. The ball screw is driven via a solid coupling by a stepping motor or manual adjuster. This motion is achieved by a combined thrust and roller bearing to eliminate any hysteresis and backlash in the unit.



Figure 1. Mirror mount.

Each of the adjusters could be manually or remotely operated but once inside the vacuum, accessibility to the drives and the vulnerability of the optics to mechanical damage led to the decision to motorise all of the adjusters with stepper motors.

The system designed to control the movement of the mirrors and gratings consists of two Parker 6K8 Motion Controllers, which provide sixteen axes of stepper motor control via Parker L25 Stepper drives. A resolution of 4000 steps per revolution is used to meet the required specification. As there is no requirement for all of the axes to be moved simultaneously, each stepper motor is wired to the chamber wall and connected to the stepper drive when motion is required. The software to control the motions and provide the user interface is written in LabView, and provides the user with incremental or specific position commands.

The mount was tested using a 30cm aperture interferometer operating at 630 nm. Vertical or horizontal fringes were individually resolvable by eye which easily enabled angular position measurement of the mount to better than $1 \mu\text{rad}$. It was not possible to test all aspects of its function due to a limited number of drive actuators. Thus, the tests concentrated on the two important aspects of its fine adjustment function – the performance of the vertical and horizontal axis fine angular adjustment and an assessment of the angular orthogonality of the vertical and horizontal axis. The vertical axis adjustment resolution was measured at $\sim 1 \mu\text{rad}$ with a reproducibility of $\sim 4 \mu\text{rad}$ over a 2 mrad adjustment cycle. The horizontal axis displayed a similar performance. There was no measurable coupling between the horizontal and vertical motions. The tests proved the mount met the exacting specification of the Petawatt optics and approval was given to incorporate this into the upgrade design.

Capacitor Bank Control System Upgrade

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Introduction

The capacitor bank upgrade for the Petawatt system has been more than just a re-fit of high-density capacitors. Individual power supply units (PSU) are now in use, one per disc amplifier assembly. The modular pulsed power installation provides a more readily serviceable assembly with independent amplifier units designed to improve system flexibility and reliability.

A more critical circuit monitoring system also provides shot to shot information about each amplifier circuit performance. The sensitivity is such that during testing the status of a faulty 8000 Amp fuse was manifested by deformation of the discharge current waveform. This is a vast improvement on the previous system sensitivity where signals were derived from the total amplifier current at the Ignitrons rather than individual lamp circuits at the amplifier. Previously, a universal PSU problem meant that up to 6 amplifiers could be out of commission at the same time. The new system allows for individual PSUs to be replaced and also adds flexibility in allowing tuning of the high voltage to cater for mismatches in the amplifier gain profiles.

Computer Control

The upgraded capacitor bank has required the commissioning of a local computer control system due to the desire to have much finer control of the capacitor bank interlocks and of the charging sequences. The local computer runs a multi-threaded Delphi application under Windows NT that continuously monitors the many interlock signals produced by each power module. It also monitors the serial communications link that enables the local computer to work with the main DOS-based

Vulcan control network. When receiving commands to, for example, test interlocks or to charge the high voltage power supplies, the system responds with the appropriate data or action.

Waveform Digitisation

As already implied, one significant improvement of the upgrade is in the use of multi-channel waveform digitizers. These are CAMAC modules each of which has 8 individual inputs typically digitizing at rates of 500 kHz. This allows 2 microsecond resolution which is fast enough to detect fast transient effects without generating too much data.

Each of the 15 disc amplifiers has four pairs of flashlamp cables and an earth return, with 3 Faraday rotators monitored as well. There are a total of 78 waveforms captured and analyzed per shot.

The graphs below show the type of data obtained from the waveform digitizers, demonstrating successful and unsuccessful firings of the amplifiers. The control computer is programmed to learn what a good shot is on the basis of the peak height and the full-width half-maximum (FWHM) of each signal and to report errors to the operator.

Development

Although only just commissioned, the capacitor control program will be under constant enhancement and is expected to aid troubleshooting by presenting detailed fault analysis or prediction of failure to the operators.

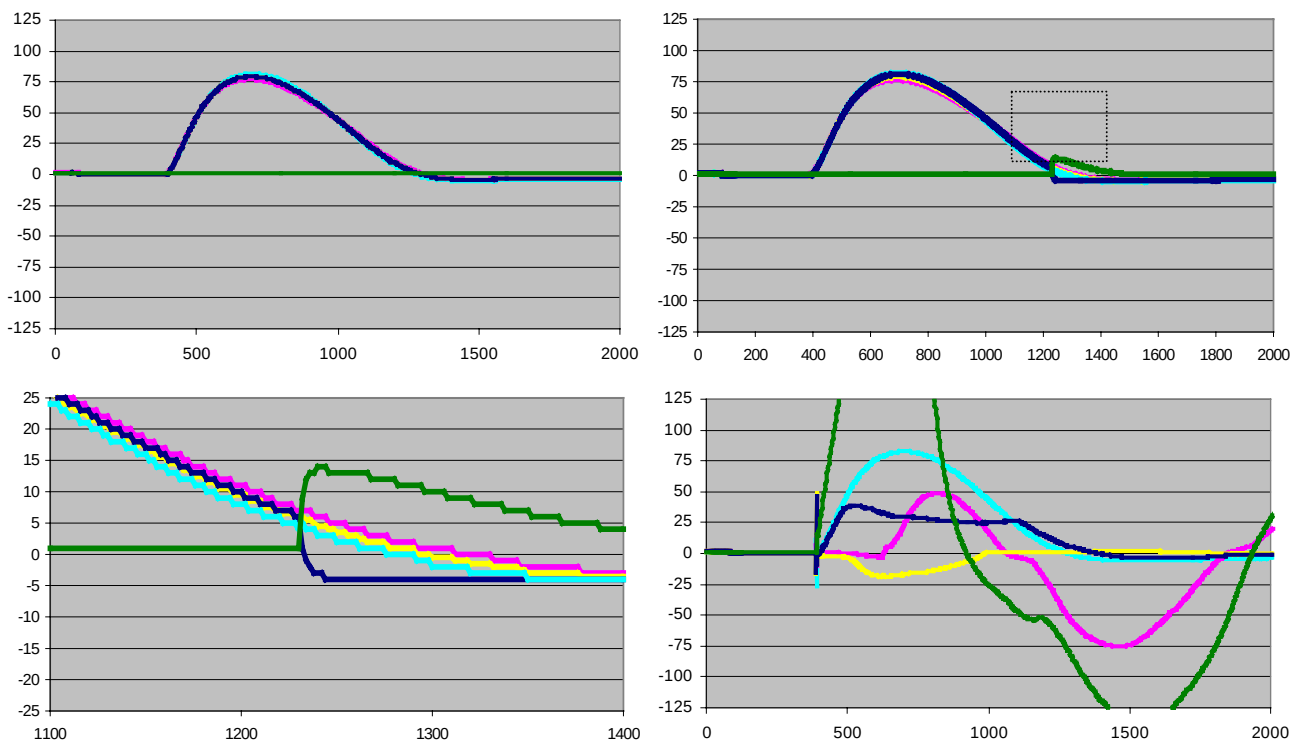


Figure 1. Graphs showing the outputs from the waveform digitizers for one of the 150 mm diameter disc amplifiers. Each disc amplifier has four flashlamps and one earth return signal, which in the diagrams above are colour coded : 1 - cyan; 2 - magenta; 3 - yellow; 4 - dark blue; earth return - green. Each graph is displaying data values in counts (y-axis) versus time in microseconds (x-axis). The top left graph shows a normal set of signals for a successful firing with a flat earth return; the top right graph shows a shot where one of the flashlamps and the earth return signal show abnormal disturbances due to a cracked lamp. This disturbance is shown in close up in the lower left graph. The lower right graph shows a shot where the amplifier had a catastrophic failure.

Adaptive optics trials on Vulcan

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Introduction

In high power lasers, such as Vulcan, large aperture adaptive optics (AO) are not only needed to correct the wavefront in order to improve their focusability, but in the Petawatt regime temporal pulse compression becomes a function of spatial wavefront quality. A large aperture dynamic wavefront corrector has been developed within the CLF for use on the Vulcan Petawatt beam line.

Experimental setup

Following the preliminary tests conducted in the Vulcan target areas, a number of improvements were made for the second round of trials, which took place in the Vulcan laser hall. These concentrated on greater quality control of optics used in the experimental setup, with all optics being better than $\lambda/8$ Peak-Valley (P-V). The local reference beam, critical for good correction, used in these trials showed a wavefront quality of $\lambda/5$ P-V.

Figure 1 details the adaptive optics trials set up in the Vulcan Laser hall. This takes Beam 7 from Vulcan and retro-reflects it with either the adaptive mirror, or a high quality reference flat. After this a beam splitter is used to generate the wavefront sensor channel and also propagates the beam to the diagnostics bench. A drop in mirror also allows the local reference beam to be injected into the setup if desired. The diagnostics used included a radial shear interferometer²⁾ for wavefront sensing, an input far-field CCD camera, a corrected far-field CCD camera, and a 16-bit far-field CCD camera.

Adaptive mirror and wavefront sensor

The adaptive mirror used in these trials is based on bi-morph

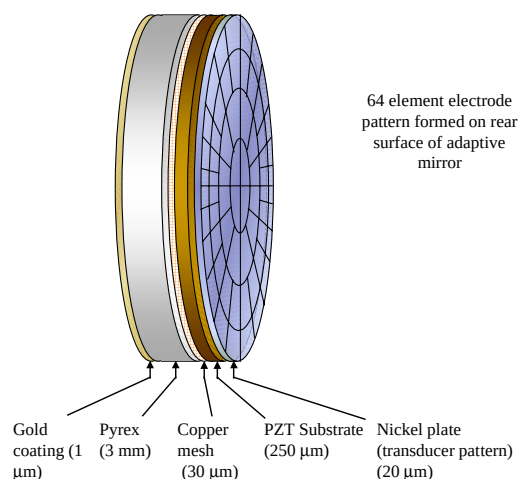


Figure 2. Bi-morph mirror architecture used in the adaptive optics trials.

technology developed in the CLF and comprises a 64-element low voltage corrective mirror, shown in Figure 2. The Bi-morph substrate is constructed from 4 separate PZT elements, glued together in quadrants to form a larger substrate.

Wavefront sensing is achieved using a Fresnel zone plate array Hartman wavefront sensor. This consists of an array of 80 amplitude Fresnel zone plates shown in Figure 3. The far-field spot locations are proportional to local wavefront gradients; hence changes in the far-field spot locations indicate changes in the wavefront gradients. The individual spot locations are

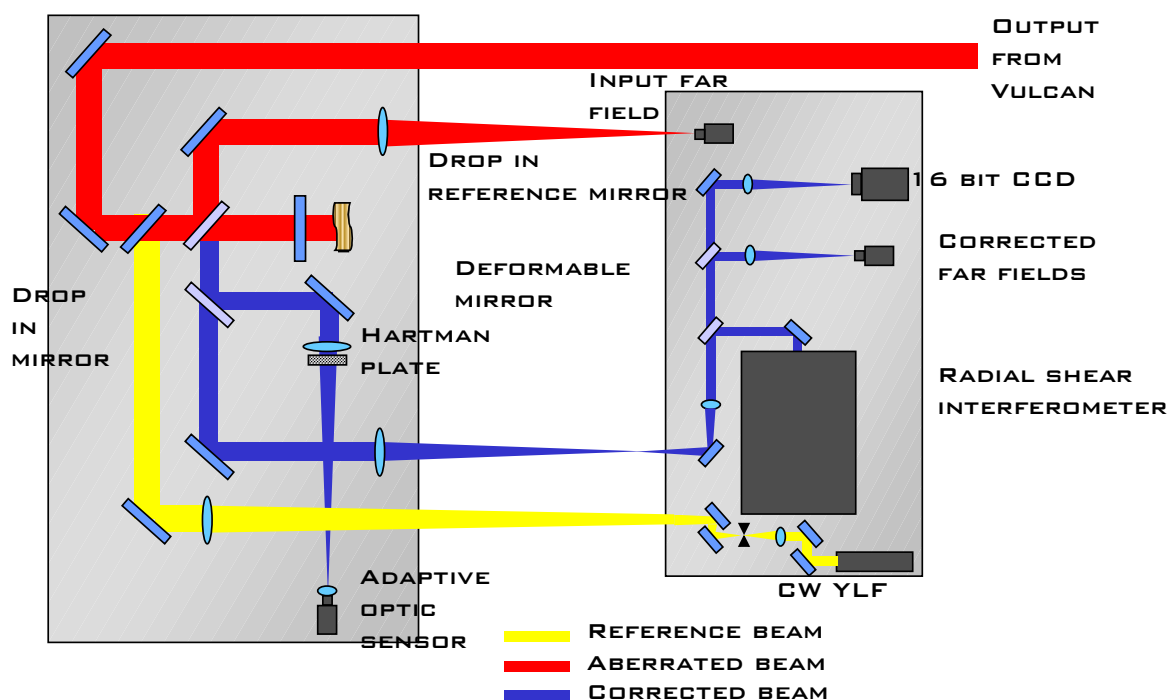


Figure 1. Experimental layout.

located to better than $1/20^{\text{th}}$ of a pixel accuracy by a centroiding algorithm in the adaptive mirror control software. The flat wavefront of the local reference beam is used to generate spot locations, shown in Figure 3, which are saved as the flat wavefront reference. The changes in the spot locations when the aberrated Vulcan beam is propagated through the Hartman sensor generate 80 'x' and 80 'y' gradients.

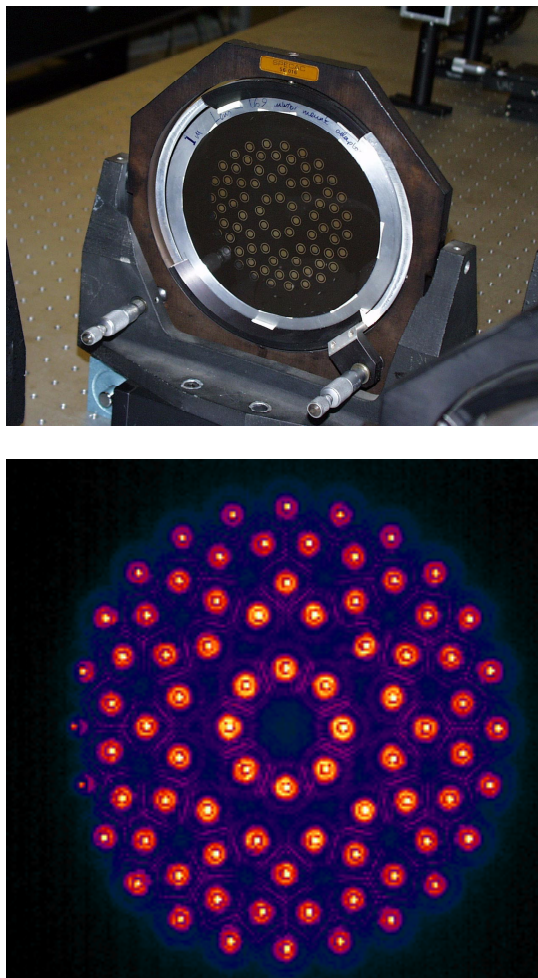


Figure 3. Hartman wavefront sensor and a typical spot pattern.

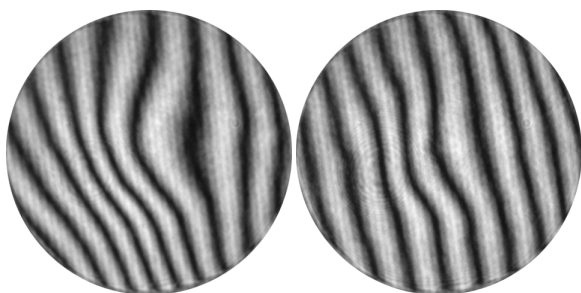


Figure 4. Interferograms showing the beam quality of the uncorrected local alignment beam (left) and after correction (right).

Computer control and program

With the local reference beam incident on the adaptive mirror a voltage is applied to each of the 64 mirror actuators in turn and the subsequent deviation of the Hartman spots is recorded. This generates a 160×64 matrix, the so-called response matrix of the mirror. Using singular value decomposition the matrix is inverted and the singular values extracted. It is a

straightforward task from this stage to obtain a control matrix in order to drive the mirror in a closed loop. Terms in the inverted matrix can be thought of as modes of the mirror, higher order terms in the matrix representing higher order modes of the adaptive mirror. In order to perform noise reduction it is possible to set the appropriate singular values to zero, effectively turning off the higher order modes of the mirror.

The aberrated Vulcan beam is then propagated onto the adaptive mirror. The control program for the adaptive mirror then applies the necessary voltage to the mirror actuators in order to move the Hartman spot positions of the aberrated beam to the positions generated from the reference beam.

Closed loop operation

In order to determine the best possible correction the adaptive mirror could obtain, the mirror was used to attempt a correction of the diffraction limited reference beam. The mirror would in effect be correcting for its own inherent aberration that Figure 4 shows to be around 1.8 waves. The second interferogram is from the mirror running closed loop correcting for this aberration. With very few aberrations present in the reference beam, the adaptive mirror can correct its 1.8 waves P-V of inherent aberration to about 0.35 waves P-V. This compares well with the 0.2 waves P-V of the reference beam. This disparity comes from the obvious central feature, which is thought to arise from the fact that the PZT substrate is not formed from a single piezo-ceramic wafer but is in fact four separate substrates glued together. The central feature was seen to increase in magnitude during the mirror trials, suggesting some deterioration in the bond between the four separate substrate elements.

Closed loop correction of a Vulcan Beam

The adaptive mirror was used to correct the 135mm clear aperture Beam 7 that was apertured to 108 mm for the purposes of these trials. Beam 7 was measured to have 1.2 waves of aberration and with the adaptive mirror run in closed loop this was corrected to 0.4 waves, as shown in Figure 5. This is close to the diffraction limit. The clarity and contrast of these interferograms is not of the same quality as those produced by the local reference beam as the Vulcan alignment laser is significantly lower in power and has a Gaussian intensity profile.

The wavefront correction by the adaptive mirror resulted in a marked improvement to the focal spot profile of beam 7 as shown in Figure 6. There is even evidence of the Airy pattern produced by a diffraction limited beam beginning to form.

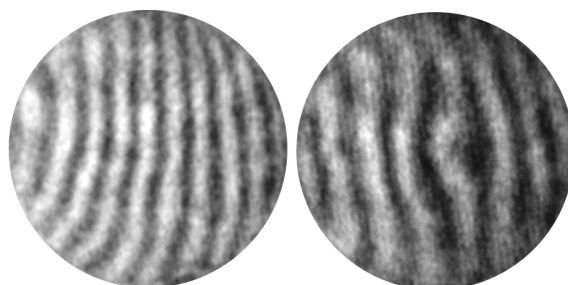


Figure 5. Interferograms showing the uncorrected Vulcan alignment laser (left) and after correction (right).

Effect of mode reduction

As mentioned previously it is possible to switch off the higher order modes of the mirror in order to reduce the amount of noise present. A series of 1000 consecutive Hartman spot patterns were recorded with different numbers of mirror modes switched on. Figures 7 and 8 show the mean pixel displacement

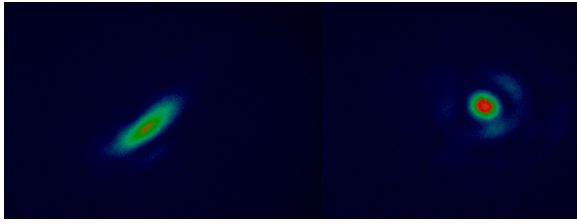


Figure 6. Beam 7 farfield images showing an uncorrected and corrected focal spot.

and pixel variance for the 5 different Hartman spot rings. Note the effect of the central feature, seen on the interferograms, on the central ring of Hartman spots. There is an optimum number of modes to use in order to make a correction. With reference to Figure 7, as more modes are introduced the mean Pixel displacement falls rapidly to a minimum value at about 20. The average pixel displacement is then seen to rise gradually, the cause of which is the introduction of more noise from the higher order modes. Figure 8 shows the pixel variance of the pixel means rising gradually as more modes are switched on.

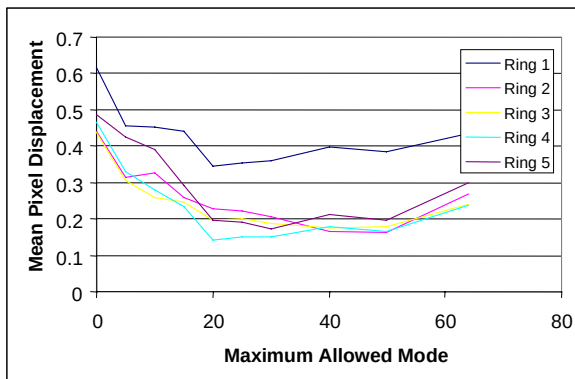


Figure 7. Mean pixel displacement.

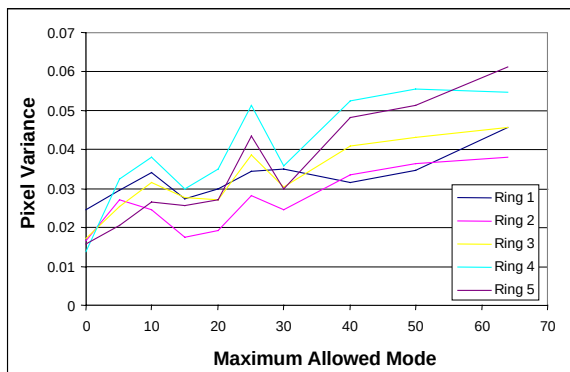


Figure 8. Variance of the mean pixel displacement.

Environmental testing

A series of environmental tests was also conducted with the adaptive mirror placed in a retro-reflective position after the beam 7 amplifier, the position it would nominally be used in the Petawatt upgrade. It is important to determine the survivability of the adaptive mirror in this electrically and magnetically hostile environment. In order to generate the maximum possible amount of noise, the entire Vulcan disc amplifier system was fired, with the adaptive optic correcting the Vulcan alignment laser. This appeared to have no impact on the effectiveness of the correction with the mirror in this position. Figure 9 shows the Vulcan alignment laser and the amplified Vulcan alignment laser, recorded when the disc amplifiers were fired. It is important to note that the far field in Figure 9 (right) is

saturated but that the performance of the mirror is in no way affected by the noise, i.e. there is no radical change to the farfield image.

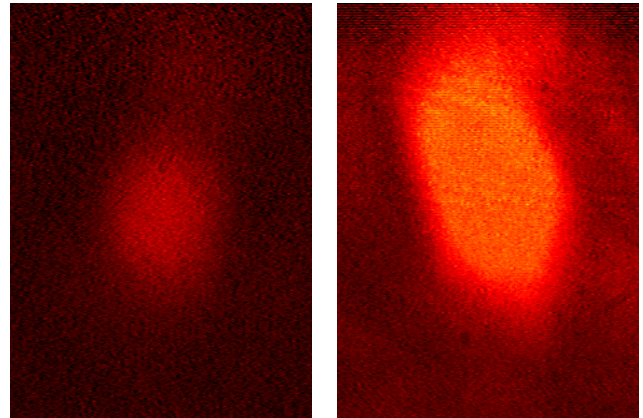


Figure 9. Beam 7 alignment laser far-field, before a disc shot (left) and on the shot (right).

Conclusions

We have demonstrated using an adaptive mirror developed within the CLF that the Vulcan beam quality can be dynamically improved to ~ 0.4 waves from ~ 1.2 waves p-v. The system has been repeatedly tested in an electrically hostile environment and proved to be unaffected.

A new mirror is currently being manufactured that will bring us close to the diffraction limit. This mirror uses a single slab of PZT to form the piezo actuators, which will in principle remove the central feature observed using the current prototype. This AO system will be installed on the Petawatt beam line.

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Scanning Third Order Autocorrelator for Contrast Measurement in Vulcan

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Introduction

A scanning cross correlator has been developed for contrast measurements in the Vulcan laser system. It is important in CPA systems to have detailed knowledge of pulse shape and contrast ratio. To measure the pulse shape of an optical signal $I(t)$ the method used is intensity third order autocorrelation $A_3(\tau)$, defined as:

$$A_3(\tau) = \frac{\int I(t - \tau) \times I^2(t) dt}{\int I(t) \times I^2(t) dt} \quad (1)$$

where τ is a delay parameter. The function $A_3(\tau)$ is asymmetric and thus it is possible to differentiate temporal activity ahead of the main pulse from temporal activity behind.

To generate this 3rd order autocorrelation function with optical signals two non-linear processes are required. The first is a process that can produce the $I^2(t)$ response to an optical signal with an intensity function $I(t)$. This can be achieved by second harmonic generation of $I(t)$. The second is a process that can produce a response that arises from the product of the two arbitrary intensity functions $I^2(t)$ and $I(t)$. Such a process is sum frequency mixing.

Layout

The autocorrelator has been designed to minimise the number of parallel surfaces which give rise to post pulses. It has also been designed to have a larger dynamic range than devices previously used to measure the contrast of the Vulcan laser ¹⁻².

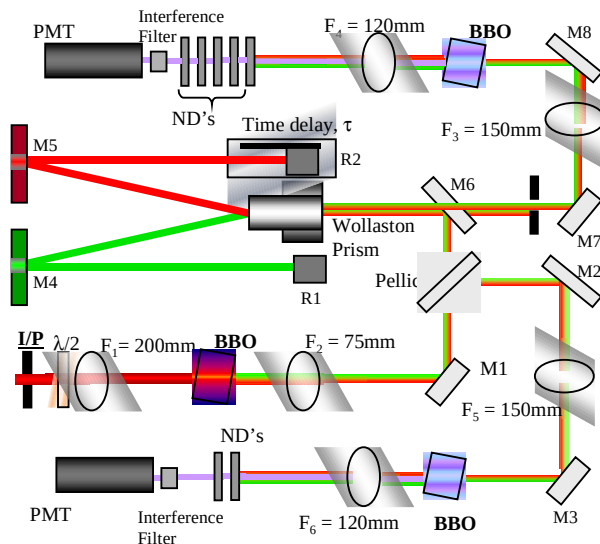


Figure 1. Schematic layout of the autocorrelator.

The layout of the autocorrelator is shown in Figure 1. It consists of two arms: the main arm and reference arm. The main arm measures the third order autocorrelation signals for different delays τ of the signal $I(t)$ i.e. the numerator in Equation (1), while the reference arm measures the 3rd order autocorrelator signal generated by the two pulses $I^2(t)$ and $I(t)$ overlapped at $\tau=0$, i.e. the denominator in Equation (1).

The input beam is focussed onto a BBO crystal to generate the initial second harmonic signal. This process is type I to ensure

that the fundamental signal and its harmonic are orthogonally polarised.

The reference arm is generated by a reflection off a pellicle as the beam is directed to the main arm. The reflected collinear pulses are then frequency mixed in a BBO crystal. The reference frequency mixed signal is then detected by a photomultiplier. An interference filter prevents the fundamental and 2nd harmonic signals reaching the photo multiplier.

In the main arm in order to impose a delay τ in the infrared pulse $I(t)$ with respect to its second harmonic $I^2(t)$ both signals are separated spatially. The collinear pulses are injected onto a Wollaston prism, which imposes an angle of $\sim 28^\circ$ between the two beams due to their orthogonal polarisation.

Once separated the fundamental pulse and its second harmonic are directed onto a pair of retro cubes. The second harmonic beam follows a fixed length path while for the infrared pulse the path can be changed on a shot to shot basis to achieve different temporal delays τ . The height of both beams is altered by the retros such that they return above the input path to the Wollaston. The Wollaston recombines the beams spatially and they are then focussed on to a BBO crystal where both signals are frequency mixed generating the autocorrelator signal. This is detected by a photomultiplier tube and an interference filter.

Characterisation

To test the diagnostic, initially the output of one of the Vulcan Front End oscillators (TiS) was examined. The result is shown in Figure 2. With a train of 150 fs pulses of 0.5 nJ, the diagnostic shows a dynamic range of 10^5 . A post pulse is clearly visible which is believed to be caused by the parallel surfaces in the input waveplate.

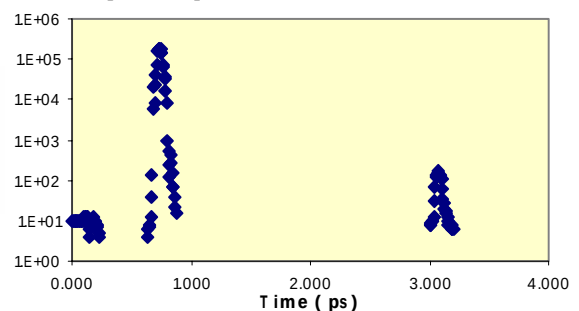


Figure 2. Contrast measurements for TiS oscillator.

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Transmissive Grating CPA System Design for the Vulcan Laser

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Introduction

Transmissive diffraction grating systems have several advantages over their reflective counterpart for high-energy laser pulse compression. They exhibit higher damage fluences, enabling more energy to be delivered to target for a given beam size, and can also be easily operated at the littrow angle, achieving maximum efficiency. This paper will show that a transmissive Chirped Pulse Amplification (CPA) system can operate optimally over pulse durations between 10 ps and 300 ps. The transmissive system proposed for Vulcan discussed in this paper will be capable of delivering up to 20 TW of power to target, and operate without the need for vacuum beam compression.

Benefits of a Transmissive Grating System

Conventional reflective CPA grating compressors are ultimately limited in their maximum energy handling abilities by the damage fluence of the grating surface. Past studies indicate that in the sub-ps to 300 ps pulse duration range, the gold-coated gratings exhibit single shot damage at $\sim 0.4 \text{ J/cm}^2$ ^{1,4,5}. The average operational fluence limit is set to around 1/3 of the single shot damage fluence threshold for safe running. This accommodates the shot to shot variations in the energy and quality of the pulse delivered, and ensures grating lifetimes of tens of thousands of shots in normal operation.

The single shot damage fluence for fused silica is ~ 10 times that of gold in the 10 ps to 300 ps regime. This is reduced slightly if anti-reflection coatings are added to the substrate to increase the total throughput efficiency of a transmissive CPA compressor.

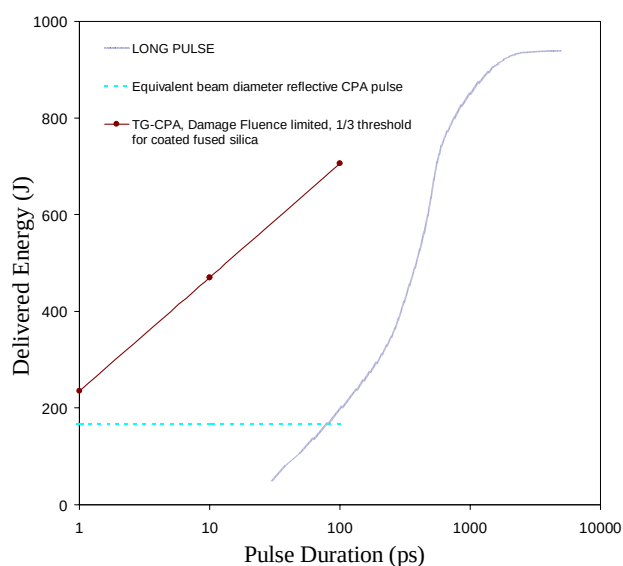


Figure 1. Deliverable energy as a function of laser pulse duration for three proposed beam lines of diameter 208 mm operating at 1053 nm.

Figure 1 gives an indication of how the deliverable energy is restricted due to the damage limits for a Transmissive Grating CPA (TG-CPA) system compared to a similar aperture (ϕ 208mm) long pulse beam line, and an equivalent reflective

CPA line. The long pulse curve is derived from operational experience and will exhibit an energy limit due to the maximum possible energy being extracted from the laser gain medium (at pulses $>1 \text{ ns}$). The central and lower sections of this curve are influenced by the B-integral damage limits for the system^{1-3,7}. Published data tells us that the damage fluence for gold-coated reflective gratings is constant up to around 100 ps pulse duration. This explains the uniform nature of the equivalent reflective CPA beam line graph. The damage fluence threshold curve for the coated transmission optics was estimated using the same published experimental data¹⁻³. Again, the intention is to operate at approximately 1/3 of this threshold fluence. The TG-CPA plot in Figure 1 indicates the damage threshold limited deliverable energy, and is independent of any beam propagation effects. Clearly, the TG-CPA line will deliver the greater amount of energy to target over a large range of pulse durations.

General Compressor Requirements

To maintain pulse fidelity it is important for any pulse recompression system to reverse the effects of the stretcher to as large an extent as possible. It is intended that Vulcan will deliver a 600 ps, 600 J chirped pulse of 2 nm bandwidth to the "Petawatt" target area.

It is essential to select a system that will not only fulfill the scientific requirements, but also fit into the target area, be viable in an engineering sense, and remain economically plausible.

The system design should contain the least possible amount of transmissive optics, keeping the B-integral to a minimum^{1,7}. Larger B-integral leads to small scale beam break-up and self focusing which can cause optical damage. It is therefore practical to suggest that the target chamber window be removed and replaced with a transmissive focusing optic, leading the beam directly to target position. Figure 2 gives a representation of how this set-up may be constructed. The transmissive gratings may simply sit on plinths with no vacuum required.

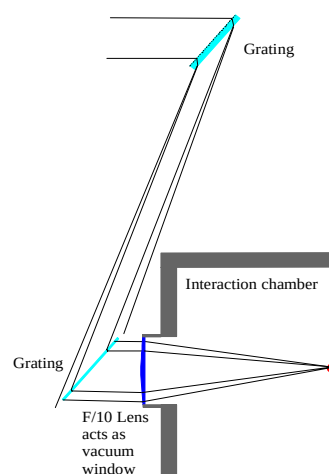


Figure 2. Target area layout diagram for the Transmissive CPA system proposed for Vulcan.

There is a large range of possible solutions for the proposed TG-CPA system. Compromises must be made between the

various parameters of grating length, line density, separation and input angle such that the most sensible design is attained.

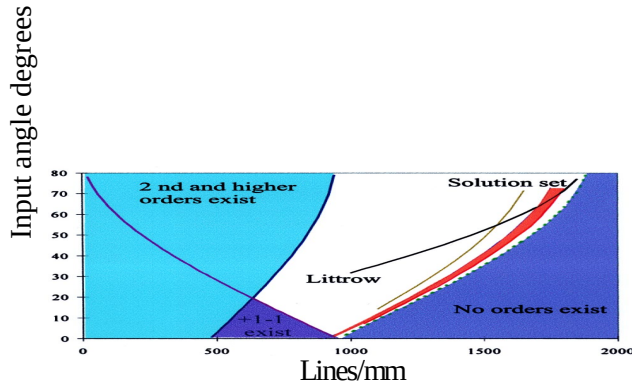


Figure 3. Available output diffraction orders as beam input angle alters over various grating line densities.

For a grating to operate at high efficiency, light should be diffracted into only one order at a time. Figure 3 shows the solution set for the existence of output diffraction orders as the input beam angle is varied as a function of grating line density for a 1053 nm beam. The region of potential high efficiency is shown in Figure 3 as the white unshaded area where only the desired first order will exist. The Littrow curve shows the solution set within this parameter range along which maximum transmissive diffraction efficiency will occur in relation to the grating line density used. The maximum diffraction efficiency for a grating with a symmetrical groove profile occurs when the Bragg conditions are satisfied. The transmissive system can easily operate under this condition thus delivering the highest possible diffraction efficiencies. Ideally, the system would operate at the intersection of the Littrow curve and the desired compression solution set. Figure 3 also includes various solution sets to show the line followed by a constant arbitrary compression rate.

Higher grating line densities essentially give larger spectral dispersion. This means that the grating separation can be smaller to give the same pulse compression value. It is this increased dispersion however, along with an increased footprint due to a larger Littrow input angle, that forces the grating length to increase. The length of the second grating must be sufficient to accommodate the footprint of a 208 mm input beam diameter at Littrow, and the spectral divergence of the first grating, at the line densities available. The useful standard line densities available are 1330, 1480, 1550 and 1740 lines/mm. A system that uses grating line densities under 1330 lines/mm will exhibit an excessively large grating separation, and any grating with over 1740 lines/mm becomes both expensive and difficult to produce. Table 1 shows the results of a geometrically modelled CPA compressor system to preserve the optimum compression of the 600ps chirped pulse from a matching stretcher.

Line density L/mm	Input angle degrees	Beam deviation degrees	Grating separation m	Fractional beam spread cm
1330	44	91	25	0.27
1480	51	78	15	0.22
1550	55	71	12	0.20
1740	66	47	5	0.17

Table 1. Geometrically modelled parameters required for a transmissive CPA system to achieve a compression of 600ps with a 2nm bandwidth, operating at the Littrow input angle, with a 208 mm diameter input beam.

Grating parallelism

It is essential to ensure parallelism between the two compression gratings to deliver optimum focusability and compressibility of the output pulse. Any non-parallelism will induce a wavefront spectral divergence anomaly in the pulse due to the residual dispersion of the laser light.

The Vulcan laser system has a number of wavelengths that can be utilized to monitor grating parallelism. These wavelengths are injected into the system and the gratings optimized until any spectral dispersion between the beams is eliminated. These injected wavelengths lie at 1047 nm and 1053 nm (dichroic Nd:YLF oscillator), and 1064 nm (Nd:YAG oscillator). At a suitable incident angle onto the first grating, these wavelengths will fill or partially fill the second of the two transmissive gratings. The extent to which they fill the second grating will determine the effective aperture with which the specific wavelength is then incident onto the focusing optic, (see Figures 2 and 4). This in turn will affect the full width half maximum (FWHM) of the resulting focal spot.

System modeling demonstrates that the 1064 nm beam will deviate from the Vulcan central wavelength of 1053 nm by such an amount as to totally miss the second grating on all four of the initially proposed grating systems. Thus, the alignment system will be limited to the use of the 1047 nm, λ_s and 1053 nm, λ_L wavelengths of the Nd:YLF when adjusting for non-parallelism.

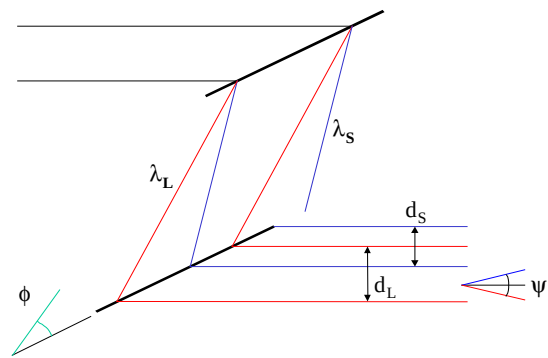


Figure 4. Extent of second transmissive grating fill at the two incremental wavelengths. ϕ represents the angular non-parallelism between the two transmissive gratings.

The maximum recompression grating misalignment error that can be permitted before seriously affecting the output angular divergence, ψ and thus, intensity in the focal plane, is assigned the term $\phi_m^{1,6}$. For an m times diffraction limited beam of spectral bandwidth $\Delta\lambda_B$ (using n th order of diffraction), ϕ_m can be approximated to the first order using the following expression:

$$\phi_m \approx \frac{m\lambda}{\Delta\lambda_B n p \tan \theta_0} \quad (1)$$

θ_0 is the resultant output angle from the first (input) grating. L and p represent the second (output) grating parameters of grating length (m), and grating period (lines/m) respectively.

The modelled data shown in Table 2 gives an indication of the tolerances associated with the setup and alignment of a transmissive compressor system, with respect to the grating line density used. The intrinsic divergence of the Vulcan beam is ~ 20 prads. Table 2 reveals that the maximum angular divergence of the 2nm bandwidth produced in alignment, ξ , has a negligible effect on the overall output beam divergence.

Optimum Compressor Design and Geometry

The line density of the gratings will determine many of the physical characteristics of the compressor system. As the line density increases the gratings operate at large incidence angles. Longer gratings are therefore required to accommodate the

beam. However, as Table 1 shows the separation between the gratings required to achieve a given pulse compression reduces as the line density increases. Also, the beam smoothing effect due to spectral dispersion on the second grating is largest for lower line density gratings. This can help minimize self-focusing effects in the final optics of the system.

Line density l/mm	Input grating length cm	Final grating length cm	ϕ_m mrads	ξ μ rads
1330	35	48	2.01	7.3
1480	40	51	0.89	5.2
1550	43	55	0.63	4.8
1740	62	72	0.20	4.0

Table 2. Table of theoretical tolerance values in non-parallelism for each compressor grating period studied. ξ is the maximum angular divergence of the 2 nm bandwidth output beam of Vulcan after the gratings are aligned, due to residual dispersion.

A survey of the Vulcan upgrade target area indicates that for the system to fit into the available space no more than 12m is permissible between the gratings. The 1740 lines/mm diffraction grating compressor system requires only 5m to obtain the correct pulse compression. However, 72 cm long grating substrates are required and manufacturing efficient high line density transmission gratings is more complex. As Table 1 indicates, the 1550 lines/mm grating system would satisfy the grating separation criteria (11.9m) with the grating length of only 54 cm.

To obtain maximum recompression of the laser pulse the compressor grating setup should 'match' the stretcher configuration exactly in terms of grating line density, input angle and grating separation. This is only true however if the shortest attainable pulse lengths are required. To operate in the desired 10-300 ps regime it is necessary to 'de-tune' the system away from maximum pulse compression. Reducing the grating separation of the compressor, or stretcher to suit can do this. It was found that it is possible to run a compressor system with grating periods differing from the stretcher. In the case of a 1480 lines/mm stretcher in conjunction with a 1550 lines/mm compressor, the recompressed pulse will exhibit a slight non-linear variation in pulse duration over the 2nm bandwidth present. This amounts to a temporal defect of ~ 0.45 ps (see Figure 5). When operating in the 10-300 ps pulse duration range this value can be seen to be negligible. The implication of this is of economic benefit, since the 1480 lines/mm stretcher gratings that are already available to Vulcan can be used in conjunction with the proposed 1550 lines/mm compressor gratings.

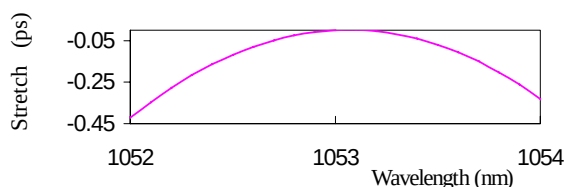


Figure 5. Graph showing the residual stretch between a 1480 lines/mm stretcher (51.2 degrees incident angle, 15.20 m separation) and a 1550 lines/mm compressor (54.7 degrees incident angle, 11.78 m separation).

Using the calculated efficiency of the grating (85% into desired order), the maximum deliverable energy for the TG-CPA system will be 420J (see Figure 6). It is considered that the maximum B-integral which could be tolerated before optical damage due to self focusing or beam breakup in the focal plane at this energy, will limit the system to $6 < B < 12$. The operating

curves (dashed curves) corresponding to $B=6$ and $B=12$ are shown on Figure 6. The marked solid line on Figure 6 shows the estimated damage fluence limits for the gratings. The flat portion of these lines is determined by the maximum deliverable energy of the 208 mm beam line for a 600 ps pulse. Clearly, the performance of the system will be restricted at the shorter pulse durations in the 10-300 ps range by self-focusing damage mechanisms rather than average fluence effects.

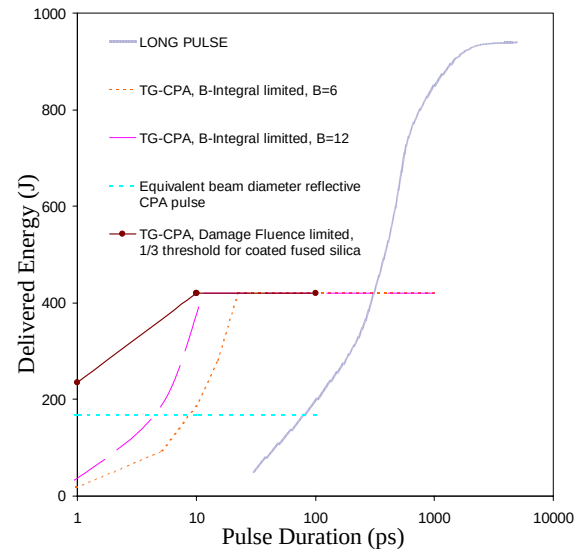


Figure 6. Deliverable energy as a function of laser pulse duration for three proposed beam lines of diameter 208 mm operating at 1053 nm. The TG-CPA plot indicates 3 variations: one theoretical damage (due to average fluence effects) threshold line, and two forecasted deliverable lines limited by damage due to self focusing at B-integrals of 6 and 12.

Conclusions

It is clear that a transmissive grating chirped pulse amplification system can efficiently deliver multi terrawatt beams to target, in the 10-300ps pulse duration range. The proposed design relies on compressing a pulse in air and then using the final focusing optic as the air/vacuum interface. The deliverable energy is ultimately limited by self focusing damage within the fused silica substrates of the final compressor grating and focusing optic. The maximum deliverable power at $B = 6$ is 20 TW at 20 ps and 1.4 TW at 300 ps. A B-integral of 12 can be tolerated before the self focusing damage mechanisms are replaced by the average fluence effects of the pulse (at the shorter pulse lengths) as the limiting threshold factor. Up to 40 TW at 10 ps can be achieved at a B-integral of 12, providing that the focal spot degradation can be tolerated.

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New Vulcan Cleanroom Complex

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The Vulcan Upgrade project established the clean-room facility within R2 for the purposes of handling and testing large aperture optics up to 1 m in diameter. The facility had a delivery area, storage area, clean handling area with class 100 cleanhoods and access to the Interferometer area with the 300 mm aperture Fizeau Interferometer¹⁾. The facility was alongside the capacitor test bank which was used to test the halfshells and completed amplifiers off-line.

At this time the clean-room complex was spread across two buildings with three non-interconnected sites. The rod amplifier assembly area was always designed to be stand-alone. However with the testing of the halfshells and disc amplifiers taking place in R2 this meant the amplifiers crossing between buildings on a regular basis as part of the assembly procedure. Following a short feasibility study it was seen that with a relatively modest investment it would be possible to reduce this to one journey between buildings.

The assembly and testing of disc amplifiers became a much smoother operation with the amplifier testing nearby. The parts for the amplifier were cleaned in the pre-clean class 10,000 area before being cleaned in the high pressure spraybooth. These clean items were then assembled in the class 100 area before moving into the amplifier test area.

The filtration systems needed to be upgraded in order to ensure that the areas were class 10,000 compatible and also to provide a positive pressure to ensure that any particulate matter was forced away when the clean-room doors were opened. This was achieved by fitting four recirculating HEPA filter units into the roof of the clean-room. Two additional HEPA filter units were fitted into the clean-room ceiling taking air from outside the clean-room complex to produce a positive pressure within. The air conditioning was also upgraded to counteract the increased heat input.

The high pressure water spraybooth^{2,3)} has been commissioned in R2 ensuring a high cleanliness route for mechanical

assembly of the disc amplifiers. The pumping system was upgraded, as it became increasingly difficult to find spares for the old diaphragm type pump. After an extensive search a supplier⁴⁾ was found of ceramic piston pumps which were compatible with the pressure requirements of 1000 psi at the spraybooth and also with the cleanliness specification.

The clean-room move brought the relocation of the high pressure water spray booth, used for the cleaning of most components within the disc amplifiers, to R2 and in the process the upgrading of the high pressure pump. The optics handling hoods have been slightly adapted to suit both their original purpose and act as a clean assembly facility. A class 100 cross flow clean hood has also been appended to the clean handling area to provide an environment for cleaning and assembly of the 108 phosphate discs assemblies. A second cross flow hood was installed in the preparation area for the handling of flashlamps and disc protection plates.

The whole clean-room complex under one roof has enabled us to streamline the clean-room processes and ensure a more efficient amplifier building programme. The clean-room move has also enabled the Vulcan Oscillator to expand to fit all the existing oscillators under one roof and to incorporate the upgrade stretcher.

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Figure 1. Robert Wellstood cleaning an amplifier chassis in the new cleanroom complex.

A Four-channel Beam Diagnostic System for Vulcan

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Introduction

Diagnostics for the Vulcan Petawatt upgrade would require customized data acquisition and analysis systems. This article describes an image capture system that would include diagnostics for laser beam analysis. It was decided to capture all images using a separate framestore board for each camera. It was found that the bandwidth of the PCI expansion ports on a standard computer's motherboard could only support a maximum of four framestore boards.

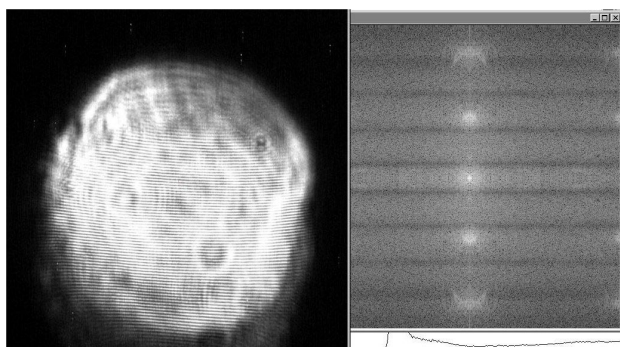


Figure 1. Beam image and 2D Fast Fourier Transform.

The system consists primarily of two programs that work together to create an integrated image capture system. Two or more networked computers, one acting as a server (Central Diagnostic, CD) and one or more acting as image capture clients (Diagnostic Workstation, DW), exchange a stream of control and feedback information via TCP/IP. This system enables a degree of control of the client(s) via a remote workstation. The DW can operate as a standalone image capture and diagnostic system under operator control.

Certain types of information produced by the Image Diagnostic program can be saved and depending on the type of data these items are saved in different ways. Supported formats are ASCII, RAW and 24-bit bitmap.

A three-dimensional plot of the image can be displayed. The mouse provides complete three dimensional control; panning, zooming and rotation using a combination of mouse buttons. A colour table can also be applied in a variety of different ways. During rotating/panning/zooming the display reduces in detail to allow for smooth movement and increases the detail once the movement has taken place.

Intensity Histogram – a histogram is produced of the intensities. The number of pixels of the same intensity are counted and displayed in a plot.

Zoom – produces a new window with zoom centred on the mouse position over the image being analysed. Different zoom levels (x2, x3, and x5) are available through the context sensitive menu.

Crosshairs – displays crosshairs with the centre at the mouse position.

Centroid – can be used to recalculate and/or display the centroid position on the selected image. If the calculated centroid is obviously not the centre of the image (this could be due to excess noise within the image) then the user can define a centroid for the image. This is important, since when the centroid is skewed, possibly due to large amounts of noise,

certain functions, integration and encircled intensity will produce invalid results.

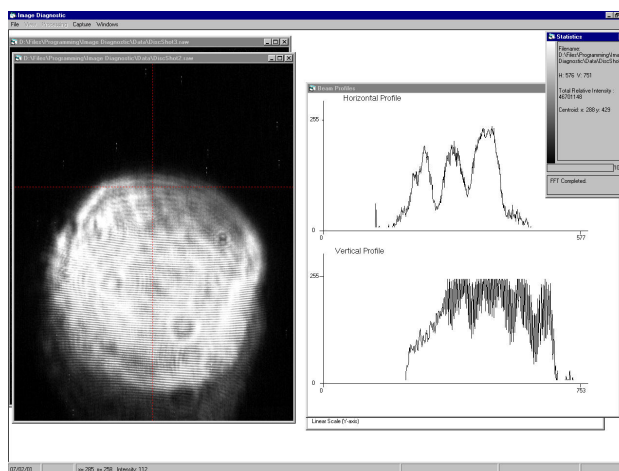


Figure 2. Beam image and image profiles.

Image Processing Options

Background Noise Subtraction – reduces the background noise and can be used in conjunction with Enhance Contrast to give a better indication of image. This is a simple algorithm that takes a sample from each corner of the image and uses this to calculate the average background noise.

Invert – inverts the colours and/or intensities of the image.

Colour Table – used to apply a look up table to the selected image.

Enhance Contrast – finds the maximum intensity and calculates a scale factor that is used to increase that intensity up to 255. This process of normalisation is applied to all pixels.

1D Fast Fourier Transform – This feature allows the user to perform an FFT on an image profile. Feedback on the selected area is given by two bars that specify a 512 region positioned using the mouse.

2D Fast Fourier Transform – FFT can be used in beam analysis to assist in the identification of different spatial frequencies. When this feature is selected a 512 by 512 selection box appears centred on the mouse pointer. The user then selects the area that is to be transformed. Performing a 2D FFT is simply a matter of transforming all the rows and then all the columns including the result of the transformed rows. This is done by repeated calling of the algorithm mentioned above.

There are three types of integration available within the program – linear, radial and annular, where necessary calculated on a sub-pixel level.

Gaussian Fit – Fitting a gaussian to the data points and using the generated data to find the FWHM is an efficient way of obtaining the FWHM of a gaussian beam. This was implemented using brute force optimization and linear regression.

Capture Functions

Up to four framestore boards can be supported with one display, shown in separate windows. To make control of these windows faster and more convenient context sensitive (right click) menus

are available for all functions. Any functions applied in this way or by using the menu system apply only to the selected window.

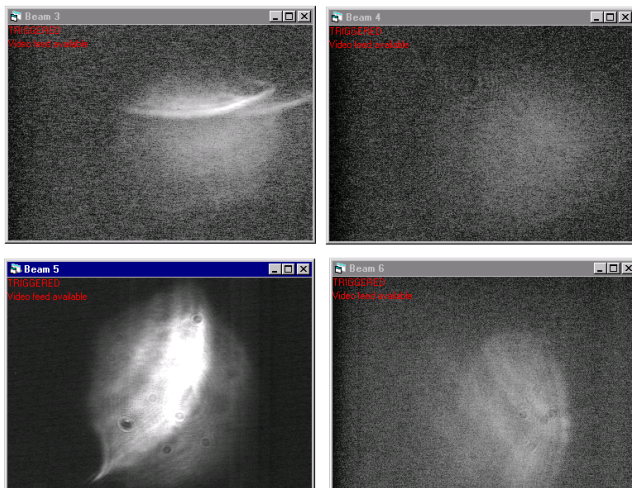


Figure 3. Four beam image display.

- Each framestore has the following functions available:
- *Arm*. A framestore can be made to capture an image upon an external signal or trigger.
- *Grab*. Captures the frame of the current input signal as soon as the function is activated.
- *Live*. Provides constant video feed direct to the display. Clearly four live video feeds direct to host video memory will put a strain upon the PCI bus.
- *Disarm*. Stops the current process of live/arm/grab.
- *Analyse*. Opens the currently displayed image in an analysis window.

In each display window there is feedback indicating the status of the video feed and the current state the framestore is in. For example 'ARM' indicates that the framestore is armed and 'TRIGGERED' indicates that the framestore has been triggered.

Networked Operation - Diagnostic Server Program

The server program allows for a practically unlimited number of Diagnostic Workstations, configured as clients (using TCP/IP), to connect and receive control instructions.

Automatic connection to control server – to enable automated functioning, the image diagnostic workstations will attempt to connect to a user specified server. If connection fails, the client will retry within a user specified retry time. If the client is

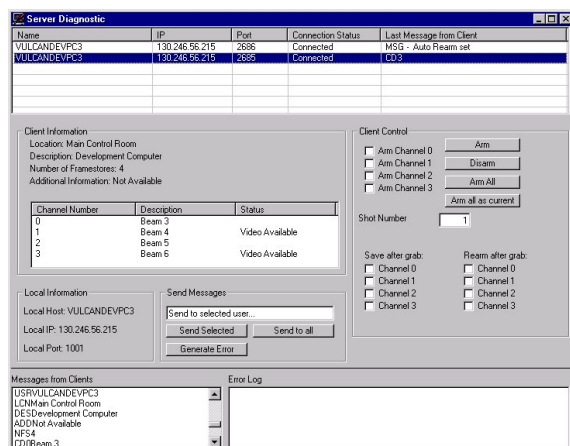


Figure 4. Networked operation.

disconnected then it will attempt to reconnect automatically.

Automatic reconnect can be disabled if the workstation is being used in standalone mode. For its application in Vulcan it is essential that the workstations be connected to the server before capture can take place.

All data must be stored on a remote server thus giving the entire CLF access to this information. In each experiment period a total of 600Mb of information will be generated. To ensure that this data can be easily interrogated a meaningful filename system was adopted. When an experimental period is over the generated data will be written to a CDR and distributed to the users.

Transmit and receive a variety of three character instruction and information messages – The messages consist of an operator and an operand, the operator defines the type of message and the operand contains the information required to complete that process.

Once connected the client sends a variety of information to the user, including computer name, workstation location and description, description of all four cameras, number of cameras available and camera status (video available/unavailable).

These options are specified by the user in the Preferences window within the client.

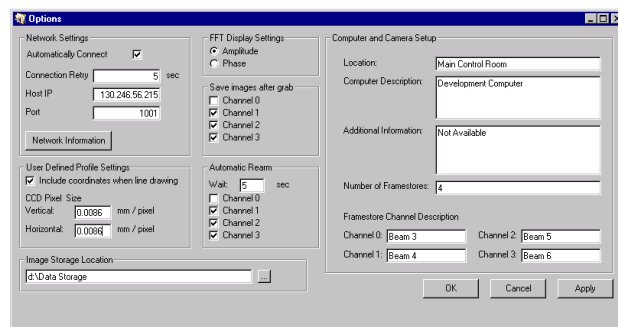


Figure 5. Preferences screen.

Other options include:

- *FFT Display Settings* - Amplitude or phase, the display type of 1D FFT information.
- *Include co-ordinates* when line drawing, indicates the co-ordinates of mouse when defining a user image profile.
- *CCD definition* - number of pixels/mm, used for calibration in determining a distance measured.

Computer and Camera Setup; primarily for the information of the person operating the server:

- *Location*
- *Computer Description*
- *Number of Framestores*
- *Framestore channel description* for channels 0 – 3, a description of each framestore/camera.
- *Image Storage Location*, where the program automatically saves the captured images.
- *Automatic rearm*, selectable for each board, allows automatic rearming after a trigger signal has been received.
- *Automatic save*, selectable for each board and specifies whether captured images should be saved after the grab.

Axial Line-Focus With A Binary-Phase Fresnel Zone Plate

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Introduction

Traditional methods to generate a line-focus along the axis of an optical system have centred on the use of axicons¹⁾. However, these devices are relatively expensive in large aperture beamlines (> 100 mm diameter), they do not produce uniform intensity along the line focus and they have a fixed focal length, limiting their use to a particular configuration. These limitations can be overcome by the use of binary phase diffractive optics that can be produced in large aperture, quickly and cheaply. We propose a novel design of a binary phase Fresnel zone plate²⁾ that uses an azimuthal variation in focal length to achieve the desired focal intensity distribution for use with a high power Nd:glass laser system.

First Principles

A Fresnel zone plate can be thought of geometrically as a lens with a focal length $\pm F_Z$. This is related to the wavelength of light (λ), the radius R_O of the central zone and the refractive index n , as given in formula (1).

It is clear then that the focal length can be changed by modifying the radius of the zone and it follows that an axial line focus can be generated by a continual change in the radius of the zone structure as one sweeps around the plate. A Fresnel zone structure of this design is depicted in Figure 1a below with almost a 40:1 variation in focal length. Figure 1b and 1c show the normal circular Fresnel zone plate structure for two different focal lengths.

Experimental Design

The application of this technique is in the generation of an on-axis line focus for plasma physics experiments. The plate was designed to be used in conjunction with a conventional lens with a 700 mm focal length (F_P), to generate a 10 mm long line

focus from a 10 cm diameter beam, using 526.5 nm laser light.

The basis for the design was to work out the range required for F_Z using the simple lens formula (2), noting that the positive order diffraction results in a line inside the principal focal plane and the negative order diffraction produces a line beyond the principal focal. Effectively then, to produce a 10 mm line focus, one requires L_L (the line length) to be 5 mm either side of the principal focal plane (making F_C equal to 700 ± 5 mm). Using these values in formula (3), F_Z is found to be around ± 97 m.

This is the minimum value of F_Z which used on its own would produce focal spots at ± 5 mm from the principal focal plane. Longer focal lengths then contribute to the axial line focus but to get to the principal plane one requires an infinite focal length! However, because of manufacturing tolerances with

$$F_Z = \pm \frac{1}{n} \left(\frac{R_o^2}{\lambda} - \frac{\lambda}{4} \right) \quad (1)$$

$$\frac{1}{F_C} = \frac{1}{F_Z} + \frac{1}{F_P} \quad (2)$$

$$F_Z = \left(\frac{1}{F_C} - \frac{1}{F_P} \right)^{-1} \quad (3)$$

$$F_C = F_P - L_S - L_L * P \quad (4)$$

$$R_O \approx \sqrt{\lambda F_Z} \quad (5)$$

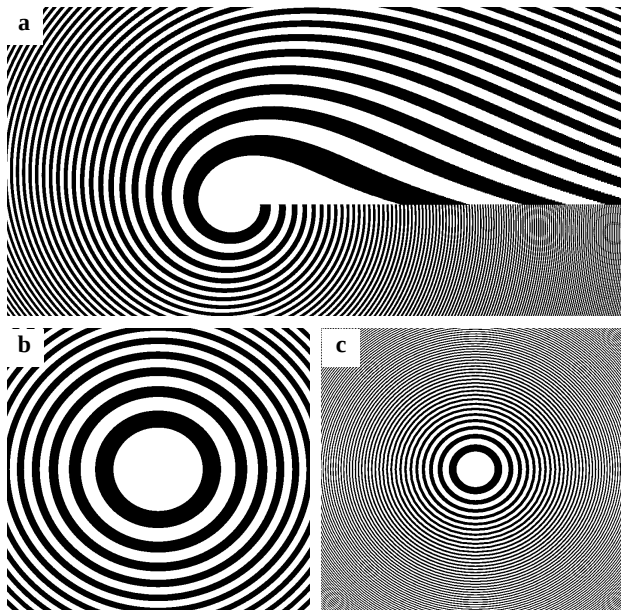


Figure 1. Fresnel zone plate structures showing:- **a)** the modified Fresnel zone structure with a continual variation of F_Z between ~ 2 m and ~ 90 m. (Arbitrary scaling). **b)** a standard plate with circular rings giving a $F_Z \sim 6$ m. **c)** a standard plate with $F_Z \sim 1$ m.

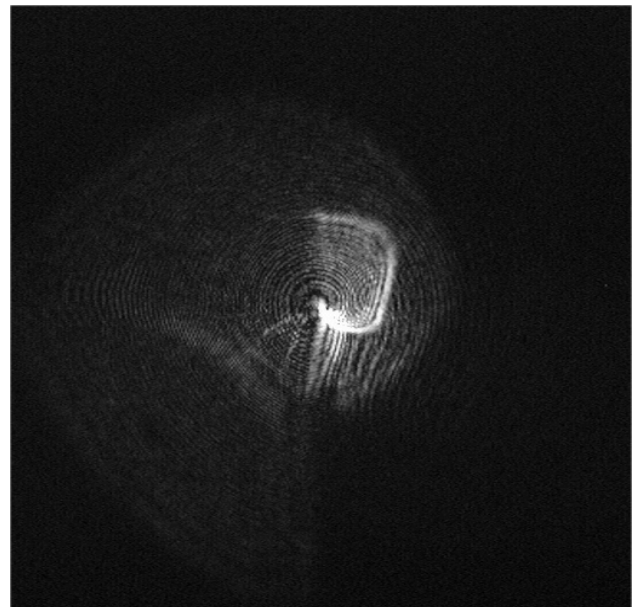


Figure 2. Image taken along the length of the axial focus, using the modified Fresnel zone design of Figure 1a, showing the high intensity cusp surrounding the central "spot".

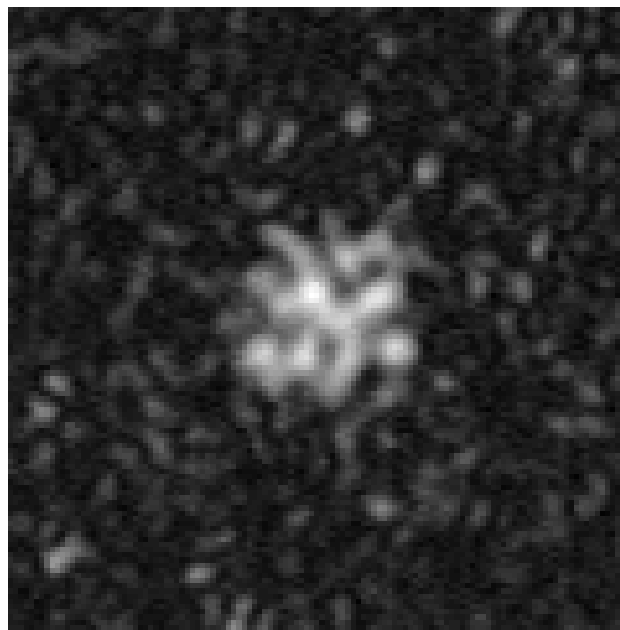
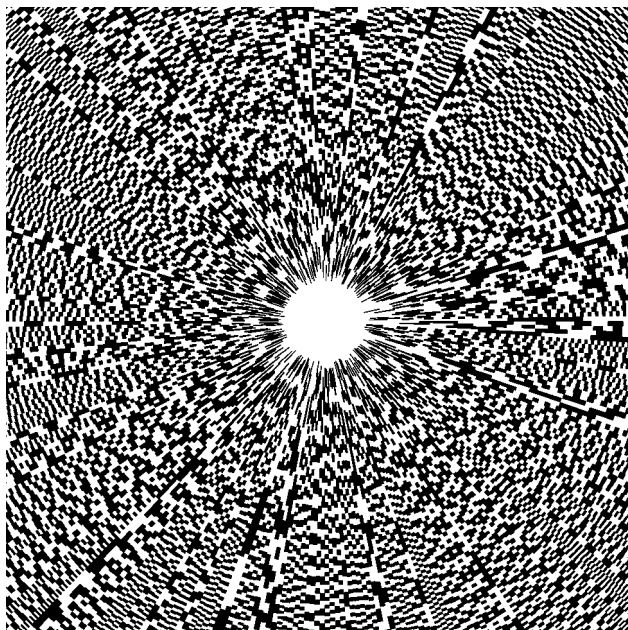


Figure 3. Left) Section of the Fresnel zone plate design with randomized focal lengths covering the range $F_z = 97$ m to $F_z = 2000$ m. Right) A $175\ \mu\text{m}$ square image of the “focal spot” taken along the axial line focus.

binary phase devices³⁾ there is often some residual zero order leakage which in this case is useful in filling in the very centre of the line focus. By choosing L_S , the line segment start, at say, $250\ \mu\text{m}$ from the principal plane (F_C is then equal to $700\ \text{mm} \pm 250\ \mu\text{m}$), the maximum F_z is found to be around 2000 m. These minimum and maximum F_z values translate into radii of $7.15\ \text{mm}$ and $32.45\ \text{mm}$ respectively.

The radius of the zone plate was then swept between these two extremes, taking into account the non-linearity of the lens equation, so as to produce an even intensity along the line focus. This was achieved by coding a ‘focal position’ parameter P to have the value 0 to 1 as one sweeps around the plate and as one traverses along the line focus; 0 at L_S ; 1 at L_L . The P parameter was then used to calculate the actual focal position F_C along the line according to formula (4) and the effective F_z from formula (3). Finally this value of F_z enabled the radius of the zone to be obtained from substitution into (5).

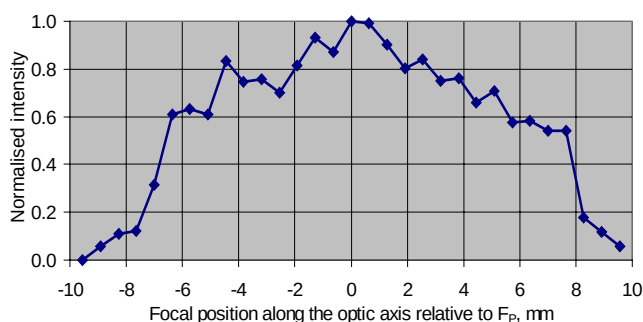


Figure 4. Graph showing the focal spot intensity (normalized at the principal focal plane, F_p) along the optic axis ± 10 mm relative to F_p . Data obtained using the randomized focal length design depicted in Figure 3.

Although the plate manufactured using these parameters did produce a line focus, as one traversed along the axis, there was

a problem. The focal “spot” is effectively a result of the whole beam collapsing from a 2D plane into the 3D optic axis and a cusp of focused light was seen swirling around the optic axis. This is demonstrated in Figure 2. The image was computer enhanced for display purposes but contained sufficient intensity around the axis that it would have made the experiment impossible. So, the design was modified in an attempt to break up this structure.

This was achieved by using a random transition instead of the smooth transition in focal length as one sweeps around the plate. The same extremes of F_z were used but each 1.5° segment has a randomised focal length.

Results

Figure 3 shows (left) a section of the final design along with (right) a typical “focal spot” obtained along the optic axis. The optical setup for testing used a $1\ \text{m}$ lens rather than the design requirement of $700\ \text{mm}$, giving a speckle pattern of around $6\ \mu\text{m}$. The FWHM of the spot is typically $30 - 40\ \mu\text{m}$ and the randomization effect has removed the cusp feature. The intensity on axis was measured and is shown in Figure 4. Clearly the axial line focus is present and as it scales with the focal length of the principal lens, it is of a length consistent with theory.

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The PIRATE Development

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Introduction

The Picosecond Infrared Absorption and Transient Excitation (PIRATE) facility at the Rutherford Appleton Laboratory brings together novel laser technology and expertise in time-resolved infrared (TRIR) spectroscopy. The laser system uses recent developments in non-linear optical materials to generate wavelengths into the mid-infrared ‘fingerprint’ region (1000 to 3000 cm^{-1}). The Ultrafast Spectroscopy Laboratory now has independently tunable light sources ($200\text{ nm} - 10\text{ }\mu\text{m}$) for pump and probe spectroscopy such as transient absorption (both infrared and visible), fluorescence and resonance Raman spectroscopy^{1,2}, with picosecond time resolution. This provides a unique combination of techniques for studying the energy relaxation, structure and reactivity of short-lived (picosecond) intermediates formed during a chemical reaction in the solution phase.

Two output configurations are possible for the PIRATE laser, either broadband 150 - 200 cm^{-1} femtosecond pulses for spectrally dispersed time resolved infrared spectroscopy or narrowband 25 cm^{-1} picosecond pulses for experiments pumping/probing specific IR active modes.

Description

The layout of the Ultrafast Spectroscopy Laboratory OPA system is shown in Figure 1. The pump laser is a Ti:sapphire regenerative amplifier operating at 1 kHz repetition rate, at *ca.* 800 nm , with an energy of 2 - 3 mJ per pulse. The regenerative amplifier is seeded by a $\sim 100\text{ fs}$ pulse from a

mode-locked Ti:sapphire laser. Spectral filtering of the seed beam produces output of *ca.* 1 to 3 ps (FWHM) pulse duration and *ca.* 15 cm^{-1} to 7 cm^{-1} bandwidth respectively. An optional femtosecond stretcher/compressor arrangement provides an output of 150 fs and $\sim 100\text{ cm}^{-1}$ bandwidth. In the picosecond mode the pulse is frequency doubled and split in order to pump two optical parametric amplifiers. Spectral filtering delivers 1 ps pulses with $\sim 35\text{ cm}^{-1}$ bandwidth (or optionally 2 - 3 ps with 10 - 15 cm^{-1} bandwidth) with pulse energies of $\sim 10\text{ }\mu\text{J}$ across the tuning range of $470 - 700\text{ nm}$ (signal). Combined with upconversion and including the idler tunability, the overall tuning range is $205 - 2800\text{ nm}$. A general description of the system can be found in Reference 1.

The PIRATE mid IR outputs are generated by frequency down conversion of the signal and idler outputs of an 800 nm pumped OPA in silver gallium sulphide (AgGaS_2). For high brightness narrow linewidth ($\sim 25\text{ cm}^{-1}$) mid IR light the picosecond mode of the pump laser is used. Spectrally dispersed time resolved IR spectroscopy uses the femtosecond mode to generate the broadband ($\sim 150\text{ cm}^{-1}$) mid IR probe beam. This OPA is similar in design to that described by Hamm et al.².

The full tuning range and approximate energy performance of the PIRATE system is illustrated at the bottom of Figure 1.

The Time Resolved IR (TRIR) system

TRIR directly probes the vibrations of molecules in a sample where a pump beam initiates a photochemical or photophysical process. A $<1\text{ ps}$ snap shot (probe) of the progress of the

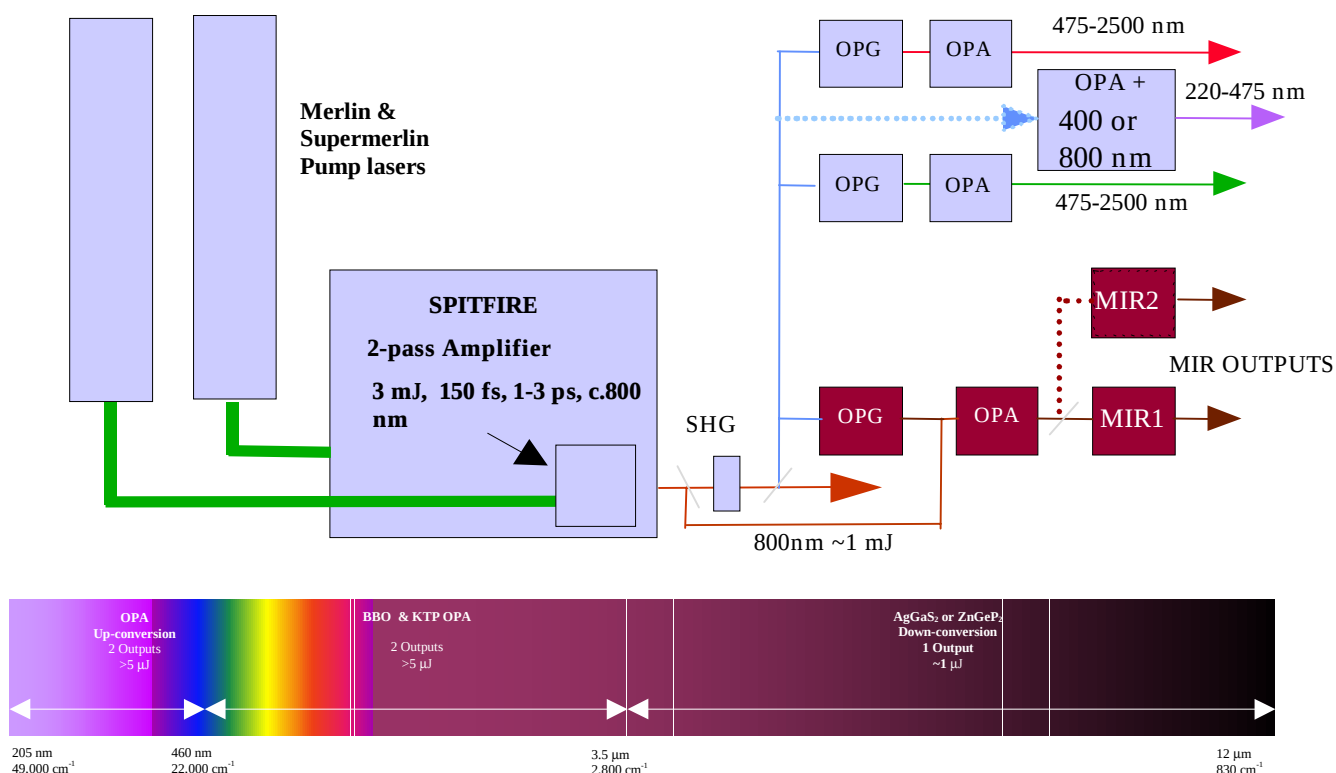


Figure 1. Ultrafast Spectroscopy Laboratory: PIRATE SYSTEM.

reaction is taken by measuring the changes in IR absorption of the initial and reactant species as a function of time delay between the pump and probe pulses. By using a broadband probe it is possible to simultaneously measure the absorption spectrum over a range of wavelengths. Vibrational transitions are generally weaker than electronic transitions and therefore an ability to observe small absorbance changes down to 10^{-5} or better is desirable. For example in the range of species we would like to probe, the expected absorption changes for very strong absorbers such as metal carbonyls are $\Delta A \sim 10^{-1} - 10^{-2}$; for strong absorbers such as -C=O , -O-H and -C-H vibrations, $\Delta A \sim 10^{-3} - 10^{-4}$ and for moderate absorbers such as C=C vibrations, $\Delta A \sim 10^{-5}$.

These low cross-sections place heavy constraints on the pulse to pulse stability of the laser output and the stability and sensitivity of the detector and data acquisition system. The Hamm paper describes the potential stability of mid IR sources based on OPA technology. In our case only modest stability of the order of $\pm 5\%$ was achievable with additional large fluctuations due to triggering and local thermal variations. To reduce the overall effects of fluctuations we developed a sensitive multi-channel IR probe and reference approach to normalise out probe variations on a shot by shot basis as described below.

A key advance in picosecond TRIR has been the recent developments in multi-channel MIR array detectors. Our TRIR apparatus comprises two 64 element mercury cadmium telluride (MCT) photoconductive detectors (MCT-13-64el detectors from Infrared Associates Inc. and MCT-64000 pre-amplifiers from Infrared Systems Development Corp.) to detect the mid IR reference and probe signals. A customised analogue multiplexer readout system has been designed and built. The data are captured and analysed in pump on/pump off pairs to create a rolling average using the following equation:

$$\Delta A_N = \log[1 + I_R/I_P] \left((I_{\text{probe}}/I_{\text{ref}})_{\text{pump on}} - (I_{\text{probe}}/I_{\text{ref}})_{\text{pump off}} \right) + \Delta A_{N-1} (N-1)/N$$

Here I_R and I_P are the final averages of the pump off spectra on the reference and probe side respectively, and N is the total number of acquisitions. Further software discrimination removes large fluctuations in the signal, such as laser 'drop outs' or other large variations such as those associated with gas bubbles in the sample flow stream, on a shot by shot basis.

The simultaneous outputs of both 64 element MCT arrays are fed into a modified HX2 analogue multiplexer test board PC20001/5 (User guide 11/7/97). The HX2 was designed at the Rutherford Appleton Laboratory by the Instrument Development Group for charge detection from multi-element X-Ray detector arrays. Each HX2 integrated circuit integrates charge (up to 60 pC +ve charge and 20 pC -ve charge) over 16

parallel input signals and has an electrical bandwidth of $\sim 1\text{MHz}$ and integration period determined by internal or external clock circuitry. The test board uses 4 HX2s to capture 64 channels simultaneously with all readouts multiplexed into a single output consisting of a sequence of 64 analogue voltages. The buffered output generates a $\sim 12\text{V}$ full scale voltage. This board incorporates pulse timing circuitry for charge integration down to $\sim 20\text{ }\mu\text{s}$ as set by the basic clocking structure that was tied to the readout rate. In order to match the detector response to the integration period we provided an external clock pulse train to define a $\sim 2\text{ }\mu\text{s}$ integration period followed by a $14\text{ }\mu\text{s}$ readout period. A second HX2 board, slaved to the first board, is used to acquire the signals from the second MCT detector. The outputs from both boards are read out in simultaneous bursts of 64 analogue signals, with each burst separated by 1 ms as defined by the laser repetition rate.

The charge injected from the detectors into the HX2 is adjusted to give $\sim 12\text{ V}$ output for a 4 V MCT detector input signal. The multiplexed output has a full scale range of about 12 V and baseline ripple of $\sim 15\text{ mV rms}$ and noise of $< 6\text{ mV rms}$. The noise derives from the MCT detectors at the $\sim 2\text{ mV}$ level and the ripple from 50 Hz mains related modulation. The mains ripple is correlated in all analogue outputs and is largely removed in the subsequent data normalisation process.

A simple low pass RF filter is used to reduce high frequency noise prior to digitisation. The HX2 board provides trigger and clock pulses to synchronise with the ADC. The analogue signals are passed into two channels of an 8 channel simultaneous sampling, 12 bit resolution, Datal 416J ADC card housed in a standard 500 MHz PC. This card has capacity to acquire at up to 250 kHz on each channel. The data is then streamed to the PC RAM via the ADC FIFO and PC direct memory access where data analysis such as signal discrimination, normalisation and averaging between detector channels is carried out on a shot by shot basis at 1 kHz . The experiments are carried out in a pump and probe configuration where the pump laser is switched on and off on an alternative shot basis using an optical galvanometer synchronised to the laser. A third channel of the ADC is used to monitor the pump on/off status of the laser.

The general layout of the time resolved IR spectrometer is shown in Figure 2. The mid infrared probe beam generated from the OPA is split into a reference and probe using a 50% germanium beamsplitter. The probe beam is focused to about $150\text{ }\mu\text{m}$ diameter into the sample cell using an $f = 30\text{ cm}$ gold coated spherical mirror. The transmitted light from the sample is then imaged onto the spectrometer input slit that is set to 0.5 mm width. A similar optical relay is used for the reference arm. Two CVI DKSP240 $1/\text{m}$ spectrometers disperse the IR beams. They have the option of 150 l/mm (4000 nm blaze) and 300 l/mm (2400 nm blaze) gold gratings with 25.6 and

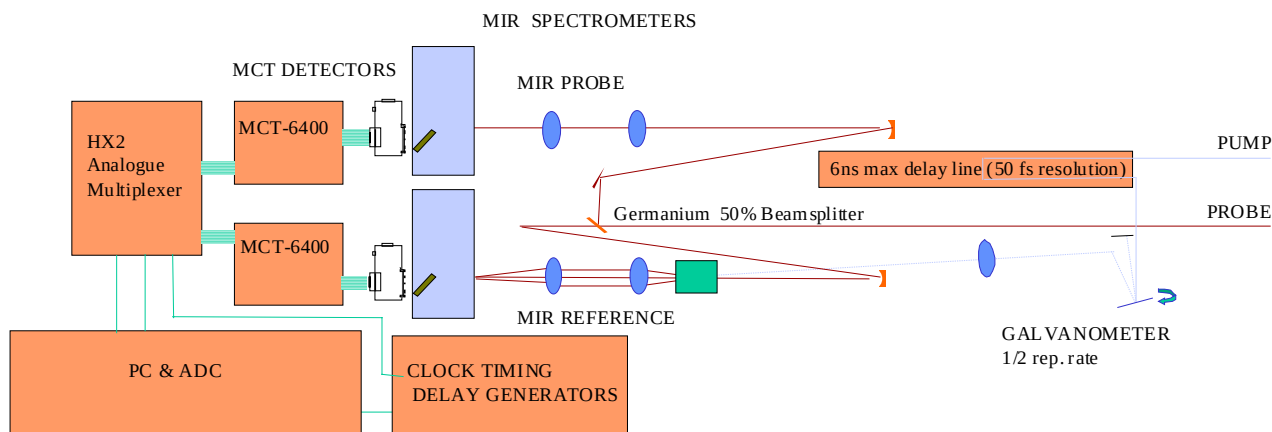


Figure 2. The PIRATE Time Resolved IR Spectrometer.

12.8 nm/mm dispersion respectively. An adaptation of the exit port and mirror increased the spectral window of the spectrometer from 25 mm to 35 mm, matching the dimensions of the MCT diode array.

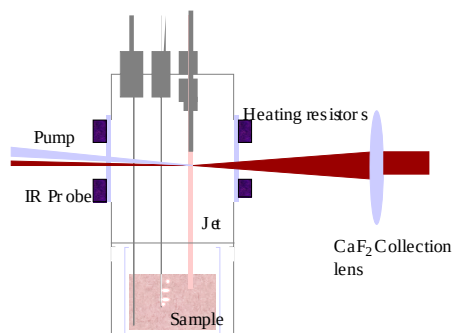


Figure 3. The open solvent jet flow system.

Figure 3 shows the sample chamber used for experiments with probe wavelengths below 5.85 μm . This open jet system is used for the many samples that are prone to pump induced degradation that often occurs on the surface of an enclosed flow cell. Low f number lenses image the jet onto the spectrometer slit. A CaF_2 windowed compartment allows an inert atmosphere, and resistive heaters on the windows stop condensation of solvent on the windows. This arrangement is also suitable for transparent solvents and for UV VIS transient absorption. For measurements in aqueous solution and below 5.85 μm , in the solvent absorption regions, a thin moving enclosed flow cell is being designed.

Results

As an illustration of the capability of the PIRATE TRIR apparatus, two spectra are given.

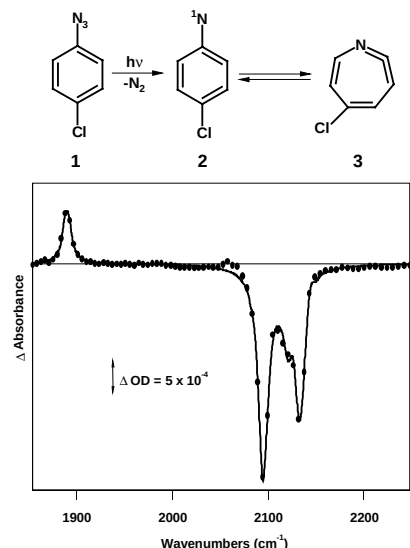


Figure 4. Transient IR spectrum of para-chlorophenylazide 20 ps time delay after the pump pulse.

Figure 4 shows the TRIR spectrum of para-chlorophenylazide (1) in n -hexane in an open flowing jet, after 2 minutes of data accumulation. Aryl azide compounds have potential as photolabels and photo-resists. The spectrum shows the azide bleach and the dihydroazepine product (3) which is formed in ~ 20 ps. The baseline noise level is better than $\Delta A = 10^{-4}$ and shows that with 100 times longer accumulation, sensitivity to better than the 10^{-5} level could be achieved.

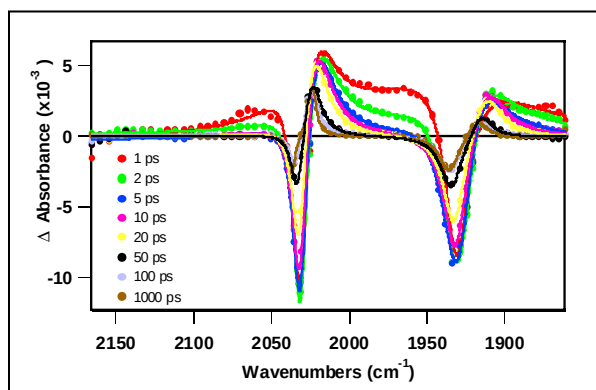


Figure 5. Time-resolved IR spectra of $[(\text{py})\text{Re}(\text{CO})_3(\text{dppz})]^+[\text{PF}_6]^-$ in CH_3CN after 400 nm photolysis. The insert shows the pump probe time delays.

Figure 5 shows the TRIR spectra of $[(\text{py})\text{Re}(\text{CO})_3(\text{dppz})]^+[\text{PF}_6]^-$ taken in the open jet over a 300 cm^{-1} spectral range (two 150 cm^{-1} spectra joined) after 2 minutes accumulation. This complex is one member of a family of compounds that have the potential to act as IR probes of the structural features of DNA and the electron transfer processes which occur only in the DNA helix. This is because the character of their lowest lying excited states can be tuned, by ligand substitution, to induce fluorescence when bound to specific sites in DNA.

The spectrum shows both negative and positive going features which relate to the ground and excited state species. The negative going peaks are a bleach of the ground state absorption bands caused by the depletion of ground state population. The broad positive going peaks are characteristic absorption bands of a π - π^* ligand based excited state.

Conclusions

The PIRATE system provides access to the complementary techniques of TRIR, IR pump spectroscopy and time resolved resonance Raman spectroscopy. Preliminary results demonstrate sensitivity down to the $\Delta A \sim 10^{-4}$ - 10^{-5} level in around 1 minute of accumulation time with an open flow jet configuration.

The RAL designed analogue multiplexer, in combination with the Dattel ADC, has potential for scaling to readout rates of 8 kHz (128 elements) or 1 kHz (1024 elements).

Acknowledgements

M. S. Platz (Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210-1173) for the azide sample. EPSRC for funding on grant GR/M40486.

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Fluorescence Suppression in Raman Spectroscopy using a High Performance Picosecond Kerr Gate

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Introduction

Raman spectra obtained using a probe beam wavelength matched to a molecular absorption band have exceptional sensitivity and selectivity. The resonance greatly enhances the Raman signal from individual transition moments of the specific molecule to be studied. Unfortunately, fluorescence is often also strong, limiting observations in ground state studies to particularly strong Raman bands. In many cases the probe beam - and the pump beam in time-resolved resonance Raman (TR³) experiments - may induce fluorescence in contaminants or the solvent. In biological or industrial cases particularly, the concentration of the molecule under study may be low. To reject the fluorescence we have adopted the temporal gating technique that uses the main distinguishing feature of the Raman scattering, its promptness. A short pulsed Raman signal is generated using a pulsed laser and the longer lived fluorescence is rejected in the time domain. Very short gating times were achieved by Tahara and Hamaguchi¹⁾ who used a streak camera with effective time gating resolution of ~10 ps limited by trigger jitter. A similar concept but relying on an optical Kerr gate²⁻⁵⁾ was proposed and demonstrated in ground state Raman spectroscopy by Deffontaine et al⁶⁾ using 25 ps gating pulses. This latter concept holds certain advantages over the streak camera due to simplicity of the design and inherent absence of jitter problems allowing potential access to shorter gating times. We have recently demonstrated the feasibility of Kerr gate fluorescence suppression with ~3 ps time resolution in Raman spectroscopy⁷⁾. The prototype device had a throughput of about 30 % (excluding Fresnel losses on optical elements) and extinction ratio 10^{-4} in the usable spectral range of 630 - 700 nm. However, we recognised the need and scope for improvement in order to detect signals from much weaker Raman scattering systems and to greatly increase its spectral range in order to use resonance enhancement for a wide range of molecules. Here we present our improved design and characterise the performance of the enhanced device. The specifications are transmittance in the open state of ~40 % (excluding Fresnel losses on optical elements), a higher rejection ratio of 10^{-5} and a substantially wider usable spectral range 300 - 700 nm attained with a single pair of polarisers. This is achieved at the expense of a marginally lower temporal resolution, ~4 ps.

Description

The basic principle of the optical Kerr gate was described in our earlier publication⁷⁾. Briefly, the Kerr gate consists of two crossed polarisers and a Kerr medium. In the closed state, light collected from the sample and collimated in an optical train is effectively blocked by the crossed polarisers. Coincident in time with the Raman scattered light from the sample, a short gating pulse of 800 nm wavelength that bypasses the polarisers creates a transient anisotropy within the Kerr medium by the optical Kerr effect. The gating beam is polarised at 45°. The intensity is adjusted to create an effective $\lambda/2$ waveplate and rotate the polarisation of the light from the sample by 90° allowing it to be transmitted through the cross polariser for the duration of the gating pulse.

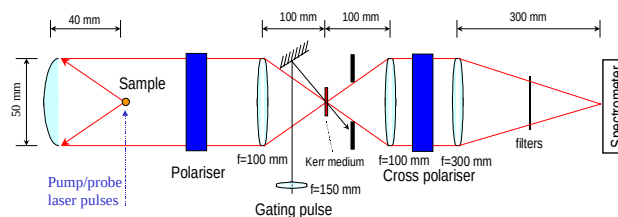


Figure 1. Optical arrangement of the Raman collection system and the optical Kerr gate.

The improved Raman collection system consists of a parabolic collection mirror ($f^{\#} = 0.8$) of 50 mm diameter, image relay fused silica lenses, a Kerr cell and two calcite Glan Taylor segmented polarisers (see Figure 1). The 800 nm gating pulse is weakly focused into the Kerr cell to a diameter of ~1 – 2 mm using a 150 mm focal length lens. The Kerr cell containing static CS₂ was custom made with a 2 mm-path length and ultrathin (300 μ m) Spectrosil B walls. The polarisers were of 41x41 mm aperture, manufactured to our specifications by Halbo Optics, replacing earlier sheet polarisers. The first polariser consists of two 20 x 41 mm segments of 20 mm thickness. The choice of 41 x 41 mm aperture is a compromise between the cost and optimum Raman throughput, with some 14 % loss due to clipping on the polariser being tolerated. The optical thickness of the polariser is uniform to within $\pm 50 \mu$ m to keep the transit time variation of the Raman signal within the gate response time. The second polariser placed after the Kerr cell is manufactured to the same specifications except that it has relaxed thickness uniformity to within ± 1 mm.

The $f = 10$ cm lens placed immediately after the first polariser images the sample interaction region into the Kerr cell. The rays emerging from the Kerr medium are then re-collimated by the second $f=10$ cm lens, passed through the cross polariser and imaged onto spectrometer entrance slit using a 30 cm focal length lens with the f-number matching that of the 3-stage spectrometer (Triplemate). A home built Triplemate filter stage by-pass option was used in the experiments described here to optimise transmission. The probe laser line was blocked using a holographic supernotch filter, glass edge absorbing filter or a solution filter. A concentrated solution of copper sulphate in water in a 1 cm thick, 2 inch diameter, optical cell was placed in front of the spectrometer slit to block the 800 nm gating beam. The spectrometer throughput was determined to be 3.5-times lower for horizontal polarisation (corresponds to measurements with the polarisers oriented in parallel) compared to the vertical orientation (polarisers crossed) at ~2250 cm⁻¹ when probing at 400 nm. All photon counts given here for measurements with the polarisers oriented in parallel ('without gate') are scaled to account for these differences.

A schematic diagram of the overall system is shown in Figure 2. Raman scattered light was collected at 90° to the probe beam direction. One CCD count corresponded to one photoelectron.

The sample solution was re-circulated in an open liquid jet of 0.5 mm diameter.

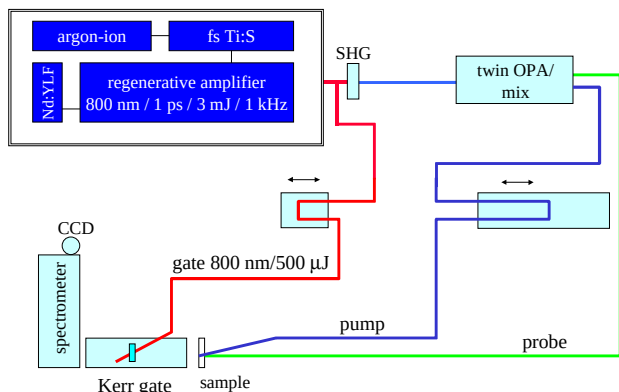


Figure 2. Schematic diagram of the picosecond time-resolved resonance Raman apparatus with the Kerr gate (K-TR³).

Our ps-TR³ apparatus uses a regenerative amplifier system followed by a two pass linear amplifier (SuperSpitfire, Spectra Physics/Positive Light) providing 800 nm, 1 ps, 2 - 3 mJ fundamental pulses at 1 kHz repetition rate. The fundamental laser output is split in two. 500 μJ is taken for the gating pulse to drive the Kerr gate and the remainder is frequency doubled to pump two home built optical parametric amplifiers that generate the synchronised, independently tunable pump and probe pulses required for TR³ experiments. This configuration also enables the delivery of frequency doubled, 400 nm, and tripled, ~266 nm, pulses with higher energies. For conventional ground state Raman measurements, the pump beam is blocked.

The low wavelength limit of the CS₂ Kerr gate is ~ 390 nm, determined by the electronic absorption of CS₂. The wavelength coverage extends to 700 nm where the limit is set by background due to stimulated anti-Stokes emission induced by the gating pulse in the Kerr medium. Coverage of the 300 - 390 nm range is facilitated by using a benzene based Kerr gate capable of achieving a throughput of about 20 %.

Results

The temporal response of the gate was determined by measuring the intensity of the 2253 cm⁻¹ Raman band of acetonitrile and delaying the Raman probe pulse with respect to the gating pulse. The data was best fit to a Gaussian profile with FWHM 4.2 ps. With ~500 μJ of gate pulse energy, the throughput of the Kerr gate in the open state is 40 % excluding losses on optical elements, i.e. Fresnel and absorption losses. In comparison with our earlier design⁷, the new gate provides an approximately 2.7-fold increase in Raman flux reaching the detector under the same experimental conditions. This is due to improved collection efficiency of Raman light (x1.7) and a higher overall transmission (x1.6) through the gate in the open state due to more efficient opening of the gate.

To demonstrate the effectiveness of the Kerr device we have recorded Raman spectra of an unpurified 'industrial' sample of unleaded petrol taken directly from a motorcar petrol tank (see Figure 3). The spectra obtained at 400 nm without the gate (polarisers oriented in parallel, gating pulse blocked) were dominated by a massive amount of fluorescence. Raman bands were resolved from over 10,000 times more intense fluorescence background using the gate. The fluorescence lifetime was estimated to be ~30 ns.

The Kerr gate was also used for a TR³ spectroscopy of the highly emissive intramolecular charge transfer (ICT) state of DMABN⁸ shedding new light on the 40 year old problem of the nature of the anomalous fluorescence observed in polar solvents. The Kerr gate was also successfully used in ground

state Raman studies of highly emissive solid samples and measurements of picosecond time-resolved fluorescence.

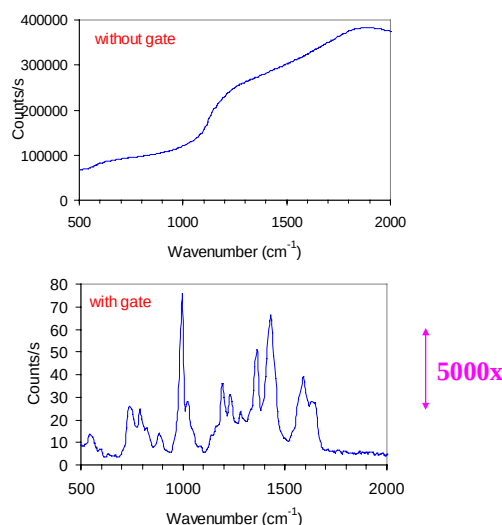


Figure 3. Raman spectra of unleaded petrol measured (top) without the gate and (bottom) with the gate at 400 nm (1 ps, 4 μJ, 1 kHz). The accumulation time was 400 s.

Conclusions

In summary, we have developed an improved, high performance device, based on an optical gate with a response time ~4 ps, for the efficient suppression of fluorescence in Raman spectroscopy. The system further increases the general applicability of Raman spectroscopy and, in particular, holds great promise for industrial and biological applications where high levels of fluorescence are common.

Acknowledgements

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Development of a Time Correlated-Single Photon Counting Multiphoton Laser Scanning Confocal Microscope

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Introduction

Fluorescence Lifetime Imaging (FLIM) is a technique that allows investigation of molecular interaction such as energy transfer and anisotropy correlation in subcellular entities^{1,2}. These cellular processes affect the quantum state of the molecule of interest and lead to a change in the natural fluorescence lifetime.

Confocal laser scanning microscopy (CLSM) allows fluorescence imaging with resolution of 200-400nm dimensions. The ability of the technique to exclude out-of-focus information makes it possible to obtain 3D images of even thick samples with clarity. However, single photon excitation normally used in this technique leads to photo-bleaching, rapid degradation and sample toxicity during the repeated raster scanning process. Multiphoton confocal microscopy³ uses near infrared light (NIR) to excite the fluorophor by a non-linear process under high laser peak power (Figure 1).

The advantage of this technique is that the excitation is confined only to the focus of a high numerical aperture microscope objective, reduced specimen toxicity due to the NIR source and less photo bleaching.

In this report, we have combined time correlated single photon counting technique, TCSPC, a technique for determining ultra short molecular lifetime, with multiphoton -CLSM to study the photo-physics of biomolecules⁴. 5-hydroxy tryptophan, the molecule of interest is incorporated within a protein in yeast cells.

Experimental

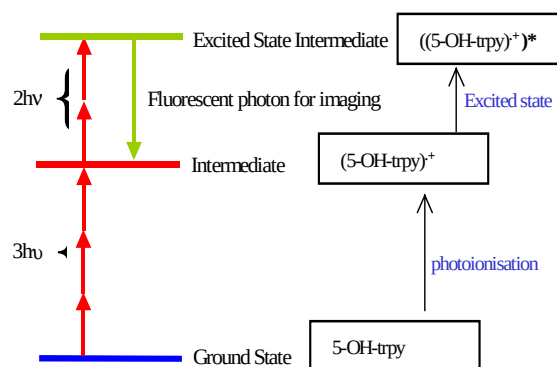


Figure 1a. Non-linear multiphoton process

Figure 1b. Multiphoton energy diagram of 5-OH trypt, leading to the green fluorescence observed at 505 nm

Figure 1. Multiphoton generation of green fluorescence.

The multiphoton microscopy apparatus consists of laser light (Titanium Sapphire, 76 MHz, mode-locked, 120 fs, from Spectra-Physics) focused to a diffraction-limited spot through an oil objective and scanned across the sample (Figure 2). Specimens were illuminated at a microscope stage (Olympus IMT-2) by passing the beam through a 750 ± 2 nm interference filter (Ealing), placed at the fluorescence attachment port of the

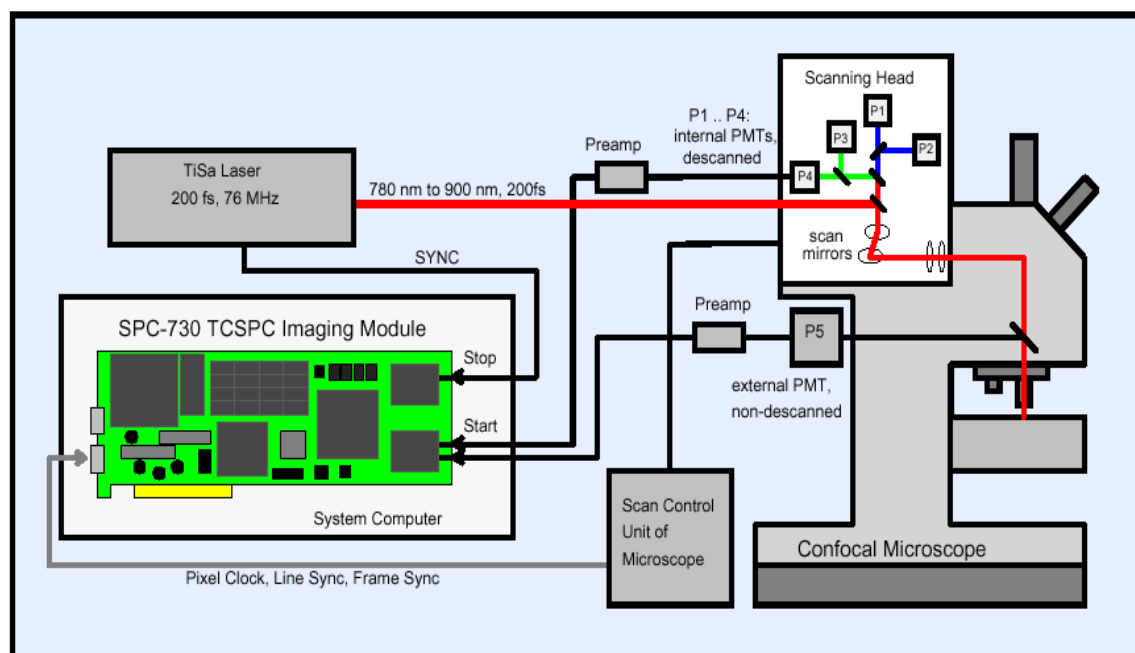


Figure 2. Instrumentation - TCSPC confocal laser scanning fluorescence microscope .

microscope.

Line, frame and pixel clock signals generated by the XY scanner were synchronised with a fast micro channel plate – photomultiplier tube, used as the detector. These were linked via a photon counting PC module (Becker and Hickl, Germany), that measures the fluorescence decay lifetimes.

Sample preparation and cell culture

Proteins were labelled by inducing their expression in the presence of 5-OH-Trp, using galactose-inducible expression vectors. Briefly 2×10^8 cells were used to inoculate a 50-ml culture containing 2% glucose, 2% bactopectone and 1% yeast extract. When the cells were in stationary phase, 5 ml of a 25% galactose solution was added to the media. After 2 hours 2.5 ml of a 0.2% solution of L-5-OH-Trp was added and the culture incubated for a further 24 hours prior to cell harvesting. For microscopy experiments the cells were placed on top of a 1% agarose gel, which prevented cell movement.

Preliminary Results

Figure 3 shows a raster scan steady-state and fluorescence lifetime map image of 5-OH-tryptophan labelled yeast cells. The control cells showed significantly less fluorescence under similar conditions.

Since each pixel that makes up the image also contains a complete decay profile (Figure 4), we are now able to scrutinize the lifetime image in greater detail.

The fluorescence lifetime map shows distribution of the different components within the steady state image. Lifetimes from different confocal planes are all similar. This is indicative of similar and homogenous environment of the 5-OH tryptophan within the yeast cellular entity. Solution studies of the amino acid showed a lifetime of 3.5 and 1.5 ± 0.3 ns for the UV (340 nm) and visible (505 nm) emission respectively.

Conclusions

- We have constructed a tuneable time resolved (TR) multiphoton laser scanning confocal fluorescence microscope with-picosecond resolution.
- Conclusions with tryptophan derivative show differences in the lifetime.
- The lifetime of the new visible emission is different from that of the natural UV fluorescence. This provides a new way to monitor certain molecules that are normally UV absorbing or emitting.
- The results highlight the potential usefulness of this set-up in the study of fluorescence dynamics of intracellular probe localisation.
- This technique provides a new way of studying protein without the need for detrimental UV light.

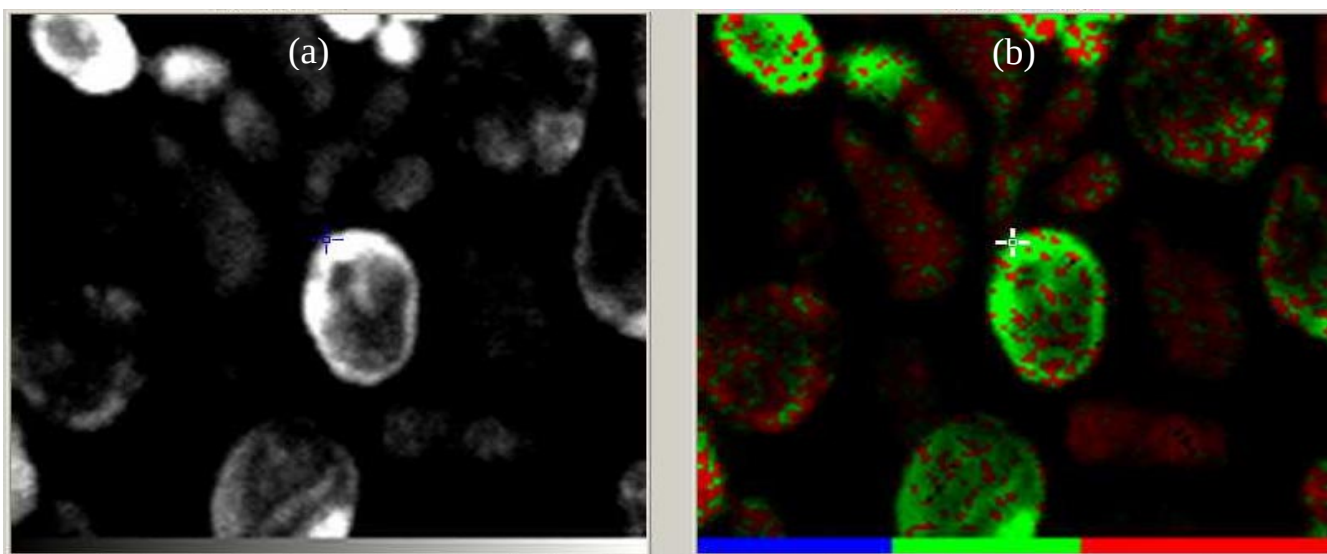


Figure 3. TR-confocal fluorescence images of yeast cells labelled a) Steady state fluorescence map b) Fluorescence lifetime map.

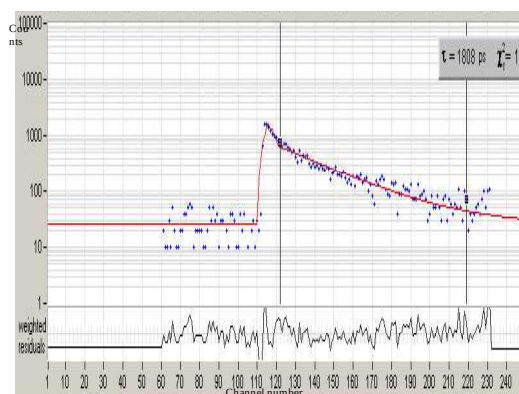


Figure 4. The fluorescence decay at a single pixel which together makes up the lifetime map.

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Developments in the EPSRC Laser Loan Pool

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During the reporting year, the laser systems in the EPSRC Laser Loan Pool have been replaced as they reach the 5-year age limit set in the terms of the Loan Pool Grant. The Loan Pool aims to provide state of the art laser systems that have a high degree of flexibility for wide ranging research while combining the reliability and robustness required for the Loan Pool environment.

The development of the Loan Pool is administered by the LSF on the basis of User requirements. We use all feedback from the UK research community such as from User report forms, meetings and questionnaires. We then purchase systems on the strength of this feedback and on our assessment of technical practicality.

Nd:YAG pumped dye lasers remain extremely useful work horse systems capable of broad tunability, very high brightness and narrow resolution. We continue to maintain five Nd:YAG laser systems in the Loan Pool. However this year the two Spectron Nd:YAG pump lasers for the Sirah dye lasers, the entire GCR11/PDL3 system, have been replaced with new lasers. The output specification range of the Nd:YAG/dye laser systems is given in Table 1.

The trial of the femtosecond system within the Loan Pool has proved very successful with it finding a wide range of applications such as multiphoton microscopy, surface harmonic generation and for the development of THz sources. In June the femtosecond system is to be replaced by a Verdi/MIRA system capable of very broad tuning range and with the option of second and third harmonic generation. The specifications of the femtosecond system are given in Table 2.

The remainder of the Pool includes the fluoride excimer, and frequency doubled argon ion. Full details of all the lasers and their specifications can be found on our web-site at: <http://www.clf.rl.ac.uk/Access/lp/alsfl.html>.

NSL1 replacement

The compact NSL1 system has been replaced with a more powerful injection-seeded YAG/dye system with doubling and infrared option. The system is a Continuum Powerlite 8010 pumping a SIRAH dye laser. The dye laser has frequency doubling and IR difference frequency mixing units to cover most of the spectral range from 215 nm to 4 μ m. Injection seeding of the Nd:YAG enables generation of IR light with linewidth matching the performance of the dye laser. Delivery of the Infrared unit is expected in mid June 2001 and is to be installed in the Department of Chemistry, Heriot-Watt University for Prof K McKendrick and will be used to study the reaction dynamics of O(3P) with vibrationally excited methane.

NSL2&3 replacements

In the first months of the year, the two Spectron Nd:YAGs were replaced with Surelite III-10 systems used to pump the existing Sirah dye lasers. These Surelite lasers are very compact in both size and weight. In the next few months the systems will be mounted on dedicated breadboards on trolleys to form a compact package that can be easily transported and wheeled in and out of User laboratories. In addition the systems are water-cooled and are supplied by a 13A plug making them versatile and easy to install. The service back up for both the Nd:YAG and the dye is from a single company to avoid downtime occasionally experienced with 'hybrid' systems. A diagram of the proposed layout is shown in Figure 1(a) and (b). One of these lasers has been used in Nottingham (Dr K Reid) and is

currently with Dr A Alexander in the Department of Chemistry, University of Edinburgh where it is being used to study interference in dissociation dynamics. The other system will shortly be used by Prof A Stace in Sussex University to study the chemistry of nanodroplets.

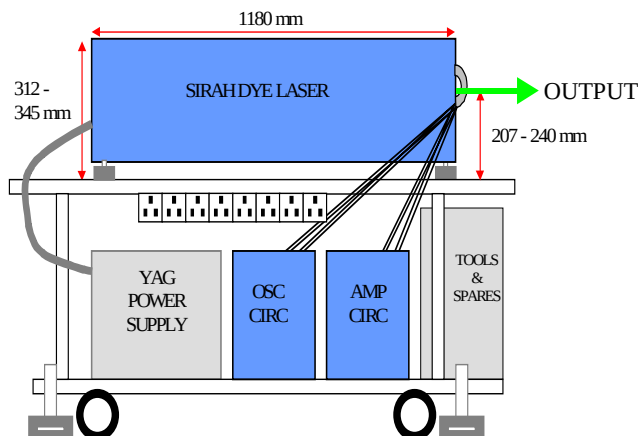


Figure 1(a). Proposed layout of Surelite/Sirah laser (side view).

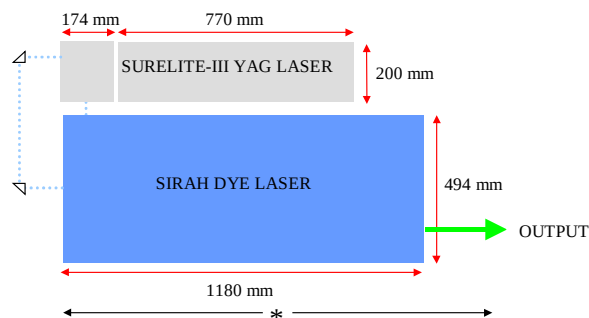


Figure 1(b). Proposed layout of Surelite/Sirah laser (top view).

The Tsunami system was placed in the Loan Pool to prove the viability of operating a femtosecond laser in the Loan Pool. The success of this project led to demand for a more modern femtosecond system and the IRA Optima 900F with 10W Verdi pump laser was purchased after normal European tender. The MIRA has a single mirror set which provides tunability from 700 to 1000 nm with <150 fs pulses. The 10W Verdi pump laser provides sufficient power to maintain the laser well above threshold and can in itself provide stable single longitudinal mode green output.

A frequency doubling and tripling option on the MIRA will allow convenient access to new regions of the spectrum in the UV, near UV and visible regions of the spectrum.

The MIRA incorporates several diagnostics to give mode locking status, power and a fluorescence monitor to help aid alignments when re-alignment or re-configuring is necessary.

The system will be provided with an optical breadboard and a small water chiller unit.

Nd:YAG/DYE systems	NSL1,2,3,4&6
Nd:YAG	Specification range
Output 1064 nm	700 – 1200mJ
532 nm	300 - 600 mJ
355 nm	100 - 300 mJ
266 nm	50 – 100 mJ
Pulse length	4 – 9 ns
Linewidth	1 cm ⁻¹ (0.05 with seeding)
Dye output	
Linewidth	<0.1 cm ⁻¹
440 nm	10 - 25 mJ
570 nm	90 - 150 mJ
640 nm	55 - 60 mJ
Doubling	215 – 400 nm ~10% of fundamental
DFG	1500-3000 nm >2 mJ 3000-4000 nm

Table 1. The general specifications of the Loan Pool Nd:YAG lasers.

FEMTOSECOND SYSTEM	CWL1
Pump laser Verdi V10	
Power	>10W
Wavelength	532 nm
Linewidth	<5 MHz (over 50 ms)
Femtosecond Laser MIRA Optima 900F	
Pulse length	~130 fs
Tuning range	700-980 nm (1000 nm typical)
Power	700 nm ~0.4W 750 nm ~ 1W 800 nm ~1.3W 850 nm ~1.1W 900 nm ~0.8W 950 nm ~0.6W 1000 nm ~0.2W
FREQUENCY CONVERSION	
SHG Tuning range	350-500 nm ~10% conversion
THG Tuning range	240-320 nm ~3% conversion

Table 2. The specifications of the femtosecond laser system.

Development of large-aperture bimorph adaptive mirrors

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Introduction

The CLF has had a programme of development of adaptive mirrors and their control systems since 1995. The mirrors have been based on bimorph technology, in which an optical substrate a few mm thick is bonded to a sheet of piezoelectric material (lead zirconate-titanate, or PZT) of about one-tenth the thickness. The PZT has an electrically conductive layer on either side. When a voltage is applied across the thickness of the PZT, it attempts to expand or contract, but because one side is constrained by the adhesive bond, the result is a localized curvature of the mirror proportional to the applied voltage. To control the shape of the mirror, positive or negative voltages are applied between control electrodes on the back surface of the PZT and a common ground electrode incorporated in the adhesive layer between the PZT and the substrate. The first operational mirror had a clear aperture of 70 mm, limited by the size of available pieces of PZT, and this was used to develop the control system and demonstrate closed-loop correction of an aberrated beam. For these devices to be useful on the CLF's large laser systems, in particular the Vulcan petawatt beam, mirrors are required which can handle beams up to 100 mm in diameter. This article discusses the techniques which have been developed for constructing such mirrors.

The first large aperture mirror, VP1

The first large adaptive mirror constructed at the CLF was 150 mm in diameter, and was described briefly in an earlier report¹. As the maximum size of PZT available was 70 mm square, the active layer of this mirror was constructed in four quadrants, separated by gaps of 1 mm (Figure 1). The 64 actuators were formed in a nickel layer coated on the back of the PZT, and were laid out in a radius/sector pattern with the majority of the actuators concentrated at the edge of the Vulcan beam. The outermost ring of actuators lies outside the beam area to provide slope control at the edge. The ground plane common to all the actuators is a layer of conducting cloth that is incorporated into the adhesive layer. To allow connection to the ground plane, two flaps of the cloth were left protruding at the edges of the substrate; these can be seen in Figure 1. In practice these flaps caused several problems. They became rigid because they were filled with adhesive, and even when folded onto the back of the mirror there were residual irregularities at the edge

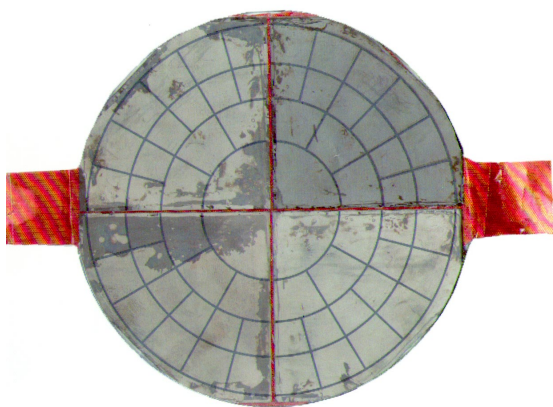


Figure 1. The rear surface of the prototype 150 mm adaptive mirror VP1, showing the actuator pattern.

of the substrate that interfered with its rotation on the polishing lap. The resulting abrasion and flexing broke the fine copper wires in the cloth, so there was no longer any electrical connection to the back of the PZT: the ground connection was eventually made through small exposed areas of the cloth around the edge of the mirror.

Because the epoxy adhesive used to attach the PZT to the mirror was known to shrink on curing, the final polishing of the mirror face was left until after the assembly was complete. The shrinkage of the adhesive changed the curvature of the substrate significantly, from an initial 14 waves concave to roughly the same amount of convexity. The polishing removed the majority of this curvature, leaving the mirror with no more than 1 wave of error across the surface. During the gold-coating process the mirror was heated significantly, causing further curing of the adhesive. The additional shrinkage pulled the shape of the mirror approximately eight waves convex, but also, because the gaps between the PZT quadrants were less stiff than other areas of the mirror, there was additional curvature across the gaps. The resulting shape was quite strongly pyramidal (Figure 2), with local curvature on a scale length of a few millimetres at the edges of the pyramid, which the relatively large actuators were unable to compensate.

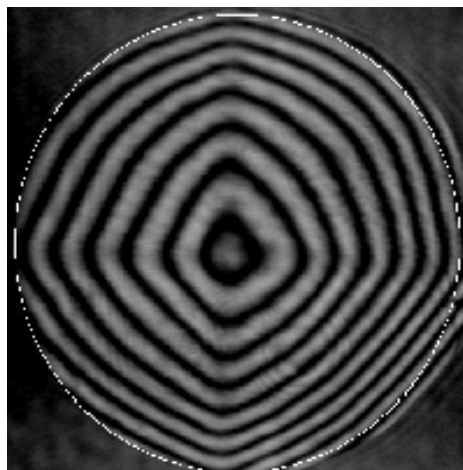


Figure 2. Interferogram of VP1 after gold coating, showing pyramidal shape.

The mirror was used for some off-line trials on Vulcan, but the size of the intrinsic errors prevented a convincing demonstration that the beam aberrations could be corrected. Before the mirror was repolished, it was annealed by heating to 80 °C for an hour: this was repeated three times, until no further change in shape was seen. The heat treatment completed the cure of the adhesive, allowing repolishing and recoating to be done without further distortion. However, there were still some residual high spatial frequency ripples which could not be eliminated, and it was noticed that after many cycles of operation, a weak pyramidal shape gradually reappeared. The results of trials of the reworked mirror are described elsewhere in this report².

Design of VP2 and VP3

The problems encountered with VP1 made it clear that some changes to the design were needed for future mirrors. In particular, the active element must be a single piece of PZT, to ensure uniform stiffness of the assembly and avoid the pyramidal effects seen with VP1. It was also decided to try a

different type of adhesive, as the shrinkage of the epoxy used in VP1 was the main cause of the change of shape of the mirror.

PZT is not available in the required thickness at the diameter needed for 150 mm aperture mirrors: discs of 120 mm diameter are supplied by the manufacturer at a minimum thickness of 2 mm. However, PZT is a ceramic material of moderate hardness, and can be ground using conventional abrasives. Rather than attempting to thin the discs to 200 microns separately, it was decided to assemble the mirror with 2 mm thick PZT, and let the glass substrate act as a support during the grinding. To test this technique, and at the same time investigate different adhesives, three test assemblies were made using 76 mm diameter by 3 mm thick Pyrex substrates and some 60 mm diameter by 4 mm thick discs of PZT that had failed quality control: these were supplied free by the manufacturer. Three adhesives were selected based on work done at Imperial College³. These were a two-part acrylic and two different UV-curing types. Each assembly was made with a layer of conducting cloth between the substrate and the PZT, to reproduce the structure that would be present in the final mirror.

One of the three adhesives (the two-part acrylic) had a working time that was far too short to allow correct positioning of the components. Of the UV-curing types, Holdtite ST3500 was selected as the easiest to use for future mirrors, subject to satisfactory performance. Grinding tests were carried out on all three samples and worked well: standard optical grinding techniques were used to thin the PZT to around 200 microns, although variations in the thickness of the adhesive layer did cause some variations in the PZT thickness. As the technique for thinning the PZT was a success, two full-sized mirror assemblies were prepared, using 150 mm diameter substrates with 112 mm PZT discs, bonded with ST3500. To avoid the difficulties experienced with VP1, the conducting cloth for the ground plane was cut as a circle 10 mm smaller than the substrate, and four areas were filled with conducting epoxy adhesive to serve as connection points to the cloth. The rear of VP3 is shown in Figure 3, together with two of the test assemblies and PZT discs.

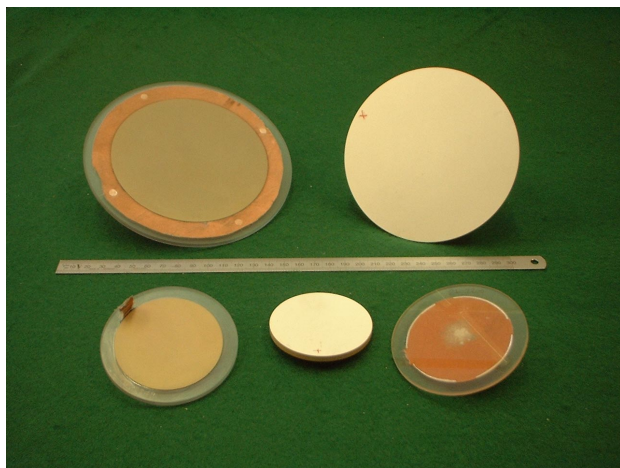


Figure 3. Adaptive optical elements. **Front:** two of the 76 mm test assemblies with 60 mm PZT ground to 0.2 mm thickness; original 4 mm thick PZT disc. **Back:** Rear surface of VP3 after grinding; 120 mm diameter x 2 mm thick PZT disc.

Coating tests

While VP2 and VP3 were in preparation, coating tests were carried out on the three small samples. As supplied, the PZT discs have a sintered silver conducting layer on each face, which is used for polarizing the material. The silver layer on the back is lost when the PZT is ground to thickness, so a new conducting layer must be applied to form the electrode structure. This could be done by either evaporation or sputtering

of a suitable metal, possibly followed by an electroplating stage to increase the thickness of the coating. Sputtering is the preferred coating process, as the PZT must be kept below the Curie temperature of 200 degrees, and the hot filament or boat required for evaporation can heat the substrate radiatively to quite high temperatures. Both nickel and copper were sputtered onto fine-ground glass substrates to determine the thickness that was achievable and to test the adhesion of the layer. Layer thicknesses of between 1 and 1.5 microns were formed with both materials, but the coatings were soft and easily scratched. For later tests the surfaces were activated with HMDS (hexamethyldisilazane), which on PZT yielded a highly adherent layer that could not be stripped with adhesive tape. The copper layers had low electrical resistance, and were ideal for forming the structure of the control electrodes. To confirm that the PZT was not depolarised by the temperature rise during sputtering, the coated electrode and the ground plane of one sample were connected to an audio-frequency signal generator: the assembly then acted as a loudspeaker, and the vibration of the PZT was clearly audible.

Electroplating was tried as a means of thickening the coating to around ten microns, and although this was successful, the adhesion of the thickened layer to the ceramic was extremely poor, so the idea of electroplating was abandoned. The final stages in fabricating the new mirrors will be (1) coating the PZT with 1–2 microns of copper, (2) creating a pattern of actuators in the copper by etching through a photoresist mask and (3) gold coating.

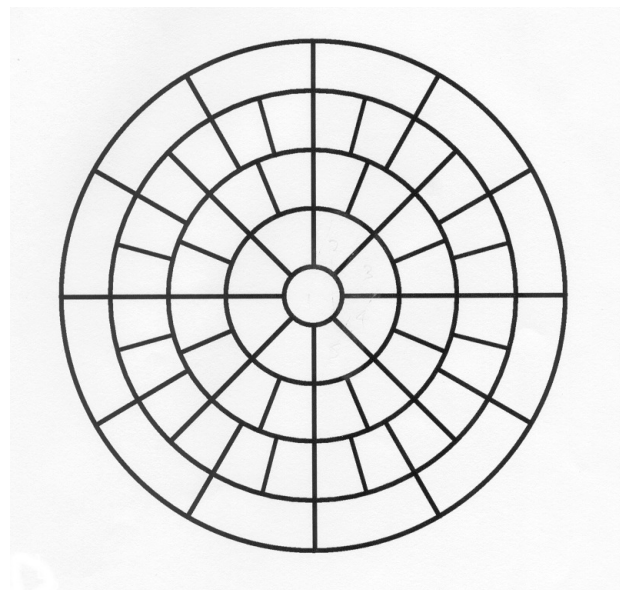


Figure 4. Proposed new actuator layout for VP3.

The actuators will be laid out in a radius/sector pattern similar to that of VP1. Experience with VP1 showed that the small number of large centrally-placed actuators (a result of concentrating the correcting power at the edge of the beam) led to an inability to correct certain types of errors. The new design (Figure 4) has 61 actuators: 49 of equal area within the beam footprint and only 12 in the outer ring. This mirror should be ready for trials on Vulcan in the autumn of 2001.

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A predictive analysis of the performance of a bimorph adaptive mirror

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Introduction

The de-formable mirror developed within the CLF is based on bimorph technology using an array of spatially distributed electrodes in a particular pattern that provide 64 independent wave front correction channels¹⁾. Each electrode of arbitrary shape produces a generally localised radius of curvature change of the mirror (i.e. change to the second derivative of the wave front, or spatial phase). Thus its influence function in terms of beam spatial phase extends appreciably beyond the local confines of a particular electrode shape. Wave front sensing is currently achieved using a modified 80 channel Hartman sensor²⁾ which provides a measurement of spatially distributed wave front gradients in the horizontal and vertical directions. (i.e. first derivative of spatial phase). Sensing is performed in 5 concentric rings about the beam centre with differing numbers of azimuthal channels.

Individual electrode influence functions in terms of the gradient changes they produce are measured by the Hartman sensor to produce a 64 x 160 element response matrix. During its inversion to a control matrix using singular value decomposition, 64 eigen vectors with associated eigen (singular) values are produced. When spatially resolved to the original Hartman sensor positions each eigen vector represents a characteristic and individual wave front gradient pattern that can be corrected. We term the eigen vector, or this pattern in a classical sense, as a mode of the system. The associated eigen value is proportional to the corrective power available to any particular mode. With this particular system, the challenge is to find an electrode pattern that generates a modal basis that best supports any wave front gradient pattern that already exists in a static way and also to accommodate those that are most likely to be encountered from thermal and other sources. A computer model has been developed to simulate this process. It predicts the modal basis of the mirror for an arbitrary electrode pattern and in turn applies this in both a static and dynamic way to the correction of known beam aberrations to predict its likely performance.

Model Description

On an (x,y) plane of a bimorph structure comprising of a sheet of PZT and a sheet of glass bonded directly together, the spatial distribution of surface deformation $W(x,y)$ is related to the spatial distribution of voltage $V(x,y)$ through the differential equation³⁾:

$$\nabla^4 W(x, y) + A \nabla^2 V(x, y) = 0$$

where A is a constant dependent in a complex way on the properties of the structure and ∇ is the Laplacian operator. The exact value of A should be determined experimentally, but is arbitrary for the simulation provided it is spatially constant. If $V(x,y)$ is expressed as a 2D Fourier series of frequencies (n,m) with Fourier co-efficients $V(n,m)$, then $W(x,y)$ can also be expressed as a 2D Fourier series with Fourier co-efficients, $W(n,m)$ ⁴⁾ where :

$$W(n, m) \propto \frac{V(n, m)}{n^2 + m^2}$$

Thus, in terms of a spatial transfer function the action of the bimorph plate is to 'filter' the applied spatial frequencies in a $1/(\text{freq})^2$ way.

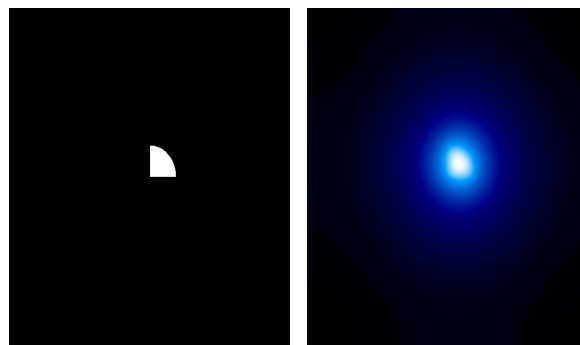


Figure 1. Applied voltage pattern (left) and the computed mirror response (right).

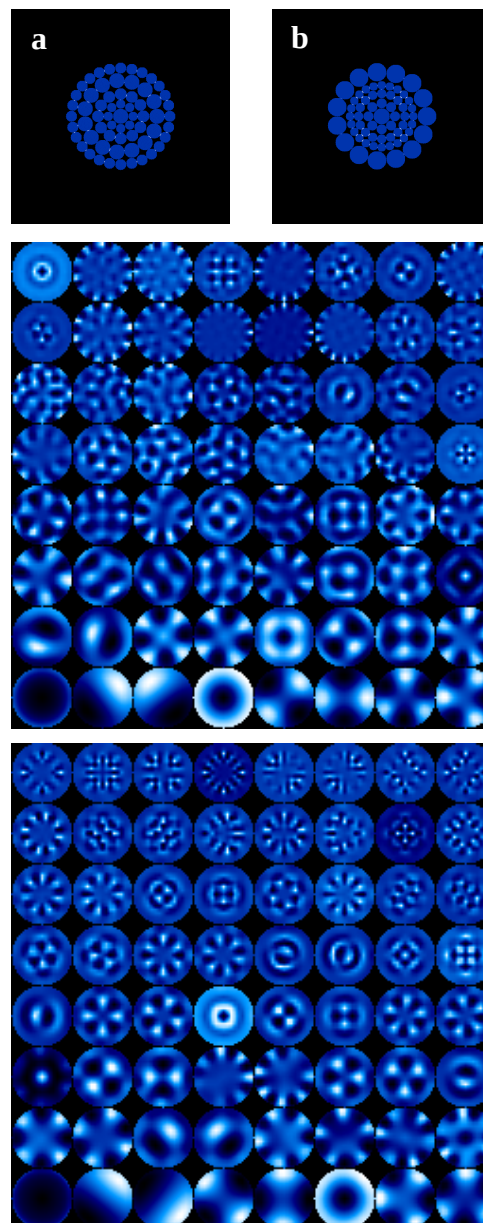


Figure 2. The modal basis for two electrode geometries – (a) top and (b) bottom.

The response of the mirror can therefore be calculated in a relatively straightforward way. An arbitrary spatial voltage pattern is defined and a 2D Fast Fourier Transform (FFT) computed. A $1/(\text{freq})^2$ amplitude filter is then applied and the inverse FFT computed. An example of an individual electrode shape and its computed response is shown in Figure 1.

For absolute phase computations (wavefront mirror modes) an individual electrode response is sampled on a grid. Alternatively for system modelling, the orthogonal differentials of the response are sampled following the Hartman pattern. The model cycles through each electrode and builds up a matrix of sampled responses as a function of electrode number, in exactly the same way as the actual system described earlier does. It is thus possible to extract the modal basis of correction for the designated pattern of electrodes. An example of the modal basis for two different electrode patterns is shown in Figure 2.

The modal patterns, shown in absolute phase (not gradient) are ordered according to their singular values with bottom left being the highest value and top right the lowest. It is evident that despite there being significant differences in the distribution and size of the electrode patterns, the lowest order modes up to approximately number 24 are extremely similar if not identical. Differences in the modal basis only start to reflect the differences in the electrode pattern above this number, and for the highest order modes they are quite distinct.

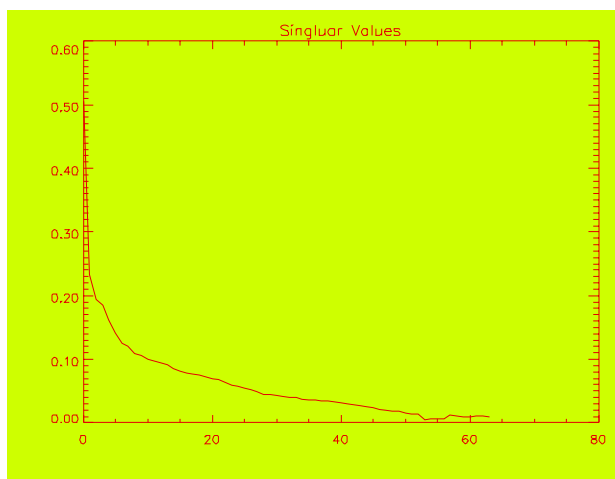


Figure 3. Eigen values of pattern (a) plotted against mode number.

The singular values for these distributions show that typically 75% of the corrective power available is concentrated in these first 24 modes as shown in Figure 3, with the remaining 40 modes accounting for some 25% only. Additionally, these highest order modes are relatively very weak and both their initial determination and their subsequent stimulation are strongly affected by noise. Indeed, it is usual during the formation of a particular control matrix to set the highest order (i.e. lowest value) singular values to zero above a certain mode number, either in a step like way or using a tapering function. Thus the variation in the electrode patterns is only likely to be effective in the mid band modes, and even then only account for 15 % to 20 % of the corrective power.

Comparison to a real bi-morph mirror

Previous measurements of the wave front quality of the primary CPA beam line of Vulcan established that the greatest static and thermally induced aberration occurred at the periphery of the beam. Because the AO mirror was being designed for this beam line, the initial electrode design concentrated on placing more actuators towards the outer edges of the beam with relatively

few in the centre of the beam. Another important element in the design of the electrode pattern was to include a ring of actuators completely outside the diameter of the beam. This was to ensure that it was always possible to correct gradients that occurred at the very edge of the beam. The electrode pattern used is shown in Figure 4 and the predicted (phase) modal basis shown alongside. The mid band shows a high number of beam edge correction modes.

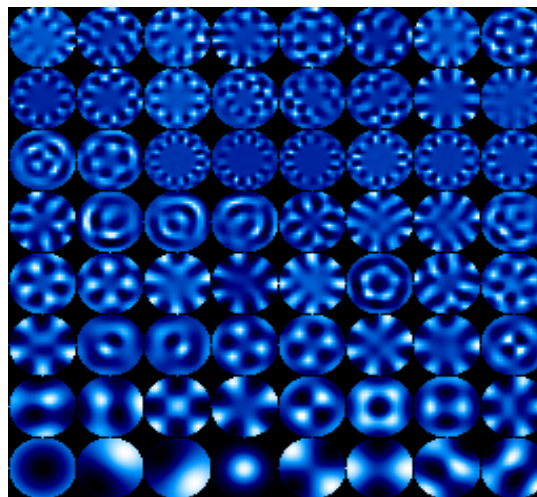
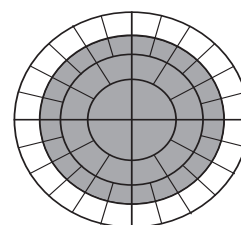


Figure 4. Electrode pattern of the AO mirror used and the computed modal basis.



The real mirror is of course unlikely to behave in the exact same way as the predicted modes above. This will be increasingly the case for higher order modes that have very little power associated with them. The two main reasons for this are the effect of noise (or errors) in the determination of the measured electrode influence functions and the fact that the “constant” A is unlikely to be constant over the whole mirror surface as a result of manufacturing and material errors. In order to make some comparison of the measured ortho-normal basis of the real mirror and that of the computed basis, the illustration of Figure 5 is presented.

In this Figure, the ortho-normal basis is measured and computed in phase gradient using a spatial sampling following the Hartman pattern for both the real mirror and the model. The

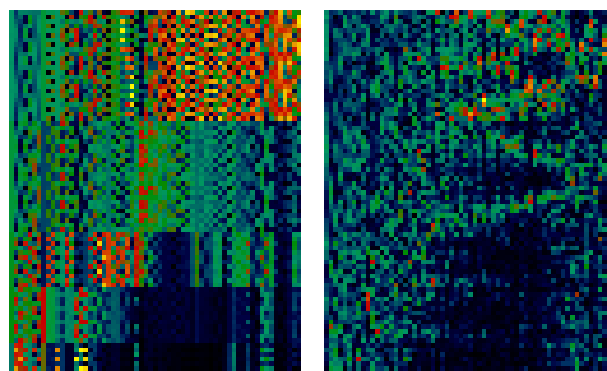


Figure 5. Comparison of the computed (left) and measured (right) ortho-normal basis of wavefront gradients. Colour level is gradient magnitude plotted against mode number (horizontal) and Hartman spot number (vertical).

comparative figure shows by colour level the magnitude of the gradient as a function of both mode number ordered according to decreasing power (horizontal axis) and Hartman spot position number (vertical axis). The spot position numbering starts at 3 o'clock on the innermost ring (bottom of axis) and proceeds anticlockwise, jumping onto the next ring at 3 o'clock and so on. The ringed structure of the sensor is evident in the computed basis, and less so in the measured one. Inspection of the Figure shows that there is a reasonable qualitative agreement between the model and the measurement, with the general re-produced. One thing to note is that as a result of its manufacture the real mirror had a number of discontinuities to its underlying bimorph structure, most notably along the central horizontal and vertical diameters and at its very centre. This is likely to perturb the modal basis away from that of a perfect plate and could explain some of the absence in the measured basis of activity predicted by the model.

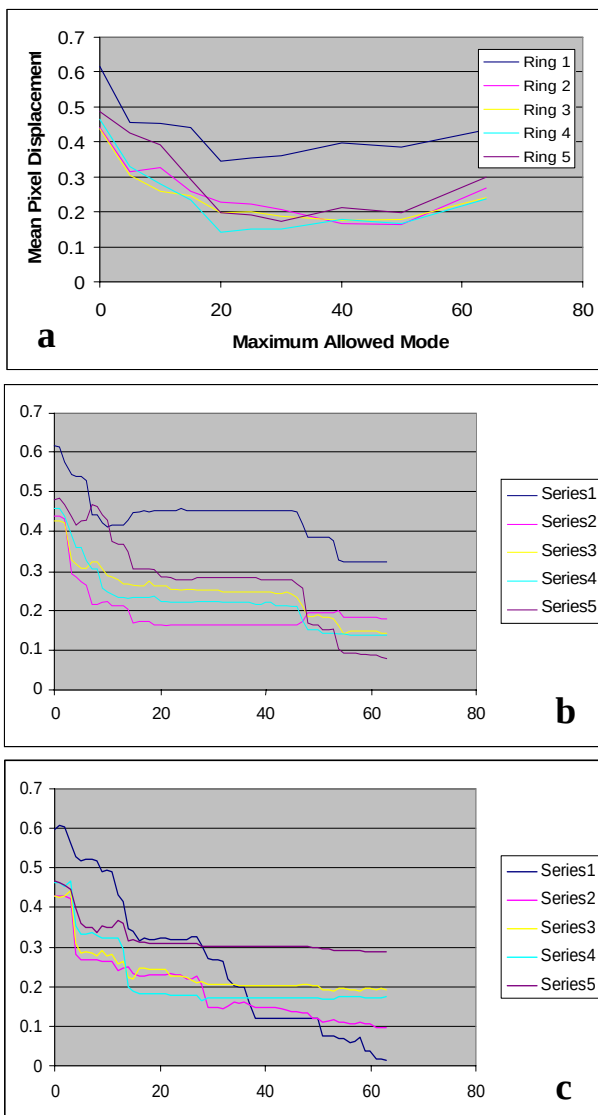


Figure 6. Measured average gradient errors within each Hartman ring (a), in comparison to predictions (b) for the actual mirror. Also shown (c) is the prediction for a mirror with the electrode pattern shown in Figure 2(b). The mirror is attempting to correct for its own aberrations only.

Model Performance

A prediction of the modal basis allows an estimation to be made of the likely performance of an electrode pattern in respect of a particular aberration. Real data was available from the use of the actual mirror illustrated in Figure 6. This mirror had an intrinsic and somewhat arbitrary aberration arising from manufacturing errors. The real performance of this mirror in correcting for itself and a prediction of its performance from the model is compared in Figure 6. Also shown in Figure 6 is a prediction of the performance of the electrode pattern shown in Figure 2(b) to correct for the same aberration. Each of the various lines is the average gradient error with respect to a diffraction limited reference within each concentric Hartman ring, plotted as a function of the maximum allowed mode number within the control matrix. Ring (also Series) number 1 is the innermost ring and ring number 5 the outermost. The singular value truncation is step-like. Figure 6(a) is the measured performance averaged over 1000 consecutive corrections. It is clear that the largest aberration is at the centre of the beam (Ring 1), which is also verified by interferometry and was known to have arisen during the mirror manufacturing process. Given the low density of actuators in the centre of the beam it is not surprising that appropriate modes do not exist to adequately address this error. Shown in Figure 6(b) is the prediction of the computer model of the response of the mirror to the same aberration. There is a reasonably good agreement between observation and expectation, although the increase of the gradient errors in the measured data above mode number 30 or so is not reproduced. Figure 6(c) also shows the predicted response of a mirror with the electrode pattern shown in Figure 2(b) which has a higher density of electrodes at the centre of the beam. Not unsurprisingly, correction is predicted to be better here for ring 1, at the expense, to some extent, of ring 5

The reduction of performance with the introduction of higher order modes in the measured data of Figure 6(a) is due to the influence of noise coupling to these higher order modes. This does not appear to be duplicated in the model. As previously stated, the measured data was taken over 1000 consecutive mirror corrections and the figure displays the mean of the means over these 1000 corrections. The data from the model however is a single correction. In an attempt to duplicate the effect of noise coupling, the model was also run over 1000 consecutive corrections, with a small random error introduced in the determination of Hartman spot positions between consecutive corrections. Figure 7(a) shows the effect of this. Clearly, the correction deteriorates, to such an extent that it becomes generally independent of the degree of mode truncation. However, for most of the rings slight minima in the truncation are observed, albeit small. The fact that the low / mid band minima are not more obviously re-produced is not so surprising because whilst going some way to illustrate the effect of noise, this is in one sense unphysical. The primary source of noise in the real system is air turbulence and thus there will be some degree of spatial correlation between errors introduced into the determination of Hartman spot positions. The effect of the spatial randomising of these errors is to introduce wavefront gradients that are more associated with higher order modes than lower ones.

However, one feature is replicated quite well and that is the effect of the noise coupling. Figure 7(c) shows the measured variance of the 1000 corrections for the real data, again as a function of maximum allowed mode. In the case of the maximum allowed mode being zero, the data is effectively illustrating the effect of air turbulence. With zero mode correction the mirror makes no change to its shape from one correction to another. Following the introduction of modes, the correction variance for all rings increases in a generally linear way, such that even though the mean correction remains approximately constant between 20 and 50 modes (Figure 6(a))

it is increasingly unstable. The model, as shown in Figure 7(b), duplicates this very well.

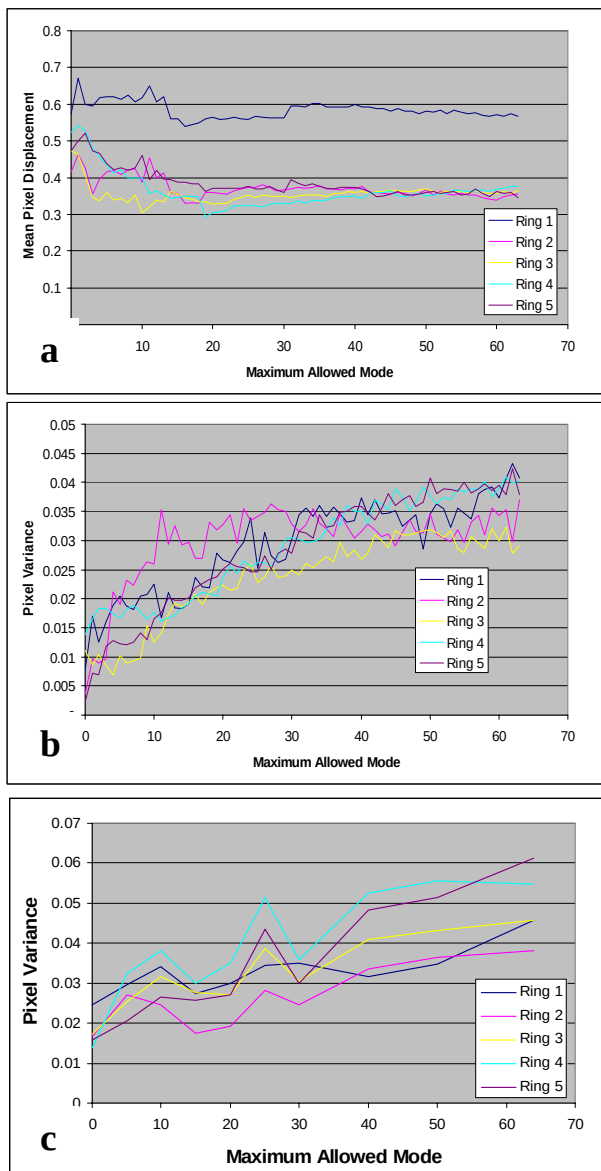


Figure 7. (a) Mean of the predicted average gradient errors within each Hartman ring over 1000 corrections with a deliberate random error introduced to the model to simulate noise. Also shown is the variance within each ring over the 1000 correction for both the model (b) and the measured data (c).

Application to Vulcan Beam 7

One of the reasons for undertaking this modelling was to attempt to determine the best electrode pattern for the aberrations that were expected on one of the Vulcan beamlines. The existing mirror has a strong localised aberration in its centre and Figure 6 has already indicated that with the existing actuator design, which was not intended to correct significant structure in the centre of the beam, the performance of the system would be limited by the mirror aberration itself. Moreover, Figure 4 also illustrated that if this aberration were to be a permanent feature of the mirror, then the electrode pattern of Figure 2(b) would be a better choice.

Thus the model was run using the known aberration of Vulcan beam 7 as an input and assuming that a next generation of mirror could be manufactured that did not possess this central feature. It is likely that the central feature of the mirror perturbed and created asymmetry to the real model basis for

correction, which the model would not have. Figure 8(a), shows the predicted performance of the existing mirror geometry to correct for the known aberrations of Vulcan beam line 7 only. Also shown for comparison in 8(b) is the predicted performance of the electrode pattern of Figure 2(b), which previously had a superior performance when using the mirror aberration as an input. The reverse is now true and indicates that the performance of the existing electrode design is likely to be better than that of Figure 2(b) as intended. Furthermore, it highlights the benefit of tailoring the electrode pattern to suit the static and or expected aberrations present in any system.

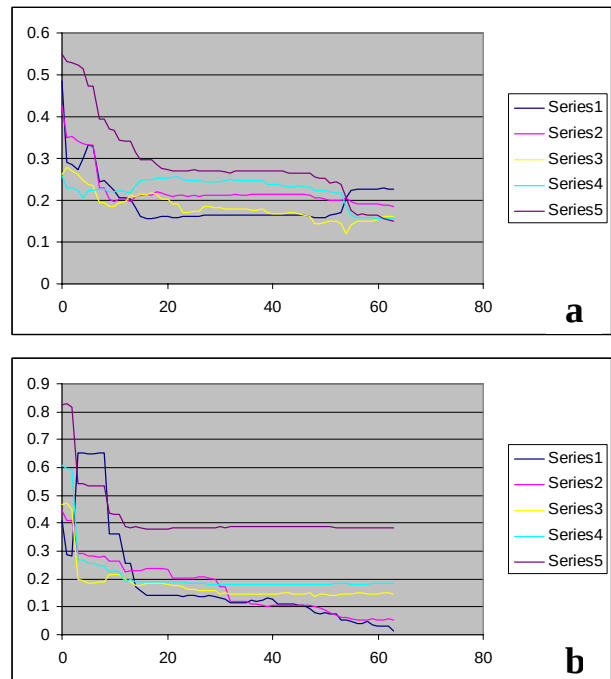


Figure 8. Predicted performance of the existing mirror electrode pattern (a) for Vulcan beam line 7 assuming that the residual mirror aberrations have been removed. Also shown for comparison in (b) is the predicted performance for the electrode pattern of Figure 2(b).

Conclusion

We have developed a computer model of a piezoelectric bimorph adaptive mirror in terms of the applied electrode pattern. It is capable of predicting performance with respect to an arbitrary wavefront aberration. This has been verified with reasonable agreement experimentally. It will be used to determine the optimum electrode pattern for a new adaptive mirror that will be installed on the primary Vulcan CPA beam line as part of the PetaWatt upgrade.

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An analysis and optimisation of optical parametric chirped pulse amplification

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Introduction

We present a detailed analysis of optical parametric chirped pulse amplification (OPCPA)¹, including ways to optimise the process. We address the following specific issues:

- The influence of chirp on the OPA process.
- The optimisation of efficiency and bandwidth, particularly in the presence of non-flat spatial and temporal pulse profiles.
- The calculation of the additional phase imposed on the amplified signal pulse by the OPA process and its influence on the final re-compressed pulse profile.
- The effect of group velocity mismatch.
- The tolerances to misalignment and input phase aberrations on the pump beam, and pump pulse bandwidth.

The primary analytical tool is a formulation based on that of Armstrong et al², which gives useful and instructive results which have good validity for parameter ranges of interest. Examples include Nd:glass and Nd:YAG pumped OPCPAs.

Analysis

The analysis of Armstrong et al is based on the plane wave solution of the coupled wave equations and assumes slowly varying pulse envelopes and a lossless medium. In a parameter range where pulse chirp can be neglected, a simple analytical solution can be obtained for the intensity and phase of the three propagating waves for the case of significant energy transfer.

It will be seen that, under conditions for maximum bandwidth of the OPCPA, the signal and idler have the same group velocity in the direction of the signal. This locks the two chirped pulses together and the requirement for validity is that the group time difference for signal and pump is small compared to the pump pulse duration.

Solution for intensity

With some manipulation and substitution the Armstrong solution (Equation 6.9) can be re-written in terms of measurable parameters as:

$$2gz = \pm \int_0^f \frac{df}{\sqrt{p(1-f)(f+\gamma_s^2)(f+\gamma_i^2) - \left(\gamma_s \gamma_i \cos \theta(0) \sqrt{p} + f \frac{\Delta k}{2g}\right)^2}} \quad (1)$$

where:

$$g = 4\pi d_{\text{eff}} \sqrt{\frac{I_p}{2\epsilon_0 n_p n_s n_i c \lambda_s \lambda_i}}$$

$$f = 1 - \frac{I_p}{I_p(0)} = \text{fractional depletion of the pump}$$

$$\gamma_s^2 = \frac{\omega_p}{\omega_s} \frac{I_s(0)}{I_p(0)}; \quad \gamma_i^2 = \frac{\omega_p}{\omega_i} \frac{I_i(0)}{I_p(0)}$$

$$p = \frac{I_p(0)}{I_p(0) + I_s(0) + I_i(0)}$$

$$\theta(t) = \phi_p(t) - \phi_s(t) - \phi_i(t)$$

$$\Delta k = \text{crystal phase mismatch per unit length}$$

Equation (1) applies to any three-wave mixing process. For an OPA with zero input idler, Equation (1) reduces to:

$$2gz = \int_0^f \frac{df}{\sqrt{p(1-f)(f+\gamma_s^2)f - \left(\frac{\Delta k}{2g}\right)^2 f^2}} \quad (2)$$

Amplification continues until, at a value of z (defined as z_A), the denominator of Equation (2) falls to zero and the pump depletion reaches a maximum value determined by:

$$f_{\text{max}}^2 - \left[1 - \gamma_s^2 - \frac{1}{p} \left(\frac{\Delta k}{2g}\right)^2\right] f_{\text{max}} - \gamma_s^2 = 0 \quad (3)$$

In the case of perfect phase matching ($\Delta k = 0$), $f_{\text{max}} = 1$ and the pump is fully depleted; the pump to signal conversion efficiency is then 100% $\times \omega_s/\omega_p$. With increasing mismatch the conversion efficiency is reduced. For $z > z_A$ the process reverses symmetrically to transfer energy back into the pump from the signal and idler.

Equation 2 has the form of a Jacobi elliptical integral, its solution being written as the elliptical function 'sn'. Since energy conservation requires that the pump depletion energy is divided between signal and idler in proportion to their frequencies respectively, we can write the signal intensity as:

$$I_s = f I_p(0) \frac{\omega_s}{\omega_p} + I_s(0) \quad (4)$$

For practical applications it is useful to estimate the pulse energies which can be calculated by integrating the intensity over space and time e.g.

$$E_s = \iint I_s dA dt \quad (5)$$

Solution for phase

With the increasing interest in shorter and shorter pulses, careful attention must be paid to the assessment of the spectral phase which is reflected in the temporal phase of amplified chirped pulses. The phase in a three-wave mixing process is obtained by solving the imaginary parts of the coupled wave equations, namely:

$$\frac{d\phi_s}{dz} = -K \frac{\omega_s^2}{k_s} \frac{\rho_p \rho_i}{\rho_s} \cos \theta; \quad \frac{d\phi_i}{dz} = -K \frac{\omega_i^2}{k_i} \frac{\rho_p \rho_s}{\rho_i} \cos \theta;$$

$$\frac{d\phi_p}{dz} = -K \frac{\omega_p^2}{k_p} \frac{\rho_s \rho_i}{\rho_p} \cos \theta \quad (6)$$

where the amplitude of each wave has been written in the form

$$\rho \exp(i\phi), \quad K = \frac{2\pi}{c^2} \chi_{\text{eff}},$$

where χ_{eff} is the effective nonlinear susceptibility.

Following the methods of Armstrong et al closed form solutions for the imaginary parts of the coupled equations can also be found, and for the case of an OPA with zero input idler these reduce to:

$$\phi_s = \phi_s(0) - \frac{\Delta k z}{2} + \frac{\Delta k \gamma^2}{2} \int \frac{dz}{f + \gamma^2}; \quad \phi_i = \phi_p(0) - \phi_s(0) - \frac{\pi}{2} - \frac{\Delta k z}{2};$$

$$\phi_p = \phi_p(0) - \frac{\Delta k}{2} \int \frac{f dz}{1-f} \quad (7)$$

Inspection of these equations leads to the following initial comments about the phase effects in an OPA.

- The phase of the amplified signal is independent of the initial phase of the pump and consequently it is possible to maintain the optical quality of the signal while using for example a pump with both spatial aberrations and having temporal phase variations resulting from a chirp.

- b) Phase changes to signal and idler only occur at wavelengths for which there is a phase mismatch ($\Delta k \neq 0$).
- c) The phase of the idler is particularly simple, see Equation (10), depending only on the initial pump and signal phases and the phase mismatch term $\Delta k z/2$.
- d) A good approximation to the phase of the signal can be obtained if the input signal is small compared to the input pump. In this case $\gamma \ll f$ and there is only a small contribution to the integral part of the equation for ϕ_s from the region of significant pump depletion. We can then use, with some manipulation, the following solution for the signal phase¹⁾:

$$\phi_s = \phi_s(0) - \frac{\Delta k z}{2} + \tan^{-1} \left[\frac{\Delta k}{2\sqrt{g^2 - (\Delta k/2)^2}} \tanh \sqrt{g^2 - (\Delta k/2)^2} \cdot z \right] \quad (8)$$

Non-collinear geometry

It is important to consider the case of non-collinear geometry³⁾ which leads to the highest gain bandwidths for an OPA. The following simple analysis can help in understanding, and optimizing, this geometry.

Gain bandwidth on the signal beam

For a narrow bandwidth pump beam and a non-angularly-dispersed signal beam the non-collinear phase matching vector diagram leads to the requirement:

$$2k_p k_s (1 - \cos \alpha) = k_i^2 - (k_p - k_s)^2 \quad (9)$$

where $k = 2\pi\nu/c$ with appropriate subscripts for pump, signal and idler beams

$$\nu_i = \nu_p - \nu_s \text{ by conservation of momentum}$$

and for type I phase-matching:

$$n_p^{-2} - n_{po}^{-2} = (n_{pe}^{-2} - n_{po}^{-2}) \sin^2 \theta \quad (10)$$

where n_{po} and n_{pe} are the ordinary and extra-ordinary indices for the pump beam.

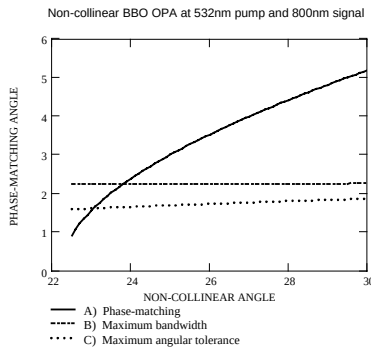


Figure 1. Conditions for phase matching, maximum bandwidth and maximum angular tolerance in an OPA.

Figure 1a shows the variation between non-collinear and phase-matching angles for BBO for a pump wavelength of 532nm and a signal wavelength of 800nm.

By setting the first differential to zero the maximum bandwidth is obtained for:

$$\cos \beta = \frac{n_{gi}}{n_{gs}} \quad (11)$$

which is just the condition for the group velocities of the signal and idler to be matched in the signal beam direction⁴⁾.

Figure 1b shows this condition as a function of the phase matching angle (which is reflected in the value of k_p) for type I BBO pumped at a wavelength of 532nm. The coincidence of the two curves 1a) and 1b) gives the point of operation for maximum bandwidth. It should be noted that this geometry results in an angularly dispersed idler wave.

Angular tolerance on the pump beam

This indicates both the maximum acceptable pump beam aberration and pump beam size and the maximum tolerance is again calculated by setting a differential of Equation (8) to zero:

$$\sin \alpha = \frac{1}{2} \left(\frac{n_p \lambda_s}{n_s \lambda_p} - \cos \alpha \right) n_p^2 (n_{pe}^{-2} - n_{po}^{-2}) \sin 2\theta \quad (12)$$

Figure 1c plots this dependence between the non-collinear and phase matching angles for the BBO example. The coincidence between this curve and the phase matching curve 1a) gives the point of operation for maximum angular tolerance.

Since the two coincidence points in Figure 1 are quite close, BBO can be operated with both high bandwidth and high angular tolerance.

Calculated examples and optimisation

Top-hat profile beams

For beams which have uniform intensity in space and time the intensity and phase of the amplified signal can be calculated using Equations (2) and (7). The chirp is taken into account through a time-dependent phase mismatch and is calculated from the known chirp and the material dispersion equations. We illustrate this calculation for an OPCPA consisting, as above, of a type I BBO crystal operating at close-to-degeneracy and pumped by a spectrally narrow line at a wavelength of 532nm (second harmonic of a Nd:YAG laser). For the purposes of comparison at high gain against the low gain of a conventional amplifier the intensity and length were chosen to give a parametric gain of 10^6 .

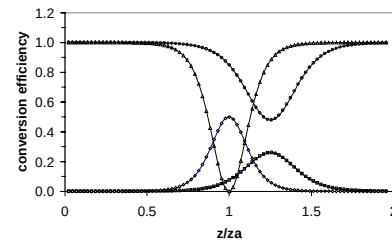


Figure 2. Pump and signal propagation in an OPA.

Figure 2 shows the calculated signal and pump intensities for zero phase mismatch as a function of the distance along the crystal up to and beyond the region of pump depletion. The cyclic nature of the process is at once apparent and indicates that 100% depletion of the pump is possible but that this can only be achieved for beams of uniform intensity and at a specific value of crystal length and intensity. Also shown is the evolution of signal and pump in the wings of the spectrum where there is a significant phase mismatch ($\Delta k L = \pi$). The peak pump depletion is now 50% and requires a greater length of crystal.

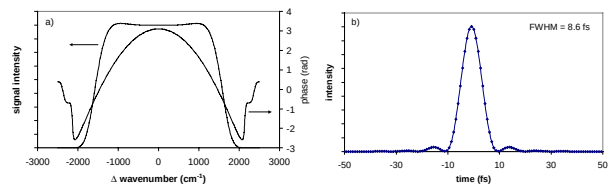


Figure 3. Amplified OPCPA spectrum, phase and recompressed pulse for collinear geometry.

Optimum conditions are taken to correspond to the maximum product of signal energy and bandwidth. An example is shown in Figure 3. Also shown is the resulting re-compressed pulse profile calculated by taking the Fourier transform of the spectral intensity and phase and assuming that the compressor is set to

compensate for linear, quadratic and cubic chirps. Although this represents only an idealised case, the potential of the OPCPA scheme is demonstrated by these calculations which give an amplified bandwidth of 3150cm^{-1} and a re-compressed pulse duration of 8.6fs.

Spectral narrowing and performance limits

Since the bandwidth of an OPA is determined by the phase mismatch (ΔkL) and the OPA gain is determined by the product $\gamma\sqrt{I_p}L$, we can achieve both high gain and bandwidth by minimising the length and maximising the pump intensity. However we must stay within the limit determined by the so-called B-integral ($=\gamma_{NL}\int_0^L Idz$) (or other nonlinear processes such as two-photon absorption or Raman generation).

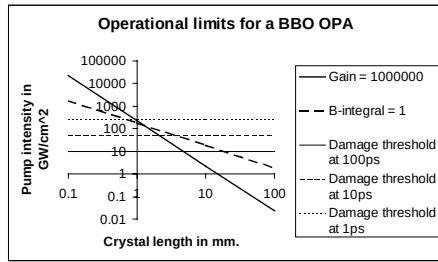


Figure 4. Operational limits for a BBO OPA.

Figure 4 plots the B-integral limit for BBO together with the curve defining a gain of 10^6 . The maximum intensity and hence also bandwidth is determined by the crossover point of these graphs.

A further limiting process, optical damage, is also represented on Figure 4. In this example the intensity limit is determined by the B-integral for pulse durations up to about 10ps. For longer pulses the damage threshold requires a reduction in the pump intensity and an increase in the crystal length, leading to reduced gain bandwidth.

Maximum bandwidth option

Amplified bandwidths greater than shown by Figure 3 are generally possible using non-collinear geometry. Figure 5 shows the gain bandwidth, phase and re-compressed pulse profile for this option for BBO. The gain bandwidth is now 4800cm^{-1} and the re-compressed pulse duration 5.7fs.

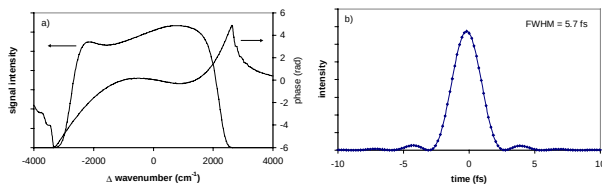


Figure 5. Amplified OPCPA spectra, phase and recompressed pulse for non-collinear geometry.

Real beam profiles

We consider the realisable example of an OPCPA with a flat-top spatial distribution for both pump and signal beams and a Gaussian distribution for their temporal profiles. Assuming equal pulse durations for pump and signal and the same example with BBO as discussed above, Figure 6 shows curves for the input and output signal when the crystal length (or pump intensity) is set for maximum product of efficiency and bandwidth. The peak efficiency in this case is 27% from pump to signal (54% depletion of the pump) with a 20% reduction in signal bandwidth during amplification. Further optimisation of the performance can be achieved by allowing a difference in pulse duration between the input pump and signal beams. Figure 7 shows the variation with pump pulse duration of the best efficiency-bandwidth product and points to an optimum value of 1.75 for the ratio of the pulse durations and a 20% higher efficiency-bandwidth product.

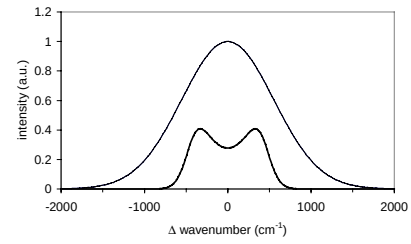


Figure 6. OPCPA input and output spectra with real beams

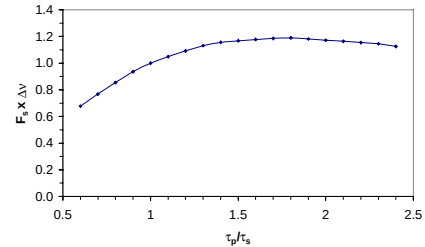


Figure 7. Optimum ratio of pump to signal pulse duration.

Optimised beam profiling

It has been demonstrated⁵⁾ that control of the beam profiles can lead to the achievement of maximum efficiency and bandwidth in an OPA. There are compensating pairs of profiles for pump and signal which give optimum performance. The simplest such pair is a flat-top profile for each. If, as is usually the case, the pump beam profile cannot be made flat-top but is typically Gaussian, the compensating signal beam profile is shaped like an 'inverted Gaussian'. This can be approximated in a multi-amplifier OPCPA by driving the earlier stages into heavy saturation.

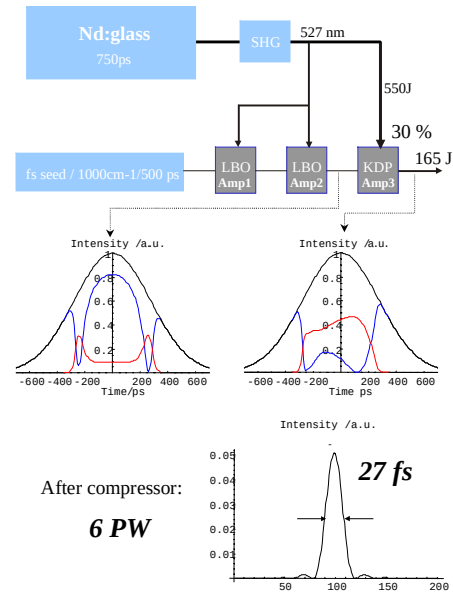


Figure 8. Optimised OPCPA design using a PW pump laser.

Figure 8 shows the optimised design for a petawatt OPCPA scheme which uses a large Nd:glass laser to provide the pump beam. The calculated temporal profile generated by the pre-amplifiers is the required shape and leads to an output signal beam with maximum efficiency and spectral bandwidth and an intensity profile which can be compressed to a short pulse with good fidelity.

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A Laser System Design for the Photo-injector Option for the CERN Linear Collider

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Introduction

This study contributes to the development of the CERN Linear Collider (CLIC). One route to the generation of the required electron injection into this system is through the use of photo-cathodes illuminated with a suitably designed laser system. The requirements of the accelerator and photo-cathodes have led to a specification for the laser system given in Table 1.

UV energy per micropulse	5μJ
Pulse duration	10ps
Time between pulses	2.13ns
Wavelength	≤270nm
Pulse train duration	91.6μs
Repetition Rate	100Hz
Energy stability	≤0.5%
Laser/RF synchronisation	≤1ps
Reliability	10 ⁹ shots

Table 1. Photo-cathode specifications.

Key laser parameters

The key parameters are those for which feasibility needs to be established and they largely determine the system design.

- 1) Laser energy stability - the 0.5% specification in the UV places a very tight requirement on the laser output. Also it must be controllable to this accuracy to meet the varying needs of the photo-cathode due to sensitivity changes etc.
- 2) Laser average power - the laser is required to deliver 430W, a high value for lasers, and one demanding careful design to prevent beam degradation due to thermal effects.
- 3) Laser pulse train power - an average output power in the pulse train of 47kW places severe demands on the laser pumping system.

Basic design features and choices

Pump source

Only diode arrays can meet the shot lifetime requirement of 10⁹ shots and have an intrinsically higher stability and lower thermal deposition in the laser material. The cost is higher but development will lead to a reduction in the cost differential.

Wavelength

A wavelength at about 1000nm is chosen since it is most efficiently pumped by laser diodes and can be conveniently converted to the UV using harmonic generation.

Gain medium

There are three principal criteria for selecting the best gain medium for the amplifiers.

The gain bandwidth must support the amplification of pulses of 10ps or less.

The material must be able to achieve a reasonable gain (greater than ~2) with quasi steady state pumping, without excessive losses due to the fluorescence decay. This loss is regarded as excessive if it is larger than the 47kW extracted power in the amplified beam.

The third is the pump power required to generate a reasonable gain in the material.

These criteria point to Nd:YLF as the best option. It also has very low thermal distortion and its birefringence ensures a well polarised output. However care must be taken not to exceed its fracture level of about 20 W/cm.

Amplifier type

Rod amplifiers are preferred, being simpler, better for optical quality and less expensive. Slab amplifiers would need to be considered if required pump powers and thermal deposition rates are too high for rod amplifiers.

Amplification can be carried out using single, multipass or regenerative amplifiers or seeded oscillators. This study mainly concentrates on single and double pass amplifiers and demonstrates that a system based on them is feasible. Four pass amplification can reduce the number of smaller amplifiers at some cost saving but with increased complexity. An injection-seeded oscillator looks a good option for the first stage of amplification especially if the master oscillator provides only low power since it is well suited to giving high power pulse trains with good stability.

System Architecture

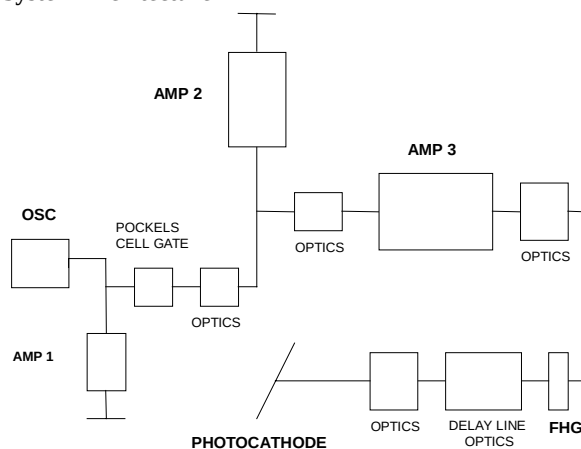


Figure 1. Basic system architecture.

An outline design architecture is shown schematically in Figure 1 and demonstrates the key features of the system.

The pulse train from a cw oscillator with the correct pulse duration and repetition rate and at the correct wavelength is amplified by a sequence of single or double pass amplifiers to the required pulse energy specification. These pulses are converted to the fourth harmonic in a pair of nonlinear crystals and the resulting UV pulse train is relayed to the photo-cathode. Other features of the system are: beam conditioning optics for beam sizing, relaying and filtering; electro-optic devices both for switching out the required pulse train and for fast feed back amplitude control; fast feedback control of pump diode array current.

Detailed design considerations

The system can be conveniently broken down into a number of aspects for detailed analysis:

- 1) General amplifier design considerations.
- 2) Amplifier designs.
- 3) Fourth harmonic generation.
- 4) Laser damage threshold.
- 5) System staging - including the disposition of the system components and the design of the beam conditioning optics.
- 6) Stability - ways to control the intrinsic instabilities of the design through design changes and through the introduction of feedback mechanisms.

Amplification

In this section an analysis is given of the dynamic gain characteristics of both single pass and double pass rod amplifiers subject to a spatially uniform pumping rate and having a spatially uniform input pulse train. Account is taken of: the diode pumping; the amplification of the beam; the depletion of the stored energy by the beam; the fluorescence losses; and the amplified spontaneous emission (ASE).

The approach taken is to specify the output requirements (pulse train power and energy stability) of the amplifier and to look for parameters which minimise the pump energy and maximise the tolerance on the input parameters. The aim is to try to establish 'steady state' operation of the amplifiers since this is most likely to be able to satisfy the stability requirement. An important feature of steady state operation is the time for it to become established, since it is necessary that this is sufficiently short that it does not lead to unacceptably high pumping losses and thermal effects.

Steady state operation

A simple and useful relationship can be found for the amplifier in steady state. In this case the extracted pulse train power is balanced by the difference between the pumping rate and fluorescence losses. This can be written:

$$P_{out} \left(1 - \frac{1}{G}\right) = \eta_p \cdot P_{abs} - \frac{\pi D^2}{4} \cdot F_{sat} \cdot \frac{\ln G}{2} \cdot \frac{(1+B)}{\tau_{fl}} \quad (1)$$

where η_p = fraction of the absorbed power (P_{abs}) reaching the upper laser state and we assume a fast energy transfer between the upper state levels.

- F_{sat} = saturation fluence = $h\nu/\sigma$
- G = amplifier gain
- B = additional losses due to ASE
- τ_{fl} = intrinsic fluorescence decay time

The factor 2 is for a double pass amplifier (1 for single pass).

For example, inserting the values for Nd:YLF, setting $B = 0$ and taking the output requirement for CLIC of $P = 47\text{kW}$ gives:

$$47 \left(1 - \frac{1}{G}\right) = 0.76 P_{abs} - 0.34 \ln G \cdot D^2 \quad (2)$$

and for a 1cm diameter rod with gain x4, absorbed power must be $= 46.4 + 0.6 = 47.0\text{kW}$ where the second term (+0.6) is the fluorescence loss.

A comparison between single and double pass amplification can also be made using Equation (1). For amplifiers with the same gain the fluorescence loss term is a factor of 2 less for double pass operation and requires less pump power to reach the same gain. For the two examples above the difference between single and double pass is only an additional 0.3kW for Nd:YLF.

Full calculation

The calculation is characterised by the following parameters:

- The absorbed pump power P_{abs} which is assumed uniformly distributed over the rod.

- The input and output fluences F_{in} and F_{out} of a pulse in the pulse train.
- The diameter D and length L of the amplifier rod.
- The pulse fluence $F(z,t)$ within the amplifier.
- The gain coefficient $\alpha(z,t)$ within the amplifier.

The calculation increments through the pulse train calculating for each pulse its amplification and the resulting gain distribution for the next pulse. An underlying assumption is that the amplifier deals with each pulse sequentially in time, and this may not be the case for multipass amplifiers. However the assumption is valid if, as in the case being considered, the pulse fluence is small compared with the saturation fluence and leads to only a small incremental change in the gain coefficient.

The pulse fluence within the amplifier can be written:

$$F(z,t) = F_{in} \exp \int_0^z \alpha(z,t) dz \quad \text{for single pass} \quad (3)$$

$$F(z,t) = F_{in} \left[\exp \int_0^z \alpha(z,t) dz + \exp \left(\int_0^L \alpha(z,t) dz + \int_z^L \alpha(z,t) dz \right) \right] \quad \text{for double pass} \quad (4)$$

The incremental change in the gain coefficient from one pulse to the next has 3 contributions: an increase due to pumping; a loss due to fluorescence enhanced by amplified spontaneous emission, and depletion by the previous pulse. Consequently:

$$\Delta \alpha(z,t) = \frac{\eta_p \eta_R}{F_{sat}} \cdot \frac{4 P_{abs} \tau_s}{\pi D^2 L} - \frac{\alpha(z,t) \tau_s (1+B)}{\tau_{fl}} - \frac{\alpha(z,t) \eta_R F(z,t)}{F_{sat}} \quad (5)$$

where: η_R = level splitting ratio in the upper laser state and it is assumed that the equilibrium in the level populations is re-established in a time very short compared with τ_s .

τ_s = time separation of the pulses in the train

An analysis of ASE is given elsewhere. In order to include its effect in this calculation approximate analytic expressions are used for B as follows:

$$B \approx 0.05 \left(\frac{D}{L} \right)^{0.3} \cdot G^{0.5} \quad \text{for decoupled double pass amplifiers}$$

$$B \approx 0.05 \left(\frac{D}{L} \right)^{0.3} \cdot G \quad \text{for single pass amplifiers} \quad (6)$$

$$B \approx 0.05 \left(\frac{D}{2L} \right)^{0.3} \cdot G \quad \text{for close-coupled double pass amplifiers}$$

Using these equations the dynamic development of both gain and pulse train fluence was evaluated to find a solution for a required output pulse train with less than 1% variation over the required pulse train length. Figure 2 shows an example of the output pulse train for the case of a double pass amplifier with its gain switched on in the presence of the input pulse train. The output pulse energy rises to become stable ('steady state') after a characteristic response time. At later times the output is seen to be stable to a very high degree. The process with the minimum response time is critically damped and evaluating a number of different simulations such as in Figure 2 we find the following approximation for critically damped Nd:YLF amplifiers:

$$\frac{4 \cdot P_{abs}}{\pi D^2} \approx 240 \text{ kW} / \text{cm}^2 \quad (7)$$

with a response time $\approx 10 \cdot \ln G \mu\text{s}$

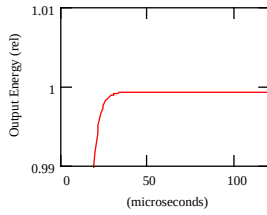


Figure 2. Double pass Nd:YLF amplifier with diodes initiated at zero time and continuous injection of pulse train.

Another important parameter of the amplifier performance is its sensitivity to variations in the pump power and the input pulse energy. These are illustrated in Figure 3 for which the input energy has been decreased by 1% and the pump power is suddenly increased by 1% after 60μs.

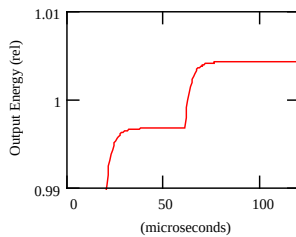


Figure 3. Effect of small changes in input energy and pump power.

The conclusion on sensitivity tests is:

$$\text{Output variation} = \text{input variation} / G + \text{pump variation} \quad (8)$$

This is simple to demonstrate analytically by differentiating Equation (1). Consequently by extending this argument through several saturated amplifiers in series, the tolerance to the input pulse energy increases with the total gain of the system. The requirement for stability of the beam energy and pump power of early amplifiers and oscillator is very much relaxed.

We also note a 1/e response time of about 4μs for a sudden pump power change.

We can conclude that good output energy stability can be achieved after an acceptable initial period of pumping to converge to steady state operation. If necessary this initial response time can be eliminated by pumping the amplifier for a short period before switching in the input pulse train.

Double pass amplification gives slightly better performance than single pass but involves additional optical elements.

Diode Pumping of the Rod

We concentrate on the requirements for the final amplifier in CLIC since these are likely to be the most difficult to meet and estimates suggested that an absorbed pump power of 47kW would be required. The problem is reduced to finding the simplest design of pumping chamber which will contain a sufficient number of diode arrays, will couple the diode power efficiently to the rod, and will allow efficient cooling of the rod.

The maximum thermal loading on the rod for the final CLIC amplifier is given by:

$$\begin{aligned} \text{Thermal Power} &= \text{Output Optical Power} \times \frac{1 - \eta_p}{\eta_p} \quad (9) \\ &= 0.32 \times \text{Output Optical Power} \quad \text{for Nd:YLF} \end{aligned}$$

Since the average output power requirement is 430W, the thermal deposition rate is 140W. This can be satisfied using simple flow-tube water immersion and a low flow rate.

The absorption efficiency of the rod has been analysed by Barnes et al¹⁾ and for the case being considered (Nd:YLF at 1% concentration, diode bandwidth = 5nm, average of both polarisations) their results can be reduced to the approximate expression:

$$\eta_{abs} \approx 1 - \exp\left(-\left(\frac{D}{0.42}\right)^{0.77}\right) \quad (10)$$

For example, for an absorption efficiency greater than 80% the rod diameter must be greater than 0.78cm. If the un-absorbed pump is reflected back into the rod for a second pass we can achieve 80% efficiency with rods of diameter 0.39cm.

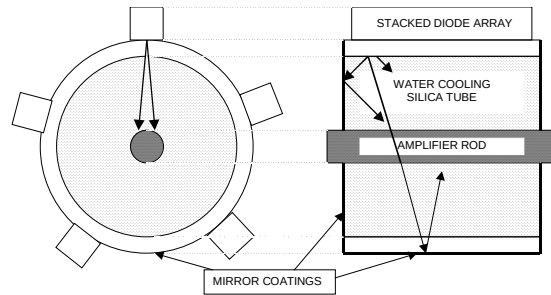


Figure 4. Schematic of diode-pumped amplifier head.

Figure 4 illustrates a simple design suitable to meet the requirements of the CLIC photo-injector system. This design stacks 5 x 9 1cm² arrays around a φ1 x 10cm laser rod, providing at a maximum total output well above the required 47kW. The estimated coupling efficiency of this design is 85% and the estimated absorption efficiency is 96%.

Thermal distortion

A significant advantage of YLF is its low value of thermal focusing. From Murray²⁾ we derive the following relationship for the thermally induced focal lengths in the 'o' (σ) and 'e' (π) planes at the principal wavelength of 1047nm:

$$f_o = 2.2 \cdot \frac{D^2}{P_{th}} \quad \text{and} \quad f_e = -0.65 \cdot \frac{D^2}{P_{th}} \quad \text{respectively} \quad (11)$$

for D in mm and P in W

or, maximum wavefront error, δ_o = 0.05P_{th} or δ_e = -0.19P_{th} μm

Although Nd:YLF has less thermal distortion than other materials it is still necessary to use spherical and cylindrical optics to correct for the resulting aberration.

Design of amplification system

The specification for the CLIC system is given in Table 1. A mean pulse train power of 47kW is required, and it is important to minimise the required pump power. A key parameter is the total gain of the amplifier system. Suitable oscillators up to 100W output power have been demonstrated so we assume for this design study that 30W is available. 30W input and 47kW output leads to the requirement for a gain of 1600.

A three amplifier system is preferred because it is more conservative and places less demands on pump power and gives less thermal effects in the final amplifier. The total pump power requirement is almost the same for all possible schemes.

The performance of the final amplifier is illustrated in Figure 5 by the dependence of the output train pulse energy on the time after initiation of the pumping, and in the presence of a constant energy input pulse train. The pump power required to achieve the specified performance is 48kW with a rod geometry of φ0.7 x 14cm. The pump pulse duration required to give a 91μs output pulse train with high stability is ≥140μs and at 100Hz the average thermal deposition in the rod is 15W/cm which is less than but quite close to the thermal fracture limit of Nd:YLF³⁾.

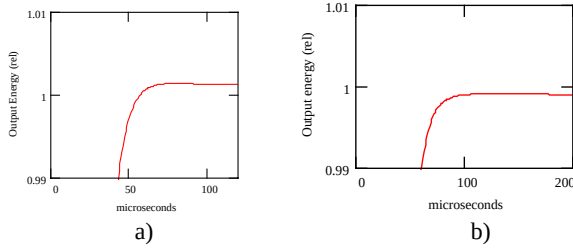


Figure 5. CLIC a) final and b) penultimate amplifier giving gains of 4 and 20 respectively.

Operating the final amplifier in double pass would result in a shorter time to reach the steady state and reduce the thermal stress in the rod by about 18%, but with increased complexity.

The penultimate amplifier operating in double pass with a gain of 20 is also illustrated in Figure 5. The required pump power is 16kW for a $\phi 0.5 \times 10\text{cm}$ rod. In this case, to ensure that the steady state is reached before the pump for the final amplifier is initiated, the pump pulse duration must be 210 μs with a resulting thermal loading on the rod of 11W/cm.

Fourth harmonic generation

Fourth harmonic generation is needed to meet the requirements of the photo-cathode and we have assumed a conversion efficiency of 10%. Although sensible to take a conservative estimate for this design study it is important to improve on this efficiency since this would lead to a significant reduction in the cost of the laser and in the loading of the final amplifier.

Fourth harmonic generation (FHG) uses two second harmonic generation (SHG) crystals in series and, in principle, each SHG process can be 100% efficient for pulses square in space and time. For many systems 50% is generated leading to an FHG efficiency of 25%, but to do this it is necessary to be able to achieve the correct conditions at the crystal. These are:

$$\text{for high efficiency: } \left(\frac{\lambda_3 d_{\text{eff}}}{\lambda_1 \lambda_2} \right)^2 \cdot IL^2 > 0.04 \quad (12)$$

for sufficient bandwidth:

$$\Delta\lambda \cdot L < \text{value for crystal and wavelengths} \quad (13)$$

for sufficient angular tolerance:

$$\Delta\alpha \cdot L < \text{value for crystal and wavelengths} \quad (14)$$

where: d_{eff} = effective nonlinear coefficient in pm/V

I = incident intensity in GW/cm²

L = crystal length in cm

subscripts 1,2 and 3 refer to the three wavelengths

$\Delta\lambda$ = input pulse bandwidth in nm

$\Delta\alpha$ = input beam divergence in mrad

Equation (13) determines the maximum length of crystal acceptable for the bandwidth of the laser. For 10ps pulses the minimum bandwidth is 1.5cm⁻¹ (the transform limit for a 10ps pulse). Having determined the crystal length, or less if appropriate, Equation (12) is used to determine the pulse intensity required to achieve high efficiency. Equation (14) determines the acceptable divergence of the input beam.

Crystal parameters suggest that, using spatially flat top beams it should not be difficult to achieve at least 50% conversion at each stage and an overall conversion efficiency to the fourth harmonic of 25%, a factor of 2.5 higher than assumed for this design study. BBO for both stages looks a good option since it allows the beams to be larger and have the same size. The most critical parameter may be the beam divergence requirement at the fourth harmonic stage as this must be close to the diffraction limit to achieve maximum efficiency. If this proves a problem then KDP offers an attractive alternative.

Optical Damage Requirement

Estimated minimum damage threshold (for anti-reflection coatings) for the CLIC output pulse train (4.2 J in 91 μs) is 40 J/cm². Allowing for a safety factor of 4, maximum fluence is 10 J/cm² and minimum beam diameter is 7 mm. This criterion allows us to have a calculated beam non-uniformity of 2:1 and still have a factor of 2 in hand.

System Staging

The layout of the system and its optical design are determined by the requirements of beam size and profile at all points in the system. These requirements are:

- The oscillator to generate a single mode beam.
- The beam diameter to match that of the amplifiers.
- For maximum efficiency the beam profile to be close to top hat at the final amplifier, harmonic crystals and photo-cathode.
- To minimise the risk of component damage, the peak to average intensity in the beam at all components should be less than 2.

The single mode generated profile is converted to as close to top hat as possible before the high efficiency amplifier stages. This profile is then image-relayed to subsequent amplifiers, into the harmonic crystals and onto the photo-cathode. The image relays also enable the beam diameter to be matched to the following stage.

The closest it is possible to approach a top hat distribution and meet the requirement that the peak to average intensity must be nowhere greater than 2 is demonstrated in Figure 6 for a 'super-Gaussian' profile. In this case the profile FWHM is 9.4mm or 94% of the final amplifier aperture.

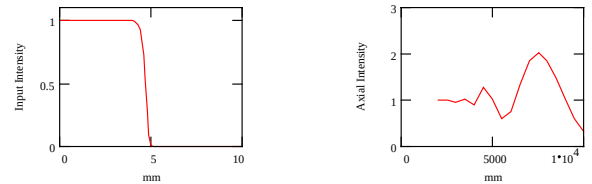


Figure 6. Super-Gaussian and down-stream diffraction pattern.

A schematic of the proposed optical layout of the system is shown in Figure 7.

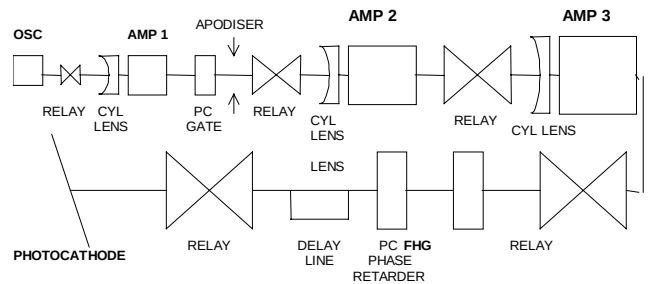


Figure 7. Optical design for the photo-injector laser system.

Conclusions

A design for a laser system has been proposed to meet the specifications appropriate for the CLIC drive beams. The feasibility of this system both in terms of performance and cost have been demonstrated.

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Design of a 5 PW Optical Parametric Chirped Pulse Amplifier for the Iodine Laser Asterix IV

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Introduction

A rapidly evolving and exciting field in the current development of lasers is the generation of ultrashort pulses and ultrahigh peak powers fostered by the technique of chirped pulse amplification (CPA). Exploiting this approach, powers up to 1 PW have been obtained¹⁾ and with comparable magnitudes projected for other systems²⁻⁵⁾. The future development of these systems to higher powers would require the generation of shorter pulses. However, the existing systems have already reached their practical limits in pulse duration given by the bandwidth of the amplifier gain medium. These limitations can be circumvented using a technique called optical parametric chirped pulse amplification (OPCPA)^{6,7)} relying on amplification within a broadband optical parametric amplifier. In this concept the energy from a narrowband, high power laser operating in an efficient energy extraction mode (typically on the nanosecond timescale) is transferred onto a broadband seed pulse generated as an ultrashort pulse and stretched to match the duration of the pump. The OPCPA technique is particularly beneficial to those high power laser systems for which the conventional CPA technique cannot be used effectively. This is especially true for a high power iodine laser because of its very narrow gain bandwidth.

In this report, we numerically demonstrate that the implementation of OPCPA to a high power iodine laser system can be used to greatly enhance its performance and generate powers up to ~5 PW, focused intensities higher than 10^{23} Wcm^{-2} and pulses with duration as short as ~20 fs. The presented design was calculated to match the existing output parameters of the Asterix IV iodine laser. The numerical simulations used in the design take into account saturation effects within the OPCPA amplifiers, and the temporal variation of the pump pulse intensity. A full account of this work can be found in Reference 8.

Optical Parametric Chirped Pulse Amplification

In the OPCPA scheme the energy from a high power laser system operating in a narrow bandwidth, energy efficient mode is transferred onto a chirped pulse in an optical parametric amplifier (OPA). The amplified pulse is then recompressed in a grating compressor. The high power laser pulse and chirped pulse act as pump and signal, respectively. The OPA typically operates in a noncollinear geometry⁹⁾ optimised to give a maximum gain bandwidth. The scheme overcomes the bandwidth limitations of conventional high power lasers and enables pulses in the region of tens of femtoseconds to be generated. Other advantages of this approach include lower amplified spontaneous emission (ASE) on target and improved beam quality stemming from the fact that pump pulse aberrations are not imprinted on the amplified chirped pulse.

The OPA process is fully described by three coupled wave equations expressing the nonlinear interactions between the pump, signal, and idler waves¹⁰⁻¹²⁾. In the nanosecond regime where the group velocity mismatch between the pump signal and idler pulses can be neglected the set of equations can be reduced in the plane wave approximation to^{12,13)}.

$$2L = \pm \int_0^{f(L)} \frac{df}{\sqrt{f(1-f)(f+\gamma^2)g_o^2 I(t) - (\Delta k(t)/2)^2 f^2}}$$

where

$$\gamma^2 = \frac{\omega_p I_s(t)}{\omega_s I_p(t)},$$

f is the fraction of energy lost to the pump and distributed between the signal and idler in proportion to their frequency at time t , L is the propagation distance within the crystal, g_o is the gain coefficient defined in⁶⁾, ω_p and ω_s are the pump and signal angular frequencies, respectively, $I_p(t)$ and $I_s(t)$ are the time dependent pump and signal intensities at the input of the crystal, respectively, and Δk is the wave vector mismatch between the three waves. It can be shown¹³⁾ that the additional phase acquired by the signal within the OPCPA can be approximated by the phase in the non-saturated case given in Reference 6.

The above equation was solved numerically in *Mathematica 3.0* for a three stage OPCPA as given in Figure 1. The dependence of the gain coefficient g_o on the signal and idler wavelengths across the pulse bandwidth was neglected as it only accounts for $\pm 1\%$ change corresponding to $\pm 2\%$ change of pump intensity which, as shown later, is insignificant in the presented design.

Asterix IV / PALS Pump Laser

The OPCPA system discussed in this paper is conceived as an upgrade to the iodine laser Asterix IV¹⁴⁾ which is integrated into a new facility named PALS (Prague Asterix Laser System)¹⁵⁾. The Asterix IV is a high power laser system consisting of a master oscillator and an array of five power amplifiers. At the fundamental wavelength (1.315 μm) it delivers in a single beam up to 1.2 kJ of energy in a pulse with a duration of 100 to 500 ps and beam diameter 290 mm. The beam can be frequency tripled to 438 nm in a DKDP crystal, with an efficiency up to 60 %. The Asterix IV also delivers up to 100 J in an auxiliary beam with 148 mm diameter, which may be converted to 438 nm with up to 30 % conversion efficiency. A particularly noteworthy feature is a good spatial quality of the output beams exhibiting intensity uniformity within a few percent of rms deviation from the ideal top-hat profile.

The Asterix IV bandwidth is less than $\sim 1 \text{ cm}^{-1}$ (1.7 $\text{\AA}$) which is more than two orders of magnitude less than that possessed by Nd:glass systems and as a result the iodine laser is not capable of the effective amplification of pulses with bandwidth larger than $\sim 30 \text{ GHz}$. This restricts its pulse duration to above $\sim 40 \text{ ps}$. Consequently the conventional direct chirped pulse amplification (CPA) technique as a means of generating sub-picosecond high-power pulses is not applicable to this type of laser. Alternative routes for producing short pulses with Asterix IV have been proposed. These include the use of the frequency tripled 483 nm beam to drive the population inversion in an auxiliary amplifier consisting of either a Raman ethanol-filled cell¹⁶⁾ or a Ti:sapphire crystal¹⁷⁾. Although the viability of both of these approaches was demonstrated at the millijoule level, their scalability to a larger system utilising the full pump power of Asterix IV is yet to be established. It is however expected that the maximum achievable peak power would not exceed $\sim 100 \text{ TW}$.

In contrast, the Asterix IV iodine laser system is ideally suited as a driver for an OPCPA as it has a high spatial uniformity and large pulse energy available in a single beam (500 J, 438 nm) of subnanosecond duration. Its third harmonic output (438 nm) can be used to pump an OPCPA consisting of LBO and KDP crystals to amplify very broad band pulses at wavelengths (~ 785 nm) which can be conveniently generated by existing commercial Ti:sapphire oscillators.

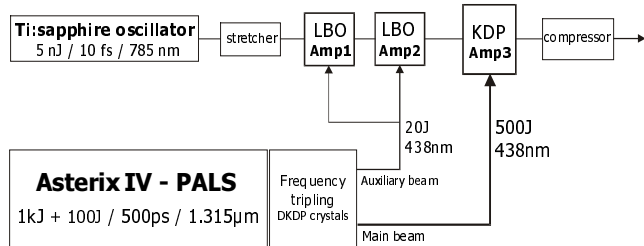


Figure 1. The proposed layout of the OPCPA system using the high-power iodine laser Asterix IV as a driver.

Design of an OPCPA Add-on System to Asterix IV

The conceptual layout of the OPCPA scheme is shown in Figure 1. The system consists of two LBO pre-amplifiers (of thickness 13.5 mm and 12 mm, respectively) of a moderate size, and a final, large aperture (270 mm diameter clear aperture, 45 mm thickness) KDP power-amplifier. The LBO stages are driven by the Asterix IV auxiliary beam using ~ 20 J at 438 nm. The final KDP stage is pumped by the third harmonic of the main Asterix IV beam with energy 500 J, which is conservatively taken lower than the highest available. The third harmonic output was favoured over the second to pump the OPCPA as its wavelength enables broader bandwidth to be amplified in the OPCPA. BBO crystals were also considered for use as pre-amplifier stages but provided narrower gain bandwidth than LBO crystals. The temporal shape of the pump pulse used in the modeling was Gaussian with a nominal FWHM of 500 ps. A suitable seed pulse can be generated from a Ti:sapphire oscillator with a sech^2 temporal profile and FWHM duration as short as 10 fs, corresponding to a spectral bandwidth ~ 1000 cm^{-1} . The seed pulse is stretched (3.2 cm^{-1}/ps) in a grating stretcher to several hundred picoseconds and injected into the first LBO stage, temporally overlapping with the pump pulse. The amplified pulse is compressed in a compressor with overall throughput 56% (assuming 70 % compressor throughput and additional 20 % loss due to spectral clipping in the compressor).

Optimized Configuration using 500 ps Pump Pulses

A non-zero angle between the signal and pump pulses was used (internal angles of 2.1 and 1.4 deg for LBO and KDP, respectively) in order

- (i) to maximise the OPCPA bandwidth,
- (ii) to enable a suitable phase mismatch to be introduced by detuning the crystals to maximise the amplifier bandwidths and
- (iii) to help separate the beams after the amplification.

An additional feature of the optimisation was the variation of both the ratio of pump and signal pulse durations and the length of individual crystals while keeping the B-integral below unity. The highest peak power was obtained with the signal pulse shorter in duration by a factor 1.6 relative to the 500-ps pump pulse (~ 310 ps). The maximum achieved energy extraction efficiency in the final KDP amplifier was 36 % giving an output energy of 180 J.

Figure 3 shows the temporal profile of the signal pulse after recompression. The resulting pulse length is 21 fs. By accounting for losses in the compressor, the simulation demonstrates that the peak powers up to 4.9 PW may be generated. The overall intensity contrast of the pulse is better than 5×10^{-2} and better than 10^{-3} outside the range ± 100 fs. The output pulse contrast can be improved by either spectral pulse shaping in the compressor or by operating the OPCPA in a regime optimised for highest contrast at some loss to the peak intensity.

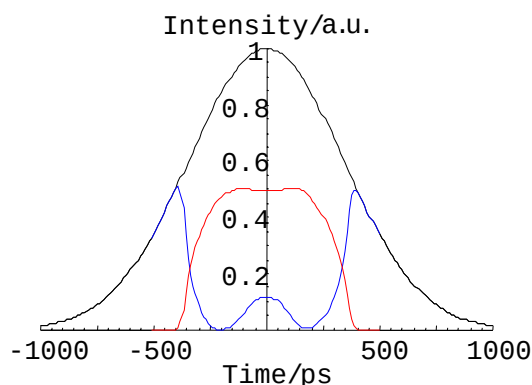


Figure 2. Intensity temporal evolution for the input pump (black), output pump (blue) and output signal (red) pulses in the final KDP amplifier.

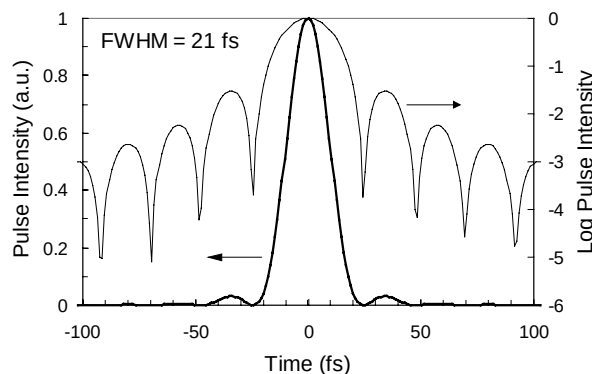


Figure 3. The temporal profile of the output pulse after recompression, obtained by taking the Fourier transform of the output signal spectrum and residual phase.

Practical Aspects of the OPCPA Design

The beams are injected into the amplifiers using dichroic mirrors at the required non-collinear angle with respect to the signal beam. The Amp3 is driven by the Asterix IV main beam which is telescoped from 290 to 270 mm to attain a higher pump fluence allowing the use of a shorter KDP crystal and to avoid possible problems with overfilling of the compressor gratings. The reduction of the Asterix IV main beam from 290 to 270 mm may be accomplished most conveniently by adapting the output end of the current final spatial filter. The Asterix IV / PALS beam divergence which is below 50 μrad is well within the pump beam angular tolerance of OPCPAs in the presented design. The input and output faces of the crystals constituting the amplifiers should be antireflection coated for the signal and idler wavelengths, to minimise the internal reflection of these beams to avoid potential parasitic oscillations.

The ~ 10 fs seed pulse can be conveniently generated using a Ti:sapphire oscillator synchronised to the 38 MHz radio-frequency driving the acousto-optical mode coupler of the Asterix IV oscillator. As the jitter of the Asterix IV oscillator is well within 100 ps, it should not be a critical factor for the shot-

to-shot stability of the performance of the proposed OPCPA chain⁸⁾. The oscillator pulse having an energy of ~ 5 nJ is frequency chirped to 310 ps in a stretcher. It is then injected to the Amp1 to match the temporal peak of the pump pulse and amplified to ~ 0.24 mJ. Both the residual pump and the idler (~ 990 nm) waves are removed from the beamline prior to the beam expander using their angular separation with respect to the signal. Upon amplification to ~ 0.5 J in Amp2, the signal beam is separated from the residual pump using a dichroic mirror while the idler wave is again eliminated using its angular separation with respect to the signal beam. The final amplification in the KDP stage is achieved with the total spatial overlap of the signal and pump beams. Residual pump and idler beams are removed as for Amp2, requiring for the idler an optical path of ~ 3.1 m. The signal fluence on the compressor gratings is ~ 0.3 Jcm⁻², which is safely below the damage threshold of currently available Au-coated gratings. In a double-pass compressor involving commercially available gratings 40 cm in size, designed to an angle of incidence of ~ 45 degrees, the signal beam will underfill the first grating and will be spectrally clipped at $\sim 4 \times$ FWHM on the second one¹⁸⁾. Assuming a 56% efficiency of the compressor, we obtain the power in the compressed beam of 4.9 PW representing an improvement by three orders of magnitude over the existing system.

Assuming a focusing reflective optic with the f -number equal to 1 and 3 and a 2-times diffraction limited beam⁶⁾ the estimated focused intensity available on target would be $\sim 1.6 \times 10^{23}$ Wcm⁻² and 2×10^{22} W/cm², respectively. This represents an improvement of five orders of magnitude over the highest attainable focused intensity from the current Asterix IV / PALS system.

Conclusions

The presented design demonstrates that the OPCPA technique promises a very large increase in peak power (1000 $\times$), focused intensity (100,000 $\times$) and reduction in duration for the high power pulse down to 21 fs.

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Possible Electro-optic Materials for use in Vacuum Ultra Violet Pockels Cells

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Introduction

Shutters have been used to modulate the output of light sources since optical science began. A very wide range of shuttering techniques is available but few of these work in the vacuum ultraviolet (VUV) part of the spectrum, usually considered to have a long wavelength limit of ~190 nm. Particular problems arise when the requirement is for high speed VUV shutters.

There are a number of applications for such devices but perhaps the most important current one is the selection of single VUV pulses from synchrotrons. These are high average power facilities, providing radiation to many users at the same time. Their output consists of pulse trains lasting for hours, with intervals of just a few nanoseconds between pulses of 10-100 ps duration. While the short inter-pulse interval is not a problem for most experiments it does restrict the study of processes with relatively long decay times. This can be accommodated to some extent by operating the synchrotron in “single-bunch” mode, where the inter-pulse interval can be hundreds of nanoseconds. However this leads to a substantial reduction in average power which is unpopular with most of the other users. A much better solution would be to provide each of the synchrotron’s beamlines with a fast shutter, allowing single pulses to be isolated. Unfortunately this is not currently practical in the VUV where the fastest shutters are based on the photoelastic effect. This involves interrupting the beam using two crossed polarisers with a quartz block between them. When the block is stressed by an acoustic wave it exhibits birefringence which alters the polarisation of the light passing through it, thereby opening the shutter. However the acoustic waves cannot be switched faster than a few hundred kilohertz, so photoelastic shutters are far too slow to select single pulses. Much faster shutters can be built using the electro-optic effect. Here the quartz block in a photoelastic shutter is replaced with a material whose birefringence depends on the applied electric field, rather than on mechanical stress. Electro-optic shutters, including one called the Pockels cell, can operate at gigahertz frequencies.

Pockels effect

The term “Pockels effect” is used to describe an electro-optic response where the induced birefringence is linearly proportional to the applied electric field. The Pockels effect can only occur in materials which are not centro-symmetric, i.e. in the case of crystals, those that have no central point through which each atom can be reflected onto an identical atom¹. This is also a necessary condition for crystals to be piezoelectric. Of the 32 crystal classes, only 20 are not centro-symmetric, so many crystals are excluded from displaying the Pockels effect. The same is true of all disordered materials e.g. glasses and liquids in their natural states, although it is possible for “poled” glasses to have linear electro-optic coefficients².

In order for a material to work successfully in a VUV Pockels cell it must be transparent in the VUV and have a sufficiently large electro-optic coefficient. To our knowledge the only non-centro-symmetric crystals which are known to transmit at wavelengths below 190 nm³ are the colquirrites, lithium calcium aluminium hexafluoride (commonly known as LiCAF) and its analogue, lithium strontium aluminium hexafluoride (LiSAF). A recent literature search revealed no reference to their electro-optic coefficients so it was decided to attempt to measure these directly.

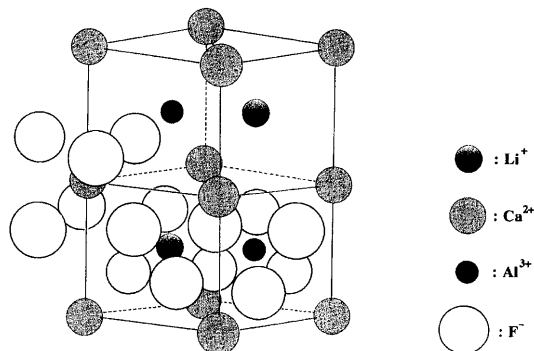


Figure 1. The crystal structure of LiCAF.

Linear electro-optic coefficient calculations

The linear electro-optic effect is described mathematically⁴) by the following equation, which relates the change in the components of the optical indicatrix, $(1/n^2)_{ij}$, to the components of the electric field vector, E_k , through the third rank electro-optic tensor, r :

$$\Delta(1/n^2)_{ij} = r_{ijk}E_k \quad (1)$$

Since r is symmetric in the first two indices, the Einstein summation rule over equal indices can be used and r can be reduced to matrix form.

The crystal structure of LiCAF is shown in Figure 1 (LiSAF is identical except that the calcium ions are replaced by strontium). The structure has 3m symmetry and it can be shown⁵) that in this case ten of the elements of r are identically zero and only four of the remaining eight are independent. In more detail:

$$r = \begin{pmatrix} 0 & r_{12} & r_{13} \\ 0 & r_{22} & r_{23} \\ 0 & 0 & r_{33} \\ 0 & r_{42} & 0 \\ r_{51} & 0 & 0 \\ r_{61} & 0 & 0 \end{pmatrix} \quad (2)$$

and

$$r_{12} = -r_{22} = r_{61}, r_{42} = r_{51}, \text{ and } r_{13} = r_{23} \quad (3)$$

The actual size of any Pockels effect will depend on the magnitudes of r_{12} , r_{13} , r_{33} and r_{42} . These are difficult to model numerically⁶) so the only way to establish whether LiCAF or LiSAF will be a useful Pockels material is to measure them.

In general applying an electric field to a Pockels material changes its refractive index in such a way as to steer, as well as retard, different polarisation components of the transmitted light. Beam steering is undesirable in a practical shutter, so particular geometrical arrangements are chosen to eliminate it. Two common arrangements are to propagate the light with its k vector perpendicular to the entrance and exit faces of the crystal and either parallel to the applied electric field or perpendicular

(transverse) to it. It can be shown that an $\mathbf{r}$ matrix constrained as in (2) and (3) leads to an identically zero birefringence when the $\mathbf{E}$ and $\mathbf{k}$ vectors are parallel, so only the transverse arrangement can be used for Pockels materials with 3m symmetry. Such an arrangement is shown in Figure 2. The retardance, Γ , i.e. the phase difference introduced between the light polarised along the material's optic axis and that polarised parallel to it, is then given by:

$$\Gamma = \frac{\omega l}{c} \left\{ n_o - n_e + \frac{n_e^3}{2} r_{33} \frac{V}{d} - \frac{n_o^3}{2} r_{13} \frac{V}{d} \right\} \quad (4)$$

where c is the speed of light, ω is its angular frequency, n_o and n_e are the crystal's refractive indices in the absence of any applied field and the other variables are as defined in Figure 2. The shutter is “closed” when the value of Γ is an even multiple of π radians and fully “open” when it is an odd multiple. The length of the Pockels material is usually adjusted so that Γ is an exact multiple of 2π radians when $V=0$.

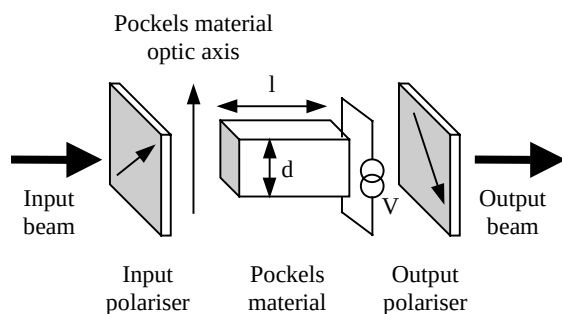


Figure 2. Transverse Pockels cell arrangement, showing the applied voltage, optic axis, polariser and beam directions.

Experimental setup

The experimental setup is shown in Figure 3. It is almost identical to the schematic in Figure 2 except that a Babinet-Soleil compensator has been added between the first polariser and the crystal. This allows the total retardance to be adjusted to an odd multiple of $\pi/2$ radians which is the value at which the output is most sensitive to small changes in Γ .

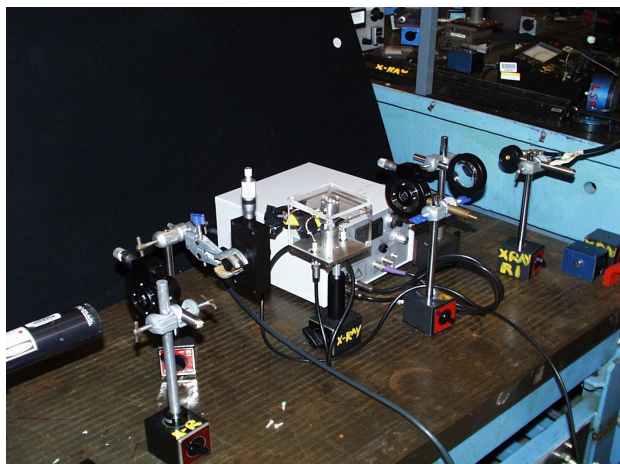


Figure 3. Photograph of the experimental set-up.

The light source is a He-Ne laser operating at a wavelength of 632.8 nm. The LiCAF and LiSAF crystals were provided by VLOC Inc⁷⁾ and are mounted between spring-loaded solid electrodes in a custom built cell. Their dimensions are given in Table 1. The high voltage comes from a commercial Pockels cell driver (Leysop Ltd) which can deliver up to 8 kV with a falltime to ground of less than 5 ns. The output signal is

monitored using a silicon photodiode (Thorlabs Inc, DET 210). To reduce the noise the system was fired repetitively and up to 64 signals were averaged.

Crystal	Length l (mm)	Height d (mm)
LiCAF	6.00 ± 0.005	6.00 ± 0.005
LiSAF	10.02 ± 0.005	9.38 ± 0.005

Table1. Dimensions of the crystals.

Under good conditions the system should detect a retardance change when the driver is fired of as little as 0.01 radians.

Results

Preliminary measurements have shown no Pockels effect in either crystal. It would seem that the upper limits to the value of $(n_e^3 r_{33} - n_o^3 r_{13})$ are approximately 4×10^{-8} cm/kV for LiCAF and 5×10^{-8} cm/kV for LiSAF. A value of the order of 10^{-6} cm/kV would be required to make a practical Pockels cell within the constraints of high voltage breakdown and useable crystal length.

However the apparent absence of any Pockels effect may be due to one or more experimental artifacts. In particular the high natural birefringence of both materials (more than 10^3 radians in each sample) means that strict crystal parallelism is required if the birefringence is not to vary significantly across the beam width. If it were present such variation would mask small Pockels signals.

It is planned to carry out more detailed measurements including a calibration of the experimental set-up using a sample of KDP – a well-characterised Pockels material.

Conclusions

The colquiriite crystals LiCAF and LiSAF have been identified as being potential transverse Pockels materials in the VUV. However to be practically useful they must exhibit sizeable electro-optic coefficients. An experimental set-up has been designed and built to measure these coefficients. Preliminary results suggest that any effects are very small. However further and more detailed experiments, including a calibration of the experimental hardware, are under way.

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Schedules and Operational Statistics

- 1) Vulcan**
- 2) Astra**
- 3) Lasers *for* Science Facility**

Vulcan Operational Statistics

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Vulcan has completed an active experimental year, with 8 full experiments taking place between April and December 2000 in the two main target areas, East (TAE) and West (TAW). The laser was shut down for the first three months of 2001 to install equipment for the Petawatt upgrade.

Table 1 below shows the operational schedule for the year, and illustrates the shot rate statistics for each experiment. Numbers in parentheses indicate the total number of full energy laser shots delivered to target, followed by the number of these that failed.

The total number of full disc amplifier shots that have been fired this year is 951 with only 44 of these failing to meet user requirements. This gives an overall system reliability figure of 95.4%. The EPSRC Service Level Agreement (SLA) requires Vulcan to be at least 90% reliable.

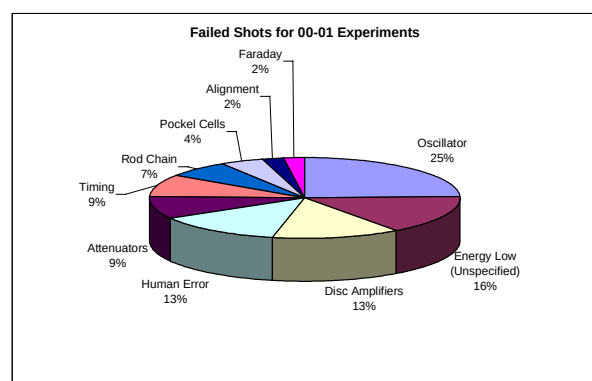


Figure 1. Analysis of Vulcan failure modes.

The SLA also requires that the laser system be available, during the four week periods of experimental data collection, from 09:00 to 17:00 hours, Monday to Thursday, and from 09:00 to 16:00 hours on Fridays (a total of 156 hours). The laser has not always met the startup target of 9:00 am but it has been common practice to operate the laser well beyond the standard contracted finish time on several days during the week and to operate during some weekends. On average, Vulcan has been available for each experiment for approximately 138 hours during contracted hours with an additional 9 hours of laser downtime giving an availability of 82%. The facility was also operated for an average of 80 additional hours per experiment outside of contracted hours giving an overall availability of 132%.

The Vulcan laser remains very reliable; the overall shot failure rate to target for the year is 4.6%. This compares with 4.6% during 1999-2000 and 5.4% for the previous year. Analysis of the reasons for failure of the individual shots enables a breakdown of these causes into specific categories. Figure 1 shows the identified failure modes and their individual failure rates. This information enables servicing and equipment refurbishment to be focused on the most serious sources of system downtime. Figure 1 shows the most serious causes of failed shots to be the oscillators (25%), energy low (unspecified) (16%) and the disc amplifiers (13%). These issues are being addressed individually. Improvements to the system continue to be made by targeting the main causes of failure. The three main causes of failure for 1999-2000 were the rod amplifier chain (19%), the alignment of the beam through the system (17%) and the oscillators (14%). Improvements to the alignment procedure included the use of CCD cameras to monitor the near field images at the output of the rod amplifier chain.

PERIOD	TAE	TAW
24 Apr – 4 June	GR/L72718 – <i>J Wark</i> Radiative transfer (115, 5)	GR/L79151 – <i>A E Dangor</i> Beat-wave acceleration (82, 3)
12 Jun – 23 Jul	Not operational	GR/M82936 – <i>K Krushelnick</i> CPA magnetic fields (174, 4)
31 Jul – 10 Sep	Not operational	Direct Access – <i>M Borghesi</i> Proton imaging (119, 7)
24 Sep – 29 Oct	GR/L72718 – <i>J Wark</i> Radiative transfer (134, 9)	GR/L04436 – <i>O Willi</i> Additional tickets (119, 5)
13 Nov – 24 Dec	LLNL access – <i>G Collins</i> EOS of planetary cores (90, 3)	GR/L79151 – <i>A E Dangor</i> Wakefield acceleration (118, 8)

Table 1. Experimental schedule for the period April 2000 – March 2001. (Shut down for Upgrade, January to March 2001).

Astra Operational Statistics

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A total of 40 scheduled experiment weeks were carried out with the Astra laser during the reporting period April 2000 to March 2001. The EPSRC sponsored 73 % of the experiments whilst the remainder were sponsored by the EU. All of the experiments were physics based.

The Astra laser was available for experiments for an average of 75 % of the time in normal day-time hours during scheduled experiments. In 6 of the 8 experiments 100 % of day-time down-time was made up in out-of-hours working. The average lost-time made up was 88 % across all experiments. Reliability defined as the time the laser was available as a percentage of the total time provided to scheduled experiments was 79 %.

Eleven weeks of development this year have helped Astra make a successful transition from a development programme to an

operational facility capable of delivering 5 TW pulses of 50 fs duration with focused intensities up to 10^{19} Wcm⁻². Facility development focused exclusively on characterising the system and optimising it for the user programme. Pulse energy and beam distribution, for example, have been improved by about 25% as the performance of the final amplifier has been enhanced with the installation of a better quality titanium-sapphire crystal. We have worked to reduce pre-pulse to $\sim 10^{-5}$ of the main pulse, an essential requirement for many experiments. A suite of diagnostics are in place to support experiments – a single-shot autocorrelator to monitor pulse duration and on-line pulse spectrum, laser energy, far and near-field detectors are in place to monitor the laser through the day. A third-order correlator (TOC) is also available.

Date	Target Area 1 (ATA1)	Target Area 2 (ATA2)	
3 Apr		Laser amplifier development	
10 Apr	Ross (RAL) Gratings damage tests		
17 Apr			
24 Apr			
1 May			
8 May	Newell/Williams (UCL/Belfast) Short pulse laser interactions with positive ions and molecules	System characterisation	
15 May			
22 May			
29 May			
5 Jun	Newell/Williams (UCL/Belfast)	Hooker (Oxford) Short wavelength lasers driven by optical field ionisation Direct access	
12 Jun			
19 Jun			
26 Jun			
3 Jul to 24 Jul	Laser maintenance and optimisation		
31 Jul		Maintenance	
7 Aug		Hooker (Oxford) Capillary waveguides for driving Short-wavelength lasers	
14 Aug			
21 Aug			
28 Aug			
4 Sep		*	
11 Sep		Maintenance	
18 Sep			
25 Sep			
2 Oct			
9 Oct		Dangor (IC) Laser plasma wave generation and electron acceleration	
16 Oct			
23 Oct			
30 Oct			
6 Nov to 18 Dec		Laser maintenance and optimisation	
25 Dec		CHRISTMAS/NEW YEAR	
1 Jan	Maintenance	Maintenance	
8 Jan	Osvay (Szeged, Hungary) Optical parametric chirped pulse amplification of femtosecond pulses between 290 – 530nm	Dangor (IC) Laser plasma wave generation and electron acceleration	
15 Jan			
22 Jan			
29 Jan			
5 Feb		Maintenance	
12 Feb			
19 Feb			
26 Feb			
5 Mar	Ledingham (Glasgow) Proton production with a TW laser interacting with thin solid targets		
12 Mar			
19 Mar			
26 Mar			

Table 1. Astra Experiment Schedule 2000/2001

* 5 week experiment over a 6 week period.

LSF Operational Statistics

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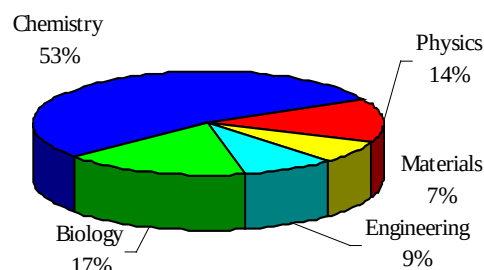
Main contact email address: S.M.Tavender@rl.ac.uk

RAL-based experiments

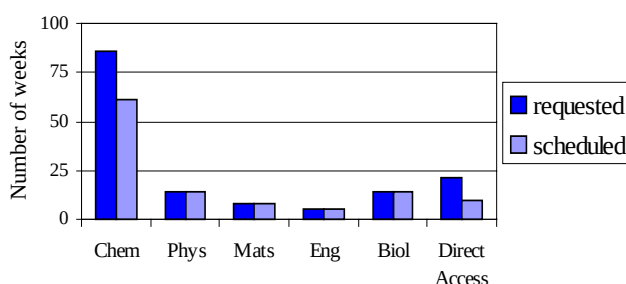
In the reporting period (April 2000 to March 2001), 21 different User groups performed a total of 58 experiments in the LSF laboratories at RAL. A total of 3978 hours laser time was scheduled throughout the year and 4371 hours delivered with only 133 hours downtime. Across the funding Councils the weeks scheduled were 75 to EPSRC, 5 to the MRC, 9 to BBSRC, 12 to Commercial Users, 5 to European Users, and 4 to Internal R&D giving 110 weeks delivered to the User community overall. Once again, a wide spread of disciplines was covered and a breakdown is shown in Figure 1 with the RAL-Based schedule Table 1. There was a total of 28 publications and 14 conference proceedings published during the reporting year.

Figure 1. RAL-based experiments.

Number of experiments per subject group.



Number of weeks requested and scheduled RAL-based experiments.

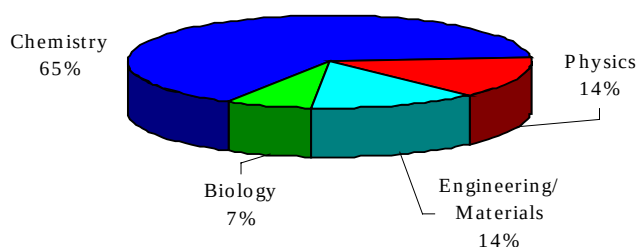


Loan Pool

The Loan Pool delivered 359 weeks of laser time in the reporting period. Downtime was 26 weeks and was mainly due to a laser being damaged during removal and transit. In the 29 laser loans there were 8 groups new to the Loan Pool. The chemistry community was once again the biggest user as shown in Figure 2 and this year there were 2 applications for the cw systems to study biological systems using LIF and confocal imaging. The Loan Pool schedule is shown in Table 2. There was a total of 13 publications, 14 conference proceedings and 1 PhD during the reporting year.

Figure 2. Loan Pool.

Number of experiments per subject group.



Number of weeks requested and scheduled in Loan Pool experiments.

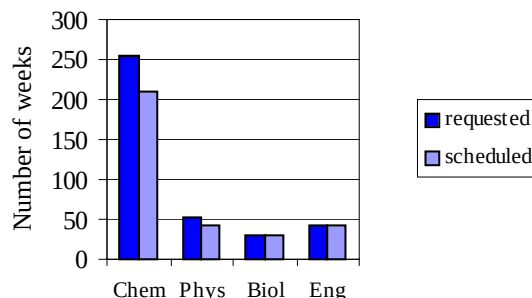


Table 1. RAL-BASED SCHEDULE April 2000 to March 2001

Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory	X-Ray Laboratory
3-Apr-00			M GEORGE (Nottingham)	
10-Apr-00				
17-Apr-00	MAINTENANCE	COMMERCIAL	P.I.R.A.T.E.	COMMERCIAL
24-Apr-00			GR/M40486	
1-May-00		MAINTENANCE	US1C1/00	
8-May-00			COMMERCIAL	H REEHAL (SBU)GR/L63044 TFCS Photovoltaics XU3E1/00
15-May-00	K BRINDLE (Cambridge)		D PHILLIPS (Imperial College)	
22-May-00	Novel fluorescence technique for studying proteins in vivo		Reorganisation Dynamics of Charge Transfer Reactions	COMMERCIAL
29-May-00	8/E11895 CM1B1/00	U JAYASOORIYA (UEA) Raman studies of the metal centre in bacterioferritin	GR/L84001 US5C1/00	G HIRST (CLF) High brightness microtomography system XU1P1/00
5-Jun-00		NL1C1/00	MAINTENANCE	
12-Jun-00			J J McGARVEY (OUB)	C THOMAS GR/K90074 TFEL Devices

Date	Laser Microscope Laboratory	Nanosecond Science Laboratory	Ultrafast Spectroscopy Laboratory	X-Ray Laboratory
19-Jun-00	BAGSHAW (Leicester) Time-resolved fluorescence anisotropy of myosin 91/C11088 CM5B2/00		DNA Interactions at colloidal surfaces GR/M45696 US2C1/00	G HIRST (CLF) High brightness microtomography system XU1P1/00 CEO
26-Jun-00				
3-Jul-00	DEVELOPMENT		MAINTENANCE	
10-Jul-00	OF LASER	D PHILLIPS Reorganisation Dynamics GR/L84001 NL2C1/00	K REID (Nottingham) A novel Probe of Intramolecular Vibrational Energy Redistribution	J CAIRNS (Dundee) Production of X-ray masks GR/M41223 XU2C2/00
17-Jul-00	OPTICAL			
24-Jul-00	TWEEZERS			H REEHAL (SBU) GR/L63044 TFCS Photovoltaics XU3E1/00
31-Jul-00	MAINTENANCE	D PHILLIPS Reorganisation Dynamics GR/L84001 NL5C2/00	GR/M83759 US4C1/00	COMMERCIAL Q99/179
7-Aug-00			D PHILLIPS (Imperial College) Reorganisation Dynamics of Charge Transfer Reactions	
14-Aug-00		MAINTENANCE	GR/L84001 US11C2/00	
21-Aug-00	S KELLY (Hull) Photoluminescence of electroluminescent liquid crystals GR/L41417 CM4M2/00		MAINTENANCE	MAINTENANCE
28-Aug-00				
4-Sep-00		M SEARLE (Nottingham) Fast time-resolved infrared analysis of beta-sheet peptide folding in aqueous solutions NL5C2/00	M GEORGE (Nottingham)	
11-Sep-00				J CAIRNS (Dundee) Production of X-ray masks GR/M41223 XU5M2/00
18-Sep-00	K BRINDLE (Cambridge) Novel fluorescence technique for studying proteins in vivo 8/E11895 CM2B2/00		P.I.R.A.T.E.	
25-Sep-00				
2-Oct-00			GR/M40486 US9C2/00A	H REEHAL (SBU) GR/L63044 TFCS Photovoltaics XU7E2/00
9-Oct-00	DEVELOPMENT OF	D McGARVEY (Keele) Nanosecond TR ⁺ of carotenoid radicals resulting from trapping phenylacetylenoxy radical in polar and non-polar solvents NL4C2/00	MAINTENANCE	
16-Oct-00	LASER		COMMERCIAL 00/0050S	M HILL (MRC) Cellular radiobiology XU6B2/00
23-Oct-00	OPTICAL TWEEZERS		J J McGARVEY (QUB) DNA Interactions at colloidal surfaces GR/M45696 US8C2/00	
30-Oct-00				C WHARTON (Birmingham) Intracellular dynamics GR/N19052 XU8P2/00
6-Nov-00	C WHARTON Intracellular dynamics CM3P2/00 GR/N19052		M GEORGE (Nottingham) P.I.R.A.T.E.	
13-Nov-00				
20-Nov-00			GR/M40486 US9C2/00B	COMMERCIAL Q99/179
27-Nov-00	MAINTENANCE		M GEORGE (Nottingham) GR/M40486 US13C3/00A	MAINTENANCE
4-Dec-00			D PHILLIPS (Imperial College) Reorganisation Dynamics of Charge Transfer Reactions	M HILL (MRC) Cellular radiobiology XU13B3/00A
11-Dec-00	C WHARTON (Birmingham) GR/N19052 CM9P3/00A			C WHARTON (Birmingham) GR/N19052 XU14P2/00
18-Dec-00	P O'NEILL (MRC) DNA Base Radical Ions CM8C3/00		GR/L84001 US14C3/00	
25-Dec-00				
1-Jan-01			X-MAS/ NEW YEAR	
8-Jan-01			MAINTENANCE	A MICHETTE (King's College) Development of the
15-Jan-01	COMMERCIAL - LASER TWEEZERS Lattice forces in 2-D crystalline monolayers CM6C3/00		P MOJZES (Czech Republic) TR3 Study of Porphyrin - Oligonucleotide Exciplex Formation USEV11C3/00	Scanning X-Ray Microscope GR/N28061/01 XU10P3/00
22-Jan-01		D PHILLIPS (IC) GR/L84001 NL8C3/00		
29-Jan-01			A VLCEK (QMWC) Early photochemical dynamics of charge transfer excited organometallic complexes GR/N11414 US15C3/00A	P O'NEILL (MRC) Energy Dependence for Base Damage in DNA by low energy Photons XU11B3/00
5-Feb-01	K BRINDLE (Cambridge) 8/E11895 CM7B3/00A			MAINTENANCE
12-Feb-01	COMMERCIAL - LASER TWEEZERS Lattice forces in 2-D crystalline monolayers CM6C3/00			
19-Feb-01				C WHARTON (Birmingham) Intracellular dynamics GR/N19052 XU8P2/00
26-Feb-01	C WHARTON (Birmingham) GR/N19052 CM9P3/00B		MAINTENANCE	
5-Mar-01	MAINTENANCE		M GEORGE (Nottingham) P.I.R.A.T.E.	J CAIRNS (Dundee) Production of X-ray masks GR/M41223 XU9M3/00
12-Mar-01				
19-Mar-01	K BRINDLE (Cambridge) 8/E11895 CM7B3/00B		GR/M40486 US13C3/00B	H REEHAL (SBU) XU12E3/00 Photovoltaics GR/L63044
26-Mar-01			A VLCEK (QMWC) GR/N11414 US15C3/00B	M HILL (MRC) Cellular radiobiology XU13B3/00B

Table 2.Delivered Loan Pool Schedule April 2000 to March 2001

Date	NSL1 YAG/Dye	NSL2 YAG/Dye	NSL3 YAG/Dye	NSL4 YAG/Dye	NSL5 Fluoride excimer	NSL6 YAG/Dye	CWL2 Ti:S	CWL3 FreD Ar Ion	CW1 Ar Ion
Apr 3		JONES	COATS			SIMONS	TAYLOR	SHIELDS	
10	UNALLOCATED	Edinburgh	Leicester		GEORGE	Oxford	Imperial College	Oxford	
17					Nottingham			GaN based	
24		Supersonic jet				UV/UV and		semiconductors	
May 1		Spectroscopy	LP15E2/99	UNALLOCATED		IR/UV		LP31P3/99	FROST
8		Density			Vibrational	Ion-dip			Heriot-Watt
15	DENNING	functional			Spectroscopy	Spectroscopy			
22	Oxford	calculations	COATS		Of	of amino acids	LP27C3/99	NEUENDORF	
29		of	Leicester		DNA base	Amides and		Birmingham	Visible laser
June 5		liquid crystal			Radical ions:	Hydrated			Induced
12	Two-photon	Molecules			A time-		BERK		Fluorescence
19	Spectroscopy		Acoustic	COLE/RAITHBY	Resolved		Manchester	Optical	Studies of
26	Of	LP28C3/99	Instability	Bath	Infrared	LP26C3/99	Two-photon	Properties	Dysplasia in
July 3	Lanthanide		Of		Investigation		Fluorescence	Of	Human
10	Ions		Fully				Correlation	Nanoscale	Colonic tissue
17		SERVICE	Premixed		LP3C1/00	SIMONS	Spectroscopy	Silicon	
24		AT SIRA	Flames	Crystallographic		Oxford	For	Structures	
31				Studies			Studying		
Aug 7		REPAIR		On	GEORGE	Ion dip	Drug		LP30B3/99
14		OF		Excited state	Nottingham	Spectroscopy	Delivery		
21	LP1C1/00	YAG		Molecular		Of	In living		
28			LP7E1/00	complexes		neurotransmitters and amino acids	Tissue	LP6P1/00	RETIRED
Sept 4					Vibrational	and their			AWARDED
11	DENNING				Spectroscopy	Hydrated			To
18	Oxford		COATS		Of		LP8B1/00		FROST
25			Leicester	LP9C2/00	DNA base				Herriot-Watt
Oct 2	Two-photon	STACE	Acoustic		Radical ions:				
9	Spectroscopy	Sussex	Instability				KLENERMAN		
16	Of		Of	COLE/RAITHBY			Cambridge		
23	Lanthanide	Spectroscopic	Fully	Bath		LP11C2/00			
30	Ions	Studies of	Premixed					POTTON	
Nov 6		transition metal	Flames				2-Photon	Salford	
13		complexes		Crystallographic		SIMONS	Scanning		
20		in the		Studies On		Oxford	Microscopy		
27	LP17C3/00	Gas phase		Excited state			and surface		
Dec 4				Molecular			Con-focal	Optical	
11				complexes		Vibrational	Imaging of	Poling of	
18	UNALLOCATED					Spectroscopy	Living cells	Glasses for	
25			LP14E3/00			Of DNA base		non-linear	
Jan 20						Radical ions		Optical	
08	LACZIK	LP2C1/00						components	
15	Oxford		REID				LP12C2/00		
22			Nottingham	LP13C2/00	LP15C3/00				
29	Use of	STACE	Photoelectron						
Feb 5	diffractive	Sussex	Angular				LINFIELD	LP16P3/00	
12	Optical		Distributions				Cambridge		
19	elements	Cluster	a Probe of	UNALLOCATED	UNALLOCATED	LP15C3/00	Development		
26	for enhanced	Spectroscopy	Intramolecular				of an optical		
Mar 5	Micro-	in Helium	and				high power		
12	machining	Nanodroplets	Photoionization			SIMONS	terahertz	LEGGATT	
19			Dynamics			Oxford	source	UMIST	
26	LP22E3/00	LP19C3/00	LP18C3/00	SMITH		LP6C1/01	LP21C3/00	LP23C3/00	

Publications

- 1) High Power Laser Programme – Vulcan Laser**
- 2) High Power Laser Programme – Astra Laser**
- 3) Lasers *for* Science Facility**
- 4) Laser Science and Development**

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Four wave sum difference frequency conversion of soft X-rays in a plasma

L M Upcraft, G J Pert
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M Borghesi
High-intensity laser-plasma interaction experiments for fast ignitor applications

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M Borghesi
Propagation and guiding of ultra-intense laser pulses through preformed plasmas

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A Bernardinello, D Batani, A Antonicci, F Pisani, M Koenig, F Amiranoff, S Baton, L Gremillet, E Martinolli, T Hall, C Rousseaux, P Norreys, H Bandulet, H Pepin
Effects of self generated electric and magnetic fields in laser generated fast electron propagation in solid materials: electric inhibition and beam pinching

A Djaoui
ICF target ignitions studies with non-local alpha particle transport

L A Gizzi, M Galimberti, A Giulietti, D Giulietti, M Borghesi, H D Campbell, A Schiavi, O Willi
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J Kuba, A Klisnick, D Ros, R Smith, P Fourcade, G Jamelot, J L Miquel, C Chenias-Popovics, J F Wyart, R Keenan, S J Topping, C L S Lewis, F Strati, G J Tallents, D Neely, R Clarke, J Collier, A G MacPhee, P Nickles, K A Janulewicz, F Bortolotto
Temporal profile of a transient x-ray laser

M Tatarakis, I Watts, K Krushelnick, M Zepf, P Norreys, E L Clark, A E Dangor
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Progress in FWSD non-linear effects with XRLs

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E L Clark, F N Beg, M Tatarakis, M Zepf, C Escoda, M Norefeldt, A E Dangor, K Krushelnick, P A Norreys, I Spencer, K W D Ledingham
Energetic particle generation from ultra intense laser plasma interactions with solids

B Dangor, Z Najmudin, K Krushelnick E Clark, M Santala, M Tatarakis, C Danson, D Neely J Faure, V Malka
The correlation of Raman side-scatter with relativistic self-focusing and implications for the generation of relativistic electrons

K Krushelnick, Z Najmudin, B Walton, M A Delannoy, R Kingham, A E Dangor, D Neely, J Collier, R Clarke, C Danson
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J D Moody, P E Young, R L Berger, L Divol, A B Langdon, E A Williams, D M Chambers, J Hawreliak, P Sondhauss, J S Wark
Observation of laser self-smoothing in an exploding foil plasma

A J Mackinnon, S Hatchett, M H Key, P Patel, R Snively, R R Freeman, S Wilks, M Borghesi, H Campbell, A Schiavi, O Willi
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P Norreys, R J Clarke, I F Watts, M Tatarakis, M Zepf, F N Beg, K Krushelnick, M Santala, A E Dangor, A Machacek
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N C Woolsey, Y Abou-Ali, P Carolan, N Conway, R O Dendy, R A D Grundy, P Helander, J G Kirk, K G McClements, P A Norreys, M M Notley, S J Peschte, S J Rose
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M Zepf

Fast particle generation and energy transport in laser-solid interactions

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M Borghesi

Laser propagation and fast particle generation in ultra-intense interaction experiments

O Willi

Laser propagation in overdense plasmas

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P Norreys

Prospects for measuring Gigagauss magnetic fields using harmonics from laser plasma surfaces

S Rose

High-energy density plasmas produced by short laser pulses

O Willi

Proton imaging of laser-produced plasmas

N Woolsey

Spectroscopy of indirectly driven spherical implosion

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Fabrication and optical properties of ordered nanoscale silicon structures

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Dynamic visualisation of flame interaction with an acoustic field

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Discharge-flow studies of reactions of halogen containing species of relevance to the atmosphere
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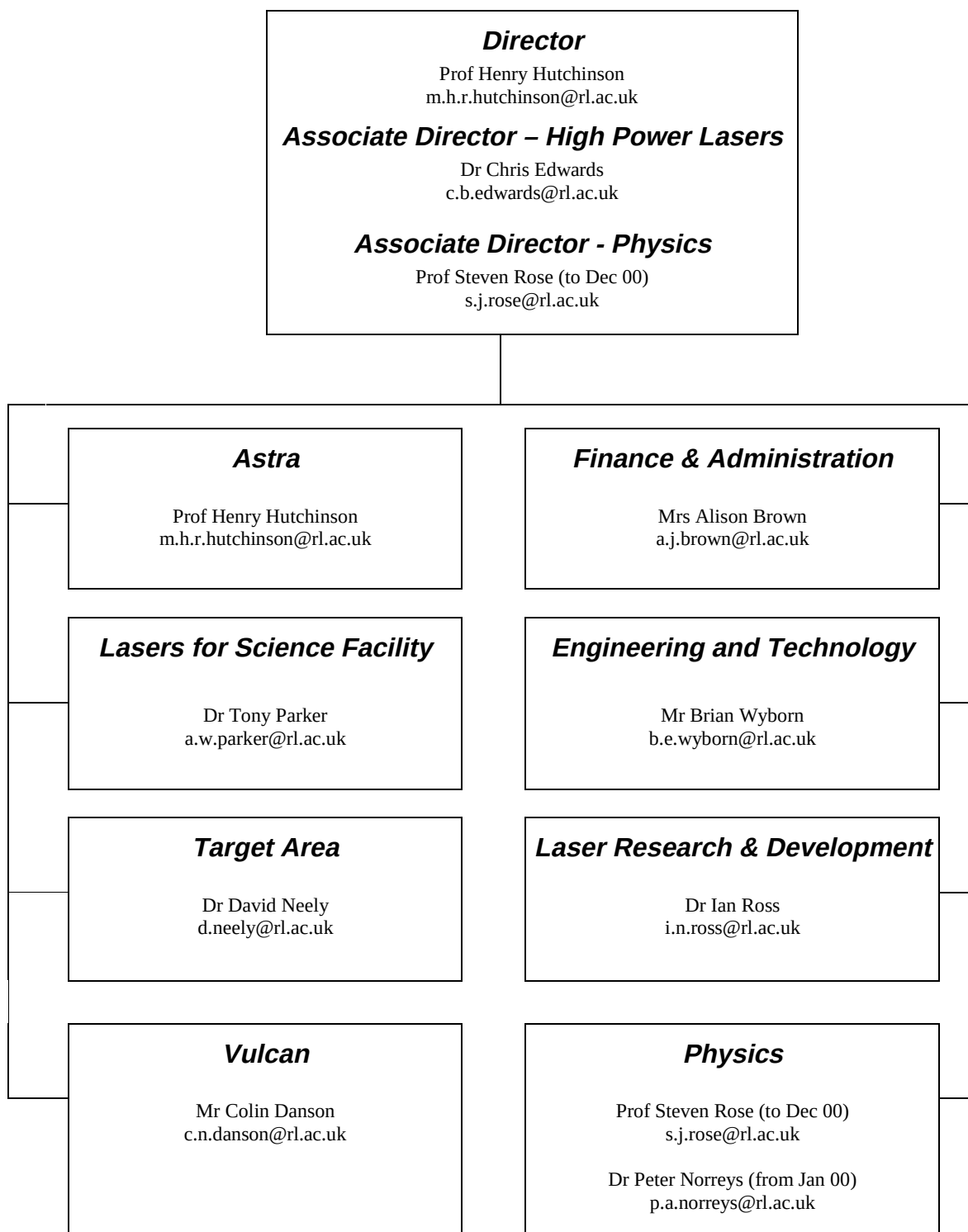
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