

Multiple Probe Spectroscopy

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Overview

Ultrafast time-resolved spectroscopy experiments apply femtosecond lasers in a “pump – probe” configuration to obtain high temporal resolution data on molecular dynamics¹. In such experiments, an ultrafast ($\ll 1$ ps) “pump” laser pulse initiates some event via electronic or vibrational excitation. Subsequent dynamics can then be probed by an ultrafast “probe” laser pulse, which can observe sample changes via absorption¹ or Raman² spectroscopy, for example. If the pump and probe pulses originate from the same laser source, their relative timing can be controlled with femtosecond resolution, and so ultrafast dynamics observed.

Ultrafast events are extremely important for understanding reaction dynamics as the movement of atoms within molecules occurs on these timescales, so processes such as bond forming and breaking are dictated by these primary events. Once these initial steps have occurred, changes will continue to take place radiating outwards in space. An example could be the release of protons occurring on an ultrafast timescale (pH jump³), the diffusion of those protons influencing a protein environment (protein folding⁴), triggering events in a living cell. This progression of events can be defined as physics, chemistry then biology (fig. 1). Therefore, it is important to be able to couple results from ultrafast pump – probe experiments with longer timescale measurements.

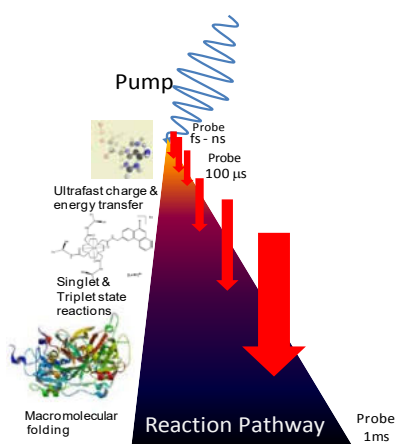


Figure 1. The range of timescales that can be addressed with time-resolved multiple probe spectroscopy and some of their applications.

Flash photolysis has been used for over 50 years⁵ to make time-resolved measurements on the microsecond timescale. This technique originally used flashlamps to create a pulse of light to trigger an event and then to monitor sample transmission or fluorescence as a probe. Time resolution here is dependent on the duration of the light pulse and the time response of the

probe measurement. Flash photolysis could be thought of as a pump – probe – probe – probe... experiment (fig. 2).

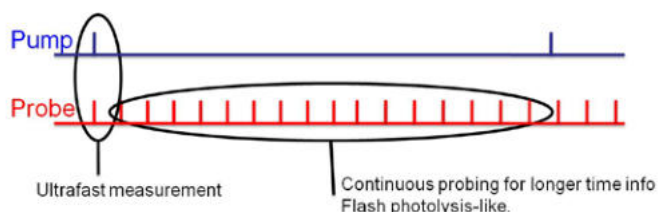


Figure 2. Pulse scheme for time-resolved multiple probe spectroscopy, allowing conventional pump – probe ultrafast measurements in conjunction with acquisition of longer timescale information.

Time-Resolved Multiple Probe Spectroscopy

In the ULTRA laboratory, we are developing techniques to couple ultrafast pump – probe data with longer time scales, by combining medium to low repetition rate lasers for ultrafast pumping (≤ 1 kHz) and high repetition rate (≥ 10 kHz) ultrafast probing. The pulse sequence shown in figure 2 shows that if the pump and probe lasers of different repetition rates are synchronised to < 1 ps, the initial probe pulse following the pump pulse can be used to obtain ultrafast information. Subsequent pulses provide information on the slower timescales, with resolution dependent on the repetition rate of the probe (nanoseconds to microseconds). The following probe pulses can be continued for the duration of the process of interest, after which the sample can be pumped again and the cycle repeated to accumulate high quality spectra.

New Facility and Future Capability

The STFC facility development project, “Time Resolved Multiple Probe Spectroscopy”, has developed novel ultrafast laser synchronisation and control, data acquisition and sample handling concepts to bring this capability to the ULTRA laboratory, for application to non-linear spectroscopy techniques, with high sensitivity. Recent successful commissioning experiments have been submitted for review and will be presented here in the near future.

References

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