Synchronised sample movement and pump laser timing in Time Resolved Multiple Probe Spectroscopy (TRMPS)

Contact *paul.donaldson@stfc.ac.uk*

P.M. Donaldson

Central Laser Facility,
STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX

G.M. Greetham

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX

R.L. Owen

Diamond Light Source LTD,
Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE

M. Towrie

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX

Introduction:

Laser pump-probe spectroscopy is a powerful generic approach to studying transient chemical and physical processes activated by a pump laser. It is usually required that long-lived photoproducts and photochemical damage accumulating in the samples studied be removed by flowing or raster movement of the sample across the pump laser focus. In TRMPS or flash-photolysis-type measurements, observed kinetics on the longest accessible timescales then become convoluted with the sample motion. When studying heterogeneous solid samples, sample motion also introduces noise and artefacts in recorded spectra. Here we demonstrate rapid 'start-stop' sample motion synchronised to the pump laser as a way of mitigating these effects.

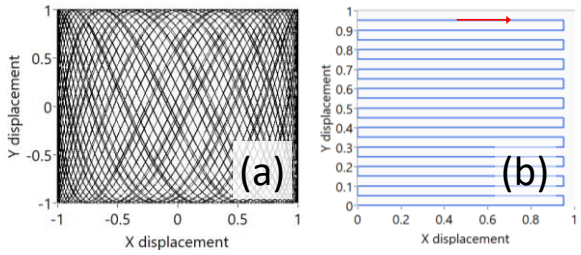

Figure 1. Position of a focussed laser spot in a moving sample for (a) 'Lissajous'-type sample motion and (b) 'Serpentine' motion.

Method:

CLF-Ultra experiments typically use a sample raster system based on linear x-y excursions of up to 15 mm driven via cams rotated with two DC motors at up to 5 Hz. The motor frequencies are asynchronous to each other and to the pump laser, and are set such that the sample is in a constant state of motion. The irradiation of the sample by the pump laser then follows a Lissajous-type motion, as shown in Figure 1(a). For a 100 um laser spot, exposure to completely un-irradiated sample shot-to-shot occurs for pump repetition rates of <1.5 kHz. This is adequate for most solution phase applications encountered, especially when the sample is also flowed. When optimal sample raster speeds for sample refresh are used in a TRMPS measurement, the movement of the sample out of the probe laser beam will inevitably enter the transient absorption signals on the longest timescales. If the linear absorption of the sample is spatially heterogeneous, as is the case for powders and crystals, the rapidly varying probe transmission introduces significant noise and the time varying linear absorption due to the raster motion is also imprinted on the transient data.

Here we examine the potential for using high speed / high precision motion controllers and linear stages for rapid sample motion, while allowing samples to be measured whilst at rest.

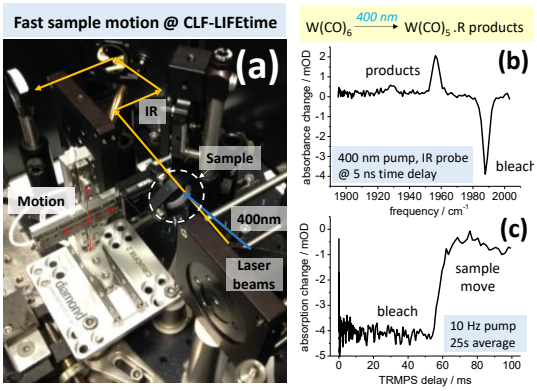

Figure 2. TRMPS-IR spectroscopy on a sample moving in synchronisation with the pump laser (a). The sample is $W(CO)_6$ in heptane. The effect of its permanent bleaching by a 400 nm laser pulse is clear in the transient infrared spectrum (b). Tracking the absorption change of the bleach (c), 50 ms after the photoproducts are created, the sample is moved 100 μm, exposing fresh sample for the next laser shot. (c) is an average of 250 pump laser /move events.

An x-y-z microcrystal scanner and controller (developed at I24, Diamond Light Source) was used to move a liquid sample cell with 100 μm steps (the diameter of the pump laser focus) in 5 ms with submicron accuracy. An x-y serpentine trajectory was executed (Figure 1(b)) and each move synchronised to the pump laser. IR-TRMPS data (captured using CLF-LIFEtime) for a 10 Hz motion rate are shown in the Figure 2 (b) and (c). At the TRMPS delay of 60 ms, the sudden movement of the sample causes the transient absorption signal to recover (Figure 2(c)). This is to our knowledge the first example of a sample studied by time resolved spectroscopy moved synchronously with the pump laser. Suppression of mechanical / servo oscillations was observed to be the key challenge in going to higher rates. A move of 100 μm in 5 ms would in principle allow moves at 100 Hz with the sample stationary for 50% of the time, however at these rates the stage would remain in motion whilst the servo feedback tries to attain the set-point. Future experiments will explore whether reducing the feedback can attain the theoretical maximum of 100 Hz.

Conclusions

The x-y-z stage tested here can be considered as a reasonable approximation for what can be expected from the best linear stages for rapid stop-start motion in TRMPS spectroscopy. The setup presented could be used for continuous scanning (with characteristics similar to rotary methods) or step scanning at frequencies of around 10 Hz.