

Femtosecond to microsecond time-resolved spectroscopy enabled using an actively Q-switched nanosecond microlasers coupled to the Ultrafast Facility lasers

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Introduction

The coupling of a 500 ps actively Q-switched laser to the Ultrafast time resolved spectrometer provides, for the first time, a seamless bridge between femtosecond and microsecond time-resolved Raman and infrared spectroscopy¹⁾.

Many ultrafast and nanosecond pump probe systems world wide use Raman and IR absorption spectroscopy to probe the structure, dynamics and optical properties of molecular systems and materials. “Pump–probe” spectroscopy employs a pump pulse to trigger a reaction then a second laser pulse to probe the progress of the reaction after a known time-delay. Although there are many pump-probe systems in existence, none can follow reaction dynamics from the ultrafast regime continuously through to the microsecond regime due to the limits of current detectors and laser technology. This capability opens up the new possibilities to study the chemical and biological reactivity of systems including free radicals, charge transfer states, triplet states and geminate ion pairs that show important dynamics in this time domain.

Figure 1 shows the schematic of the PIRATE TRIR spectrometer and nanosecond AOT-YVO-20QSP/MOPA Nd:Vanadate diode pumped microlaser. The nanosecond laser is an optional pump source, replacing the conventional ultrafast

pump beam, at time delays of greater than 2 ns. The laser repetition rate is adjustable from (1-20 kHz), has pulse duration (~0.6 ns) and sub 0.2 ns statistical jitter (to one standard deviation) with respect to an external trigger. The microlaser triggers at 1 kHz synchronous with the ultrafast Ti:S amplifier. The ultrafast laser’s master clock provides triggers to a Stanford DG535 pulse delay generator used to fire the nanosecond laser. Time delays are programmed through the new PIRATE software described in this section of this CLF Annual Report. The relative jitter between the Ti:S amplifier and nanosecond light pulse outputs was measured to be 0.3 ns (to one standard deviation).

The nanosecond laser generates a fundamental of 1064 nm (40 μ J/pulse) and harmonics at 532 nm (20 μ J/pulse), 355 nm (12 μ J/pulse) and 266 nm (5 μ J/pulse). The 355 nm and 267 nm second and third harmonics of the Ti:S amplifier pulses, frequently used to pump photochemical reactions.

To illustrate the performance of the system we looked at metal carbonyl systems with known excited state dynamics that would allow us to characterise the apparatus.

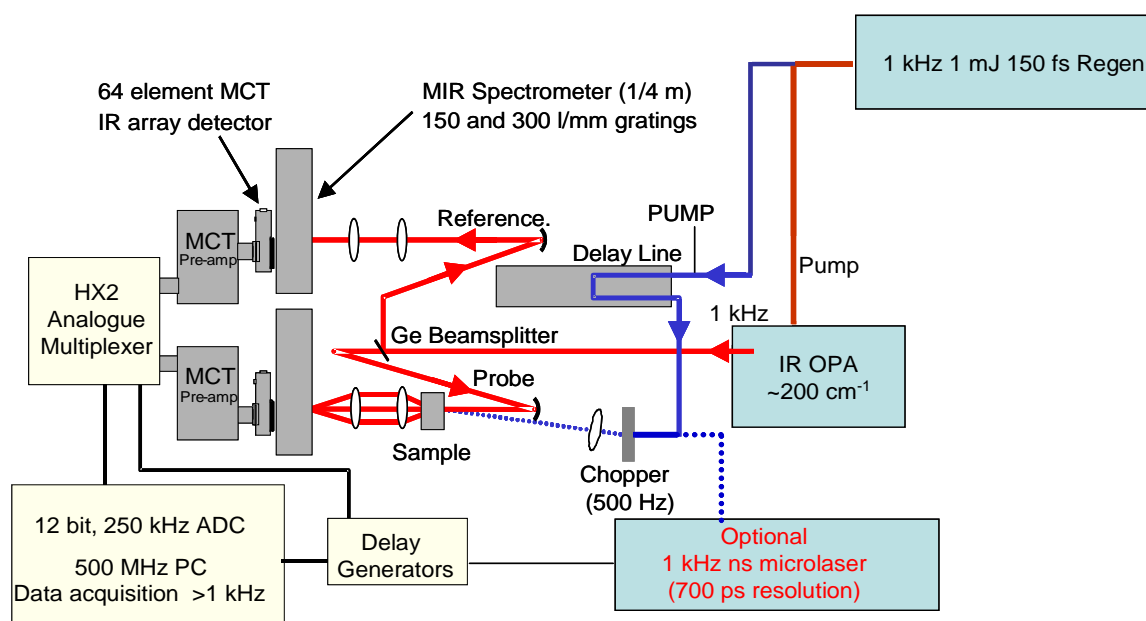


Figure 1. Schematic showing layout of PIRATE experimental apparatus.

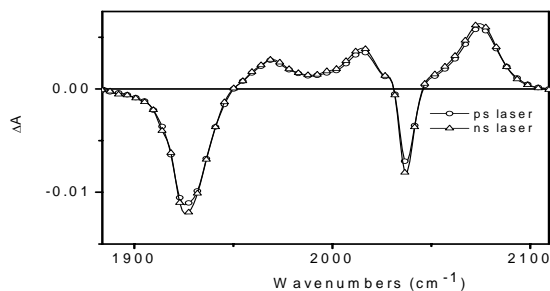


Figure 2. Un-corrected data comparison of the TRIR of $[\text{Re}(\text{CO})_3(\text{Etpy})(\text{dmb})][\text{PF}_6]$ at 2 ns delay obtained with fs (267 nm) and ns (266 nm) pump excitation source with otherwise identical conditions.

Pump probe measurements on $\text{fac-}[\text{Re}(\text{CO})_3(\text{Etpy})(\text{dmb})]^+$ where Etpy = 4-ethyl-pyridine and dmb = 4,4'-dimethyl-2,2'-bipyridine showed that the instrument response of the nanosecond laser was 0.7 ns. Figure 2 shows the good comparison between a pump probe IR spectrum taken of the $\text{fac-}[\text{Re}(\text{CO})_3(\text{Etpy})(\text{dmb})]^+$ at 2 ns delay using the 266 nm 4th harmonic of the nanosecond laser and 267 nm third harmonic of the Ti:S. The spectra are almost identical, showing that it is possible to follow dynamics from the ps through to μs regime without systematic changes in the spectra (normally very difficult to attain for conventional approaches).

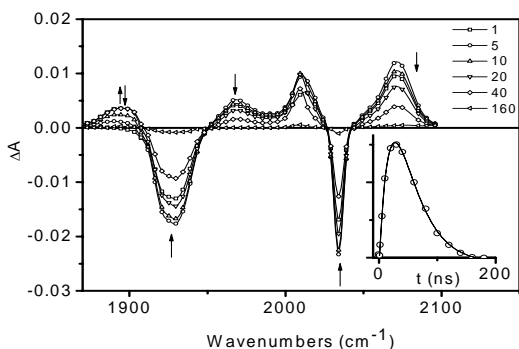


Figure 3. TRIR of $[\text{Re}(\text{CO})_3(\text{trppy})(\text{bpy})][\text{PF}_6]$ showing reductive quenching of the MLCT state, producing the charge-shifted state.

A rhenium metal carbonyl complex that undergoes an irreversible excited state bond cleavage demonstrated the time range accessible to the apparatus. Spectra taken out to the hundred microsecond timescale displayed a drop in signal that relates to movement of the photo-excited sample away from the probe interaction region due to the raster and flow of the sample needed to avoid photo-damage. However, useful data out to $\sim 200 \mu\text{s}$ may be attained. Figure 3 shows spectra obtained for a donor acceptor assembly $[\text{Re}(\text{CO})_3(\text{trppy})(\text{bpy})][\text{PF}_6]$. On excitation at 400 nm(fs), 355 nm (ns), population of the MLCT excited state occurs, this undergoes quenching to produce a charge-shifted state (as indicated by band at 1886 cm^{-1}). This system could not be reliably measured before because its kinetics are on the 20 ns timescale. The inset shows the rise of the charge transfer state with time constant 23 ns followed by decay to the ground state with a life time of 35 ns.

TRIR spectra of 1,5-dihydroxyanthraquinone in the crystal phase, Figure 4, demonstrate the ability to follow a relaxation process over timescales from 1 ps to 4 μs . This compound undergoes intramolecular proton transfer on the femtosecond

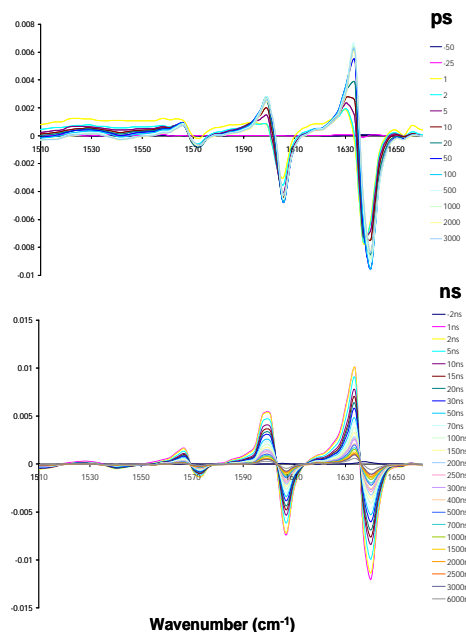


Figure 4. TRIR spectra of 1,5 dihydroxyanthraquinone measured on timescales from 1 ps to 4 μs . Pump wavelengths 400 nm for the ps data and 355 nm for the nanosecond data under similar pump intensity.

timescale after photo-excitation. We were interested in comparing proton transfer and energy relaxation between solution and crystalline environments. The crystalline spectra produce a series of transients living for 100's of nanoseconds not present in solution. The origin of the transients is not clear but as the molecule decays back to the electronic ground state on a femtosecond timescale, they do not stem from excited electronic states instead they are indicative of rapid heating and cooling of the crystals or local phase changes induced within the lattice.

Conclusions

We describe a spectrometer capable of providing a seamless bridge between femtosecond and microsecond time-resolved vibrational spectroscopy. Its performance is illustrated by a number of experiments on metal carbonyl photo-reactions that could not be measured in the past because their dynamics fell outside the range of spectrometer technology. The sub 1 ns time resolution and $10^{-4} \Delta\text{OD}$ in sensitivity in one second exceeds that of current technology thus providing an instrument able to probe samples with lower photo-stability and IR transition strength than possible with today's nanosecond resolving time-resolved techniques. In its current state the nanosecond microlaser has wavelength coverage limited to its harmonics. However, the future LSF ULTRA programme will scale the laser to higher pulse energy at 10 kHz repetition rates, sufficient to access the 5th harmonic at 213 nm and drive optical parametric amplifiers to provide greater tunability. Combining this nanosecond laser with Kerr gate Raman spectrometer would also bring the unsurpassed sensitivity of the time resolved resonance Raman technique in the ns to μs domain.

References

1. M Towrie, A Gabrielsson, P Matousek, A W Parker, A-M Blanco Rodriguez and A Vleček Jr., *Appl. Spectrosc.*, **59** (4) 467 (2005)