Nanosecond Step-scan FTIR Spectroscopy in Conventional and Supercritical Fluids

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Introduction

Time-resolved IR spectroscopy (TRIR) is a technique for probing the rate and mechanism of photochemical reactions. It involves the use of a pulsed UV/visible laser to initiate the reaction, and fast IR detection to monitor the generation of short-lived intermediates. The technique is becoming widespread and has already made a major impact on the study of organic and organometallic reactions both in the gas phase and in solution. Traditionally the TRIR apparatus at Nottingham has consisted of an IR diode laser which is tuned to a particular IR frequency and is used to monitor changes in IR absorption of a reaction solution following a UV laser pulse. The IR laser is then re-tuned to another frequency and the process is repeated. Thus IR spectra are built up point-by-point by plotting change in absorbance versus wavenumber. The relatively narrow line widths of absorptions make it possible to monitor several key species in solution at the same time; destruction of reactants and formation of excited states, intermediates and products can all be followed. Our current point-by-point laser-based approach to TRIR limits the IR range that can be studied due to the long acquisition time required for a complete spectrum (indeed, recording a 300 cm

intensity following excitation is measured producing time-dependant interferograms. Fourier transformation of an interferogram at a particular time delay following excitation of the reactions yields the spectral intensity changes at that particular time slice and this can be easily converted to the corresponding absorption spectra. Repeating this process at a variety of time delays following excitation results in a series of time-resolved spectra. Kinetic traces can be obtained by plotting the change in absorbance at any frequency as a function of time. However the acquisition of time-resolved step-scan FTIR data has required a large amount of signal averaging (up to weeks) to improve signal-to-noise. This is due in part to imperfection in stopping the moving mirror. Consequently time-resolved IR investigations have been largely restricted to cyclic or photoreversible reactions such as bacteriorhodopsin, halorhodopsin, photosynthetic reaction center, myoglobin and hemoglobin. Here we have used a combination of new interferometer design, with increased precision in mirror position, and a nanosecond Nd:YAG laser (Laser for Science Facility) to construct a new nanosecond step-scan time-resolved IR spectrometer. Our objective is to construct a time-resolved Step-scan spectrometer that can obtain ns-TRIR spectra without the need for extensive signal averaging, thus opening up this technique to study chemical reactions rather than photo-reversible systems.

Experimental Set-up

Step-scan FTIR experiments were conducted using a combination of a Nicolet Magna 860 Interferometer and a Nd:YAG laser (Spectrum SL805G) from the laser loan pool. Figure 1. Synchronisation of the Nd:YAG laser with data collection was achieved using a pulse generator (Stanford DG535).

Figure 1. Experimental set-up for step-scan TRIR experiments.

The interferometer is equipped with both an internal 100 kHz 16-bit digitiser and an external 100 MHz 12-bit digitiser. In these experiments two different photovoltaic MCT detectors were used. A 0.5 mm detector with a 50 MHz preamplifier was used for measurements < 50 ns and a 1.0 mm detector with a 20 MHz preamplifier was used for measurements > 50 ns. These detectors have both AC and DC outputs and both outputs are digitized simultaneously to ensure proper phase matching. Single sided interferograms were obtained using only one laser pulse at each mirror position.

Results and Discussion

We have recently shown that the combination of TRIR and super-critical fluids allows the detection of organometallic noble gas complexes in solution at room temperature. M(CO)$_5$(Xe) and M(CO)$_5$(Kr) (M = Cr, Mo and W) were generated by flash photolysis of M(CO)$_5$ in supercritical Xe (scXe) or Kr (scKr) solution. We will use the combination of W(CO)$_5$(Xe) in scXe as a diagnostic of our new instrument. Figure 2 shows the step-scan FTIR spectrum following irradiation of W(CO)$_5$ in scXe (3100 psi) in the presence of CO (30 psi).

Figure 2. Time-resolved Step-scan FTIR spectra obtained in 1 μs time-slices following irradiation of W(CO)$_5$ in scXe. These data were obtained from one scan of the interferometer.

The parent W(CO)$_5$ absorption is clearly bleached and two new ν(C=O) bands are formed and can be assigned to W(CO)$_5$(Xe) by comparison to previous TRIR studies. We were intentionally not completely rigorous in the preparation of the solution of
W(CO)₆ in scXe. W(CO)₆(Xe) decays to reform the parent and a new species with a band at 1944 cm⁻¹. This new species can be assigned to W(CO)₅(H₂O) and indicates the presence of a H₂O impurity in the Xe solution. This result emphasizes the advantage of using step-scan FTIR for kinetic measurements since using a diode laser (at a single frequency) to obtain the decay kinetics of W(CO)₅(Xe) may have missed the formation of W(CO)₅(H₂O) and anomalous results may have been obtained. The simultaneous acquisition of both spectral and kinetic information results helps address this problem. We have used the formation of W(CO)₅(Xe) to probe the risetime of our instrument, which was found to be 10 ns, Figure 3.

We have used the photochemistry of trans-[CpMo(CO)₃]₂ in supercritical CO₂ (scCO₂) as a model system to compare the step-scan FTIR instrument with IR diode lasers for obtaining kinetics information. The photochemistry of trans-[CpMo(CO)₃]₂ in scCO₂ has recently been investigated using TRIR. ³⁶

Visible irradiation (532 nm) of trans-[CpMo(CO)₃]₂ in scCO₂ results only in cleavage of the Mo-Mo bond to produce CpMo(CO)₃ radicals. The CpMo(CO)₃ radicals recombine at a diffusion controlled rate to form both trans-[CpMo(CO)₃]₂ and the unstable gauche-[CpMo(CO)₃]₂, Figure 4. This is followed by slow isomerisation of gauche-[CpMo(CO)₃]₂ to trans-[CpMo(CO)₃]₂. The IR spectra shown in Figure 4 are averaged over 4 scans.

We have chosen to study the photochemistry of [CpFe(CO)₂]₇ in n-heptane solution following visible excitation using step-scan FTIR. Visible irradiation of [CpFe(CO)₂]₇ causes cleavage of the Fe-Fe bond and formation of CpFe(CO)₂ radicals. These radicals recombine in 5-10 µs to form either cis-[CpFe(CO)₂]₇ or trans-[CpFe(CO)₂]₇ thus producing a non-equilibrium concentration of cis-[CpFe(CO)₂]₇. ⁷ Slowly cis-[CpFe(CO)₂]₇ isomerises to the more stable trans-[CpFe(CO)₂]₇. Early TRIR measurements using CO lasers showed that the radicals had ν(C-O) bands at ~2005 and 1938 cm⁻¹ in n-heptane. The high frequency ν(C-O) band could not be accurately determined because of the strong overlap with the absorption of the parent. Hochstrasser and co-workers investigated the photochemistry of or trans-[CpFe(CO)₂]₇ in cyclohexane using picosecond TRIR and detected a transient with absorption maximum at 1933 cm⁻¹ and claimed that the 5 cm⁻¹ shift was significant and assigned the 1933 cm⁻¹ to a precursor of the radical. ⁸ The original microsecond TRIR experiments were carried out using a CO laser and were therefore quoted with an error of ±4 cm⁻¹. High resolution TRIR experiments using the diode laser based TRIR spectrometer demonstrated that the CpFe(CO)₂ radicals had a ν(C-O) absorption at 1935 cm⁻¹ in n-heptane and 1933 cm⁻¹ in cyclohexane and the difference between the microsecond and picosecond TRIR results was due to a solvent shift in the ν(C-O) bands of the CpFe(CO)₂ radical. ⁹ Figure 6 shows the step-scan TRIR spectra obtained following irradiation of trans-[CpFe(CO)₂]₇ in n-heptane solution. It is clear that we can obtain TRIR spectra with excellent signal-to-noise ratio even at microsecond timescale and the isomerisation of gauche-[CpMo(CO)₃]₂ to trans-[CpMo(CO)₃]₂ is a first order process on the millisecond timescale. In principal the use of diode lasers for the measurement of kinetics at one IR frequency should produce better signal-to-noise ratio because of the higher IR photon flux these lasers provide. The TRIR decay traces of CpMo(CO)₃ in scCO₂ are compared in Figure 5. It can be seen that under these conditions both approaches produces excellent kinetic information and using both approaches the decay of CpMo(CO)₃ is second order. Similarly, on a slower timescale there is no difference between using the two techniques for obtaining the first order decay of gauche-[CpMo(CO)₃]₂ to trans-[CpMo(CO)₃]₂. From this we conclude that comparable kinetics can be obtained from using step-scan FTIR and IR diode lasers for TRIR measurements.
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high resolution 0.5 cm⁻¹). The correct band position was only obtained using high spectral resolution (<2 cm⁻¹).

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All the experiments described above have used time-resolved step-scan FTIR to probe the photochemistry of metal carbonyl complexes, which have very intense ν(C-O) bands in the infrared. We have also been interested in applying TRIR to organic photochemistry, particularly to azides and benzoyl radicals. Benzoyl radicals are key intermediates in many photopolymerisation reactions and have a characteristic band at 1800-1850 cm⁻¹ depending upon the nature of the substituents on the benzene ring. Here we have used the photochemistry of (1-hydroxycyclohexyl)phenyl ketone to probe the capability of our step-scan spectrometer to detect transient species with weak IR bands in irreversible photochemical systems. Irradiation of (1-hydroxycyclohexyl)phenyl ketone in n-heptane generates benzoyl radicals recombine to reform the parent or couple together to form the other products.

We have achieved 1 μs TRIR spectra of very small absorptions (ΔOD < 5 x10⁻⁴ with a signal-to-noise ratio > 10 in a few hours).

The benzoyl radicals recombine to reform the parent and the benzoin photoproduct. The TRIR decay trace (1827 cm⁻¹) of the benzoyl radical is shown in Figure 8.

Figure 6. Step-scan FTIR spectra obtained 1μs after irradiation of trans-[CpFe(CO)]₂ in n-heptane solution at 16,8,4,2,1 and 0.5 cm⁻¹ resolution.

Figure 7 shows the step-scan FTIR spectrum obtained 1 μs following irradiation of (1-hydroxycyclohexyl)phenyl ketone in n-heptane. In this experiment a low UV laser power was used to produce small IR transients. The spectrum obtained 1 μs after photolysis clearly shows depletion of the parent absorption and the production of the benzoyl radical at 1827 cm⁻¹. The data shown in Figure 7 was obtained by averaging 32 scans.

We have demonstrated that this step-scan FTIR can be used to probe a variety of chemical reactions.

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