

# Multidimensional infrared spectroscopy using Ultra

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## Introduction

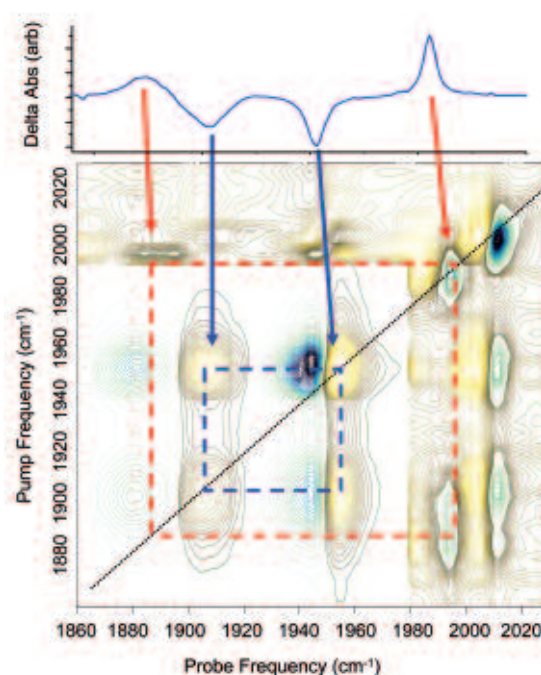
Ultrafast two dimensional infrared (2D-IR) spectroscopy has developed over the last decade to become established as a powerful tool for studying a range of chemical and biological processes. Examples include investigations relating to solvent-solute dynamics, chemical exchange, and applications ranging from determining the structure of small peptides in solution to the ultrafast fluctuations of complete proteins. These studies have been the subject of several recent review articles.<sup>[1-4]</sup> Two advantages of 2D-IR, the inherent ultrafast time resolution and the ability to obtain molecular structural information have provided the driving force for the extension of 2D-IR methods into studies of non-equilibrium problems. Transient 2D-IR (T-2D-IR) spectroscopy uses an additional excitation pulse to perturb a system with the 2D-IR experiment employed as a time-delayed probe of the subsequent evolution.<sup>[4,5]</sup>

In this report we focus on applications of two types of multidimensional infrared spectroscopy, T-2D-IR and two-colour 2D-IR, to the spectroscopy and photochemistry of the cyclopentadienyl tungsten tricarbonyl dimer [CpW(CO)<sub>3</sub>]<sub>2</sub> [**1**]. This molecule and its structural analogues exhibit a rich photochemistry<sup>[6,7]</sup> and, in line with many organometallic species, plays a key role in catalytic processes. Here, we use T-2D-IR methods to study the formation and vibrational dynamics of the 17e<sup>-</sup> radical species CpW(CO)<sub>3</sub> [**2**] following excitation of **1** at 490 nm. In addition, we present preliminary results using two colour 2D-IR methods, which reveal vibrational interactions of the carbonyl stretching modes of **1** with low frequency vibrational modes.

All the experiments featured here were carried out using the ULTRA spectrometer, which consists of a 65 MHz Ti:sapphire oscillator seeding two synchronised regenerative amplified lasers operating at a repetition rate of 10 kHz. The system produces two trains of pulses with pulse durations of 1-2 ps and 50 fs respectively at a wavelength of 800 nm. 2D-IR spectra were obtained using the double resonance technique, employing tunable narrow band pump and time-delayed broadband probe pulses. A 2D-IR spectrum was thus generated by scanning the pump frequency and recording dispersed pump-probe spectra for a given inter-pulse time delay<sup>[8,9]</sup> The mid-IR pump pulse

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**Figure 1.** TRIR (top) and T-2D-IR spectra (bottom) following excitation of **1** at 490 nm in dichloromethane solution. Blue arrows and dashed lines show peaks due to loss of **1** while red arrows and dashed lines highlight photoproduct peaks. Colour scale runs from blue (negative) to yellow (positive).

(ca 10 cm<sup>-1</sup> bandwidth) originated from a white light-seeded optical parametric amplifier (OPA) pumped by the ps amplified pulse train and equipped with difference frequency mixing of signal and idler beams. The probe pulse was generated by a similar OPA pumped by the fs duration pulses. The IR<sub>pump</sub> pulse was amplitude-modulated at half the laser repetition rate in order to extract pump-on-pump-off difference spectra. When performing T-2D-IR measurements, an additional ps duration visible wavelength pulse was generated by a third OPA and used to excite **1** prior to the 2D-IR experiment. Recording data alternately with and without this excitation pulse allowed the extraction of T-2D-IR difference spectra. For T-2D-IR experiments, the additional inter-pulse delay time between the visible pulse and the 2D-IR infrared pump

pulse allowed control over the time following photolysis that the 2D-IR experiment probed the evolving system, while the  $IR_{\text{pump}}-IR_{\text{probe}}$  time delay then probed vibrational relaxation of the photoproducts.

Two colour 2D-IR spectra are acquired in a similar manner to that described, except that the  $IR_{\text{pump}}$  and  $IR_{\text{probe}}$  frequency ranges were different and thus, only the off-diagonal region of the spectrum is obtained. This technique has been used to study the coupling of N-H and C=O stretching modes peptides<sup>[10]</sup> and vibrational energy transport across complex molecules.<sup>[11]</sup>

### T-2D-IR spectroscopy

Fig 1 shows time resolved infrared (TRIR) and T-2D-IR difference spectra following excitation of **1** at 490 nm. For acquisition of T-2D-IR spectra the time between the excitation pulse and the  $IR_{\text{pump}}$  pulse of the 2D-IR probe experiment was set to 300 ps. The lifetime of the  $17e^-$  radical **2** was shown to be in excess of 1 ns in dichloromethane solution. Thus, T-2D-IR experiments were performed in a regime where the population of **2** was slowly-varying with respect to the timescale of the experiment, which employed  $IR_{\text{pump}}-IR_{\text{probe}}$  delays of  $\sim 2$ -50 ps.

In the TRIR spectrum, (Fig 1) bleaches at 1909 and  $1955\text{ cm}^{-1}$  correspond to the  $b_u$  and  $a_u$  carbonyl stretching modes of **1** respectively,<sup>[6]</sup> while the positive peaks near 1890 and  $1995\text{ cm}^{-1}$  represent the  $e$  and  $a_1$  modes of **2**.<sup>[12]</sup> In the T-2D-IR spectrum, these features appear on the diagonal of the spectrum, highlighted by the blue and red dashed lines, as pairs of peaks: One, due to the  $v=0-1$  transition, is observed on the diagonal while the accompanying peak, shifted to lower frequency along the probe axis by the anharmonicity ( $\sim 5$ -10  $\text{cm}^{-1}$ ) of the mode, corresponds to the  $v=1-2$  transition. In the case of the peaks due to **1**, the  $v=0-1$  peaks are positive while the  $v=1-2$  peaks are negative (blue dashed lines). The phase is reversed for the photoproduct peaks (red dashed lines). This phase reversal arises from the fact that the photoproduct population is increased by the photolysis pulse while that of the dimer is decreased; the T-2D-IR difference spectrum represents the changes caused by the photolysis pulse. In each case, the diagonal peak pairs are linked by similar pairs in the off-diagonal region, indicating vibrational coupling and population transfer between the carbonyl stretching modes of the respective molecules. Additional lines are observed near probe frequencies of  $2010\text{ cm}^{-1}$  arising from the gauche structural isomer of **1**.<sup>[13]</sup>

Variation of the  $IR_{\text{pump}}-IR_{\text{probe}}$  time delay in the T-2D-IR experiment allows determination of the vibrational dynamics of the radical species. These exhibit a single exponential decay with a lifetime of  $\sim 25$ -27 ps. This is in contrast to **1**, which shows bi-exponential relaxation dynamics corresponding to fast population equilibration between the carbonyl modes on a  $\sim 2$  ps timescale followed by  $\sim 30$  ps vibrational relaxation.<sup>[13]</sup> A possible explanation is that the vacant coordination site of **2** allows increased solvent interaction and a faster IVR rate, moving the short relaxation timescale beyond the time-resolution of the spectrometer (1 ps).

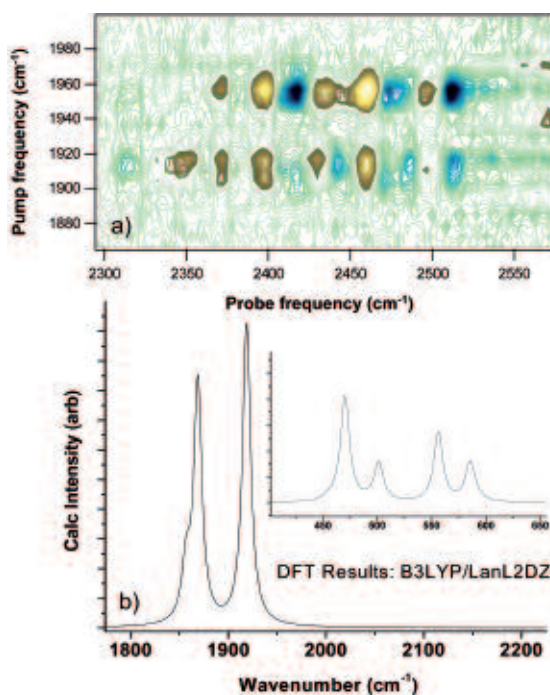


Figure 2. a) Two colour 2D-IR spectrum of **3**. (b) Calculated infrared spectra of **3** in the CO stretching and bending (inset) mode region of the mid-IR.

### Two-colour 2D-IR spectroscopy

Two colour 2D-IR spectroscopy was carried out by scanning the pump pulse frequency from  $1900$ - $1960\text{ cm}^{-1}$ ; corresponding to the carbonyl stretching modes of the dimer molecule. The probe pulse wavelength covered the region  $2300$ - $2550\text{ cm}^{-1}$ . A derivative of **1** was used featuring a propyl-substituted Cp ring ligand [**3**]; the increased solubility in alkane solvents allowed use of heptane solutions, which in turn yielded narrower linewidths than the polar solvents used for the T-2D-IR experiments and reduced spectral congestion. As can be seen in Fig 2(a), for a pump-probe delay of 2.5 ps, a large number of peaks are observed in this off-diagonal region. These appear to consist of pairs of negative and positive peaks. Though a complete assignment is yet to be obtained, it was however established that they are due to vibrational modes of the dimer **3** and that they show a relaxation timescale similar to the diagonal peaks of **3** in the carbonyl stretching region.

A tentative assignment of these peaks can be obtained by examining the infrared absorption spectrum of **3** in the region near  $400$ - $500\text{ cm}^{-1}$  where several peaks arising from the carbonyl bending modes of the molecule are located.<sup>[14]</sup> These are also displayed in Fig 2(b) where the results of simulating the infrared spectrum of **3** using DFT methods are shown. The probe frequencies of the peaks observed in the two colour 2D-IR spectra correspond well to combination band modes featuring one quantum each of the stretching and bending modes of **3**, the presence of cross peaks indicate coupling or population transfer between these and the C=O stretching fundamental modes. The large number of peaks arises from the range of possible combinations.

That these combination band modes are observed in the two colour 2D-IR spectra but only very weakly when the pump and probe pulses were tuned to the 2300-2550  $\text{cm}^{-1}$  region arises from the weaker transition dipole moment of the combination bands as compared to the C=O stretching fundamental modes. The latter show strong absorptions and, as 2D-IR peaks depend upon the transition dipole moments of the involved modes, off-diagonal peaks between combination bands and the fundamental modes will be stronger than combination band diagonal peaks due to the high intensity of the stretching modes.

### Conclusions

T-2D-IR spectroscopy and two-colour 2D-IR methods have been employed to study the spectroscopy and vibrational dynamics of the tungsten tricarbonyl dimer and the  $17e^-$  radical species arising from homolytic cleavage of the intermetallic bond. New insights have been possible into the relative vibrational dynamics of the radical versus the parent dimer, which may have implications for the understanding of photochemical reaction mechanisms. In addition, new insights have been obtained into the interactions of high and low frequency vibrational modes via two colour 2D-IR spectroscopy.

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