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Transient 2D-IR Spectroscopy of Inorganic Excited States

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Time-resolved infrared spectroscopy has been proven to be a powerful tool for investigating the structure, dynamics and reactivity of electronically-excited states of inorganic molecules. As applications drive the production of ever more complex molecules however, experimental tools that can deliver more detailed spectroscopic information, or separate multiple contributions to complex signals will become increasingly valuable. In this Perspective, the extension of ultrafast infrared spectroscopy of inorganic excited states to a second frequency dimension using transient 2D-IR spectroscopy (T-2D-IR) methods is discussed. Following a brief discussion of the experimental methodologies, examples will be given of applications of T-2D-IR ranging from studies of the spectroscopy, structure and dynamics of photochemical intermediates to new tools for correlating vibrational modes in ground and excited electronic states and the investigation of excited state solvation dynamics. Future directions for these experiments are also discussed.

Introduction

The use of infrared (IR) spectroscopy to probe the electronically-excited states of inorganic molecules is well-established. In particular, the use of IR absorptions allow the experimentalist to gain insights into changes in molecular structure at the level of the chemical bond that complement the information on electronic reorganisations provided by UV/visible spectroscopy or fluorescence measurements. The introduction of time-resolved spectroscopy methods, employing an IR probe of an electronically-excited system, opened up further possibilities for following photochemical processes or dynamics associated with, or subsequent to, excitation.¹⁻¹⁰ Implementation of these techniques has progressed in line with laser technology development to the extent that spectrometers with high time resolution (~50 fs) and broad spectral bandwidths (>300 cm⁻¹) are readily achievable using commercially-available bench-top laser systems.

As chemical research in the inorganic sector advances and the molecules become more complex, the need arises to understand, and so eventually control, their excited state chemistry and dynamics at ever more nuanced levels. This means that new spectroscopic tools are required that can provide the enhanced levels of information needed to match this synthetic progress. Obvious examples of areas in which such advanced spectroscopies could be of value include separating contributions to overcrowded or broadened linear spectra or interrogating rapidly changing mixtures of

photoproducts. More complex issues that need to be addressed include understanding the vibrational dynamics of electronically excited or photochemically-produced molecules or the interactions between excited states and their molecular environment, be that solvent or matrix. Finally, spectroscopies that provide the ability to correlate vibrational modes in ground and excited states will provide useful information on the molecular changes caused by excitation and the coupling of electronic and vibrational degrees of freedom.

One approach to achieving these aims is to extend the multidimensional infrared spectroscopy methods that have found increasing application in the ground state,¹¹⁻¹⁵ to electronically-excited states. Two-dimensional infrared (2D-IR) spectroscopy, first implemented in 1998,¹⁶ has its basis in the multidimensional NMR experiments that have made major contributions to structural biology research in recent years.¹⁷ Briefly, 2D-IR methods use a sequence of ultrafast laser pulses, analogous to the radio frequency pulse sequences used for 2D-NMR, to spread the linear IR absorption spectrum of a molecule over two frequency axes by creating a correlation map of excitation and detection frequency. The resulting spectrum is similar to that derived from 2D-NMR in that the 1D spectrum appears on the diagonal, while off-diagonal peaks reveal the coupling of spectroscopic transitions, be they nuclear in NMR or vibrational for 2D-IR. One important advantage of 2D-IR lies in the high time resolutions accessible. These typically lie in the range 100 fs to 1 ps depending on the

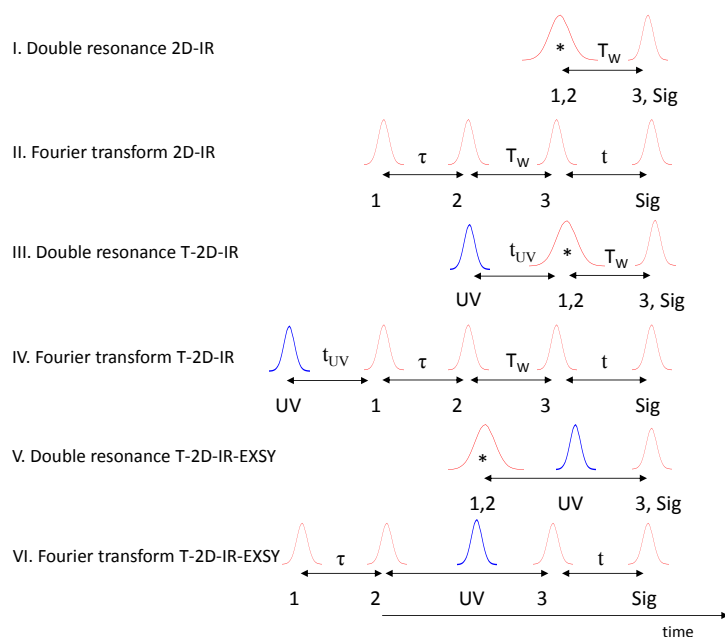


Figure 1: Schematic diagram of the pulse sequences employed in 2D-IR and T-2D-IR spectroscopy. Red pulses numbered 1-3 indicate the three time-ordered interactions between IR laser pulse and sample necessary to generate the 2D-IR signal (Sig). The blue pulse marked 'UV' indicates the UV or visible excitation pulse. Asterisks indicate the use of tuneable narrow bandwidth pulses.

methodology employed *vide infra*; many orders of magnitude higher than the millisecond timescales accessible via NMR.

2D-IR is now employed extensively in the study of ground state systems.¹¹⁻¹⁵ Exemplars of this include the analysis of off-diagonal peak patterns to determine molecular geometries,^{18, 19} deconvolute complex spectra²⁰ or reveal vibrational^{21, 22} or chemical dynamics,^{23, 24} while 2D-IR lineshapes report on the fluctuations in a system introduced by interaction with its surroundings, typically nearby solvent molecules.²⁵⁻²⁷ Crucially, much of this information is either impossible or technologically challenging to extract from 1D experiments.

The extension of 2D-IR spectroscopy to excited states via so-called transient or non-equilibrium 2D-IR spectroscopy (T-2D-IR) experiments was first reported in 2003²⁸ and it has since been demonstrated for a selection of inorganic molecules.^{29, 30} The advantage of T-2D-IR is that the additional structural and dynamic insight and sub-picosecond time resolution offered by ground state 2D-IR spectroscopy becomes accessible for probing electronically-excited states and for following photochemical processes. Thus far however, the uptake of these methods within the inorganic chemistry community remains small. Indeed, the total number of articles employing transient 2D-IR methods numbers significantly less than 50, with the majority of these being utilised for biological or related systems.³¹⁻³⁹ This is largely due to the technical challenge of the method, which typically adds a UV/visible/near IR laser pulse to the two or, more commonly, three pulses needed to generate the 2D-IR signal and so is, formally at least, a 5th order non-linear spectroscopy. As a result, the signals obtained are smaller

in comparison to linear UV-IR spectroscopies and are often overlapped by larger peaks from the ground state 2D-IR response. Despite this, significant benefits can accrue from application of T-2D-IR methodologies to inorganic systems. The aim of this Perspective is to provide a basic introduction to the experiments, and then to discuss, through a series of examples, ways in which they can contribute to inorganic excited state chemistry research.

Experimental

Ground State 2D-IR Spectroscopy

In order to discuss the use of T-2D-IR spectroscopy, it is necessary to outline, briefly, the experimental approach associated with 2D-IR methods and the types of spectral signals that are obtained under ground state or 'equilibrium' conditions. Owing to the availability of a number of articles, reviews and, recently, a textbook that discuss the methodology in detail, the intention here is to focus on the spectroscopy and the information content of the data obtained.¹¹⁻¹⁵

A 2D-IR spectrum is obtained from a 3rd order nonlinear optical process in which three resonant interactions occur between ultrashort infrared laser pulses and vibrational transitions of the sample. A diagram of the various pulse sequences discussed below is given in Figure 1 where the IR interactions are numbered 1-3 in temporal order. Various methods exist to achieve this but all result in a 2D-IR spectrum, which is a correlation map of the pump (excitation) frequency, *i.e.* the frequency of the first laser-sample interaction, and the probe (detection) frequency, *i.e.* the frequency of the third interaction. In all versions of the 2D-IR experiment, the three interactions lead to the generation of a signal (Sig) by the sample that is then frequency-dispersed and detected via a grating spectrometer, thus providing the 'probe frequency' or 'detection frequency' axis of the spectrum.¹¹⁻¹⁵

The origin of the 'pump frequency' or 'excitation frequency' axis depends on the experimental methodology employed. The simplest and perhaps most accessible method to non-specialists is the frequency-domain 'double resonance 2D-IR' spectroscopy that uses a tuneable narrow bandwidth pump pulse. Double resonance 2D-IR is represented by pulse sequence I in Fig 1 where it is noted that the narrow bandwidth pump pulse is differentiated from broad bandwidth pulses by an asterisk. The narrow bandwidth pump pulse is obtained via an optical filter, or similar, that selects a small portion of the laser bandwidth, which is then used in the manner of a traditional pump-probe experiment; the pump pulse constitutes the first two light-sample interactions with the probe pulse providing the 3rd. A diagram of the spatial arrangement of the pulses is given in Fig 2(a). In this experiment the 2D spectrum consists of a series of narrow-band pump, broadband probe

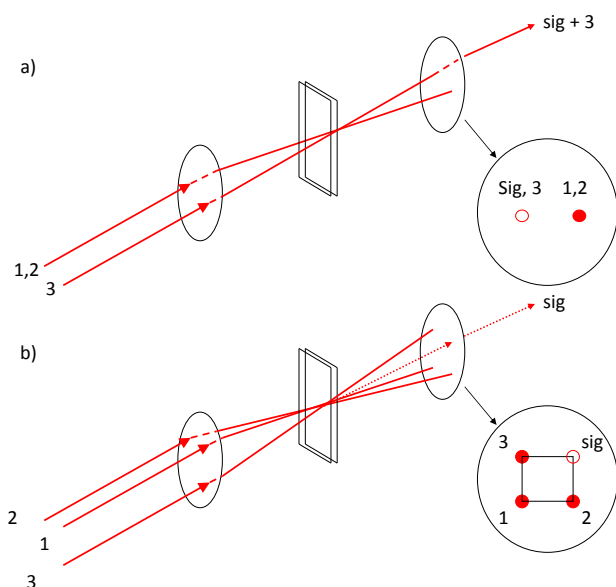


Figure 2: Schematic diagram of 2D-IR experimental pulse arrangements: a) shows 'pump-probe' geometry while b) shows the box geometry used for some Fourier Transform experiments.

slices as the pump frequency is scanned for a given pump-probe time delay (T_w in Fig 1), providing a 2D-plot showing the pump frequency-resolved response of the sample.¹⁶ Repetition of this process for multiple pump-probe delay times (T_w in Fig 1) then facilitates observation of dynamic processes. It is noted that the use of narrow bandwidth pulses in the double resonance methodology limits the time resolution achievable to, typically, 1 ps.

An alternative, time domain, 2D-IR method employs three separate broadband pulses with controllable time delays between them (pulse sequence II in Fig 1). The beams are arranged in either a pseudo pump-probe geometry (with two 'pumps' and one probe pulse as in Fig 2(a))^{40, 41} or with the pulses arranged at the three corners of a square (the box-CARS geometry as in Fig 2(b)) prior to being overlapped in the sample, whereupon the signal is emitted towards the fourth corner of the square.¹⁹ In both cases, the signal is frequency-dispersed and recorded as a function of the time delay between the first two pulses. The signal is heterodyne-detected either intrinsically, using residual light from the probe beam in the pump-probe geometry experiment (as is also the case in the double resonance experiment) or from an additional pulse in the box-CARS experiment. The use of heterodyne detection offers twofold benefits. Firstly, it amplifies the signal; secondly, it enables measurement of the interference pattern produced between the emitted signal and the local oscillator field. This means that information relating to the phase and sign of the signal field, which would be lost if the signal were detected directly, is retained. Fourier transformation of the interference pattern recovered generates the pump frequency axis of the 2D-IR spectrum. In the time domain experiment, the delay between the 2nd and 3rd pulses (T_w in Fig 1, referred to as the waiting

time) is the equivalent of the pump-probe delay time from the double resonance experiment and is fixed for a given 2D-IR spectrum acquisition. Typically, the time resolution of such Fourier-transform methods is around 50-100 fs.

The spectral features obtained using double resonance and Fourier transform 2D-IR methods have been shown to be largely equivalent and so the choice of methodology is determined by individual experimental requirements.⁴² For example, the double resonance method is perhaps simplest to implement, being a relatively straightforward modification of an existing pump-probe spectrometer. This approach does however suffer from reduced time resolution and some pump-axis spectral broadening of the line-shapes recovered as a result of the use of a narrow bandwidth pump pulse. Conversely, the Fourier transform method using the box geometry offers high sensitivity via the background-free signal at the expense of more complex post-experiment data processing. The latter arises from the need to remove the effects of unwanted 'non-rephasing' experimental signals by summing spectra obtained with those in which the ordering of the first two pulses is reversed.¹¹⁻¹⁵ This process occurs automatically when using the pseudo pump-probe Fourier transform methodology, which combines this advantage with the straightforward implementation of double resonance 2D-IR (particularly if a mid-IR pulse shaper is used to generate the pulses as described in some cases⁴³) and also maintains the high time resolution of the FT approach. This method foregoes the sensitivity benefits of the background-free measurement however. Each of these approaches is amenable to extension to T-2D-IR spectroscopy through the inclusion of an additional visible or UV pulse to the sequence (sequences III-VI in Fig 1) as will be discussed below.

In order to establish the spectral information content of a typical 2D-IR spectrum it is instructive to consider the schematic example shown in Fig 3 of an idealised system with two vibrational modes in the spectral region of interest. In effect, the 2D-IR experiment can be considered to be an excitation of each of the vibrational modes individually, with the probe axis reporting on the coupling or energy transfer pathways that exist between the excited mode and others in the sample. Fig 3 shows that excitation of the lower frequency of the two modes visible in the absorption spectrum gives rise to two peaks (1&2) located near the diagonal of the 2D-IR spectrum. These peaks can be described using the language of a standard, linear IR pump-probe experiment: on the diagonal (i.e. with equal pump and probe frequencies) is a peak corresponding to the bleach (and stimulated emission) of the $v=0-1$ transition of the excited mode (1). This is accompanied by a peak of the opposite sign attributable to the $v=1-2$ excited state absorption feature, arising from population of the $v=1$ state by the pump pulse (2). This feature appears at the same pump frequency as the diagonal peak but is shifted to lower probe frequencies due to the anharmonicity of the excited mode. These two features arise for every excited mode in the experiment and so all features seen in the IR absorption spectrum appear on the diagonal of the 2D-IR plot.

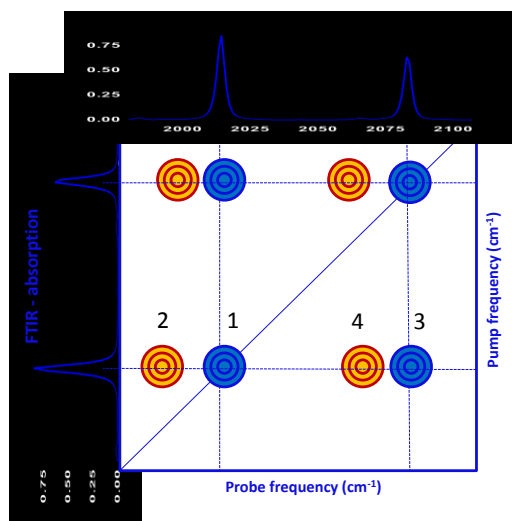


Figure 3: Schematic diagram of a 2D-IR spectrum of a system with two vibrational modes.

Additional information regarding the sample starts to be gleaned from the 2D methodology in the event that the excited mode is coupled to another vibrational mode. In this case, excitation of the lower frequency mode leads to changes in the vibrational potential of the higher frequency mode and the two modes can be considered to share a common ground state. As a result, a second pair of peaks (Fig 3, **3&4**) are observed in the off diagonal region of the spectrum, with a pump frequency equal to that of the diagonal peak but at probe frequencies corresponding to transitions involving the higher frequency mode. The peaks are assignable to the bleach/stimulated emission of the $v=0-1$ transition of the high frequency mode (**3**) and a transition from the $v=1$ mode of the pumped (low frequency) mode to the combination band of the coupled modes (**4**). When the pump pulse frequency is tuned into resonance with the higher frequency mode an analogous set of peaks is obtained giving rise to the characteristic pattern shown in Fig 3. These off-diagonal peaks arising from vibrational coupling can be applied to decipher spectral contributions in mixtures or to aid spectral assignment.¹¹⁻¹⁵ In addition, structural information on the studied molecule can be obtained from the 2D-IR spectrum. This is achieved through monitoring the relative amplitudes of diagonal and off-diagonal features with parallel and perpendicular polarization relationships between the pump (denoted 1&2 in Figs 1 and 2) and probe (3) pulses.¹⁹ From this, it is possible to extract the angles between transition dipole moments of two coupled modes. In the event that these dipole moments correlate strongly with bond directions it is possible to obtain direct measurements of molecular structure.

Recording 2D-IR spectra at a range of pump-probe delay (or waiting) times (T_w in Fig 1) allows the 2D-IR spectroscopist to gain further insights into the origin and nature of the off-diagonal peaks in the spectrum as well as the dynamic processes occurring in the sample following vibrational

excitation. For example, off-diagonal peaks of the type described indicate vibrational coupling and will be present from the earliest pump-probe delay times. As the delay time increases however it is possible to observe changes in the peak amplitudes, or the appearance of new peaks, as a result of vibrational relaxation. For example, all of the peaks described in Fig 3 will diminish in size due to vibrational relaxation of the pumped mode. Indeed, this vibrational relaxation time determines the maximum accessible range for dynamic measurements in a 2D-IR experiment. In addition, new peaks in the off-diagonal region can be observed due to the presence of vibrational population transfer (Intramolecular Vibrational Redistribution, IVR) between the pumped mode and other modes in the sample. These new peaks correspond to transitions between the newly excited 'receiving mode' and higher-lying vibrational states that were not accessible without IVR from the pumped mode.⁴⁴ As such, they occur at the pump frequency of the excited mode but with a probe frequency corresponding to transitions from the newly-populated mode and so lie in the off-diagonal region of the spectrum. More typically in the inorganic systems studied to date, the two modes between which the population transfer is occurring are coupled and the relative sizes of the diagonal and off-diagonal anharmonicities are such that the individual off-diagonal peaks from coupling and IVR are not clearly separated and this phenomenon is actually manifest as the apparent growth of the off-diagonal peaks shown in Fig 3 relative to the diagonal ones as the waiting time increases and vibrational energy is transferred between coupled states. Good examples of this effect are reported in Refs.^{21, 22} In this event however, it must be remembered that the effect is caused by the accidental overlap of peaks of different origin.

Off diagonal peaks in a 2D-IR spectrum can also report on chemical processes occurring during the pump-probe delay time. In a manner analogous to NMR chemical exchange experiments, if two species are interchanging on timescales comparable to the 2D-IR pump-probe delay time then a component of the sample can be excited in one form and transfer to the other form before it is detected and *vice versa*. In this case, an off diagonal peak with pump frequency equal to a transition of the initial species but probe frequency equal to a transition of the second grows into the spectrum with dynamics that indicate the rate of exchange.⁴⁵⁻⁴⁷ This effect has been widely exploited in 2D-IR spectroscopy to report on ground state isomerisation⁴⁸ or hydrogen bonding dynamics in inorganic species.⁴⁹

Finally, in addition to peak positions and amplitudes, the 2D diagonal lineshapes can report on solvation dynamics. An inhomogeneously broadened mode gives rise to a diagonally elongated 2D-IR diagonal peak at pump-probe delay times that are short on the timescale of the underlying dynamics causing the inhomogeneity. This reflects the fact that the individual microenvironments that make up the broadened IR absorption of the ensemble of molecules that constitutes the sample have not had sufficient time to interconvert. As the pump-probe delay time increases, this correlation, or elongation, is reduced as dynamics lead to randomisation and the sample loses the

memory of its initial configuration. Quantification of the lineshape change then provides a measure of the frequency-frequency correlation function (FFCF); an indication of the size and frequency of the ultrafast fluctuations caused by solvent motion on the studied mode.^{25, 50-52} This will be described in more detail in relation to extension of the method to excited state solvation dynamics below.

T-2D-IR Spectroscopy

The 2D-IR experiments described thus far all relate to systems in the electronic ground state. In order to transfer these measurements to electronically excited states, one has to introduce an additional laser ‘pump’ pulse into the experiment that is resonant with the molecular transition of interest. This has been demonstrated for all of the 2D-IR experimental methodologies described above.

The simplest type of T-2D-IR experiment has a UV/visible wavelength pulse arriving at the sample before the IR pulses (sequences III and IV in Fig 1). In this way the 2D-IR experiment becomes a time delayed ‘2D-IR probe’ of the excited system.²⁸ Examples will be given below of this type of arrangement being used to investigate a range of excited states and to probe photochemical reaction intermediates. The introduction of an additional laser pulse into the sequence means that T-2D-IR signals arise from 5th order non-linear processes rather than the 3rd order ones of ground state 2D-IR. However it is often useful to consider the relative time delays between the ‘UV pump’ and ‘2D-IR probe’ in such an experiment; denoted t_{UV} in Fig 1. If this time delay is sufficiently long that molecular rotation and excited state vibrational relaxation following the electronic excitation have reached a pseudo equilibrium within the excited state potential, then the 2D-IR spectrum may be considered from the point of view of a 3rd order non-linear spectroscopy experiment. In short, the type of spectral interpretations mentioned in the preceding section may be employed. Examples of this will be shown below for studying the vibrational dynamics of intermediates. If the time delay between the UV pump and 2D-IR probe is short however, a formal 5th order treatment of the data is required.⁵³ This has been described in detail and examples of this will be shown below for studies of the solvation dynamics of electronically-excited species.⁵⁴

A second type of T-2D-IR experiment that has been applied to inorganic excited states also employs a UV/vis pulse to transfer the system to an elevated electronic state but this occurs *after* the first two laser-sample interactions of the 2D-IR experiment (after the narrowband pump in double resonance 2D-IR methods, sequence V in Fig 1, or after the first two pulses in a FT 2D-IR experiment; sequence VI).⁵⁵ This type of T-2D-IR exchange (T-2D-IR-EXSY) experiment⁵⁵ can be used to monitor the correlation of vibrational modes in the ground and excited electronic states. In simplified terms, the experiment ‘labels’ vibrational modes of the ground state and by transferring these labels into the excited state, the position of

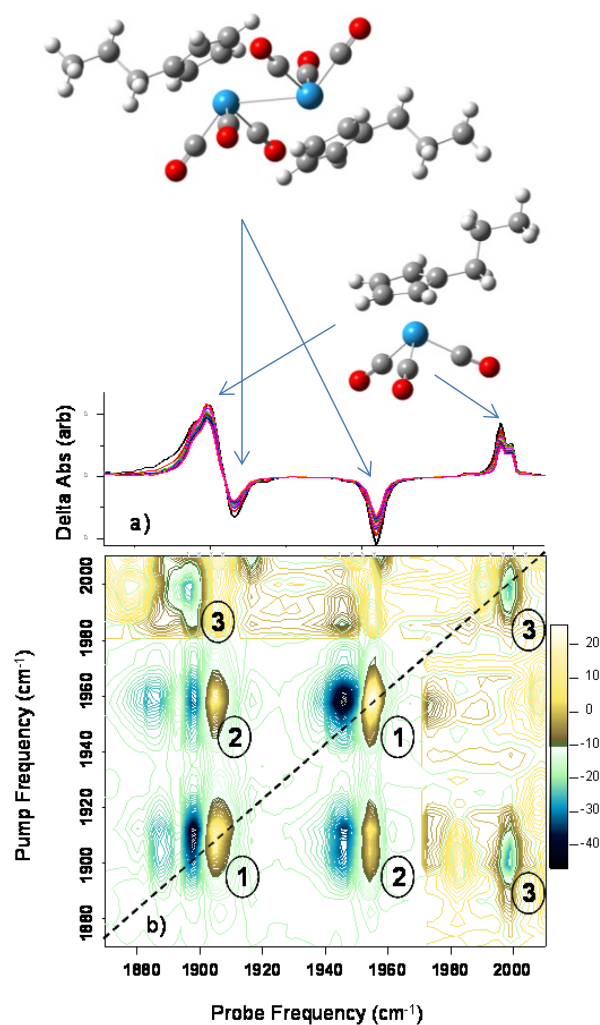


Figure 4: TR-IR (a) and T-2D-IR spectrum (b) following photodissociation of $[(nPr-Cp)W(CO)_3]_2$. Relevant molecular structures of $[(nPr-Cp)W(CO)_3]_2$ and $(nPr-Cp)W(CO)_3$ are also shown: W atoms are shown in blue; C in grey, O in red and H in white. Arrows indicate TR-IR resonances assigned to the dimer and monomer species. In (b) peak pairs labelled (1) are assigned to parent molecule diagonal transitions; Peaks labelled (2) are parent molecule off-diagonal peaks. Each corresponds to negative, bleaches in the TR-IR spectrum. Peaks labelled (3) are due to photoproduct diagonal and off-diagonal modes corresponding to positive peaks in the TR-IR spectrum. Note that the peak pairs (3) have the opposite sign to pairs (1) and (2). The region of the 2D-IR spectrum beyond 1970 cm^{-1} has been expanded to show the peaks more clearly.⁵⁶

the off diagonal peaks then reveals which excited state vibrations these transitions map to; information which can be very useful in assigning complex electronic excited state spectra. This example will be discussed in detail below.

T-2D-IR Spectroscopy of Short-lived Inorganic Photoproducts

The first implementation of the T-2D-IR methodology was reported in 2003,²⁸ using a UV pulse to excite photoisomerisation in an azobenzene moiety to create a non-equilibrium structure in a short, 8 residue, cyclic peptide. In this case, the 2D-IR pulse sequence III (Fig 1), employing the double resonance approach, was used to observe changes in the

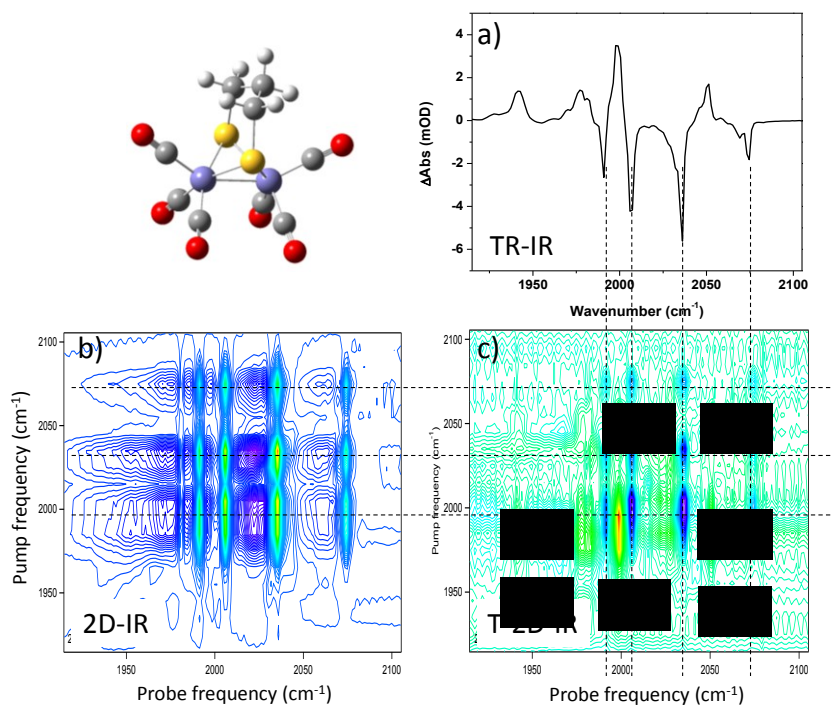


Figure 5: (a) TR-IR, (b) ground state 2D-IR and (c) T-2D-IR spectra of a model system of the hydrogenase enzyme active sub-site, as reported in Ref.⁵⁷ Arrows in the T-2D-IR spectra show the position of photoproduct peaks. The relevant molecular structure of the parent species is shown in the top left quadrant: Fe atoms are shown in purple; C in grey, O in red; S in yellow and H in white.

2D-IR spectrum of the peptide as it relaxed to its new equilibrium configuration. Though not directly relevant to inorganic excited state spectroscopy, this article is nonetheless important in that it lays the groundwork for all that follows.²⁸ In particular, characterisation of the T-2D-IR peak shapes and positions was established along with an experimental approach that allowed separation of the equilibrium and non-equilibrium 2D-IR spectral responses. The latter is based upon techniques used to record the characteristic difference spectrum datasets established for pump-probe experiments, which feature negative bleach peaks and positive-going transient absorptions for species that are reduced or increased in number by the UV/vis pump pulse respectively.

In pump-probe spectroscopy, this is done by recording two sequential probe pulses with the pump pulse on and off respectively, these are then subtracted to give the experimental signal. When applied to double resonance T-2D-IR spectroscopy, the data is obtained over four pulse sets, which incorporate every possible combination of pump pulses (both pumps, IR pump only, UV pump only and no pumps) such that, by taking the appropriate pulse combinations, the time-resolved linear IR (TR-IR), the ground state 2D-IR and the T-2D-IR spectra can be obtained in the same measurement.²⁸

The T-2D-IR spectrum that results from this approach is a difference spectrum in a manner analogous to that of the linear TR-IR pump-probe experiment in that a 2D spectrum is obtained showing the changes caused by the presence of the

UV pump pulse. Thus, 2D-IR signals arising from the loss of parent or ground state species have diagonal and off diagonal pairs of peaks as in peaks 1-4 in Fig 3 but the signs of the peaks are reversed, reflecting a loss of these species caused by the UV excitation. Similarly, peaks due to the gain of excited state species have sets of peaks in the T-2D-IR plot that exhibit the normal positive/negative amplitudes as shown in Fig 3. Thus, it is possible to differentiate between 2D-IR ‘bleaches’ and ‘transient absorptions’ by the relative signs of the peaks observed.²⁸

A demonstration of this type of experiment performed on inorganic molecules can be seen in a study of the photoproducts obtained following photodissociation of the intermetallic bond of the *n*-propyl-cyclopentadienyl tungsten tricarbonyl dimer [(*n*Pr-Cp)W(CO)₃]₂.⁵⁶ This T-2D-IR spectroscopy study built on linear photochemical studies of this species establishing that irradiation at 490 nm led to

cleavage of the dimer into two 17e⁻ (*n*Pr-Cp)W(CO)₃ monomers.⁵⁸ The double resonance T-2D-IR spectrum obtained for this system in the CO stretching region of the IR is reproduced in Fig 4, where it is accompanied by the linear TR-IR spectrum.

From Fig 4(a) it can be seen that bleaches of the parent CO stretching modes of the dimer appear as negative peaks in the TR-IR spectrum while two new positive peaks arise due to formation of the 17e⁻ photoproduct. Signals from each of these features are present in the T-2D-IR (Fig 4(b)) spectrum, which was obtained using pulse sequence III from Fig 1. Diagonal peaks assignable to the parent molecule transitions occur on the spectrum diagonal, labelled (1), as the type of peak pairs described in Fig 3. It can also be seen that the two modes attributable to the dimer are vibrationally coupled from the presence of off-diagonal peak pairs linking the diagonal peaks (labelled (2)). Similarly, the photoproduct peaks give rise to new diagonal and off-diagonal modes in the T-2D-IR spectrum (labelled (3)). Only one of the two sets of expected photoproduct diagonal peaks is visible on the T-2D-IR diagonal due to overlap of the lower frequency diagonal peak with the parent bleaches, however, the position this signal is clearly shown by the off-diagonal peaks arising from coupling of the two modes of the 17e⁻ monomer. The difference in phase of the pairs of peaks in the T-2D-IR spectrum arising from parent bleaches (1,2) and photoproducts (3) can be clearly seen in Fig 4(b).

In the T-2D-IR experiments described,⁵⁶ the 2D-IR pulse sequence was delayed by 300ps relative to the 490 nm excitation pulse ($t_{UV} = 300$ ps). This allowed T-2D-IR datasets to be obtained in the pseudo 3rd order regime where the monomer had undergone rotational and vibrational relaxation

following photodissociation. In addition, owing to a diffusive recombination time for the monomers that had not undergone geminate recombination that was found to be in excess of 4.5 ns, the monomer population was not changing significantly on the timescale for 2D-IR data acquisition. By acquiring T-2D-IR spectra at a fixed UV/vis-2D-IR delay time (t_{UV}) of 300 ps but with a range of 2D-IR-pump-probe delay times (T_w), the vibrational relaxation dynamics of the monomer were determined.⁵⁶ The vibrational relaxation of the unsaturated species was found to be faster than that of the parent, suggesting a change in the interactions between monomer and solvent, possibly arising from the weak coordination of a solvent molecule to the vacant site of the monomer. Perhaps less important than the specific molecular spectroscopy derived, this experiment provides an indication of how T-2D-IR spectroscopy can be employed to transfer the types of 2D-IR experiment carried out in the electronic ground state to short lived species produced by UV/vis excitation.⁵⁶

A similar experimental approach was employed to exploit the ability of 2D-IR spectroscopy to unravel complex spectra following excitation. In this case, the photoproduct spectrum arising from excitation of the metal to ligand charge transfer (MLCT) transition of an inorganic active sub-site analogue of the hydrogenase enzyme system was studied.⁵⁷ TR-IR spectroscopy of (μ -propanedithiolate) $Fe_2(CO)_6$ (see Fig 5 for structure) following $\lambda < 350$ nm excitation demonstrated that CO photodissociation was the main photochemical pathway observed, though the photoproduct spectra produced were found to be complex and assignment to a specific photoproduct or to a mixture was not possible, with density functional theory simulations suggesting more than one species could be present.⁵⁹

T-2D-IR spectroscopy was employed to unravel the spectroscopy subsequent to photodissociation. Once again, the experiments were performed in the pseudo 3rd order limit in order to reveal the 2D-IR spectrum of the photoproduct species.⁵⁷ The result is shown in Fig 5 where the TR-IR and ground state 2D-IR spectra are shown alongside the T-2D-IR spectrum (obtained using pulse sequence III from Fig 1). In this case the TR-IR and 2D-IR datasets are needed to separate the peaks due to the photoproduct from large parent molecule resonances in Fig 5. Dashed guidelines extend from the parent molecule signals in the TR-IR and ground state 2D-IR spectra so that the intersections of these guides in the T-2D-IR plot show the positions of parent molecule peaks. The photoproduct peaks are seen in the T-2D-IR spectrum, some of which are indicated by arrows, lying between these guides and at frequencies which correspond to the positive signals in the TR-IR spectrum. T-2D-IR spectra were obtained both as a function of the IR pump-IR probe delay time (T_w) and polarisation geometry. This showed that all photoproduct peaks in the spectrum were vibrationally coupled, while T-2D-IR datasets obtained as a function of UV pump-2D-IR delay time (t_{UV}) showed that all photoproduct peaks exhibited the same kinetics. Together, this allowed T-2D-IR spectroscopy to establish that a single photoproduct was being generated; (μ -propanedithiolate) $Fe_2(CO)_5$ (heptane). Once

again, vibrational relaxation dynamics were used to infer the formation of a solvent adduct species.⁵⁷ Finally, a further demonstration of the potential benefits of 2D methods was obtained via the use of the polarisation dependence of the T-2D-IR off-diagonal photoproduct peaks to determine the likely structure of the photoproduct.⁵⁷

Both of these examples serve to show how 2D-IR methods can be used to enhance the information available from TR-IR spectroscopy by further interrogating the structure and dynamics of short-lived species and photochemical intermediates. It is noted however that the magnitude of the signals obtained in these T-2D-IR studies is much smaller than that from ground state 2D-IR spectroscopy. In this, the use of metallobonyls with their intense CO stretching mode absorptions makes for very tractable systems. Typically, one can expect a millimolar solution of metallobonyl to yield an IR absorption in the region of 0.4 OD at the kinds of sample pathlengths typically used for ultrafast spectroscopy (50–100 μ m). Of these molecules, perhaps a few per cent are photolysed by a given UV pulse and it is from these molecules that the photoproduct peaks in the T-2D-IR spectrum are generated. This means that data acquisition times are longer for T-2D-IR spectra, though in the intervening period since these articles were published several advances have been made to reduce this parameter.^{40, 43, 60, 61} Along with the need for longer acquisition times, it must be considered that the sample must also be refreshed between laser shots meaning the use of a constantly moving sample cell and/or flowing sample. In the case that the photochemistry is not reversible, this can necessitate the provision of large volumes of sample solutions. These factors serve to highlight that, while powerful, T-2D-IR spectroscopy methods do not represent a blanket replacement for TR-IR datasets and it is wise to reserve them for situations in which additional insight is needed that cannot be obtained from linear measurements.

T-2D-IR Spectroscopy of Inorganic Excited States

An important issue associated with inorganic excited states is the need to understand the assignments of vibrational modes in the same way as for ground states. Tools that allow us to understand the coupling of vibrational modes in the excited state or the mapping of ground state vibrational modes onto their excited state partners will thus provide a valuable new layer of information.

The ability of T-2D-IR methods to deliver such insight was demonstrated by the advent of T-2D-IR-EXSY spectroscopy (pulse sequences V and VI in Fig 1) in 2004.⁵⁵ The method was demonstrated using the $[Re(CO)_3Cl(dmbpy)]$ molecule, where dmbpy indicates a dimethylbipyridine ligand. Once again, the linear spectroscopy of this species was relatively well-established with a blue shift of the three carbonyl stretching mode absorption bands of $[Re(CO)_3Cl(dmbpy)]$ (labelled $a''(2)$; a'' and $a'(1)$ respectively in order of increasing frequency) being observed upon excitation at a wavelength of 390 nm.⁶²

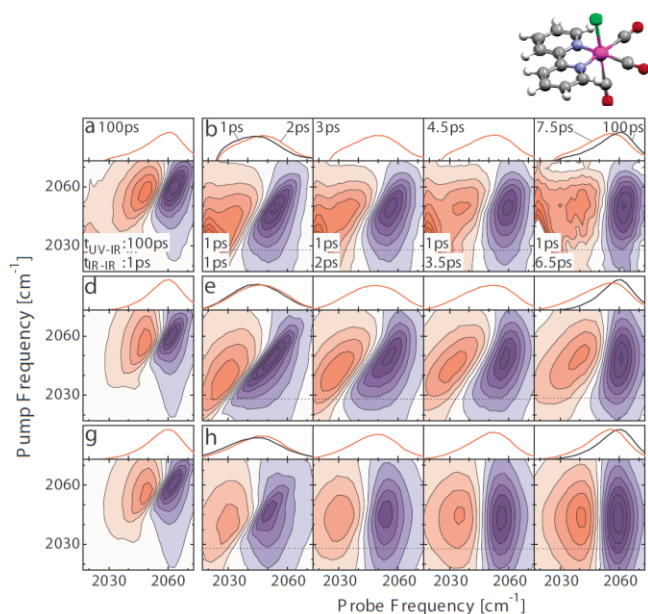


Figure 6: (a and b) IR absorption and T-2D-IR spectra of $\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})$ as a function of UV pump-2D-IR probe time delay and also 2D-IR pump-probe time delay following excitation. (d-h) show the results of simulating T-2D-IR spectra using models (see text). Relevant molecular structure is shown top right. Re atoms are shown in mauve; C in grey, O in red; Cl in green and H in white. Reprinted figure with permission from J. Bredenbeck, J. Helbing and P. Hamm, *Phys Rev Lett*, 95, 083201 2005. Copyright (2005) by the American Physical Society.

What was not clear however were the individual magnitudes of the blue shifts occurring for each band, with a conflict between the implicit assumption that the bands shifted in a linear fashion and so maintained the same frequency ordering in the ground and excited states (*i.e.* $a'(2)$; a'' ; $a'(1)$) and calculations predicting that the lowest frequency pair of modes became reversed upon excitation (*i.e.* a'' ; $a'(2)$; $a'(1)$).

This matter was solved conclusively by the use of the T-2D-IR-EXSY method using pulse sequence V (Fig 1).⁵⁵ By placing the UV pulse between the pump and probe pulses of the double resonance 2D-IR experiment, off-diagonal peaks in the 2D-IR spectrum reported the correlation of the ground-state vibrational modes with their excited state counterparts.

In more detail, in the T-2D-IR-EXSY experiment a mode is first of all excited at an IR frequency corresponding to its ground state vibrational absorption frequency, defining the pump axis position of the peak in the T-2D-IR spectrum. The electronic excitation of the molecule then transfers this vibrational excitation to the upper electronic state such that when the final IR interaction with the sample occurs, the probe, or detection, frequency of the 2D-IR signal is at the frequency of this mode in the excited state; defining its probe axis position. In this manner, off diagonal peaks between ground and electronically excited state vibrational modes were observed in the T-2D-IR-EXSY spectrum of $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ that demonstrated clearly that the

frequency shifts occurring upon excitation led to a reversal of the order of two out of the three CO stretching modes.⁵⁵

This experiment demonstrates an alternative approach to applying 2D methods to study excited states. In the case described, the CO modes studied were found to be sufficiently similar in the two electronic states that a straightforward one-to-one mapping was appropriate. In the event that the upper electronic state produced modes of significantly different character or that the extent of any delocalisation of the modes became vastly different, such an experiment would be more challenging to interpret. Similarly, the complexity of the spectra recorded will place limitations on the ability to resolve the off-diagonal peaks due to overlap with ground state species. To a certain extent this can be overcome using the relative polarization of the pulses to suppress ground state off-diagonal peaks and reveal the peaks of interest but this too will become difficult if more crowded or significantly broadened spectra are involved.

More recently T-2D-IR and T-2D-IR-EXSY methods were used to study the spectroscopy and dynamics associated with charge injection in dye-sensitised nanocrystalline thin films.⁶³ This example of T-2D-IR-EXSY spectroscopy was technically different to the initial demonstration in that it featured the use of a mid-IR pulse shaper to generate the 2D-IR pulse train and the 2D-IR spectroscopy was achieved using the FT method rather than double resonance spectroscopy (sequence VI in Fig 1).⁶³ In this case a Re-carbonyl-based dye was used to sensitise a TiO_2 film. The benefits of T-2D-IR in this application were found to be threefold: the lack of off-diagonal peaks in the 2D-IR spectrum of the dye revealed the presence of structural isomers of the dye not found in solution; 2D-IR spectra, which require anharmonic absorption modes to generate signals, were not affected by the presence of a broad, intense free-electron absorption in the same way as linear IR methods and finally, the use of the T-2D-IR-EXSY pulse sequence made it possible to establish that the three conformers exhibited different charge injection timescales.

T-2D-IR Spectroscopy of Excited State Solvation Dynamics

Solvent effects can be an important factor in determining the dynamics and subsequent photochemistry of excited electronic states. As such, it is important to understand the molecular-level response of the solvent to the electronic excitation of a solute. Ultrafast 2D-IR has demonstrated that it provides a route to determining solvent-solute dynamics via approaches that measure the frequency-frequency correlation function (FFCF) of a particular vibrational mode. In the ground state, this is achieved via changes in the 2D-IR diagonal lineshape as a function of the pump-probe delay time (waiting time).

The effect of solvent dynamics on a vibrational transition is to create a continuum of microenvironments for the solute, each of which will have a slightly different vibrational frequency. More formally, one can consider that the vibrational transition of a molecule is coupled to the low frequency density of states of the solvent. The result of this in the IR absorption spectrum of

an ensemble of molecules is inhomogeneous broadening of the IR lineshape. In a 2D-IR experiment at waiting times that are short in relation to the solvent dynamics that are causing the broadening, this results in a diagonal elongation of the peaks arising from the $\nu=0-1$ (and $\nu=1-2$) transition of the mode; the pair of peaks located on or near the spectrum diagonal. The reason for this can be visualised as the sample being pumped and probed in quick succession such that no evolution of the continuum of states occurs leading to a lineshape broadened chiefly along the spectrum diagonal. As the waiting time is allowed to increase and becomes comparable to the dynamic timescale, a solute excited in one part of the continuum may have evolved into a different part via solvent motion such that, when probed, it has a different frequency to when it was pumped. Overall, this process means that the correlation of the pump and probe frequency of the 2D-IR peak (the diagonal elongation) is lost as the waiting time increases because the sample loses the memory of its initial state. This spectral diffusion results in a change in the profile of the 2D-IR peak toward a more circular shape. Quantification of this lineshape evolution as a function of waiting time then gives rise to an exponential-type decay with the timescales reporting the dynamics of the FFCF, which in turn report on solvent motion near the vibrational mode in question.

Various methods have been developed to achieve this quantification,^{25, 50-52} of which perhaps the simplest to visualise extracts the gradient of the nodal plane between the $\nu=0-1$ and $\nu=1-2$ parts of the 2D-IR diagonal feature (the Nodal Line Slope method⁵¹) or the gradient of a line through the highest points of the $\nu=0-1$ peak at each pump frequency (the Central Line Slope method⁵⁰). All methods have been shown to be largely equivalent in terms of extraction of dynamic timescales from 2D-IR data.

It is stressed that this type of information relating to solvation dynamics is not exclusively available from 2D-IR spectroscopy. Indeed it can be extracted by other methods such as the 3 pulse photon echo peak shift experiment and linear hole burning experiments. Having said this, 2D-IR offers a relatively direct, graphical approach to extracting the data and so has become a popular approach, being employed for biologically-related samples as well as solute-solvent systems.^{11, 26, 64-70}

Transferring this experiment to the excited state has been achieved. The first instance of this was the application of T-2D-IR spectroscopy to observe the behaviour of the symmetric CO stretching vibration of $\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})$ upon excitation of the metal to ligand charge transfer transition in DMSO.⁵⁴ This excitation resulted in a significant shift in the frequency of the vibrational mode, allowing a clear spectral separation of the T-2D-IR peaks from the ground and excited states. By utilising the double resonance 2D-IR experiment as a time-delayed probe of the system (sequence III in Fig 1) at a fixed UV-pump-2D-IR-probe delay time (t_{UV}) of 1 ps and varying the 2D-IR pump-probe delay time (T_w) from 1-6.5 ps, the evolution of the distribution of CO frequencies immediately following electronic excitation was captured via changes in the 2D-IR lineshape. Figure 6 reproduces part of the data from this study.

Fig 6b shows the results of the experiment described⁵⁴ and the change in the slope of the plane between the red and blue parts of the lineshape as the 2D-IR pump-probe time delay increases can clearly be seen, reflecting the spectral diffusion of the mode as described above.

Obtaining experimental insight into the reorganisation of a solvent following the change in dipole moment of the solute associated with electronic excitation is not commonplace and such experiments provide important new information. In particular, it was noted that dynamic evolution following excitation was complex, featuring a fast band shifting of the hole burned by the IR pump pulse on different timescales to the evolution of the lineshape observed in the TR-IR data. It was also observed that, although the 2D-IR lineshape in Fig 6(b) has evolved to near vertical within 6.5 ps of the electronic excitation, this spectrum does not match the T-2D-IR spectrum obtained at a UV-pump-2D-IR-probe delay time of 100 ps in which the system has fully equilibrated (Fig 6(a)). The implication was that the system evolved on two timescales, with spectral diffusion within the ensemble being probed occurring more quickly than the recovery to equilibrium conditions. In addition, changes in the homogeneous linewidth of the studied mode were reported as the system relaxed. These observations were found to be inconsistent with widely-applied linear response models where fast homogeneous processes are independent of, or decoupled from, the slower processes underpinning inhomogeneous broadening.⁵⁴

These experiments further demonstrated this by comparing the data to two models, only one of which departed from linear response by introducing a non-linear coupling of relaxation timescales. The results of using these to reproduce the spectral data are shown in Fig 6(d-h). Overall, the results showed that both models reproduced the linear and ground state 2D-IR datasets well but only the model that included this dynamic, nonlinear coupling parameter was able to reproduce the T2D-IR data; thus the need for a 5th order experiment to establish the interactions between relaxation phenomena was established. This arises from the fact that the 5th order T-2D-IR dataset is sensitive to higher order contributions to the correlation function that are not revealed by 3rd order experiments.⁵⁴

Two further applications of T-2D-IR methods have been reported that provide insight into the interaction of electronically excited inorganic species with their solvent environment. Employing the Fourier transform-derived T-2D-IR method (sequence IV in Fig 1), it was shown that geminate recombination of the $\text{CpMo}(\text{CO})_3$ photoproducts formed from 400 nm photodissociation of the $[\text{CpMo}(\text{CO})_3]_2$ dimer favoured the *trans* form over the *gauche*.⁷¹ The measurement was supported by *ab initio* theoretical simulations that predicted a barrierless recombination process that was directed toward the *trans* isomer via diffusion within the solvent cage. This provides useful insight into the time spent by radicals within the solvent cage following photodissociation, though it is also the case that the *trans* form was found to be the most thermodynamically-stable species under equilibrium conditions and the recombination time of ~ 30 ps will be comparable to the

rotation time of the species formed. It is however interesting that no *gauche* isomer recovery was noted and raises the possibility that a role exists for the solvent in controlling the photochemical reaction coordinate.⁷¹

A second application of the same FT-2D-IR methodology was used to probe the orientational relaxation of a similar system following photodissociation.⁷² The $\text{Mn}_2(\text{CO})_{10}$ dimer was used to generate two $\text{Mn}(\text{CO})_5$ species with 2D-IR used to measure the rotation time as a function of time following excitation. In this case it was shown that orientational dynamics became progressively slower as the time following excitation increased. This was attributed to the cooling of a localised rise in temperature caused by dissipation of excess energy from the electronic transition into low frequency solvent modes; the higher temperature giving rise to faster rotational motion of the photoproduct.

Future Directions

As mentioned in the introduction it is clear that uptake of T-2D-IR methods for inorganic chemistry research has been limited, with far greater translation of methods that were developed using inorganic systems occurring into the biological research sector. In some respects this is surprising as the inorganic systems described benefit from vibrational modes that have larger transition dipole moments and so larger signals than their biological counterparts. It is noticeable that every example given here has employed a metallobonded molecule, which as a family, benefit from intense IR absorption signals that are narrow and yet both structurally- and environmentally-sensitive as well as being well-separated from absorptions of the solvent background. In this, the metallobonds make for excellent samples for demonstrating new methods. Having said that, the T-2D-IR techniques described offer a wealth of new information on the spectroscopy, dynamics and solvent interactions of the excited states and photochemistry ensuing from UV-visible excitation and constant developments in lasers and 2D-IR methodology now mean that the experiments are becoming both more accessible (2D-IR spectroscopy equipment is now commercially available) and more sensitive, such that they are by no means limited to metallobonds.

One example of a future direction for this class of spectroscopy is given by a recently published article reporting the use of mixed IR/vis pulse trains to lengthen the time window over which 2D-IR-derived dynamics can be extracted.⁷³ In these experiments, an off resonant UV/visible pulse is inserted into the 2D-IR pulse train such that only the molecules vibrationally 'labelled' by the infrared excitation are elevated into an electronically excited state. The advantage of this is that a normal 2D-IR signal is limited in terms of its temporal range by vibrational relaxation of the modes excited. By lifting these molecules into electronically excited states, the signal persistence is then dependent upon the electronic state lifetime, which is generally much longer than the vibrational one. While the example reported utilises the method to extend the interrogation time of ground electronic state dynamics, such methods could in future be used to probe excited state processes

and the coupling or electronic and vibrational degrees of freedom, offering new tools to extend the T-2D-IR-derived suite of experiments.

Acknowledgements

NTH acknowledges funding from the European Research Council, the Science and Technology Facilities Council and the Engineering and Physical Sciences Research Council for work featured in this manuscript. The provision of artwork for Figure 6 by Prof Peter Hamm is also gratefully acknowledged.

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NTH Biography

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