

Two-dimensional IR spectroscopy of transient species

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Abstract: Transient two-dimensional infrared spectroscopy (T2D-IR) extends 2D-IR spectroscopy to the non-equilibrium regime. We demonstrate different types of T2D-IR experiments for a charge transfer state of $[\text{Re}(\text{CH}_3\text{-bpy}(\text{CO})_3\text{Cl}]$, including the vibrational analogue of NMR-exchange spectroscopy.

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1. Introduction

Ultrafast two-dimensional infrared spectroscopy (2D-IR) is a promising tool for the investigation of molecular structures [1] and their equilibrium fluctuations [2]. The outstanding feature of 2D-IR spectroscopy is the combination of its structure resolution power with a sub-picosecond time resolution. Thus it is particularly suited for application to fast dynamical processes, offering means to resolve distributions and dynamics of rapidly interconverting species in *equilibrium*. Highly promising is the extension of 2D-IR to the *transient* regime. Non-linear IR spectroscopy can then be applied to a system that is prepared far from equilibrium such as a folding protein or a solvated molecule after a sudden change in charge distribution. First steps in this direction have been reported recently for the picosecond conformational transition of a photoswitchable cyclic peptide, employing *transient* 2D-IR spectroscopy (T2D-IR) [3]. T2D-IR allows to record snapshot 2D-IR spectra of transient species in the course of a photo-triggered event like a photo-reaction. The reaction is triggered by an additional UV laser pulse preceding the IR pulses which constitute the 2D-IR part of the experiment (pulse sequence Fig. 1a). In this publication we discuss two novel T2D-IR experiments corresponding to Fig. 1b and c, which vary the original T2D-IR experiment to yield different types of information: Sequence 1b constitutes a dynamic 2D hole burning experiment on the non-equilibrium ensemble created by the UV_{pump} pulse. The sequence 1c is referred to as “band labeling spectroscopy”, as it allows to label a specific vibration by the narrowband IR_{pump} pulse before the UV_{pump} pulse is applied and follows this label in the course of the subsequent photo-reaction.

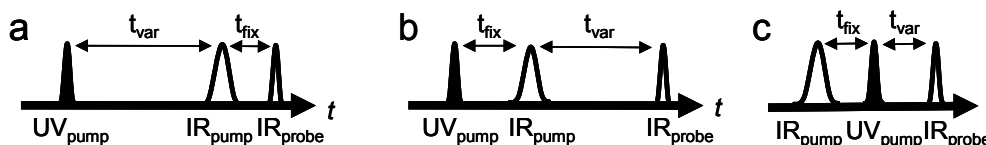


Fig. 1. T2D-IR experiments: a – regular T2D-IR spectroscopy. b – hole burning T2D-IR spectroscopy. c – band labeling T2D-IR spectroscopy.

The experiments are demonstrated for the photo-triggered metal-to-ligand charge transfer (MLCT) in $[\text{Re}(\text{CH}_3\text{-bpy}(\text{CO})_3\text{Cl}]$ (Fig. 2a), which occurs upon 400 nm excitation. MLCT induces a strong blue shift in the CO vibrations of the complex due to the change in electronic structure and subsequent solvation [4]. Fig. 2a shows the bands of the three CO modes in the C_3 -symmetric complex and their shift upon MLCT.

2. Band labeling T2D-IR

The band labeling pulse sequence in Fig. 1c relates vibrations of a transient state generated by the UV_{pump} pulse to vibrations in the initial state [5]. Here we demonstrate its application to obtain an assignment of the CO vibrations in the MLCT state of $[\text{Re}(\text{CH}_3\text{-bpy}(\text{CO})_3\text{Cl}]$. Fig. 2a shows the T1D-IR spectrum at a $\text{UV}_{\text{pump}}\text{-IR}_{\text{probe}}$ delay of 20 ps. The spectrum does not reveal which vibrational band shifts where upon UV excitation. The intuitive assignment used in the literature corresponds to the dotted arrows in Fig. 2 [4]. However, there are theoretical investigations on similar compounds that support an assignment according to the solid arrows [6], where a'' undergoes only a small shift, but the shift of a'(2) is large. Problems like this can be addressed by band labeling T2D-IR spectroscopy in a very direct manner: In the labeling T2D-IR experiment, the narrowband IR_{pump} pulse precedes the UV_{pump} pulse. The IR_{pump} pulse ‘labels’ the vibration to which it is tuned by transferring population from the $v=0$ to the $v=1$ state. This

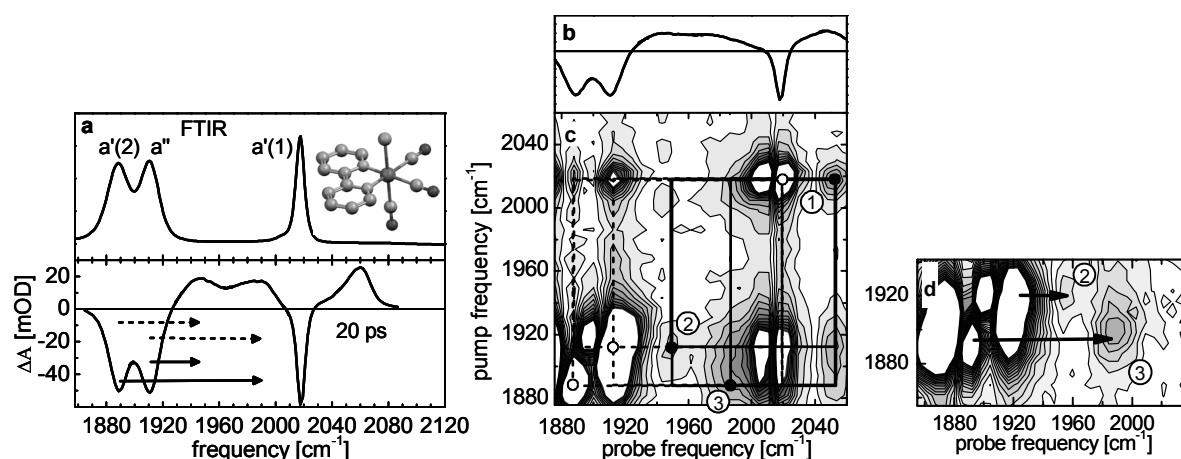


Fig. 2. (a) Rhenium complex, absorption spectrum of the electronic ground state with assigned CO vibrations, transient spectrum after 20 ps. Arrows mark the shift of the $a'(2)$ and a'' bands upon electronic excitation. Dotted arrows: old assignment for the bands in the MLCT state, solid arrows: band shift as revealed by labeling T2D-IR. (b) T1D-IR spectrum after 2 ps. (c) Labeling T2D-IR spectrum, $UV_{\text{pump}}-IR_{\text{pump}}$ delay 2 ps, $IR_{\text{pump}}-IR_{\text{probe}}$ delay 2 ps. Empty circles mark diagonal peaks of the MLCT state. (d) Labeling T2D-IR spectrum employing special polarization conditions to suppress ground state contributions. The solid arrows correspond to the solid arrows in (a)

happens while the molecule is still in the electronic ground state. The UV-pulse then excites the molecule to the MLCT state and induces the frequency shift. The IR_{probe} pulse records the frequency of the labeled and shifted vibration. In the labeling T2D-IR spectrum (Fig. 4), the vibrational shift from ground to MLCT state occurs parallel to the x-axis, since the IR_{pump} excitation takes place in the electronic ground state. In other words: the y-position (IR_{pump} frequency) of the peak does not change upon electronic excitation, staying at the ground state value, while on the x-axis, the frequency in the MLCT state can be read off. Thus excited state and ground state vibrations are correlated by this pulse sequence. This can be nicely seen for the $a'(1)$ mode in the upper right corner of Fig. 2c (Pos. 1). For the a'' and $a'(2)$ modes (Fig. 2c, Pos. 2 and 3) the effect is not that obvious. It can be enhanced using special polarization conditions that suppress disturbing contributions from the electronic ground state (Fig. 2d), giving direct evidence for the new assignment as indicated by the solid arrows in Fig. 2a. The labeling experiment constitutes the vibrational analog of NMR-exchange spectroscopy on a non-equilibrium ensemble in that it generates off-diagonal peaks connecting frequencies of the initial and of the final state of a reaction. Future applications of labeling T2D-IR are not limited to CO modes and excited electronic states. A variety of photo-triggered reactions including isomerization, rearrangement and dissociation can be addressed by this technique.

3. Hole burning T2D-IR of excited state solvation – looking underneath transient absorption lineshapes

Conventional 2D-IR spectroscopy, i. e. 2D-IR spectroscopy on an equilibrium ensemble, provides information on the equilibrium frequency fluctuation correlation function $c(t) = \langle \delta\omega(t)\delta\omega(0) \rangle$. Like other 3rd-order nonlinear spectroscopies such as photon echo and dynamic Stokes shift experiments, 2D-IR spectroscopy allows to distinguish between different line broadening mechanisms. T2D-IR spectroscopy is a 5th-order experiment, where the UV_{pump} pulse creates a non-equilibrium ensemble on which a 2D-IR measurement is carried out. T2D-IR is therefore well suited to address problems of non-equilibrium statistical mechanics.

MLCT of $[Re(CH_3\text{-bpy}(CO)_3Cl)]$ prepares the system in a state far from equilibrium. T2D-IR can be used to test whether the subsequent solvation dynamics occurs within the regime of linear response. Solvation is monitored by the dynamics of the $a'(1)$ CO vibration. It shifts with a time constant of 5.5 ps from its electronic ground state frequency of 2017 cm^{-1} to 2060 cm^{-1} in the completely solvated MLCT state, which marks the new equilibrium. T2D-IR spectra are recorded as described in Ref. [3]. Fig. 3a shows the transient 1D (T1D-IR) and T2D-IR spectra after 100 ps when solvation of the long-lived MLCT state is completed and the system is in its new equilibrium state. The T2D-IR spectrum features a characteristic tilt, which is a clear signature of inhomogeneity on the picosecond timescale. The tilt as a function of $IR_{\text{pump}}-IR_{\text{probe}}$ delay time is a direct measure of the equilibrium frequency fluctuation correlation function $c(t)$ [7]. Within linear response theory, the relaxation kinetics of the mean of a non-equilibrium ensemble $\Delta\bar{\omega}(t)$, as monitored by the overall shift of the band, should be exactly the same as that of the decay of the equilibrium autocorrelation function $c(t)$, as monitored by the tilt.

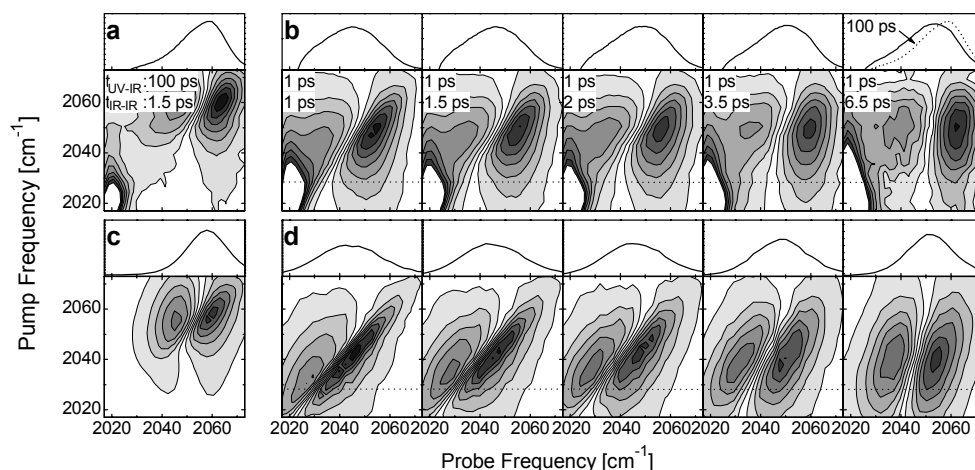


Fig. 3 (a) T2D-IR spectrum of the $a'(1)$ band after equilibration in the MLCT state. (b) T2D-IR spectra during the solvation shift. The decay of the signal due to vibrational relaxation is normalized out. The T1D-IR spectra are measured at corresponding times with the IR_{pump} pulse blocked. (c+d) corresponding data from a linear response model calculation.

Fig. 3b shows T1D-IR and T2D-IR spectra of the excited state $a'(1)$ band with an $UV_{\text{pump}}-IR_{\text{pump}}$ delay time of 1 ps and an $IR_{\text{pump}}-IR_{\text{probe}}$ delay varied between 1 ps and 6.5 ps. At first sight, the T2D-IR spectra evolve, as one intuitively expects: First, the T2D-IR spectrum is strongly tilted, reflecting strong inhomogeneity. With increasing $IR_{\text{pump}}-IR_{\text{probe}}$ delay, the band orients vertically as a result of the loss of memory of the initial pump frequency. At the same time, the 2D-IR band center shifts towards the right, away from the diagonal and in parallel with the solvation shift in the T1D-IR spectra. However, at a time of 6.5 ps, where the shift of the band is not finished, the tilt has completely disappeared, in contrast to what is expected from linear response. Furthermore, we made the surprising observation, that a transient hole burned at the red wing of the absorption band *narrows with time*. The FWHM of the hole at 2028 cm^{-1} pump frequency at an $IR_{\text{pump}}-IR_{\text{probe}}$ delay of 6.5 ps is only 65% of that at 1 ps (Fig. 3b, dotted line). Since the width of the hole represents the homogeneous width of the band (convoluted with the IR_{pump} laser bandwidth), this result suggests that the homogeneous width decreases as the system approaches equilibrium. A similar observation has been made recently in the case of the ultrafast conformational transition of a small peptide [3]. For comparison we simulated the experiment within the framework of linear response. The results are shown in Fig. 3c and d. They reproduce the general trend of a shifting and tilting band, however, they cannot reproduce the narrowing of the hole, indicating that a time dependent homogeneous width is not conform with linear response theory. Also the fact, that the relaxation of the tilt is faster than the overall shift, is not reproduced. As expected, there is still an appreciable tilt after 6.5 ps in the simulation.

These findings demonstrate that T2D-IR holeburning allows to monitor ultrafast spectral diffusion within the shifting vibrational band of a system that was prepared in a non-equilibrium state. T2D-IR holeburning measurements therefore provide previously inaccessible information and could in the present case show that a description of solvation within linear response theory is not sufficient. Based on the T2D-IR data a more sophisticated description of solvation should be attempted.

4. References

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