

Transient two-dimensional infrared spectroscopy – towards measuring ultrafast structural dynamics

Jens Bredenbeck, Jan Helbing, and Peter Hamm

Physikalisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

1. INTRODUCTION

Ultrafast two-dimensional infrared spectroscopy (2D-IR) is a promising tool for the investigation of molecular structures [1-3] and their equilibrium fluctuations [2, 4]. Similar to 2D-NMR spectroscopy [5], cross-peaks between coupled states emerge in 2D-IR spectra, and contain structural information [2, 6]. The outstanding feature of 2D-IR spectroscopy is the combination of its structure resolution power with an intrinsic sub-picosecond time resolution, freezing in all but the fastest molecular motions. This makes it particularly suited for application to fast dynamical processes, offering means to resolve equilibrium distributions of fast interconverting structures [7]. Most promising is the extension of the 2D-IR technique to the non-equilibrium regime, where its high time resolution can be put to full use [8]. This is the topic of this contribution. In principle, changes of molecular structures can thereby be followed from the sub-ps timescale up to milliseconds. We have recently reported first steps in this direction, employing transient 2D-IR spectroscopy (T2D-IR) to study the picosecond conformational transition of a photo-switchable cyclic peptide [9,10]. Here we demonstrate the application of T2D-IR to an electronically excited state, the metal-to-ligand charge-transfer (MLCT) state in rhenium(I) carbonyl complex [Re(CO)₃Cl(dmbpy)] (dmbpy=4,4'-dimethyl-2,2'-bipyridine). MLCT in rhenium(I) polypyridyl carbonyls and other metal carbonyls has been studied in considerable detail by time resolved IR spectroscopy (see [11-13] and references therein). Upon excitation at 390 nm MLCT occurs and a large frequency shift of the CO vibrations is observed (see the FTIR and UV-IR pump-probe spectra in Fig. 1 a and d). This change in vibrational frequency can be attributed to an ultrafast change in the electronic structure and the subsequent vibrational Stokes shift due to solvation, which takes place on a picosecond timescale [11, 12]. We present two dimensional infrared spectra of the transient species in the course of the solvation process, with characteristic cross peaks that depend on the relative orientations and couplings between the three carboxyl groups of the complex.

2. METHOD AND RESULTS

Fig. 1 b shows the 2D-IR spectrum of the rhenium complex in the electronic ground state. The 2D-IR spectrum is measured according to our double-resonance scheme [2, 14], employing a spectrally narrow IR pump pulse and a broadband IR probe pulse as depicted in the pulse se-

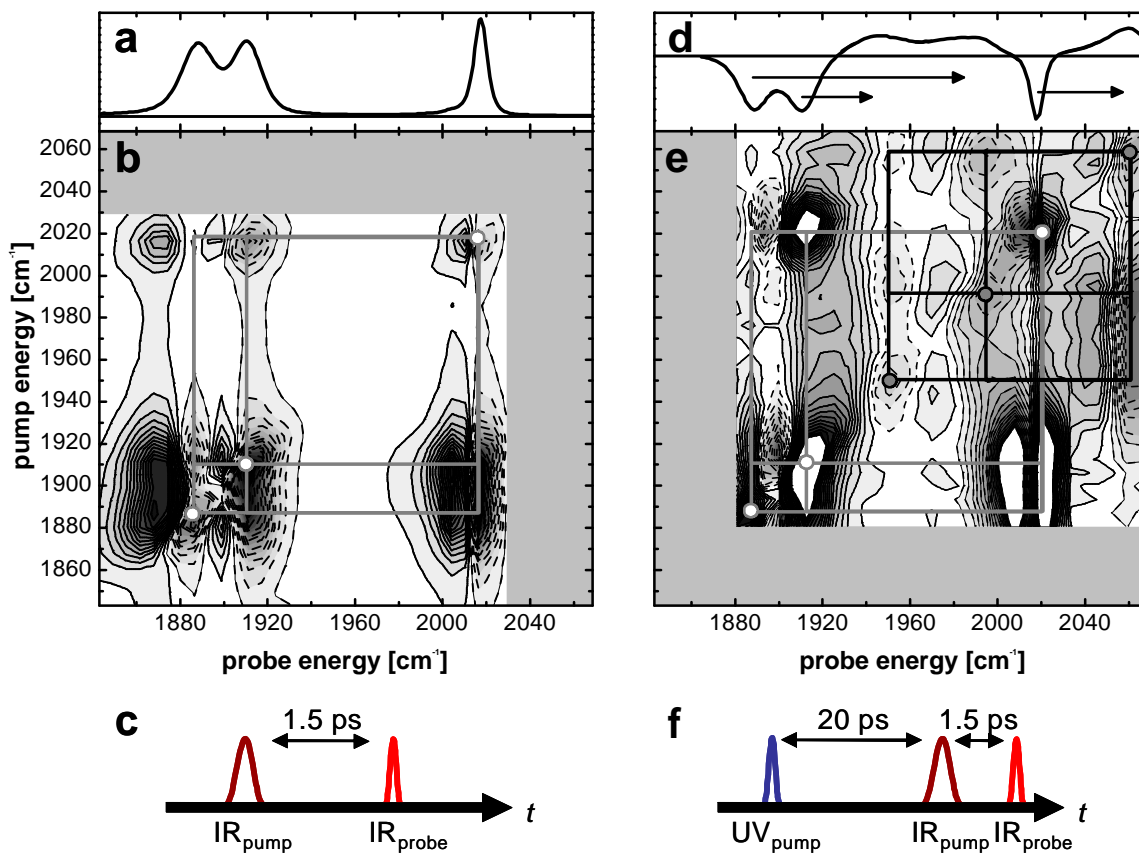


Fig. 1: left: FTIR spectrum (a) and 2D-IR spectrum (b) of the ground state for perpendicular polarization of pump and probe pulse. A broadband IR probe pulse measures the spectral change as a function of delay and frequency of a narrowband IR pump pulse (c). right: time resolved absorption spectrum (d, magic angle polarization) and transient 2D-IR spectrum (e) recorded 20 ps after UV excitation. The T2D-IR spectrum was recorded with magic angle between UV-pump and IR-pump polarizations and perpendicularly polarised IR-pump and probe beams.

quence in Fig. 1 c. To construct 2D-IR spectra as a function of pump and probe frequencies, the center frequency of the narrowband IR pulse (700 fs) is scanned across the spectral range of interest (vertical axis) and the absorption changes are recorded by dispersing the broad band probe pulse (100 fs) and imaging it onto an array detector (horizontal axis). Like in a 2D-NMR spectrum the 2D-IR spectrum features diagonal peaks and cross-peaks that report couplings, in this case not coupling between spins but between vibrations [2]. In Fig. 1 b the diagonal peaks are marked by open dots and the respective cross-peaks are connected by grey lines. In contrast to 2D-NMR, each 2D-IR peak is a double-peak consisting of a negative and positive contribution indicated by the dashed and solid contours. The negative signal at the position of the $v=0$ to $v=1$ transition is due to bleaching and stimulated emission while the positive absorption signal stems from the $v=1$ to $v=2$ transition, and is shifted to the red by the anharmonicity of the CO vibration. Structural information is encoded in the cross-peaks of the 2D-IR spectrum in essentially two ways [2]. Their *polarization dependence* can be deduced from 2D measurements employing parallel as well as perpendicular polarization of the pump and probe pulse. This yields the relative orientation of the vibrational transition dipole moments, which is essentially a model-free information. It can be translated into structural information if the orientation of the transition dipole moments in the molecular structure is known, for example from symmetry considerations or quantum chemistry calculations. This

works particularly well for localized modes. Another source of structure information is the *cross-peak intensity*. It is related to the constants of coupling between vibrations. The coupling constants can be translated into structural information based on structure dependent coupling models. This has been successfully demonstrated for the amide-I mode of peptides and proteins [1, 2, 15-17]. A prerequisite for the extension of this structure determination approach to the non-equilibrium regime is the ability to resolve transient cross-peaks in T2D-IR spectra as it is demonstrated here.

The T2D-IR experiment is essentially a UV-pump IR-narrowband-pump IR-broadband-probe scheme as displayed in the pulse sequence of Fig. 1 f. It can be regarded as the combination of time resolved UV-IR and 2D-IR pump-probe spectroscopy. Instead of just measuring transient changes in IR absorption after UV excitation, a more sophisticated probe is applied in form of a 2D experiment [10]. As one can typically not convert 100 % of the initial species into the product species, the 2D-IR spectrum recorded after the UV pulse always contains contributions from both excited and not excited molecules. In order to obtain a signal that is only due to molecules that have absorbed a UV photon, we therefore collect two sets of 2D-IR spectra simultaneously - one with the UV pulse on and one with the UV pulse off - and subtract them from each other. Hence, as it is common practice in conventional pump-probe spectroscopy, the T2D-IR spectra are difference spectra. Fig. 1 d shows the UV-pump IR-probe spectrum after 20 ps, where negative signals originate from the depleted ground state and positive signals from the excited state. Similarly the T2D-IR spectrum, shown underneath, features signals originating from the depleted ground state, as well as the signals of the excited state. The ground state diagonal peaks are again marked by open dots and the respective cross-peaks are connected by grey lines. The excited state signals are shifted along the diagonal and are marked in black. However, in the transient spectrum the signs of the ground state signals are interchanged with respect to the excited state signal, which is coded like the conventional 2D-IR spectrum. The most intriguing features in the T2D-IR spectrum of the rhenium complex are the well resolved cross peaks in the excited state. The same information as contained in the regular 2D-IR spectra can now be inferred for transient species from T2D-IR spectra, by exploiting the polarization dependence and relative intensity of the *transient* cross-peaks [19]. In addition, the dynamics of homogeneous and inhomogeneous contributions to the excited state lineshapes can be resolved from the shape of the transient diagonal peaks [10], which can also help to resolve distributions of structures [2, 16,18] as well as the anharmonicity of the vibrations [14] - in this case for the excited state.

3. ALTERNATIVE PULSE SEQUENCES

The above experiment, which corresponds to the pulse sequence in Fig. 2a, is the straightforward extension of the 2D-IR concept to the non-equilibrium regime i. e. recording a 2D-IR spectrum after a variable delay with respect to the UV pulse. However, we have also carried out other types of T2D-IR experiments. For example, T2D-IR measurements can be performed in a hole-burning mode (pulse sequence Fig. 2b): At a distinct time after the UV-pulse, the narrowband IR pulse burns a hole into the transient spectrum. The subsequent evolution of this 2D hole in time is then monitored by varying the delay of the broadband IR probe pulse. In this way ultrafast 2D-IR hole burning experiments on a non-equilibrium ensemble, generated by the trigger pulse, are possible. Interesting effects like the spectral narrowing in time can be observed [19]. Another useful set of T2D-IR spectra is generated by exchanging the order of the pulses and applying the narrowband IR pump pulse before the UV

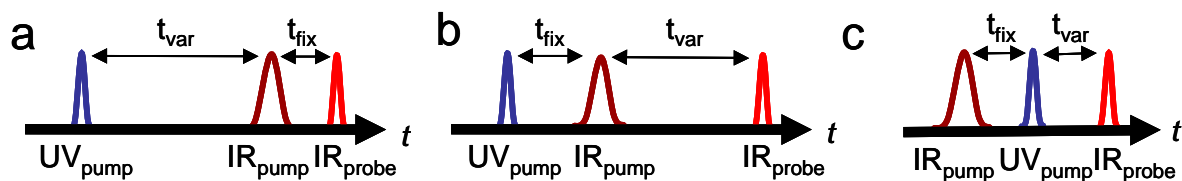


Fig. 2: Pulse sequences for a - regular T2D-IR spectroscopy. b - transient 2D hole burning spectroscopy. c - T2D-IR in the band labeling mode.

pulse arrives on the sample (pulse sequence in Fig. 2c). In this way it is possible to "label" selectively certain vibrations of the initial state by transferring population from the $v=0$ to the $v=1$ state of this vibration. After triggering the photo-process with the UV pulse, the subsequent evolution of this label can be monitored, correlating vibrations of the initial and the transient state [20]. By applying this method to the rhenium carbonyle complex we were recently able to show that the order of the vibrational modes is interchanged upon MLCT as indicated by the arrows in the top right hand spectrum of Fig. 1 [20].

The use of T2D-IR spectroscopy in its various modes is not limited to MLCT. It is applicable to all kinds of photo-triggered processes. Besides the investigation of electronically excited states, photo-chemical reactions like isomerizations and dissociations can be explored. Application to a photo-switchable peptide has already been demonstrated [10]. Conformational dynamics of biomolecules that are triggered by laser-induced T-jump or the control of pH by photo-acids, can also be investigated.

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