Labeling Vibrations by Light: Ultrafast Transient 2D-IR Spectroscopy Tracks Vibrational Modes during Photoinduced Charge Transfer

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Ultrafast two-dimensional infrared spectroscopy (2D-IR) is a promising tool to investigate molecular structure and its equilibrium fluctuations with subpicosecond time resolution. These experiments can be regarded as IR analogues of COSY and NOESY in NMR, Recently, the method has been extended to the non-equilibrium regime to investigate the conformational transition of a photoswitchable cyclic peptide by transient 2D-IR spectroscopy (T2D-IR). In this communication we report on a novel T2D-IR laser pulse sequence that allows “labeling” certain vibrational modes in the reactant of a photoreaction by an IR pulse and tracks their evolution on the way to the product. In this way the experiment correlates vibrational bands of reactant and product. The experiment can be regarded as an IR analogue of 2D-NMR exchange spectroscopy under non-equilibrium conditions in that it generates off-diagonal peaks between related vibrations of reactant and product in the T2D-IR spectrum.

We have chosen the photoinduced metal-to-ligand charge transfer (MLCT) in [Re(CO)3Cl(dmbpy)] (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) in DMSO as an interesting application to demonstrate this technique. MLCT in rhenium(I) polypyridyl carbonyls and similar metal carbonyls has been studied in great detail. Various aspects have been investigated, such as solvation dynamics, electronic structure, photocatalyzed CO2 reduction, photochemistry, or use as luminescent markers. Among other techniques, time-resolved vibrational Raman and UV–vis spectroscopy, as well as quantum chemical calculations were used. Nevertheless, there is no generally accepted assignment for the CO vibrations in the excited (MLCT) state of [Re(CO)3Cl(dmbpy)] and similar complexes. In this communication we show how an unambiguous assignment can be achieved by T2D-IR spectroscopy.

Figure 1a shows the absorption spectrum of the ground state. The bands at 1889, 1910, and 2018 cm⁻¹ have been assigned to a′(2) (antisymmetric stretching of axial CO and equatorial COs), a′ (antisymmetric stretching of equatorial COs), and a″(1) (symmetric stretching of all COs) modes, respectively. Upon excitation of [Re(CO)3Cl(dmbpy)] at 390 nm, MLCT induces a large frequency shift of the CO vibrations (Figure 1b). An assignment is widely used that maintains the ordering of the bands in the excited state as indicated by the red arrows in Figure 1b. To the best of our knowledge this assignment is not based on any direct experimental evidence as also pointed out in ref 9.

The instantaneous change of the electronic structure and the subsequent slower vibrational solvation shift have been identified as the effects responsible for the change in vibrational frequency. DFT calculations for the similar complex [Re(CO)3(4-Etpy)4]⁺ (4-Etpy = 4-ethylpyridine) predict the shift for a′(2) to be twice as large as for a″. Furthermore the contribution of the vibrational solvation effect is expected to be small for the a″ vibration, as its frequency change is the effects responsible for the change in vibrational frequency. DFT calculations for the similar complex [Re(CO)3(4-Etpy)4]⁺ (4-Etpy = 4-ethylpyridine) predict the shift for a′(2) to be twice as large as for a″. Furthermore the contribution of the vibrational solvation effect is expected to be small for the a″ vibration, as its frequency change.

Figure 1b. Figure 1a shows the absorption spectrum of the ground state. The bands at 1889, 1910, and 2018 cm⁻¹ have been assigned to a′(2) (antisymmetric stretching of axial CO and equatorial COs), a′ (antisymmetric stretching of equatorial COs), and a″(1) (symmetric stretching of all COs) modes, respectively. Upon excitation of [Re(CO)3Cl(dmbpy)] at 390 nm, MLCT induces a large frequency shift of the CO vibrations (Figure 1b). An assignment is widely used that maintains the ordering of the bands in the excited state as indicated by the red arrows in Figure 1b. To the best of our knowledge this assignment is not based on any direct experimental evidence as also pointed out in ref 9.

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The original T2D-IR experiment was designed to investigate transient structural dynamics of small peptides. It is an UV-pump IR-narrowband-pump IR-broadband-probe scheme (pulse sequence in Figure 2c). Common transient IR absorption spectroscopy employs just one IR-probe pulse after UV pumping. In contrast, the T2D-IR spectrum is obtained using a combination of two IR pulses as a probe process, where the narrowband pulse is scanned over the spectral range of interest. In Figure 2b shows such a T2D-IR spectrum of [Re(CO)3Cl(dmbpy)] at a UV delay of 20 ps. As in a 2D-NMR spectrum, the T2D-IR spectrum features diagonal peaks and cross-peaks that report couplings— in this case not between spins but between vibrations. Each 2D-IR peak consists of a negative and positive contribution represented by blue and red colors. The T2D-IR spectrum features signals originating from the ground state, which is the “reactant” of the photoreaction, as well as the signals of the excited MLCT state, which is the “product”. The ground-state diagonal peaks are marked by green dots and are connected to their respective cross-peaks by green lines. The excited-state signals are shifted along the diagonal relative to the ground state and are marked in red.

In the new labeling T2D-IR experiment introduced here, the narrowband IR pulse precedes the UV pulse (pulse sequence in Figure 2f). It “labels” the vibrations by transferring population from the ν = 0 to the ν = 1 state, while the molecule is still in the electronic ground state. The UV pulse then transfers the molecule into the excited electronic state and induces a frequency shift. In the labeling T2D-IR spectrum (Figure 2e), the shift from ground.
the bond order of the C=O group.

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state. Furthermore, the modes largely maintain their character, i.e.,
their delocalization among the various C=O groups. Upon photo-
excitation, the labeled vibrational mode is projected onto the newly
generated product normal modes, forming a wave packet. If
remixing of the modes were substantial, the experiment would be
difficult to interpret in terms of single vibrations. However, the
spectator modes in this proof of principle experiment allow for a
straightforward assignment of the excited-state spectrum. Future
applications of labeling T2D-IR are not limited to CO modes and
excited electronic states. The sensitivity of our current setup also
allows the investigation of much weaker transitions. A variety of
phototriggered reactions including isomerization, rearrangement, and
dissociation can be addressed.

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(17) Pulse parameters: UV_pump: 390 nm, 5 μJ, 400 fs; IR_pump: 0.1 μJ, 1 ps,
bandwidth 12 cm^-1, tunable between 1880 and 2050 cm^-1; IR_probes, 150
fs, 1960 cm^-1, bandwidth 200 cm^-1; for details see ref 6.
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(19) The positive part of the 2'' band is not visible as it overlaps with the
ground-state diagonal peak.

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Figure 2. (a) Time-resolved IR spectrum after 20 ps. (b) T2D-IR spectrum.
(c) Pulse sequence for normal T2D-IR. First, the UV-pump pulse arrives,
then a 2D-IR measurement is carried out. (d) Time-resolved IR spectrum
after 2 ps. (e) Labeling T2D-IR spectrum. (f) Pulse sequence for labeling
T2D-IR. The narrowband IR-pump pulse arrives first now and labels the
electronic ground state. The UV-pump pulse transfers the molecule into
the excited state. The IR-probe pulse arrives last.

Figure 3. Labeling experiment for the a(2) and a'' bands employing special
polarization conditions. The green arrows indicate the shift upon excitation.