

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^{1–3} and its equilibrium fluctuations^{2,4} with subpicosecond time resolution. These experiments can be regarded as IR analogues of COSY and NOESY in NMR.^{2,5} 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).⁶ 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^{7,8} 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 $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ ($\text{dmbpy} = 4,4'$ -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,⁹ electronic structure,^{10,11} photocatalyzed CO_2 reduction,¹² photochemistry,^{13,14} or use as luminescent markers.¹⁵ Among other techniques, time-resolved vibrational^{9,13,16} Raman¹⁶ and UV–vis spectroscopy,¹¹ as well as quantum chemical calculations^{10,12} were used. Nevertheless, there is no generally accepted assignment for the CO vibrations in the excited (MLCT) state of $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ 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.⁹ Upon excitation of $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ at 390 nm, MLCT induces a large frequency shift of the CO vibrations (Figure 1b). An assignment is widely used^{9,16} 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.^{9,10} DFT calculations for the similar complex $[\text{Re}(\text{CO})_3(4\text{-Etpy})]^+$ ($4\text{-Etpy} = 4\text{-ethylpyridine}$) predict the shift for $a'(2)$ to be twice as large as for a'' .¹⁰ Furthermore the contribution of the vibrational solvation effect is expected to be small for the a'' vibration, as its transition dipole moment is perpendicular to the symmetry plane and therefore perpendicular to the permanent dipole moment change

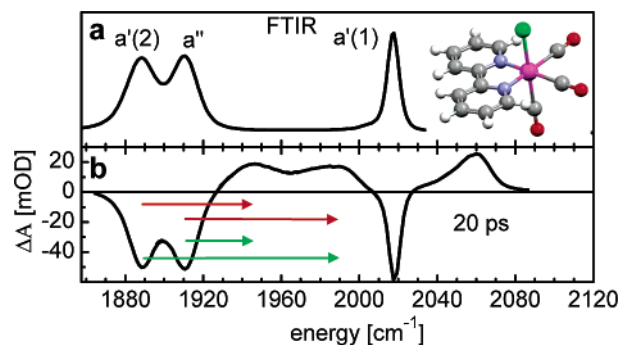


Figure 1. (a) Ground-state absorption spectrum. (b) Time-resolved IR spectrum recorded 20 ps after excitation. Negative signal originates from the depleted ground state of $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ (inset, methyl groups of dmbpy omitted), whereas positive signal corresponds to the excited state. Red arrows: band shift according to previous assignment, green arrows: band shift as revealed by T2D-IR.

upon MLCT.⁹ Nevertheless the common assignment^{9,16} attributes the strongest shift to the a'' mode (long red arrow in Figure 1b). However, in this communication we will show with the help of T2D-IR spectroscopy that the $a'(2)$ and a'' modes indeed change their ordering upon excitation, as indicated by the green arrows in Figure 1b.

The original T2D-IR experiment was designed to investigate transient structural dynamics of small peptides.⁶ 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.² Figure 2b shows such a T2D-IR spectrum of $[\text{Re}(\text{CO})_3\text{Cl}(\text{dmbpy})]$ at a UV delay of 20 ps.¹⁷ 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 contribution² 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 $\nu = 0$ to the $\nu = 1$ 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

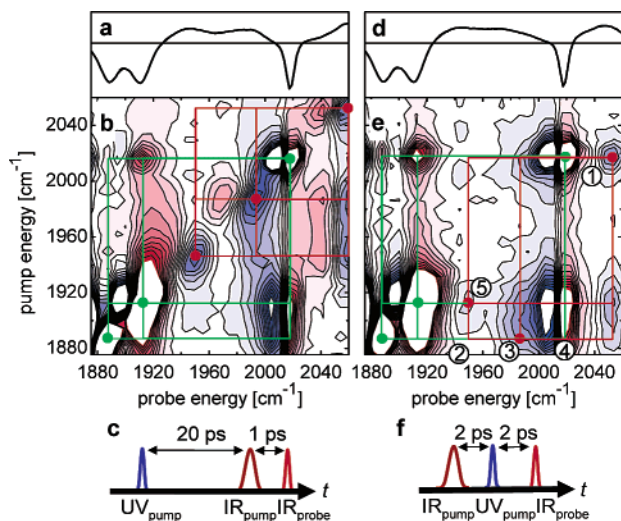


Figure 2. (a) Time-resolved IR spectrum after 20 ps. (b) T2D-IR spectrum. (c) Pulse sequence for normal T2D-IR. First, the UV-pump pulse arrives, then a 2D-IR measurement is carried out. (d) Time-resolved IR spectrum after 2 ps. (e) Labeling T2D-IR spectrum. (f) Pulse sequence for labeling T2D-IR. The 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.

to excited state now occurs no longer along the diagonal but parallel to the x -axis, since the IR excitation takes place in the electronic ground state. This means the following: the y -position of the peak does not change upon excitation, staying at the ground-state value. On the x -axis, the frequency in the transient excited state can be read off. Therefore, excited-state (product) and ground-state (reactant) vibrations are correlated by the pulse sequence. This can be nicely seen in the case of the $a'(1)$ vibration (Pos. 1) in the upper right corner of the T2D-IR spectrum. The peak shifts from its ground-state position at 2017 cm⁻¹ (green dot) to 2048 cm⁻¹ (red dot) within 2 ps after the UV pulse. To our surprise, however, in the case of the $a'(2)$ band at 1888 cm⁻¹ we did not find any corresponding excited-state signal at 1944 cm⁻¹ (Pos. 2) where we had expected it on the basis of the old assignment.^{9,16} Instead the a'' peak is shifted to 1944 cm⁻¹ (Pos. 5).

The $a'(2)$ band is shifted to 1985 cm⁻¹ (Pos. 3) where it is hidden by the strong reactant cross-peaks (Pos. 4) between both the $a'(2)$ and a'' modes and the $a'(1)$ mode. To bring out the effect more clearly, it is desirable to suppress the reactant cross-peaks (Pos. 4), while maintaining the product peaks (Pos. 3 and 5), that have been shifted off the diagonal now. This can be achieved by utilizing the different polarization dependences of the various peaks.¹⁸ The experiment offers two polarization degrees of freedom: the angle α between UV-pump and IR-pump and the angle β between UV-pump IR-probe. Figure 3 shows the T2D-IR spectrum of the $a'(2)$ and a'' bands measuring $\text{Signal}(\alpha = 45^\circ, \beta = 45^\circ) - \frac{1}{2}\text{Signal}(\alpha = 45^\circ, \beta = -45^\circ)$. This polarization condition suppresses the strong cross-peak (Pos. 4).¹⁸ The excited-state bands are now well resolved.¹⁹ Their shift along the x -axis is indicated by green arrows. Figure 3 provides direct evidence for the new assignment of the excited-state bands, as it was proposed in Figure 1b and predicted by DFT calculations.¹⁰

Apparently, vibrational labeling is robust and survives the photoreaction—despite the abruptly changed electronic structure (i.e. the bond order of the C=O groups) in the electronically excited

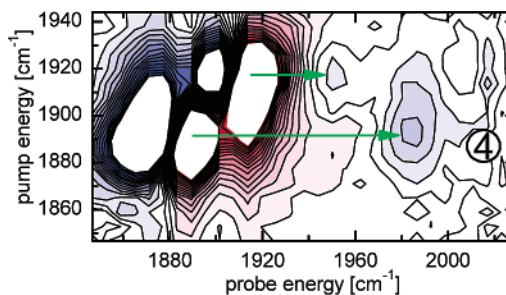


Figure 3. Labeling experiment for the $a'(2)$ and a'' bands employing special polarization conditions. The green arrows indicate the shift upon excitation.

state. Furthermore, the modes largely maintain their character, i.e., their delocalization among the various C=O groups. Upon photoexcitation, 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.

Acknowledgment. This work has been supported by the Swiss Science Foundation (2100-067573/1).

References

- (1) Hamm, P.; Lim, M.; DeGrado, W. F.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 2036–2041.
- (2) Woutersen, S.; Hamm, P. *J. Phys. Condens. Matter*, **2002**, *14*, R1035–R1062.
- (3) Golonzka, O.; Khalil, M.; Demirdöven, N.; Tokmakoff, A. *J. Chem. Phys.* **2001**, *115*, 10814–10828.
- (4) Woutersen, S.; Mu, Y.; Stock, G.; Hamm, P. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 11254–11258.
- (5) Ge, N.-H.; Hochstrasser, R. M. *PhysChemComm* **2002**, *5*, 17–26.
- (6) Bredenbeck, J.; Helbing, J.; Behrendt, R.; Renner, C.; Moroder, L.; Wachtveitl, J.; Hamm, P. *J. Phys. Chem. B* **2003**, *107*, 8654–8660.
- (7) Schleucher, J.; Schwörer, B.; Thauer, R. K.; Griesinger, G. *J. Am. Chem. Soc.* **1995**, *117*, 2941–2942.
- (8) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: New York, 1987.
- (9) Asbury, J. B.; Wang, Y.; Lian, T.; *Bull. Chem. Soc. Jpn.* **2002**, *75*, 973–983.
- (10) Dattelbaum, D. M.; Omberg, K. M.; Schoonover, J. R.; Martin, R. L.; Meyer, T. J. *Inorg. Chem.* **2002**, *41*, 6071–6079.
- (11) Zális, S.; Farrell, I. R.; Vlček, A. *J. Am. Chem. Soc.* **2003**, *125*, 4580–4592.
- (12) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724–5729.
- (13) Koike, K.; Okoshi, N.; Hori, H.; Takeuchi, K.; Ishitani, O.; Tsubaki, H.; Clark, I. P.; George, M. W.; Johnson, F. P. A.; Turner, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 11448–11455.
- (14) Farrell, I. R.; Matousek, P.; Towrie, M.; Parker, A. W.; Grills, D. C.; George, M. W.; Vlček, A. *Inorg. Chem.* **2002**, *41*, 4318–4323.
- (15) Kam-Wing Lo, K.; Hui, W.-K.; Chun-Ming Ng, D. *J. Am. Chem. Soc.* **2002**, *124*, 9344–9345.
- (16) Schoonover, J. R.; Strouse, G. F. *Chem. Rev.* **1998**, *98*, 1335–1355.
- (17) Pulse parameters: UV_{pump}: 390 nm, 5 μ J, 400 fs; IR_{pump}: 0.1 μ J, 1 ps, bandwidth 12 cm⁻¹, tunable between 1880 and 2050 cm⁻¹; IR_{probe}: 150 fs, 1960 cm⁻¹, bandwidth 200 cm⁻¹; for details see ref 6.
- (18) Bredenbeck, J.; Helbing, J.; Hamm, P. To be published.
- (19) The positive part of the a'' band is not visible as it overlaps with the ground-state diagonal peak.

JA0380190