

Ultrafast Time-Domain Raman Study to Visualize Large-Amplitude Distortions in Copper Complexes

Satoshi Takeuchi^{1,2}, Munetaka Iwamura³, Tahei Tahara^{1,2}

¹Molecular Spectroscopy Laboratory, RIKEN, 2-1, Hirosawa, Wako 351-0198, Japan E-mail: stake@riken.jp

²Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako 351-0198, Japan

³Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

Abstract: Time-resolved impulsive-Raman with narrowband photoexcitation was utilized to study structural dynamics of bis-diimine copper complex in solution. A copper-ligand symmetric stretch band showed up with frequency oscillation, demonstrating its anharmonic coupling with large-amplitude distortional motions.

OCIS codes: (300.6500) Spectroscopy, time-resolved; (300.6450) Spectroscopy, Raman

1. Introduction

Transition metal complexes play important roles in both fundamental science and numbers of applications because of their variety of photochemical properties. In particular, a photoinduced metal-to-ligand charge transfer (MLCT) state of Cu(I) complexes attracts much interests as a prototype system showing ultrafast “Jahn-Teller” distortions. As shown in Fig. 1, a representative bis-diimine copper complex forms a perpendicular structure in the S_0 state, where the two ligands are aligned perpendicularly to each other. Once excited to the S_1 state, on the other hand, it is considered to distort toward the square-planar structure, which is most typical for Cu(II) complexes, by decreasing the dihedral angle between the two ligands. In fact, a nanosecond X-ray absorption study confirmed such a “flattened” structure in the T_1 state formed in later times [1]. Our recent femtosecond emission [2] and absorption [3] measurements have further shown that the initial perpendicular S_1 state has a well-defined vibrational structure and that it exhibits emission spectral changes with a time constant of 0.7 ps. However, we still have limited structural knowledge on the early stage of this fundamental phenomenon, i.e., when and how such a large-amplitude distortion actually takes place. Therefore, it is highly desirable to clarify the initial structural events with firm enough vibrational evidences.

Motivated by this idea, we investigated the ultrafast structural dynamics of this copper complex in the MLCT state by time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) [4, 5] that we developed and upgraded to date. With careful bandwidth control in actinic excitation, we successfully observed intrinsic time evolution of the Raman vibrational structure, which is free from unwanted fifth-order contributions. It further enabled us to recognize frequency modulation of a key vibration, leading to a visualization of the vibrational anharmonic coupling in the excited state.

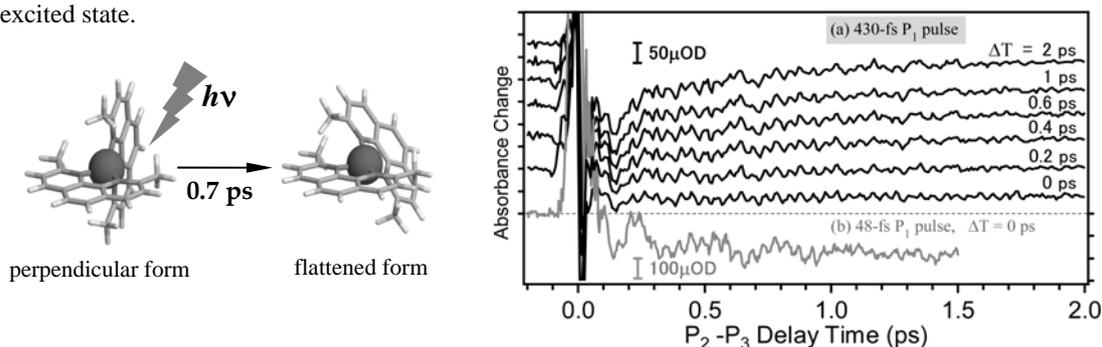


Fig. 1. TR-ISRS experiment of $[Cu(dmphen)_2]^+$ in dichloromethane. (Left) Photoinduced flattening distortion in the MLCT state. (Right) TR-ISRS signals at selected ΔT times obtained with (a) 430-fs and (b) 48-fs actinic pump (P_1) pulses.

2. Experimental

The TR-ISRS measurements were carried out using a combination of actinic pump (P_1), Raman pump (P_2), and Raman probe (P_3) pulses. Briefly, the fundamental output of a 1-kHz Ti:sapphire amplifier (840 nm) was equally divided into two parts. The first part was frequency-doubled in a BBO crystal, and the second harmonic pulse was used as the P_1 pulse for photoexcitation after spectral filtering by a grating-slit setup. The second part of the amplifier output was used to drive a home-built one-stage noncollinear optical parametric amplifier (NOPA). The

NOPA output was tuned to a wavelength range of 600 - 700 nm, and it was compressed in time down to 12 fs using a prism pair and a grating pair simultaneously. This ultrashort pulse was divided into two, and they were used as the P_2 and P_3 pulses for the ISRS measurements. All the three pulses were focused together into a 0.3-mm-thick flow cell, where the sample solution was circulated. The TR-ISRS signal, i.e., the P_2 -induced absorbance change monitored by the P_3 pulses, was evaluated by chopping every other P_2 pulse. A dichloromethane solution (8.8 mM) of $[\text{Cu}(\text{dmphen})_2]\text{PF}_6$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) was prepared and used in the TR-ISRS measurements.

3. Results and discussion

In our TR-ISRS measurement, the copper complex was initially excited to the S_2 state by the P_1 pulse at 420 nm, and then it undergoes a rapid internal conversion to the S_1 state. To track the structural dynamics, we introduced the ultrashort P_2 pulse at a ΔT delay and generated the vibrational coherence in the S_1 state. The resultant nuclear wavepacket motion was monitored by the P_3 pulse as oscillatory features in the P_2 -induced absorbance change. It was found that the oscillatory feature substantially differs, depending on the duration of the P_1 pulse (48 fs and 430 fs), as shown in Fig. 1. This difference arises, since the P_1 -induced vibrational coherence is still remaining in the molecule when the P_2 pulse reaches the sample at ΔT , i.e., the fifth-order contribution that does not reflect the vibrational structure at ΔT is significant. To remove this unwanted contribution, we carefully narrowed the spectral bandwidth of the P_1 pulse, and confirmed that the vibrational coherence is no longer generated by the 430-fs P_1 pulse having a bandwidth as narrow as 63 cm^{-1} . As shown in Fig.1, the TR-ISRS data taken under this condition, which is free from the fifth-order processes, showed clear oscillations, reflecting the intrinsic vibrational structure of the S_1 state. Therefore, their Fourier transform gives “instantaneous” Raman spectrum at each ΔT delay (Fig. 2). Most importantly, the copper-ligand symmetric stretch at 125 cm^{-1} is not observed around $\Delta T = 0\text{ ps}$, but it gradually shows up within a few picoseconds. The time scale of this Raman spectral change is fully consistent with the 0.7-ps dynamics that we observed in both emission and absorption [2, 3]. Therefore, the present Raman result provides a vibrational evidence for the ultrafast distortion occurring on the femtosecond time scale.

A close look at the Raman spectra suggested that the peak frequency of the symmetric stretch band changes with the ΔT time. In fact, a plot of the peak frequency versus ΔT time (Fig. 2) seems to show a slow oscillation with a period of ca. 1.5 ps. Interestingly, this period coincides well with that of the flattening mode ($\sim 22\text{ cm}^{-1}$), in which the dihedral angle between the two ligands oscillates with time. This observation implies that the symmetric stretch mode is anharmonically coupled with the flattening mode. Our TDDFT calculation also supported this idea, and showed that the symmetric stretch frequency varies, depending on the dihedral angle. The present observation of the frequency change with ΔT time provides a new scheme to visualize the vibrational anharmonic coupling in the excited state.

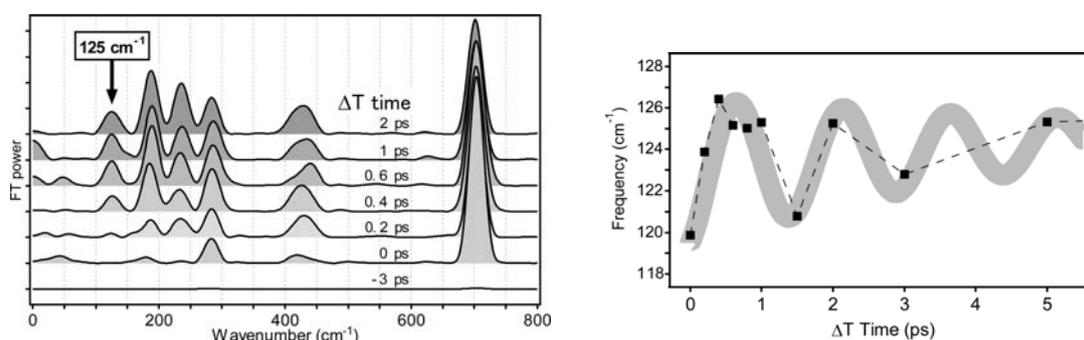


Fig. 2. Fourier transform analysis of the TR-ISRS signal. (Left) FT power spectra of the oscillatory component at selected ΔT times. (Right) Plot of the peak frequency of the 125-cm^{-1} mode against the ΔT time, showing an oscillation feature.

References

- [1] L. X. Chen, G. B. Shaw, L. Novozhilova, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer, P. Coppens, *J. Am. Chem. Soc.* **125**, 7022 (2003).
- [2] M. Iwamura, S. Takeuchi, T. Tahara, *J. Am. Chem. Soc.* **129**, 5248 (2007).
- [3] M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, T. Tahara, *J. Am. Chem. Soc.* **133**, 7728 (2011).
- [4] S. Fujiyoshi, S. Takeuchi, T. Tahara, *J. Phys. Chem A*, **107**, 494 (2003).
- [5] S. Takeuchi, S. Ruhman, T. Tsuneda, M. Chiba, T. Taketsugu, T. Tahara, *Science* **322**, 1073 (2008).