

Tracking multiple components of a nuclear wavepacket in photoexcited Cu(I)-phenanthroline complex using ultrafast X-ray spectroscopy

The mixing of electronic and vibrational wavefunctions has a substantial impact on ultrafast non-adiabatic chemical reactions owing to the breakdown of the adiabatic Born-Oppenheimer approximation at the conical intersections of multidimensional potential energy surfaces. This means that one should disentangle the coupling between electronic and nuclear degrees of freedom to understand the underlying photoreaction mechanism. The coupled electronic and vibrational energy flows can be explored by tracking a nuclear wavepacket that propagates along the reaction pathway and finally dissipates the excess energy into various electronic and nuclear degrees of freedom. In the last four decades, the time evolution of the nuclear wavepacket has been studied with pump-probe optical spectroscopies. However, although these methods can capture spectral signatures arising from specific vibrational motions, it is often difficult to reveal nuclear movements of polyatomic molecules with a sub-angstrom resolution owing to the lack of atomic structural sensitivity.

Structural information at the atomic level can be obtained by time-resolved X-ray absorption near edge structure (TR-XANES). This X-ray technique is sensitive to the local structural dynamics in the close vicinity of the absorbing atom and applicable to the investigation of the ultrafast dynamics of small systems without long-range order, e.g., ligated transition metal complexes in solution phase. The recent advent of X-ray free-electron lasers (XFELs) has enabled TR-XANES to achieve both an unprecedentedly high signal-to-noise ratio and high time resolution, and consequently allows tracking of the nuclear wavepacket.

Here, we describe the femtosecond (fs) TR-XANES study [1] of a prototypical transition metal complex, [Cu(dmphen)₂]⁺ (dmphen = 2,9-dimethyl-1,10-phenanthroline), dissolved in acetonitrile. Previous studies [2,3] revealed that after the excitation of [Cu(dmphen)₂]⁺ into the metal-to-ligandcharge-transfer (MLCT) manifold by absorption of a visible photon, significant structural flattening occurs, so that the dihedral angle of two dimethylphenanthroline ligands is reduced from 90° to ~70°; this is known as the pseudo Jahn-Teller (PJT) distortion (Fig. 1). Our TR-XANES experiment performed at SACLA **BL3** successfully revealed to what extent detailed vibronic motions are observable



Fig. 1. Schematics of the structural change of $[Cu(dmphen)_2]^+$, known as the PJT distortion. The symmetry is reduced by the reduction of the dihedral angle between two dimethyl-phenanthroline ligands.

during this PJT relaxation process.

In the transient Cu K-edge XANES difference spectra (Fig. 2(a)), the pre-edge (8979.5 eV) intensity is slightly increased. This feature is associated with the $1s \rightarrow 3d$ transition and adds some dipole character to the transition by 3d-4p mixing. Consequently, the preedge intensity is sensitive to the molecular structural symmetry, i.e., the PJT flattening. The spectral features at 8985.0 eV and at 8986.5 eV are associated with the $1s \rightarrow 4p$ transition. The intensity decrease in this spectral region is attributed to the blueshift of the absorption edge, reflecting the oxidation of the Cu ion from d^{10} to d^9 by the MLCT excitation. The fs temporal evolutions were measured at these three probe energies (Fig. 2(b-d)). Damped oscillatory signals originating from coherent molecular vibrations were observed at 8979.5 eV and at 8985.0 eV, while no oscillatory features were found at 8986.5 eV. This difference illustrates that the selection of the X-ray probe energy is critically important for capturing the nuclear wavepacket dynamics.

The observed oscillatory signals were extracted from the large electronic backgrounds by picking up residuals after the global fitting analysis (Fig. 3). At the pre-edge (8979.5 eV), three types of oscillations were found at 83–122 cm⁻¹, 165–195 cm⁻¹, and 269–287 cm⁻¹ in the time-dependent Fourier transform map (Fig. 3(c)). They are assigned to the normal modes of v_8 (the breathing mode), v_{21} (the symmetrybreaking mode), and v_{25} (the symmetry-breaking mode), respectively. In contrast, at the rise of the absorption edge (8985.0 eV), only a single band was found at 100–122 cm⁻¹, corresponding to the breathing mode (Fig. 3(d)). The amplitude of the breathing mode corresponds to ± 0.1 Å in the first halfpicosecond (ps) and decays with a time constant of 0.54 ps, which is interpreted to be the time constant of the PJT dynamics. On the other hand, the symmetrybreaking modes fade at away around ~0.2 ps, indicating the redistribution of the coherent vibrational energies. This redistribution process is faster than the PJT dynamics (0.54 ps) and demonstrates that the symmetry-breaking modes are strongly coupled to the ligand flattening motion, while the breathing mode is rather irrelevant but still dominates the wavepacket dynamics.

The observed wavelength-dependent sensitivity of TR-XANES to these nuclear motions was interpreted as follows. At the pre-edge (8979.5 eV), the intensity is dominated by the dipole contribution derived from the 3d-4p mixing, which is enhanced by the symmetry-breaking of the molecule or modulated by the metal-ligand covalency. Therefore, both the symmetry-breaking modes and the breathing mode are observable at the pre-edge. On the other hand, at the rise of the absorption edge (8985.0 eV), the



Fig. 2. Femtosecond transient Cu *K*-edge XANES. (a) Top: Cu *K*-edge XANES spectra of the $[Cu(dmphen)_2]^+$ ground and excited states. Middle: Difference spectrum between these two spectra. Bottom: Magnified view of the difference spectra. The blue, red, and green dotted lines indicate the photon energy positions where the fs temporal traces were measured. (b-d) Time dependences of the transient XANES signals measured at (b) 8979.5 eV, (c) 8985.0 eV, and (d) 8986.5 eV. The gray solid and dotted lines are the results of the global fitting analysis and the individual components, respectively. The arrows correspond to the signal intensities at 10 ps after photoexcitation.

intensity is associated with the shift of the absorption edge, which is sensitive to the effective charge state of the Cu ion and the average Cu-N bond length. This explains why only the breathing mode is observable at the rise of the absorption edge. The capability of TR-XANES to disentangle multiple contributions to the wavepacket dynamics demonstrated here is highly advantageous in gaining a deeper understanding of ultrafast nonadiabatic chemical reactions.



Fig. 3. Extracted coherent nuclear wavepacket. (**a,b**) Residual profiles after the global fitting analysis. (**c,d**) Time-dependent Fourier transforms of (**a,b**). (**e,f**) Vertical projections of (**c,d**) with a time window of 0-0.4 ps.

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