

Pulsed X-rays Revealed Rapid Excited-State Structural Reorganization Faster than 10^{-10} Seconds

Photoexcited molecules are vehicles to many important processes in solar energy conversion and storage, molecular photonics, photovoltaic and catalysis. However, the excited state molecular structures in fluids at room temperature, where most of the photochemical reactions take place, have not been directly characterized by x-rays until recently.¹ Due to the reason that many of these excited states only exist in 10^{-12} to 10^{-6} seconds after the photoexcitation, pulsed x-rays with comparable durations are required to probe the structure within such a short time after the photoexcitation. Using pulsed x-rays from the Advanced Photon Source, scientists in the Chemistry Division of Argonne National Laboratory revealed, for the first time in the world, the structural reorganization of a photoexcited copper complex in solution using x-ray pulses with less than 10^{-10} second duration from the Advanced Photon Source at Argonne National Laboratory. The photoexcited state structures captured by this technique revealed that the copper(I) center in the complex was temporarily oxidized after the photoexcitation by a laser pulse, which induced structural reorganization to form a solute-solvent complex even with so-called “non-interacting” solvents. The variation of the bond lengths between the copper center and the neighboring atoms in the excited state copper complex can be related to the interaction strength of the excited copper center with the solvent that determines the excited state lifetimes of this copper complex. The results from this pioneering experiment provides new insights into the mechanisms for light-driven molecular devices, and will lead to a wider variety of improved and new technologies reliant upon the excited states. The scientific results of this work have been published in two papers on Journal of American Chemical Society,^{2,3} and in one review on Angewandte Chemie, International Edition.⁴

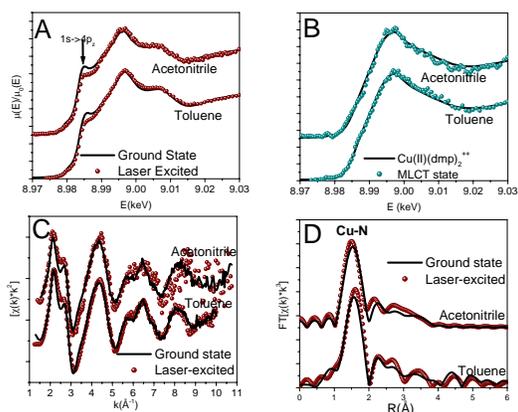


Fig. 1. XANES and XAFS spectra of Cu(I)(dmp)_2^+ .

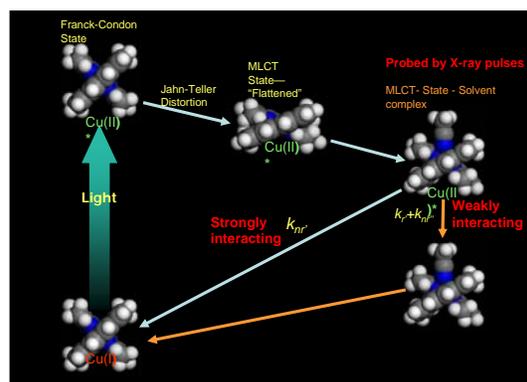


Fig. 2 Newly established excited state pathways based on pulsed X-ray results (see text).

Copper (I) diimine compounds were suspected to display unique structural reorganization following energy absorption that induces metal-to-ligand charge-transfer (MLCT) excited states. The photoexcitation of such a compound, $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$, otherwise known as copper(I) 2,9-dimethyl-1,10-phenanthroline in toluene, a non-interacting solvent, and in acetonitrile, a strongly interacting solvent, was induced by illumination with 527 nm light from a Nd:YLF laser with 5 ps pulse duration. Then, single x-ray probe pulses with

energies near the copper K-edge and a pulse duration of less than 10^{-10} seconds was introduced at a time delay from the laser pulse at which the optimal excited state molecules were present. This x-ray energy corresponds to the Cu K-edge at which the XANES (x-ray absorption near edge structure) and XAFS (x-ray absorption fine structure) techniques were exercised.

This particular experiment examines the MLCT transition to determine the amount of electrons transferred from copper(I) to its ligand and, additionally, how the thermally equilibrated MLCT-state differs in structure from the ground state, and what are structural origins accounted for a factor of 50 shortening of the excited state lifetime in strongly interacting acetonitrile compared to in non-interacting toluene. In the MLCT excited state, time-resolved optical spectroscopic measurements revealed the existence of the reduced dmp ligand. The ground-state and excited Cu(I)(dmp)_2^+ XANES spectra show in Fig. 1A that the attenuation of the shoulder feature at 8.983 keV in both solvents demonstrates the existence of 20% MLCT excited state molecules that bound to an additional solvent molecule to form a penta-coordinated geometry, instead of the tetrahedral ground state geometry. Subtraction of the background – the ground state – reveals the spectra in Fig. 1B that agree with the copper(II) center with a penta-coordination. Therefore, the whole electron or equivalent is transferred from copper(I) to the ligand upon the formation of the MLCT excited state. From the XAFS and the Fourier-transformed XAFS spectra for the ground-state and laser –illuminated Cu(I)(dmp)_2^+ revealed the bond lengths from the copper center to the ligands of the MLCT excited states. The bond length of the Cu-N peak is demonstrated as 0.04 Å longer in toluene and 0.04 Å shorter in acetonitrile, and there is a suspected increase in the coordination number in both solvents as revealed by a higher amplitude and shift in the Fourier-transformed XAFS, confirming the ligation with an additional solvent molecule in both non- and strongly- interacting solvents.

In summary, excitation via a visible laser leads to a complete charge transfer from copper(I) to a dmp ligand in this copper diimine system and the coordination number as well as the geometry changed due to an inner-sphere reorganization. Although a factor of 50 differences in the MLCT excited state lifetime of Cu(I)(dmp)_2^+ in non-interacting toluene and in strongly interacting acetonitrile was thought due to the formation of the excited state - solvent complex only in the later, but not in the former, XAFS spectra indicated formation of the MLCT-solvent complex in both. However, the longer average copper to ligand bonds in the former and shorter in the latter differentiate the interaction strengths with the solvent that is responsible for the factor of 50 difference in the excited state lifetime in the two solvents. Therefore, by controlling the solvent environment of the molecule, we can alter the excited state structure and properties of the molecule. The results demonstrate a confirmed method in quantifying the effects of transient energy-driven charge-transfer excited state structural reorganizations that may be applicable to numerous other inorganic as well as inorganic compounds.

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