

Excited-state Molecular Structure in Disordered Media Studied by X-ray Pulses from the APS with 100-ps Time Resolution

L.X. Chen,¹ G.B. Shaw,¹ T. Liu,¹ G. Jennings,² K. Attenkofer²

¹Chemistry Division and ²Advanced Photon Source (APS),

Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

In a majority of photochemical reactions, ranging from natural and artificial photosynthesis and photocatalysis to molecular photonics and devices, the excited-state molecules are reactants generated by light and transformed into products. When a molecule absorbs a photon with energy ranging from ultraviolet to near infrared, its valence electron density is redistributed, and its nuclei experience a new field while retaining the same configuration as the ground state. However, within femtoseconds (fs) to a few picoseconds (ps), the nuclei of the excited molecule rapidly adjust themselves to accommodate the new field via structural relaxation, forming a configuration that differs from the ground state and retains this thermally equilibrated configuration for picoseconds to milliseconds (ms). Despite sophisticated studies done with ultrafast laser spectroscopy on excited-state dynamics, energetics, and coherence, the structures of excited states remain largely indirect and elusive, which severely hinders advances in photochemistry.

Methods and Materials

The unprecedented photon flux in each x-ray pulse and the timing structures of x-ray pulses that are provided by the APS allow excited-state structures to be probed by single x-ray pulses with a time resolution limited only by the duration of the x-ray pulse (i.e., 30-100 ps). Although such a time resolution is still too slow for directly following atomic movements from the initial Franck-Condon state to the structural relaxed excited state, it is sufficiently fast for capturing the thermally equilibrated excited-state structures with lifetimes from hundreds of picoseconds to milliseconds. However, several challenges were encountered in the laser pulse pump, x-ray pulse probe x-ray absorption experiments as a result of mismatches in the (1) repetition rates of the laser pump and the x-ray probe pulses, (2) absorption coefficients for optical and x-ray photons, (3) sample concentration preferences of x-ray absorption fine structure (XAFS) and photochemistry, and (4) response times of detectors and the intrinsic time resolution provided by 100-ps

x-ray pulses. In spite of these challenges, pump-probe XAFS experiments were carried out at beamline 11-ID at the APS.

Results and Discussion

Following our initial successful studies in fiscal years 2000 and 2001 [1], we conducted pump-probe XAFS measurements with 100-ps time resolution obtained by using single x-ray pulses from the APS during the asymmetric fill operation. We investigated the structural origins of the metal-to-ligand charge-transfer (MLCT) excited-state behavior of $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ (where dmp is 2,9-dimethyl-1,10-phenanthroline), which is strongly solvent-dependent [2, 3]. Absorption of a visible photon promotes an electron from Cu^{I} to one of the dmp ligands, achieving intramolecular charge separation with a $\text{Cu}^{\text{II}*}$ center coordinated to one reduced and one neutral dmp ligand. The initial Franck-Condon MLCT state has a pseudotetrahedral coordination geometry identical to that of the ground state, but the $\text{Cu}^{\text{II}*}$ center with a d^9 electronic configuration is susceptible to a Jahn-Teller distortion, resulting in a MLCT state with flattened tetrahedral coordination (Fig. 1A). In noncoordinating solvents such as toluene, the MLCT state is luminescent and has lifetimes up to over 100 nanoseconds (ns) at room temperature. In contrast, in strongly coordinating solvents such as acetonitrile, the MLCT state is almost nonluminescent and has lifetimes as short as 1-2 ns at room temperature. The large “Stokes-like” shift observed between the absorption and the emission is consistent with significant structural changes in the MLCT state; either it returns to the ground state via a radiative decay pathway in noncoordinating solvents, or it forms a pentacoordinate complex with a strongly coordinating solvent molecule, resulting in the “exciplex” quenching.

Transient spectra with femtosecond time resolutions were also measured in a coordinating solvent (acetonitrile) and a noncoordinating solvent (toluene), revealing three time constants in the excited-state dynamics in each solvent. The first two fast time constants of 500-700 fs and 10-20 ps are

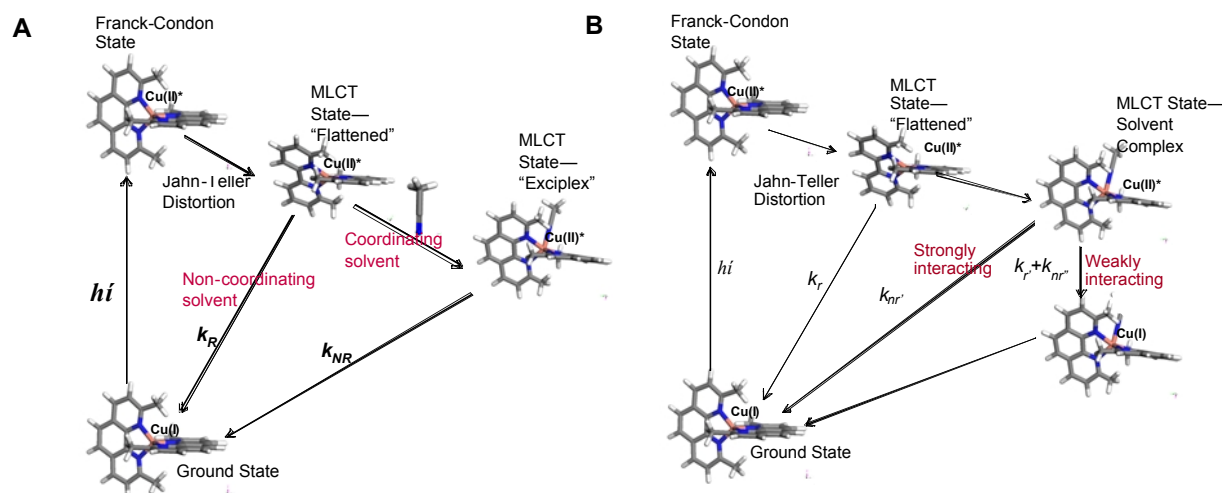


FIG. 1. Left panel A shows previously accepted mechanism in the literature for photoinduced MLCT excitation of $\text{Cu}(\text{dmp})_2^+$ in solution. Right panel B shows the revised mechanism based on pump-probe XAFS results.

similar in both solvents, but the third time constant is 1.7 ns in acetonitrile and 100 ns in toluene, representing a difference of about 60-fold! The optical transient absorption data suggest that the subpicosecond time constant is due to the formation of the triplet state via the intersystem crossing and that the 10-ps time constant is due to the structural flattening of the tetrahedral coordination in the excited state. Because these two time scales are beyond the reach of the current x-ray probe with single pulses, pump-probe XAFS was carried out to investigate the structures of the thermally equalibrated MLCT state with 1.7- and 100-ns lifetimes, respectively.

Laser pulses at 527 nm were used to excite the copper complex. Differences between the x-ray absorption near-edge structure (XANES) spectra of the ground state and of the laser-excited $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ in acetonitrile and in toluene are clearly visible in Fig. 2. The shoulder feature at 8.985 keV was reduced upon laser excitation, accompanied by a slight increase of the peak intensity at 8.996 keV. After subtracting the 80% remaining ground-state spectrum from the laser-illuminated sample spectra in both solutions, the MLCT-state XANES spectra were extracted in both solvents. In both cases, the shoulder feature for the ground-state $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ is missing in the MLCT state, and the transition edge is shifted by about 3 eV to the same edge energy as that of the ground-state $[\text{Cu}^{\text{II}}(\text{dmp})_2]^{2+}$ obtained via *in situ* electrolysis of the $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ in acetonitrile. The shoulder feature at 8.985 keV is due to the $1s \rightarrow 4p_z$ transition that is pronounced in $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ and missing from $[\text{Cu}^{\text{II}}(\text{dmp})_2]^{2+}$. This is a typical

observation for transformation from four- to five- or six-coordinate geometry.

The copper coordination number and the Cu-to-ligand bond lengths for the MLCT-state $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ were extracted from the XAFS data. Interestingly, the Cu-N peak shifts to a shorter distance in acetonitrile and a longer distance in toluene, when compared with the average Cu-N distance at 2.07 Å for the ground state. The average Cu-N distance for the laser-excited sample in acetonitrile fits to two distances of 2.07 and 2.03 Å, whereas in toluene, that distance fits to two distances of 2.06 and 2.11 Å, while the relative ratio of the two distances is kept to 4:1. Clearly, the first Cu-N distance is from the ground state, and the second is from the MLCT state. The results of the experiment demonstrated that (1) light excitation generated a formally $\text{Cu}^{\text{II}*}$ center, (2) the inner-sphere reorganization changed the coordination number of the MLCT state from four to five in presumed noncoordinating toluene, and (3) the average Cu-ligand bond distances lengthened in the MLCT state in toluene but shortened in acetonitrile.

The XANES spectra provided strong evidence for the pentacoordinate $\text{Cu}^{\text{II}*}$ in both acetonitrile and toluene. These results are in accordance with the fact that $\text{Cu}^{\text{II}*}$ in the MLCT excited state is formally a 17-electron d^9 system prone to the addition of a fifth ligand. It is well-known that MLCT excited states in general follow the energy gap law, in that the nonradiative rate constant increases exponentially with decreasing energy separation between the ground state and the excited state. The formation of the “exciplex” stabilizes the MLCT state, reducing the energy gap between the ground state and the

MLCT state. As the energy gap becomes small enough as a result of the strong interaction of the Cu center with the ligand, the nonradiative decay dominates the relaxation pathway, and no emission is detected (e.g., as in the acetonitrile solution case). However, the above statements are unable to explain the solvent dependency of the MLCT-state behaviors.

The XANES results for $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ in both toluene and acetonitrile solutions support the formation of a pentacoordinated $\text{Cu}^{\text{II}*}$ center in the MLCT state, based on the attenuation of the shoulder feature in the transition K edge of copper in the spectra. However, a broad range of the Cu-to-ligand bond distances for the fifth ligand could smooth the transition edge, as seen in previous studies. The respective elongation and shortening of the average Cu-N bond distance for the MLCT-state $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ in toluene and in acetonitrile, respectively, signal the difference in the interactions of the copper with the fifth ligand. Such variation was also evidenced by a broad range in the MLCT-state lifetimes in various Lewis base solvents with different electron-donating capabilities. The variation of the MLCT-state structure in different solvents confirmed that the origin of distinctly different excited-state behavior is the formation of MLCT-state solvent complexes with different electronic interactions (Fig. 1B). When the interaction is strong, the MLCT-state lifetime is shortened significantly, and the luminescence is

quenched, which has been characterized by the “exciplex” formation in previous literature. Therefore, the pump-probe XAFS measurements in the time domain provide new insights into the fundamental aspects of structural factors that may influence photoinduced electron and energy transfer processes.

Acknowledgments

This work was supported by the Division of Chemical Sciences and Materials Science in the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. The authors would like to thank the BESSRC beamline staff at the APS for their assistance. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.

References

- [1] L.X. Chen, W.J.H. Jager, G. Jennings, D.J. Gosztola, A. Munkholm, and J.P. Hessler, *Science* **292**, 262-264 (2001).
- [2] L.X. Chen, G. Jenings, T. Liu, D.J. Gosztola, J.P. Hessler, D.V. Scaltrito, and G.J. Meyer, *J. Am. Chem. Soc.* **124**, 10861-10867 (2002).
- [3] L.X. Chen, G.B. Shaw, I. Novozhilova, L. Tao, G. Jennings, K. Attenkofer, G.J. Meyer, and P. Coppens, *J. Am. Chem. Soc.* **125**, 7022-7034 (2003).

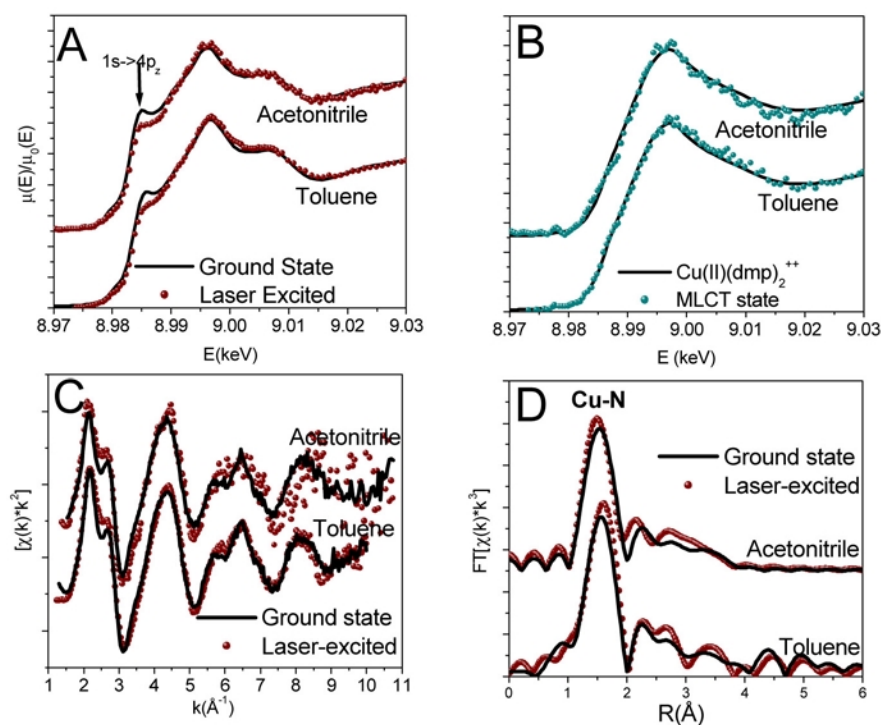


FIG. 2. Graph A shows XANES spectra of $\text{Cu}(\text{dmp})_2^+$ in solutions. Graph B shows the MLCT state XANES spectra after subtraction of the remaining ground-state spectra. Graph C shows XAFS spectra. Graph D shows Fourier transform (FT)-XAFS spectra of the ground and laser-illuminated samples.