

# Towards Ultrafast Excited State Molecular Structural Studies in Disordered Media Using Pulsed X-rays

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## Introduction

Excited state molecules are created by absorbing a visible or UV photon (Fig. 1). They are

- highly energetic,
- Short-lived,
- adopting new structures,
- reactants in photochemistry and photophysics,
- useful in many applications (Fig. 2).

Excited state structural evolution is divided into

- coherent atomic movements within a single potential surface on the time scale of fs to a few ps (i.e. vibrational relaxation);
- incoherent motion involving potential barrier crossing and thermal equilibrium on the time scale of ps to ms (i.e., populational decay).

Synchrotron x-ray pulses with 30-100 ps FWHM are suitable to take snapshots of excited state structure at thermally equilibrated state, but are too long for following atomic motions during the coherent processes.

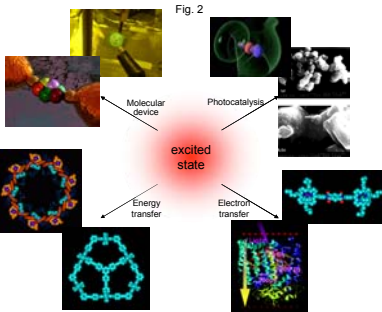


Fig. 2

## Approach

Pump-probe approach has been extensively used in ultrafast laser spectroscopy with time resolution as high as fs, where the first pump laser pulse triggers photochemical and photophysical processes, and the second probe laser pulse monitors excited state kinetics, energetics and coherence through the changes in the optical properties of the molecules. In order to obtain the excited state structures, the second laser probe pulse is replaced by an x-ray pulse in diffraction, scattering and absorption studies.

For most of the photochemical processes take place in disordered media, x-ray absorption and scattering approaches are needed to extract structural information of the excited state molecules. We started our excited state structural study with x-ray absorption near edge structure (XANES) and x-ray absorption fine structure (XAFS) measurements in solutions.

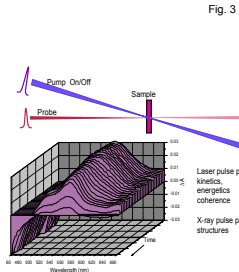


Fig. 3

## Experimental

In our laser pump, x-ray probe x-ray absorption spectroscopy (XAS) experiments, a hybrid timing operation mode of the storage ring was employed (Fig. 4), where a single electron bunch is separated from other bunches in the storage ring. The design of such an operating mode is simultaneously enables a sufficient time window for single X-ray pulse extraction for time-resolved studies and a high average X-ray photon flux for steady-state studies. Such a time separation allows the most commonly used solid state Ge detector array for the fluorescence XAFS to recover fully before signals from adjacent X-ray pulses enter the detector. Thus, the signal from the single X-ray probe pulse can be extracted via electronically gating the detector signals without an X-ray shutter.

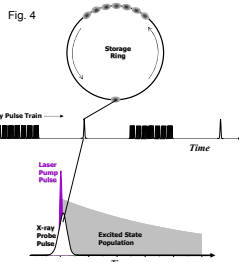


Fig. 4

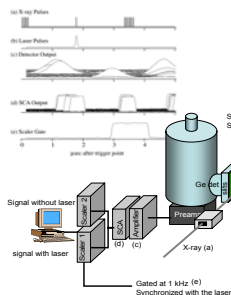


Fig. 5

Illustration of the experimental setup for the pump-probe XAFS. The signals shown in the upper left are marked at corresponding points in the letter.

## Future Studies

The initial success of using single x-ray pulses from the APS with 100-ps time resolution enables the structures of thermally equilibrated excited state to be determined. This is the first step toward to ultrafast x-ray studies for excited state structures during coherent motions after interactions with photons with energies in the visible and UV regions. Future studies include,

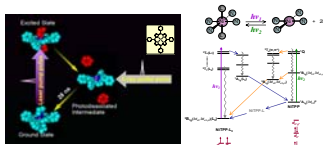
- Other excited state molecular structures and their implication in photochemistry and solar energy conversion and storage;
- Extend the pump-probe approach to x-ray scattering to obtain the excited state structure on different spatial resolutions for self-assembled nanostructured materials;
- Excited state dynamics for coherent and incoherent processes by ultrafast laser spectroscopy;
- Molecular modeling of excited state structure and dynamics;
- Transient structural studies using fs x-rays from other sources.

## Selected Publications

1. L. X. Chen, G. B. Shaw, I. Novozhilov, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer, P. Coppens, *J. Am. Chem. Soc.* **125** 7022-7034 (2003).
2. L. X. Chen, G. Jennings, T. Liu, D. J. Gozstola, J. P. Hessler, D. V. Scaltrito, G. J. Meyer, *J. Am. Chem. Soc.* **124**, 10861-10867 (2002).
3. L. X. Chen, *Faraday Discussion*, **122**, 315-329 (2002).
4. G. Jennings, W. J. H. Jäger, L. X. Chen, *Rev. Sci. Instr.* **73**, 362-368 (2002).
5. L. X. Chen, *J. Electronic Spectroscopy*, **119**, 161-174 (2001).
6. L. X. Chen, W. J. H. Jäger, G. Jennings, D. J. Gozstola, A. Munkholm, J. P. Hessler, *Science*, **292**, 262-264(2001).

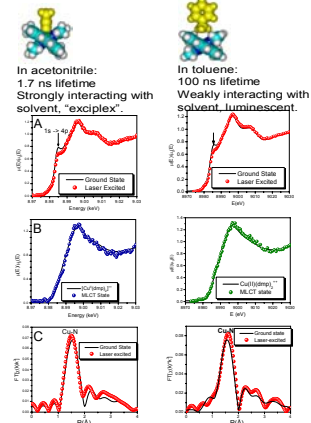
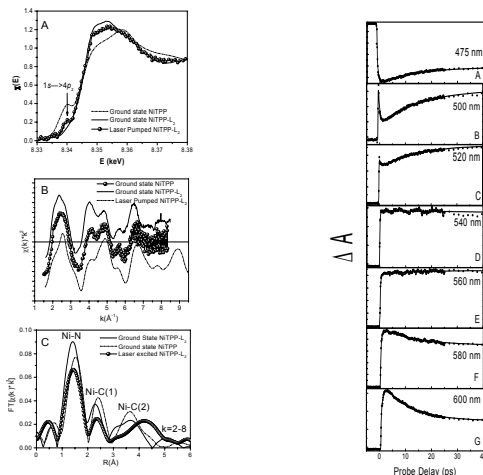
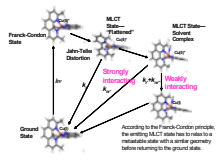
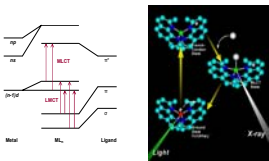
## Acknowledgement

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## Photoexcited metal-to-ligand-charge-transfer state Copper(I) diimine complex in different solvents

*J. Am. Chem. Soc.* **124**, 10861 (2002); *J. Am. Chem. Soc.* **125**, 7022 (2003).



The pump-probe XAFS revealed the structure of photodissociation intermediate is square-planar NiTPP, rather than NiTPP-L. Therefore, the ligand recombination follows either concerted mechanism or the step-wise mechanism with first step much slower than the second step. This the first ns structural study conducted with pump-probe XAS.

The experimental results indicated that the copper ion in the thermally equilibrated MLCT state in both coordinating and non-coordinating solvents have the same oxidation state as the corresponding Cu(II) complex in the ground state and was found to be penta-coordinate with an average nearest neighbor Cu-N distances 0.04 Å longer in toluene and 0.04 Å shorter in acetonitrile than that of the ground state [Cu(dmp)<sub>2</sub>]<sup>+</sup>. The results further revealed that what distinguishes the MLCT state structures in non-coordinating and coordinating solvents is not the "exciplex" formation, but whether strength of the interactions between the solvent and the Cu(II)\* species at the MLCT state. This is the first XAFS experiment with the time resolution of ~100 ps limited by the pulse duration of synchrotron x-rays.