X-ray Transient Absorption (XTA) Spectroscopy: 
A Decade and Beyond

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Time-Resolved X-ray Absorption Spectroscopy of Carbon Monoxide–Myoglobin Recombination After Laser Photolysis

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X-ray Absorption Structural Study of a Reversible, Photoexcited Charge-Transfer State

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X-ray Absorption Studies on Electronic Spin State Transitions of Fe(II) Complexes in Different Media

Lin X. Chen,*† Zhiyu Wang,‡ Jeremy K. Burdett,‡ James R. Norris,*‡
A decade ago....

Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure
Lin X. Chen,1* Vighard J. H. Jäger,1 Guy Jennings,2 David J. Gosztola,1 Anneli Munkholm,1‡ Jan P. Hessler1

Several years later....

JACS (2007); Chemical Science (2010)
## Challenges in New Decades

- Control chemical reaction dynamics with structural parameters;
- Coherence in electronic coupling and nuclear motions;
- Coupling single photon excitation events with multiple electron redox reactions (water splitting);
- Projecting reaction coordinates via polarization dependent studies;
- Interfacial energy and electron transfer (catalysis, solar cell);
- A higher time resolution beyond the synchrotron x-ray pulse limit (fs – 10 ps);
- High data quality to extract transient structural information;
- Transient structures in systems beyond models and feasibility experiments (sustainable energy, environment, etc);
- Ultrafast non-photon trigger sources (E-field, thermal, etc.);
- Accurate theoretical and simulation methods

...
Control chemical reaction dynamics with structural parameters: the MLCT state of Cu(I) complexes

$$[\text{Cu}^{I}(\text{dmp})_2]^+ \xrightarrow{h\nu} [\text{Cu}^{II}\text{(dmp}^-)(\text{dmp})]^+ + e^-$$

Metal to ligand charge transfer

ES lifetime: 100 ns or longer;

Solar Cell Eff.: 2%

Excited state reorganization

Labile Cu(II)

Can we make the MLCT state Cu(I) complexes to behave like Ru(II) complexes in some solar energy conversion processes?

$$[\text{Ru}^{II}\text{(bpy)}_3]^2+ \xrightarrow{h\nu} [\text{Ru}^{III}\text{(bpy}^-)(\text{bpy})_2]^2+ + e^-$$

Metal to ligand charge transfer

ES lifetime: 300 ns or longer;

Solar Cell Eff.: 11%

Rigid structure

Ru(III) species stable
Control chemical reaction dynamics with structural parameters: the MLCT state of Cu(I) complexes

McMillin, Meyer, Karpishin, Sauvage...

XTA identified that the MLCT state is Cu(II) species and the exciplexes between the solute and solvent molecules can be formed in both toluene (non-coordinating) and acetonitrile (coordinating solvent) with different average bond distances of Cu-N.

Control chemical reaction dynamics with structural parameters: the MLCT state of Cu(I) complexes

Nosaki et al. 2003

MLCT state dynamics by three rate constants:

\[ \tau_1 = 500 - 700 \text{ fs}; \quad \tau_2 = 10 - 15 \text{ ps}; \quad \tau_3 = 2 - 100 \text{ ns} \]

Solvent independent
Flattening

\[ \tau_2 = 10 - 15 \text{ ps} \]
Solvent independent
Intersystem crossing

\[ \tau_3 = 2 - 100 \text{ ns} \]
Solvent dependent

\[ 3\text{MLCT state population decay} \]

Structural dependence excited state dynamics

\[ \langle 1\Phi_{1B1}|H_{SO}|3\Phi_{1A}\rangle: \quad \frac{d[S_1(t)]}{dt} = k_{ic}[\Phi(t)] \cdot [S_3(t)] - \{k_r[\Phi(t)] + k_{nr}[\Phi(t)] + k_{isc}[\Phi(t)]\} \]

The MLCT excited state properties are structural-dependent: ISC < 1 ps in orthogonal dihedral angle geometry, and ~ 10 ps in flattened geometry.
What we have learned...

- Two main structural factors control the MLCT state properties: dihedral angle and solvent accessibility.
- The optical TA spectra could infer but not directly resolve the flattening and ligation dynamics.
- The flattening is mainly inner sphere processes not significantly affected by media.

Unanswered questions:

1. What is the time scale for the solvent ligation?
2. Can we control the MLCT dynamics by structural constraints that will alter the two main reaction coordinates?
3. Which geometry can prolong the MLCT state lifetime, orthogonal or flattened?
4. Can Cu(I)diimine be used as a dye sensitizer in DSSC to replace Ru dye?
Changing the constraint for “flattening”:
S1 to T1 is fast in orthogonal geometry while S1 in flattened geometry has a lower energy. To look for the energetically, dynamically and structurally optimal complexes for DSSC applications.
MLCT state dynamics of “flattened” complexes

\( \tau_1 = 0.3 - 0.9 \) ps
\( \tau_2 = 9 - 11 \) ps
\( \tau_3 \approx 100 \) ns (ACN)

\( \tau_1 = ----- \)
\( \tau_2 = 12 - 15 \) ps
\( \tau_3 >> \) ns (water)

- dpp ligands at 2,9-positions block solvent accessibility
- Bis-dpp complex may could still have flattening in the excited state;
- Its energy minimized structures show possible multi-conformations with both orthogonal and flattened geometry in the ground state (also UV/vis evidence);
- additional –SO\(_3^−\) locks flattened conformation with a slow intersystem crossing without the exciplex in coordinating solvent.
The Cu K-edge XANES spectra are highly sensitive to the coordination geometry and oxidation state of Cu which can be used to probe details of correlations between the electronic distribution and the nuclear geometry.
Moving to a new time window:

- Two main structural factors control the excited state properties: dihedral angle between two ligand planes, and space for the ligation.
- The clear signatures in XANES spectra have been identified to future studies using fs x-ray pulses in LCLS (beamtime proposal has been approved).
Coherence in electronic coupling and nuclear motions
Excited State Structures of Pt Phenylpyridine Pyrazolate Dimer [Pt(ppy)(μ-R₂pz)]₂ Complexes

Aaron Rachford and Felix Castellano
Evidence of electronic coherence of two states

\[
\phi_1 = (ppy1)^-(Pt - Pt)^+(ppy2)^0 \quad \Longleftrightarrow \quad \phi_2 = (ppy1)^0(Pt - Pt)^+(ppy2)^-
\]

Electron transfer coherence

\[
|\Psi(t)|^2 = \frac{1}{2}\Psi_+^2 + \frac{1}{2}\Psi_-^2 + \Psi_+ \Psi_- \cos[(E_- - E_+) t / \hbar]
\]

\[
|\Psi(t)|^2 = \cos^2(\beta t / \hbar) \phi_1^2 + \sin^2(\beta t / \hbar) \phi_2^2
\]
Coupling single photon excitation events with multiple electron redox reactions

Multiple laser pulse excitation, Multiple colors; Pulse separation control; Stepwise probe.
Long term goal is replacing Ru with the first row transition metal dyes;

- Is this system energetically feasible;
- Can we control the singlet excited state lifetime to be long enough for e-injection?
- Does the triplet state have sufficient energy for e-injection?
- Are the linkers at right place for e-injection?
- Can the transient Cu(II) species be stable complex?
- Does the surface restructure?
- Synthesis, kinetics and transient structural characterization as well as theory will be pursued.

Bessho, et al., Chem. Comm. 3693 – 3808 (2008), ~2% PCE

Interfacial energy and electron transfer in Dye Sensitized Solar Cells
Table 1. Structural parameters of RuN3 adsorbed to TiO2 nanoparticle surface extracted from XAS spectra.

<table>
<thead>
<tr>
<th>Ru-N Bond</th>
<th>RuN3</th>
<th>RuN3⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-N(dcbpy)</td>
<td>2.04 Å</td>
<td>2.05 Å</td>
</tr>
<tr>
<td>Ru-N(NCS)</td>
<td>2.05 Å</td>
<td>1.99 Å</td>
</tr>
</tbody>
</table>
The results confirmed a step-wise mechanism:
1. Electron density locates at Ru-(NCS)2 moiety in the ground state;
2. Electron density shifts and is localized on fs-ps time scale onto bpy ligands at the excited state, which cannot be resolved with current synchrotron x-ray pulse;
3. Electron transfer from bpy ligands anchored on the nanoparticle surface to the TiO2 lattice, causing the net loss of electron density in Ru-(NCS)2 moiety.

The net electron density change depletion at NSS-Ru(II) when it changes to Ru(III)
The bpy ligands act like a relay transport electron from NCS to TiO2 while Ru-N(dcbpy) bonds unchanged after the electron injection;
Ru-N(NCS) change with less hindrance.
Other thoughts:

- High repetition pump-probe cycle for better s/n ratio (Anne Marie March)
- A higher time resolution beyond the synchrotron x-ray pulse limit;
  - LCLS and other fs x-ray sources
- High data quality to extract transient structural information;
  - High S/N ratio required to extract precise transient structures
- Transient structures in systems beyond models and feasibility experiments;
  - Small quantities, low concentrations, fragile samples, irreversible processes, multiple transient species, biological samples
- Ultrafast non-photon trigger sources;
  - THz, ultrafast E-field, shock wave, thermal pulses, etc.
- Accurate theoretical and simulation methods
- Detector development
- Simultaneously employing multiple techniques on the same sample.
Transient XAS-WAXS combo

XTA probes inner sphere structural changes, metal oxidation state change due to photoinduced electron transfer, coordination geometry change due to dissociation and ligation, and electronic structure change due to metal to ligand charge transfer.

XTS probes outer sphere structural changes, molecular shape changes, interactions with solvent, e.g. cage effect, and pair density distribution functions.
Time-Resolved X-ray Absorption Spectroscopy of Carbon Monoxide–Myoglobin Recombination After Laser Photolysis
Thank you.