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

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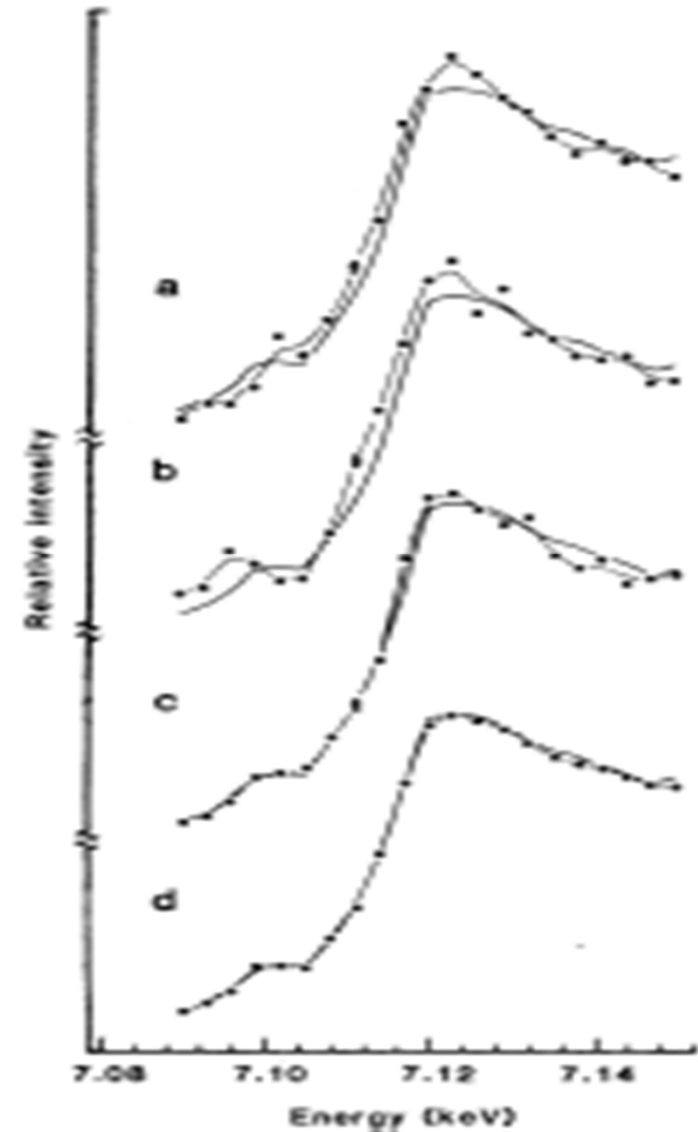
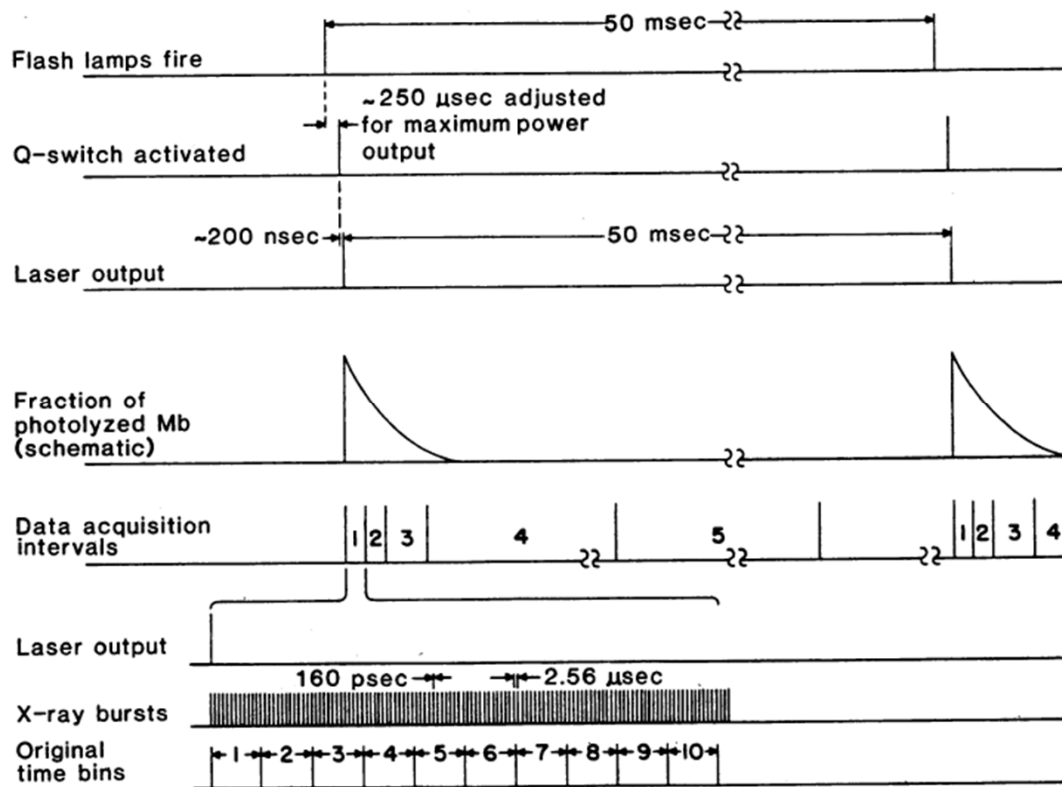


**NORTHWESTERN  
UNIVERSITY**

*Support from US Department of Energy,  
Office of Science, Basic Energy Science*



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



D. M. MILLS

*Cornell High Energy Synchrotron  
Source, Cornell University,  
Ithaca, New York 14853*

A. LEWIS

A. HAROOTUNIAN

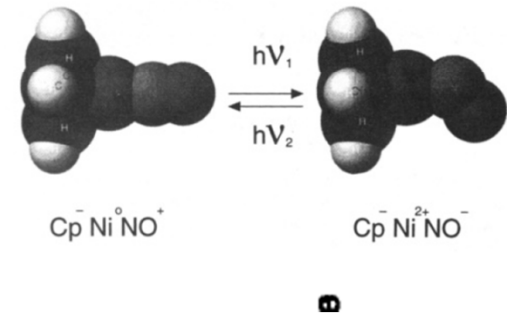
J. HUANG

B. SMITH

*School of Applied and Engineering  
Physics, Cornell University*

**Before the APS...**

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



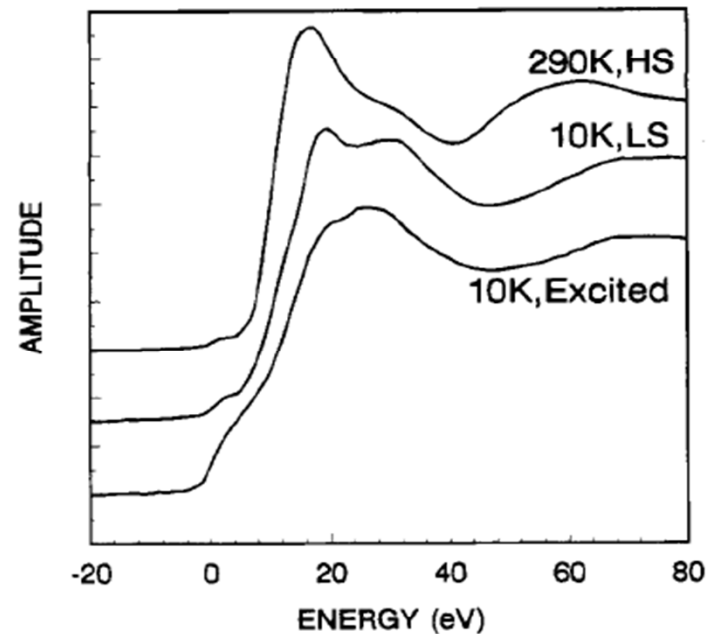
Lin X. Chen, Michael K. Bowman,<sup>1</sup> Pedro A. Montano,<sup>2</sup> and  
James R. Norris<sup>\*,3</sup>

7958

*J. Phys. Chem.* **1995**, *99*, 7958–7964

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

Lin X. Chen,<sup>\*,†</sup> Zhiyu Wang,<sup>‡</sup> Jeremy K. Burdett,<sup>‡</sup>  
James R. Norris<sup>†,‡</sup>

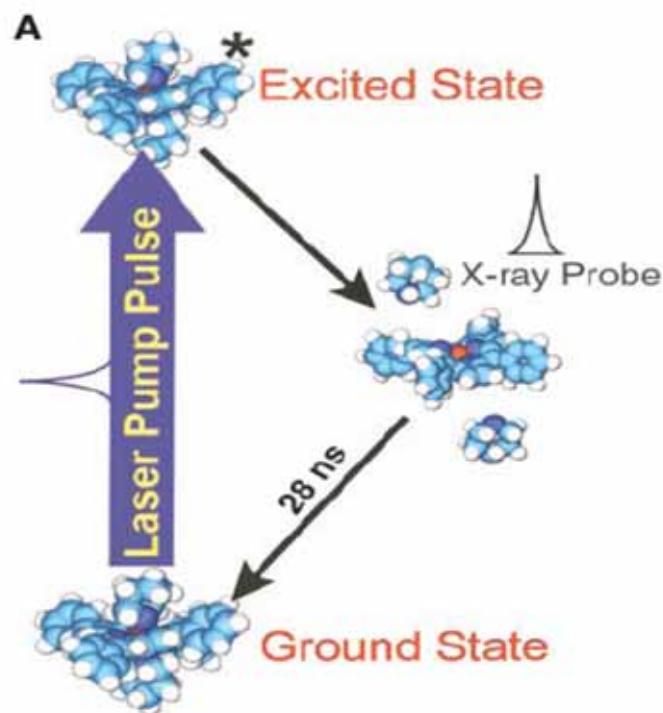


A decade ago....

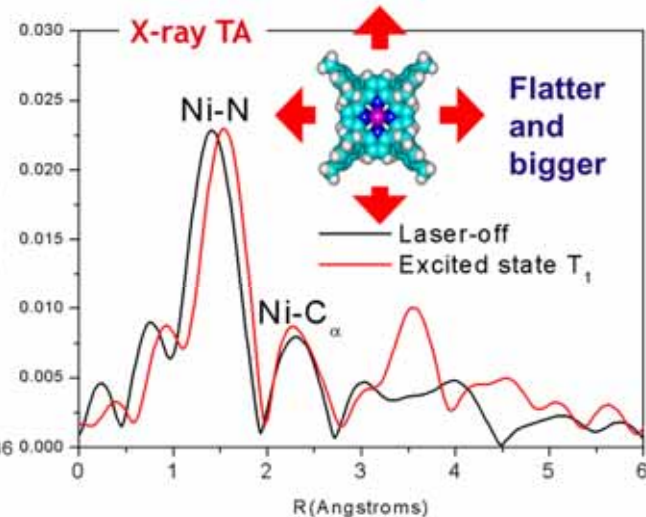
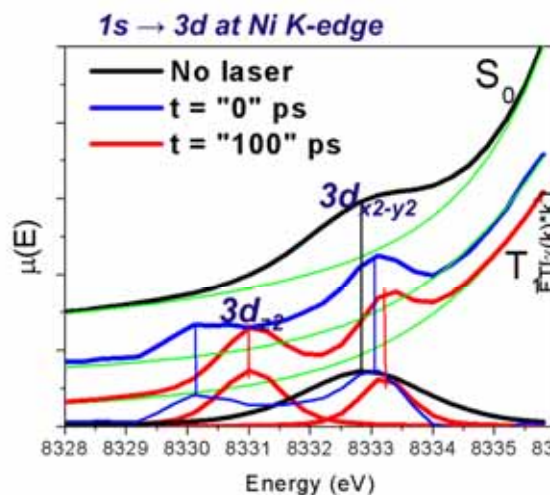
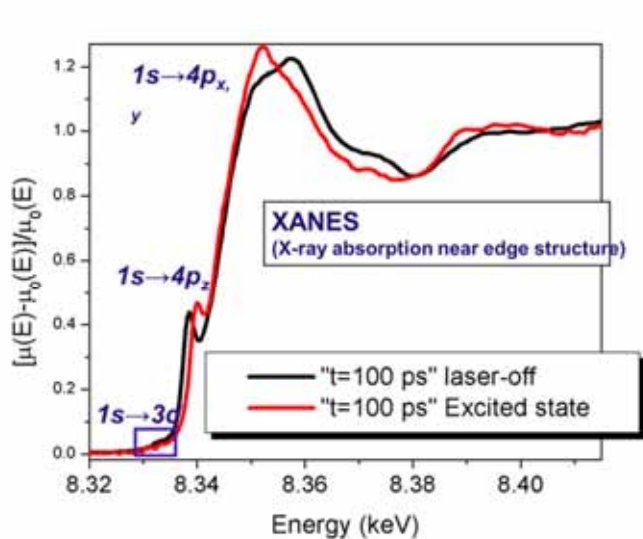
SCIENCE VOL 292 13 APRIL 2001

# Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure

Lin X. Chen,<sup>1\*</sup> Wighard J. H. Jäger,<sup>1</sup> Guy Jennings,<sup>2</sup>  
David J. Gosztola,<sup>1</sup> Anneli Munkholm,<sup>1†</sup> Jan P. Hessler<sup>1</sup>



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



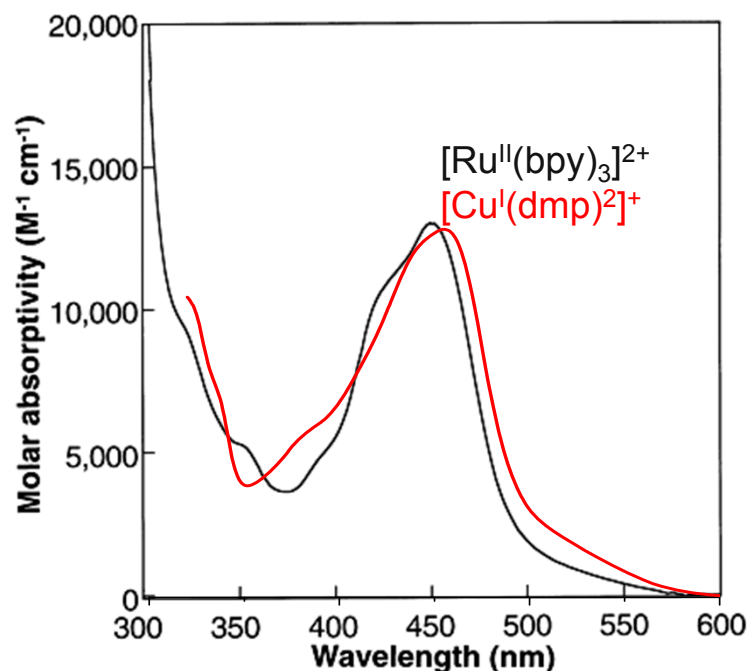
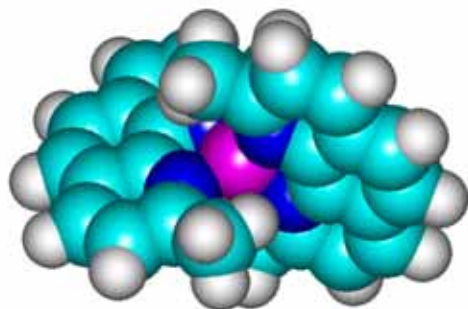
Metal to ligand charge transfer

ES lifetime: 100 ns or longer;

Solar Cell Eff.: 2%

Excited state reorganization

Labile Cu(II)



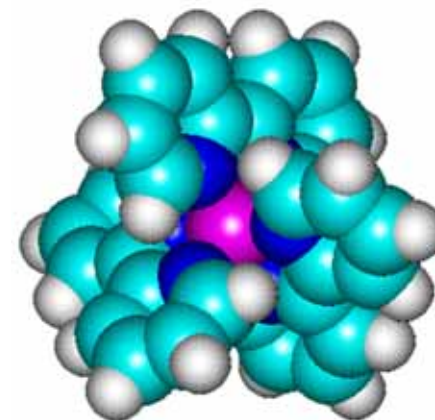
Metal to ligand charge transfer

ES lifetime: 300 ns or longer;

Solar Cell Eff.: 11%

Rigid structure

Ru(III) species stable

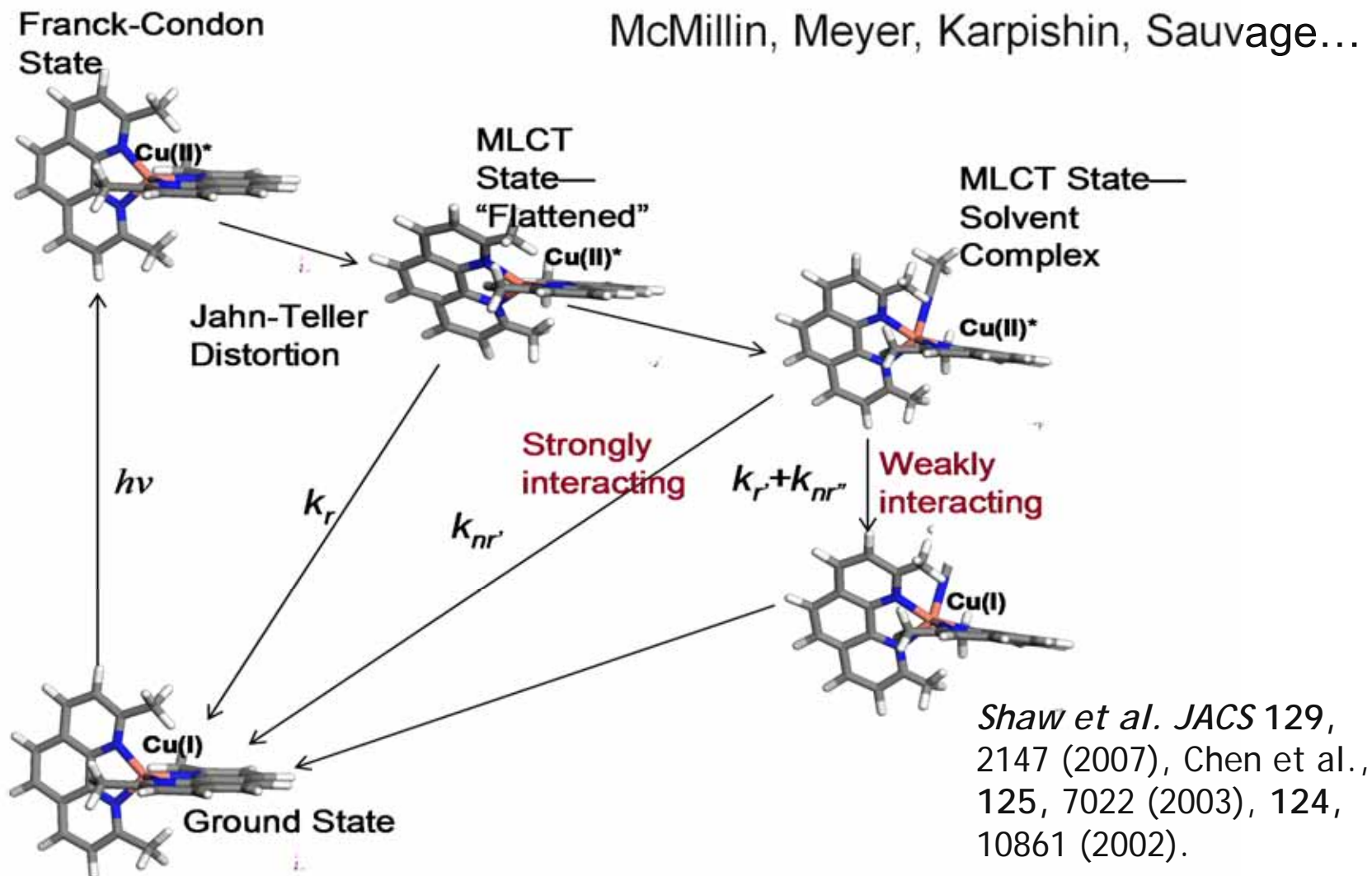


Can we make the MLCT state Cu(I) complexes to behave like Ru(II) complexes in some solar energy conversion processes?



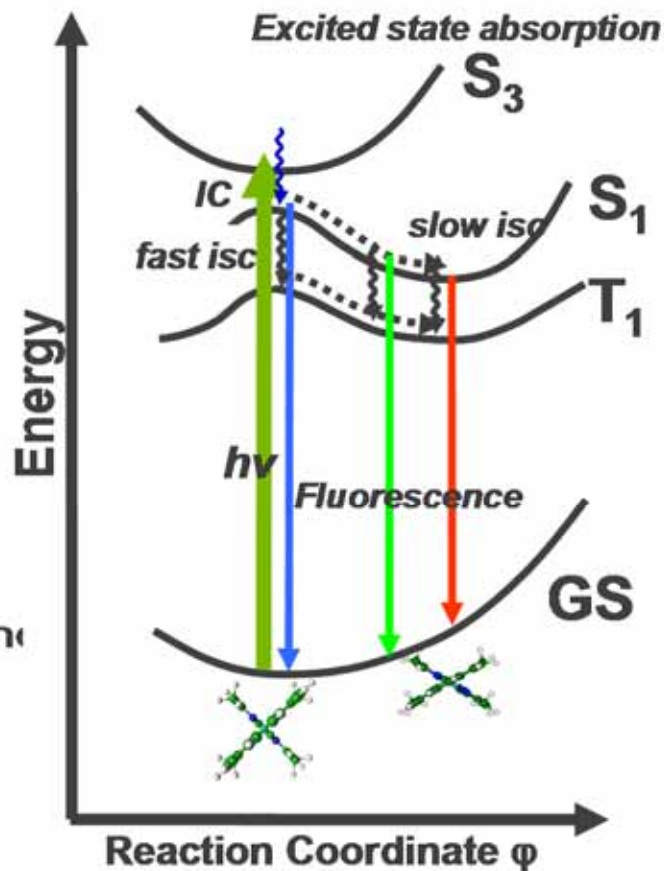
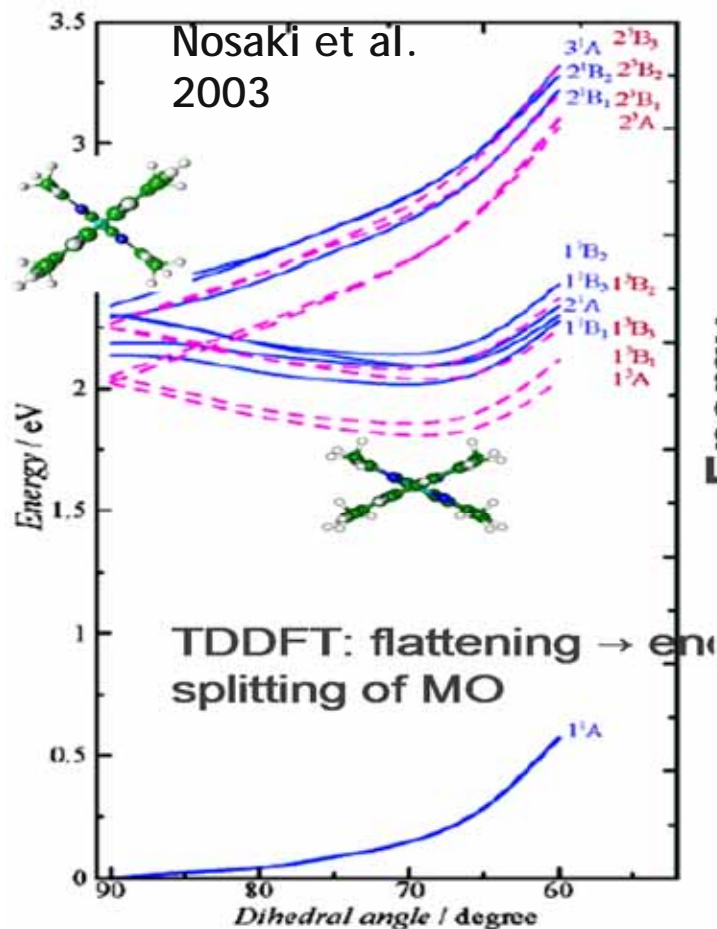
# Control chemical reaction dynamics with structural parameters : the MLCT state of Cu(I) complexes

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



MLCT state dynamics by three rate constants:

$\tau_1 = 500 - 700$  fs;  
Solvent independent  
Flattening

$\tau_2 = 10 - 15$  ps  
Solvent independent  
Intersystem crossing

$\tau_3 = 2 - 100$  ns  
Solvent dependent  
 $^3$ MLCT state population decay

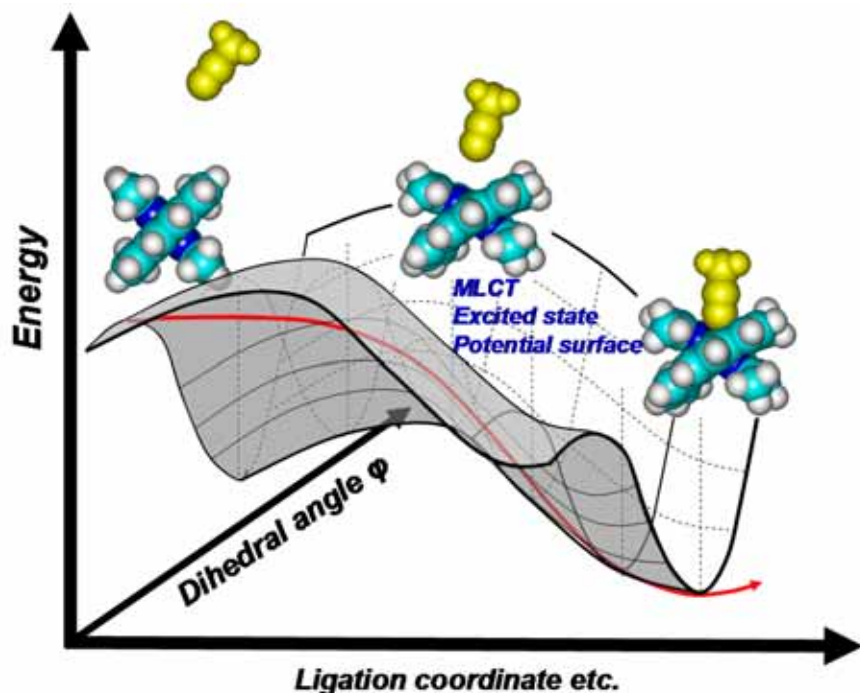
Structural dependence excited state dynamics

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

The MLCT excited state properties are structural-dependent: ISC  $< 1$  ps in orthogonal dihedral angle geometry, and  $\sim 10$  ps in flattened geometry.



## What we have learned...

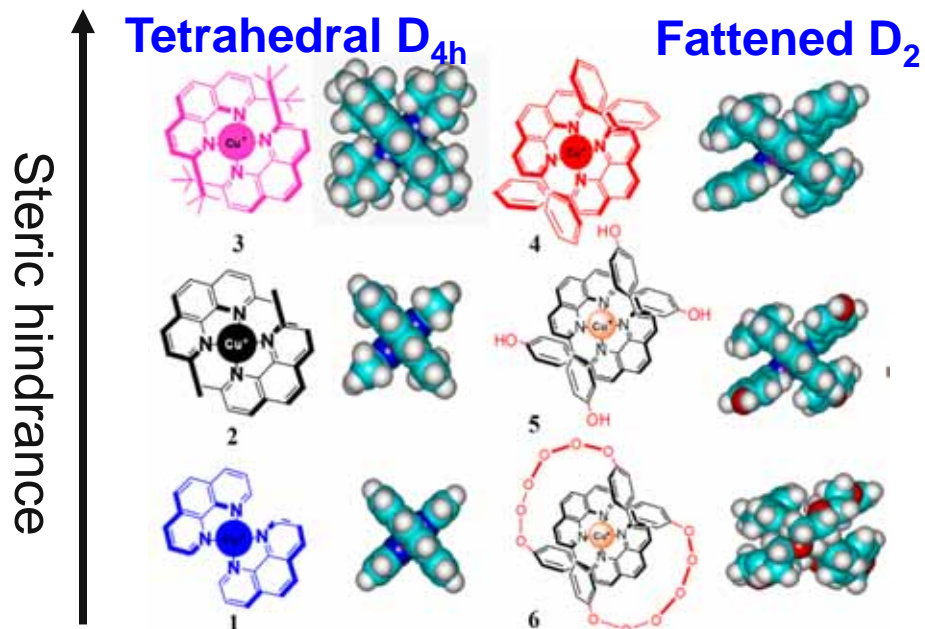


- Two main structural factors control the MLCT state properties: dihedral angle and solvent accessibility.
- The optical TA spectra could infer but not directly resolve the flattening and ligation dynamics.
- The flattening is mainly inner sphere processes not significantly affected by media.

## Unanswered questions:

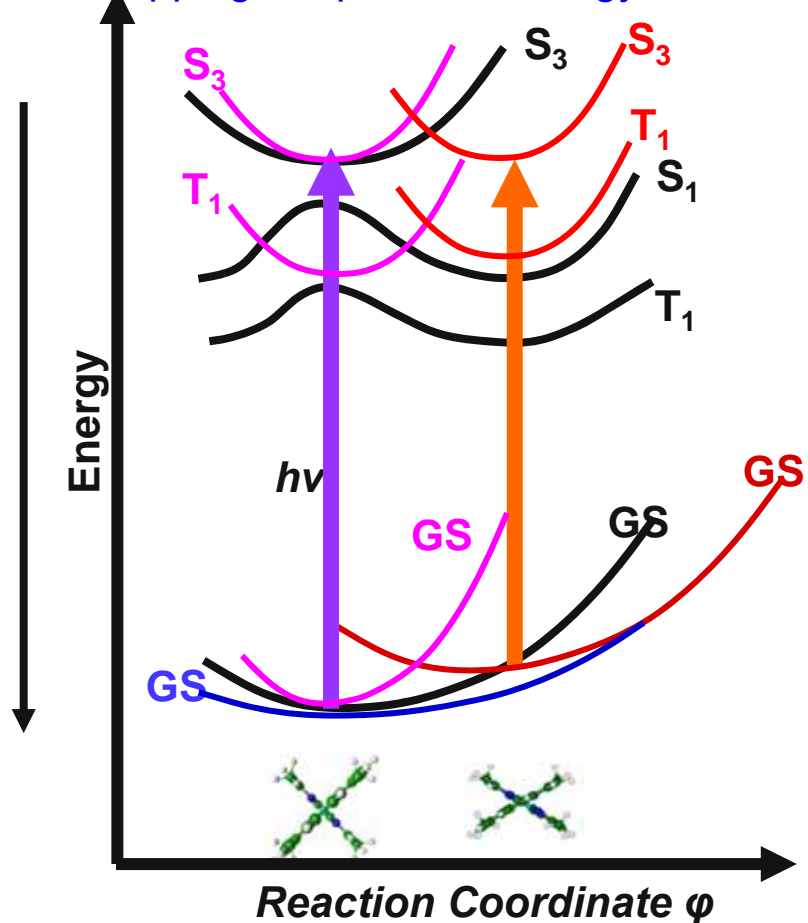
1. What is the time scale for the solvent ligation?
2. Can we control the MLCT dynamics by structural constraints that will alter the two main reaction coordinates?
3. Which geometry can prolong the MLCT state lifetime, orthogonal or flattened?
4. Can Cu(I)diimine be used as a dye sensitizer in DSSC to replace Ru dye?

# Varying excited state properties by altering the potential surfaces through structural constraints



- Confirmed sub-ps component is due to flattening in the MLCT state;
- Both “non-coordinating” and “coordinating” solvents will interact with the MLCT state while their interactions vary;
- Solvent shielding will prolong triplet MLCT state lifetime.

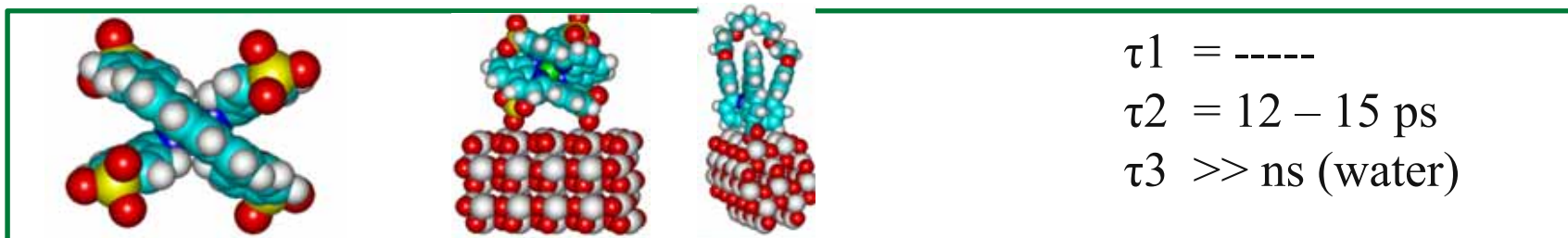
Mapping the potential energy surfaces



Changing the constraint for “flattening”:

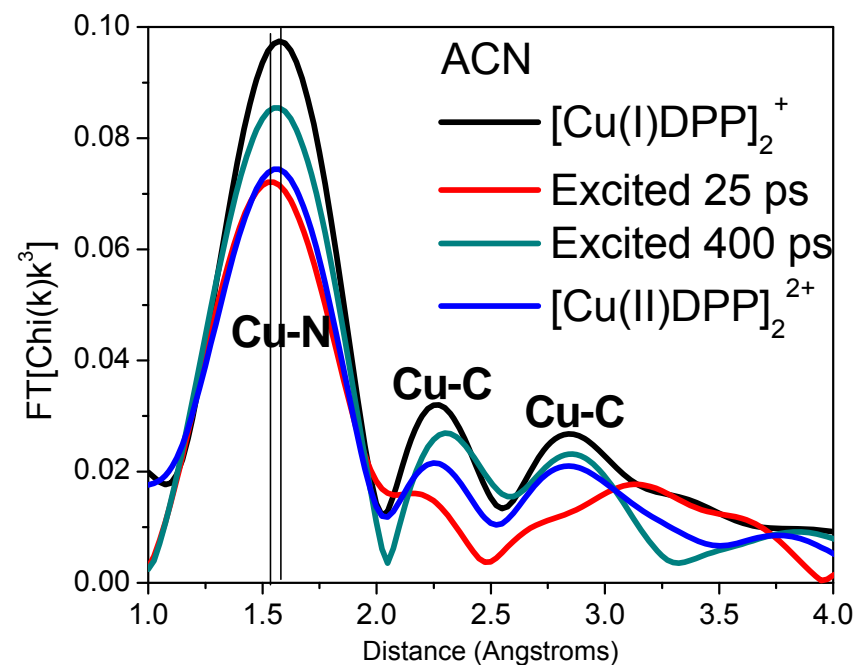
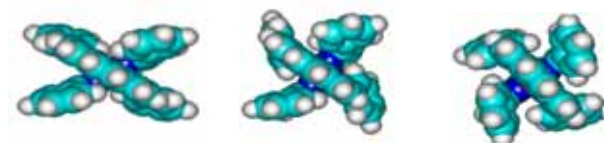
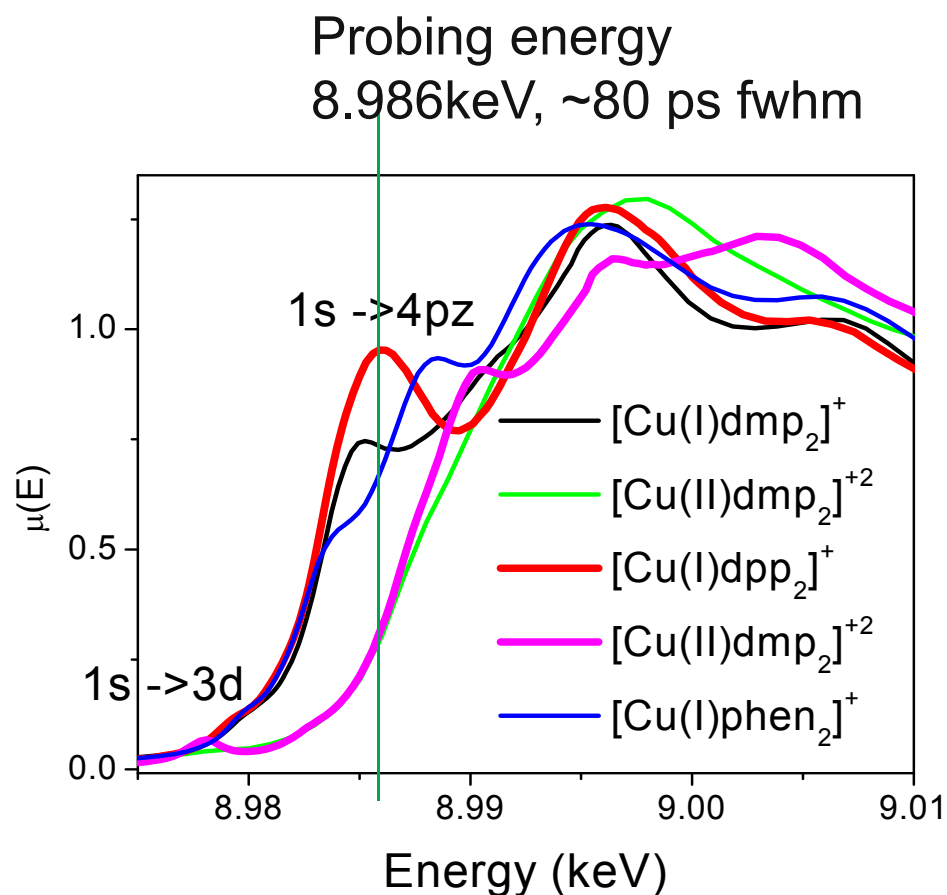
$S_1$  to  $T_1$  is fast in orthogonal geometry while  $S_1$  in flattened geometry has a lower energy. To look for the energetically, dynamically and structurally optimal complexes for DSSC applications.

## MLCT state dynamics of “flattened” complexes



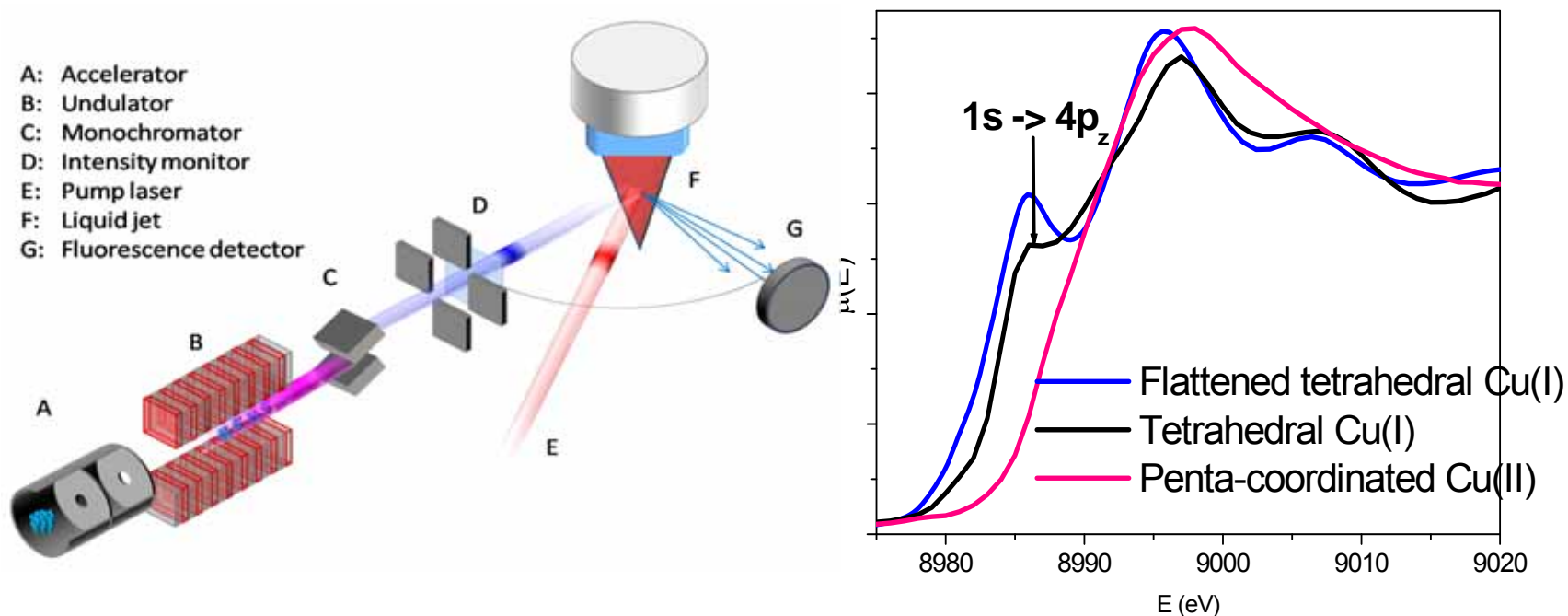
- dpp ligands at 2,9-positions block solvent accessibility
- Bis-dpp complex may still have flattening in the excited state;
- Its energy minimized structures show possible multi-conformations with both orthogonal and flattened geometry in the ground state (also UV/vis evidence);
- additional -SO<sub>3</sub><sup>-</sup> locks flattened conformation with a slow intersystem crossing without the exciplex in coordinating solvent.

# Investigating MLCT structures of $[\text{Cu(I)(dpp)}_2]^+$ by XTA (X-ray TA)



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:

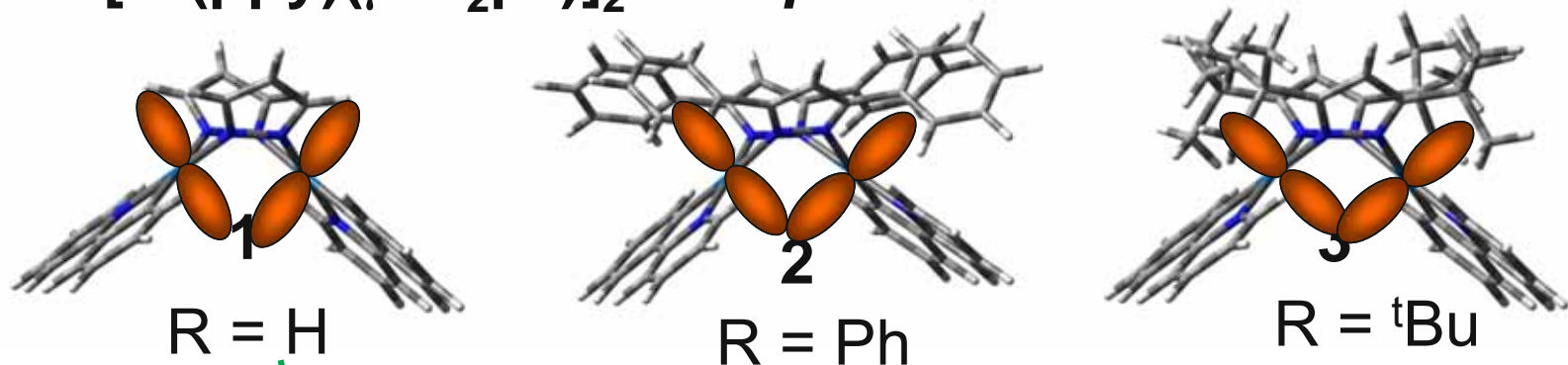


- Two main structural factors control the excited state properties: dihedral angle between two ligand planes, and space for the ligation.
- The clear signatures in XANES spectra have been identified to future studies using fs x-ray pulses in LCLS (beamtime proposal has been approved).

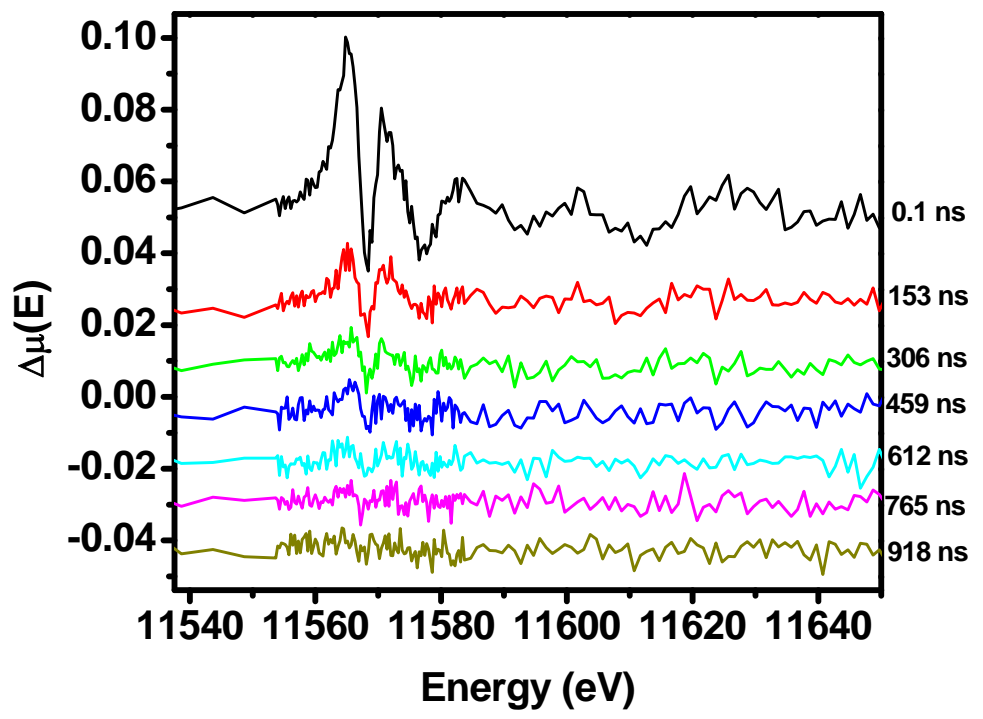
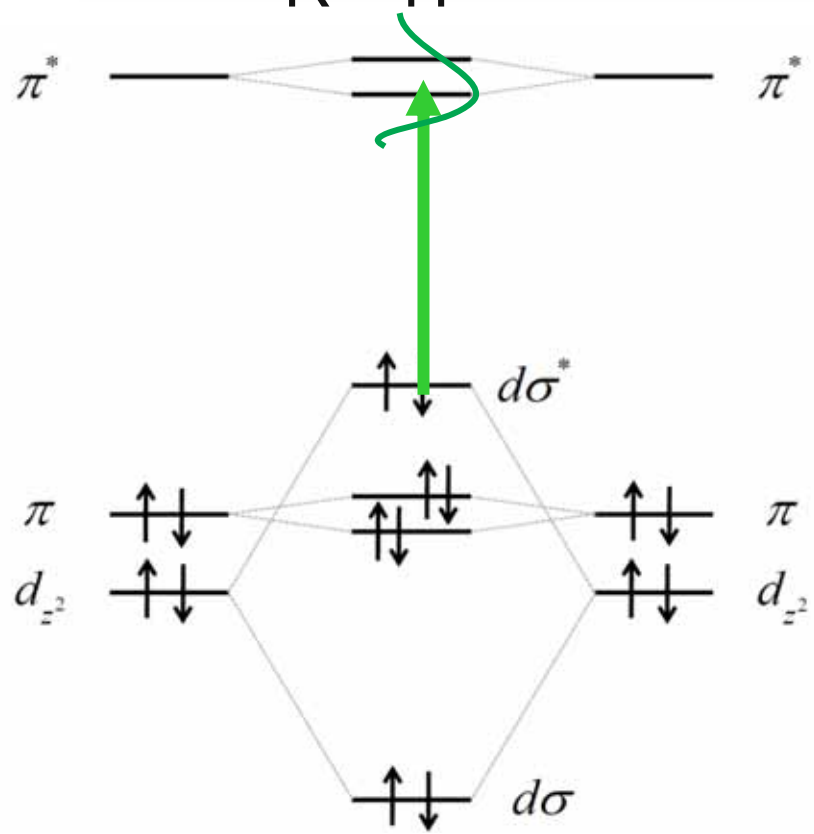


# Coherence in electronic coupling and nuclear motions

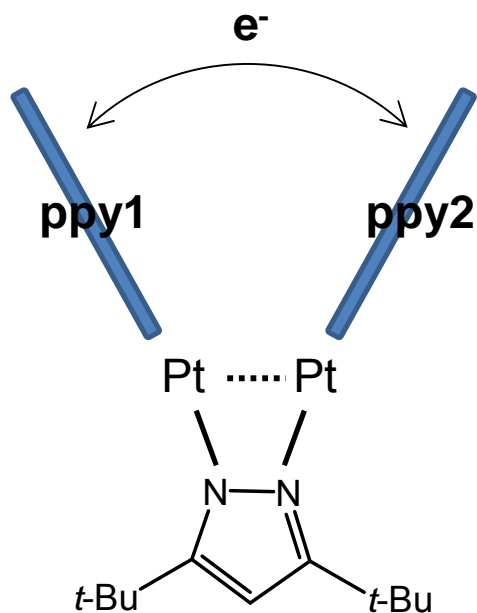
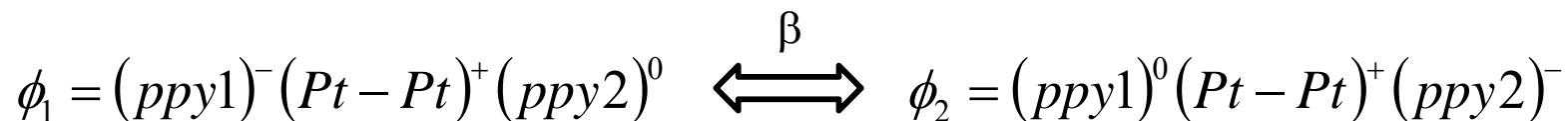
## Excited State Structures of Pt Phenylpyridine Pyrazolate Dimer $[\text{Pt}(\text{ppy})(\mu\text{-R}_2\text{pz})]_2$ Complexes



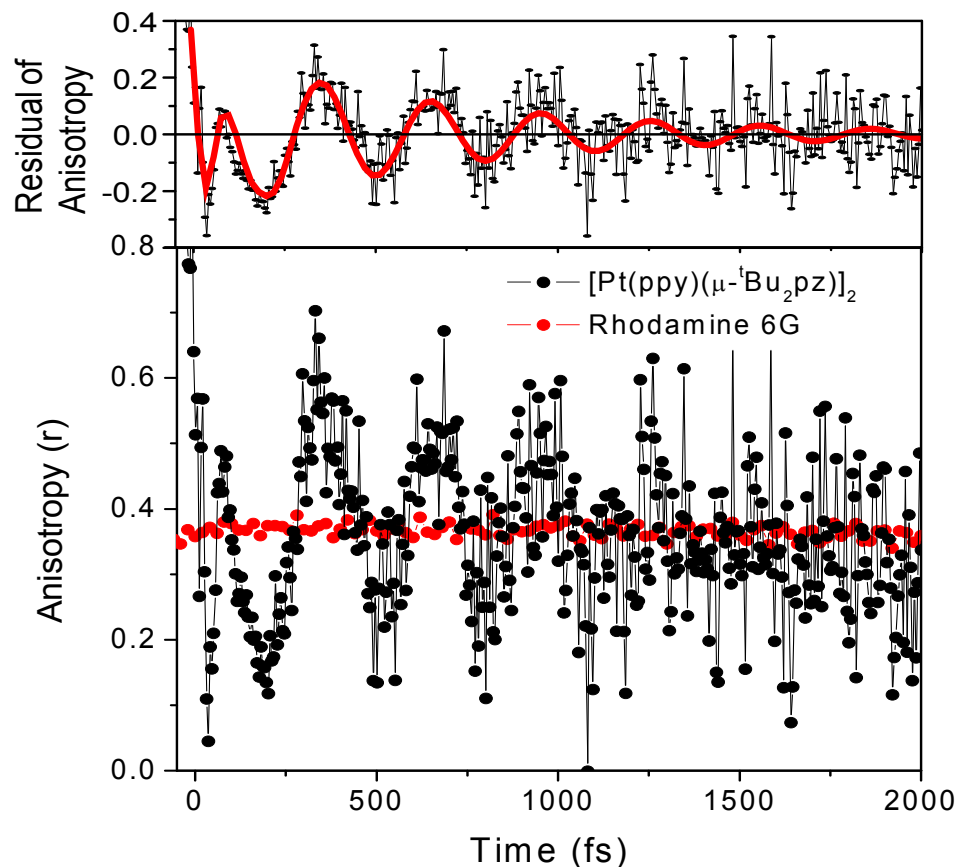
Aaron Rachford and Felix Castellani



# Evidence of electronic coherence of two states



Electron transfer  
coherence

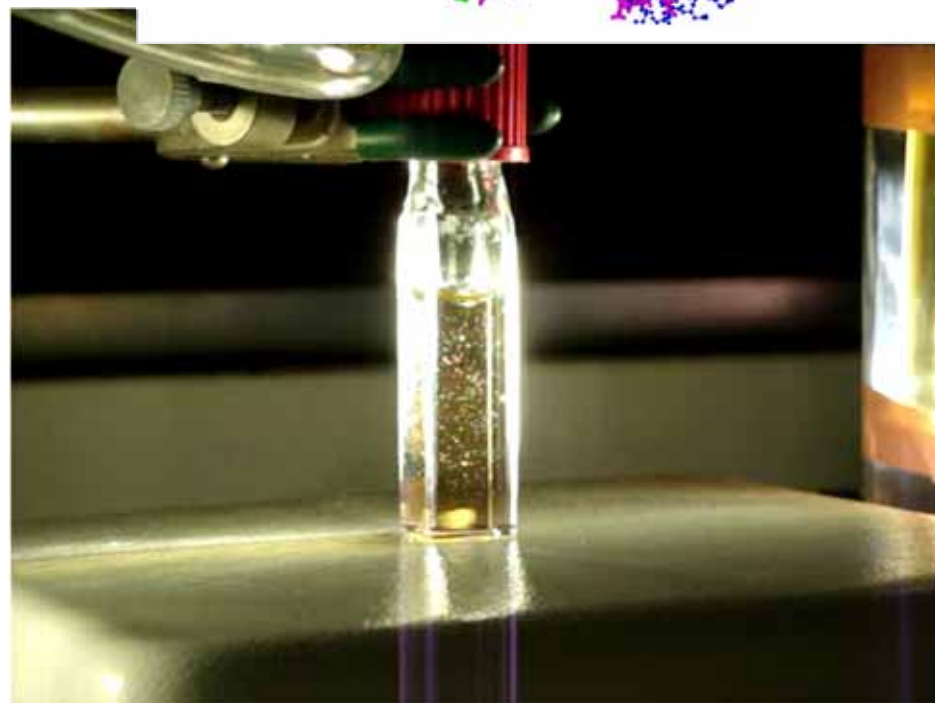
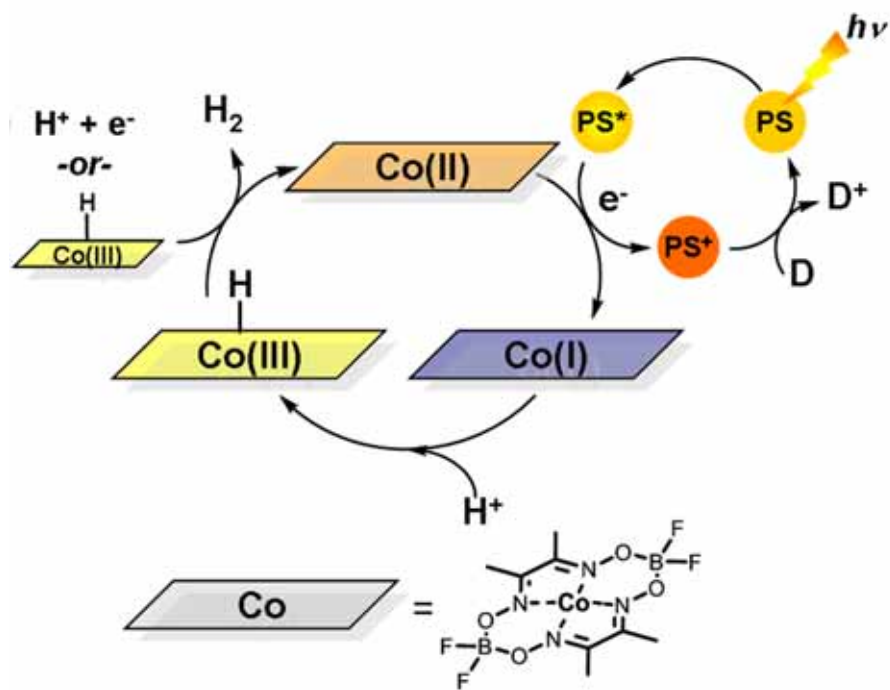
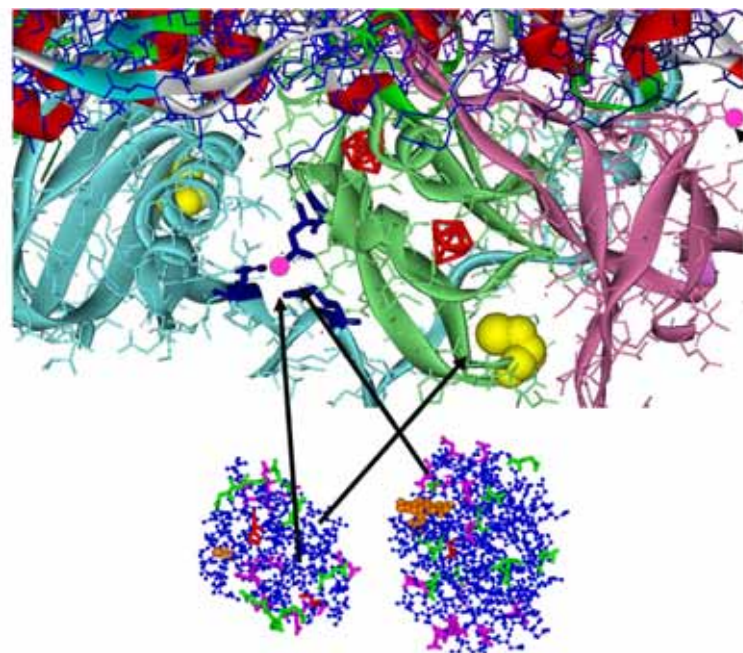


$$|\Psi(t)|^2 = \frac{1}{2} \Psi_+^2 + \frac{1}{2} \Psi_-^2 + \Psi_+ \Psi_- \cos[(E_- - E_+) t / \hbar]$$

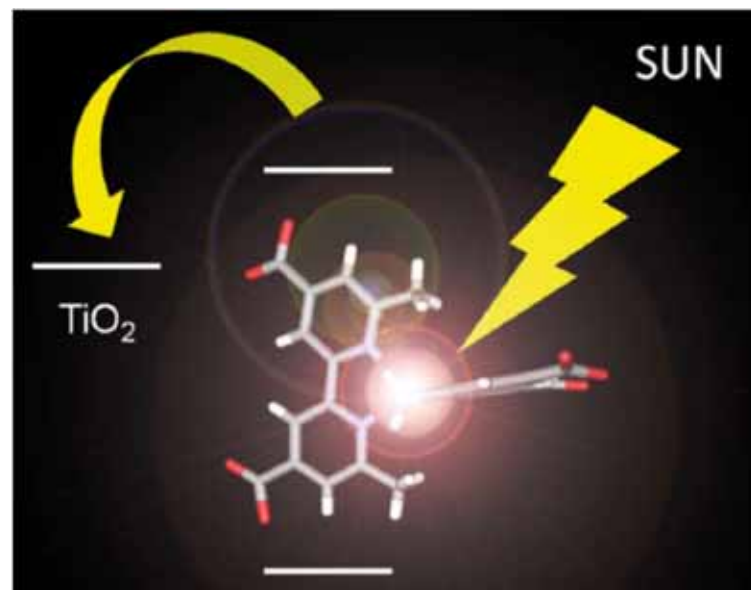
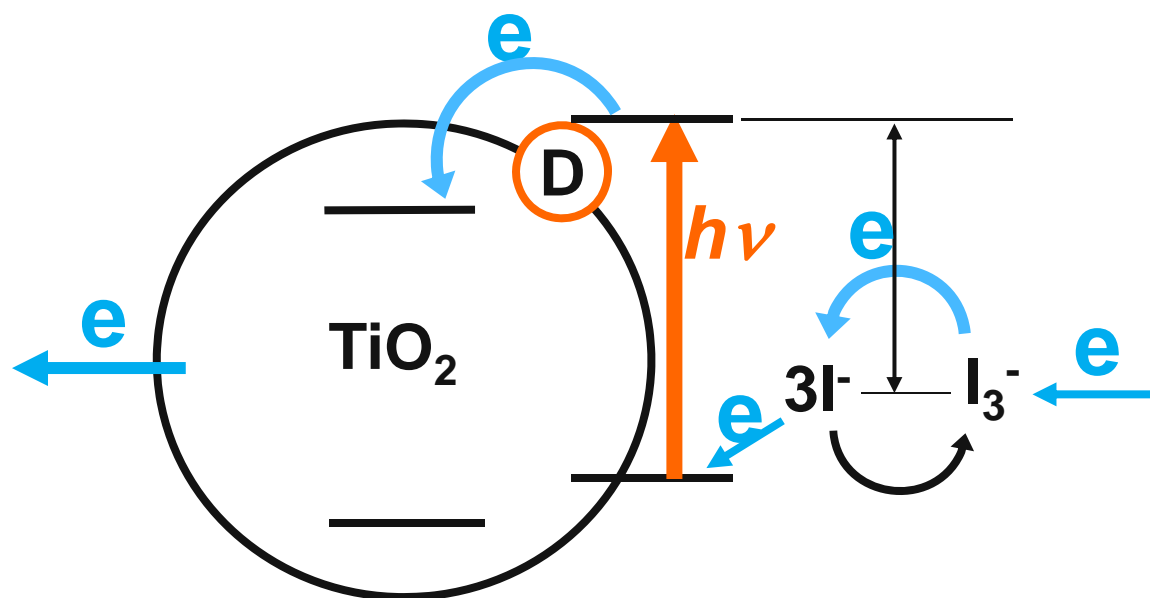
$$|\Psi(t)|^2 = \cos^2(\beta t / \hbar) \phi_1^2 + \sin^2(\beta t / \hbar) \phi_2^2$$

# Coupling single photon excitation events with multiple electron redox reactions

Multiple laser pulse excitation,  
Multiple colors;  
Pulse separation control;  
Stepwise probe.



## Interfacial energy and electron transfer in Dye Sensitized Solar Cells

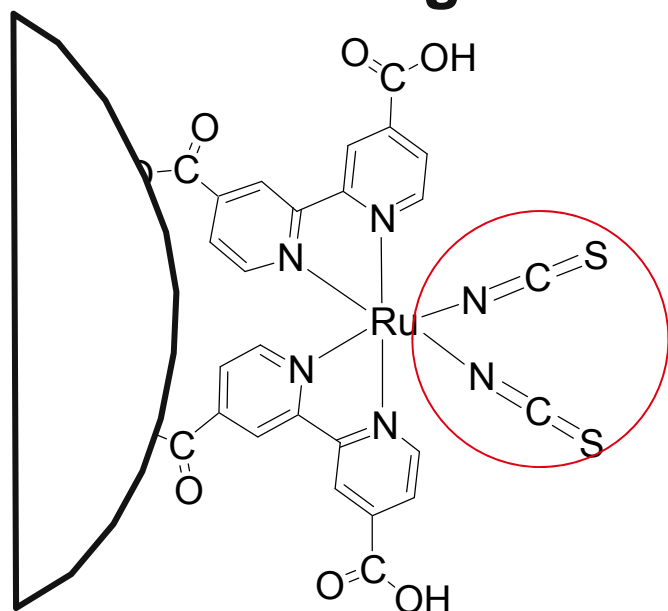


Bessho, et al., Chem. Comm.  
3693 – 3808 (2008), ~2% PCE

Long term goal is replacing Ru with the first row transition metal dyes;

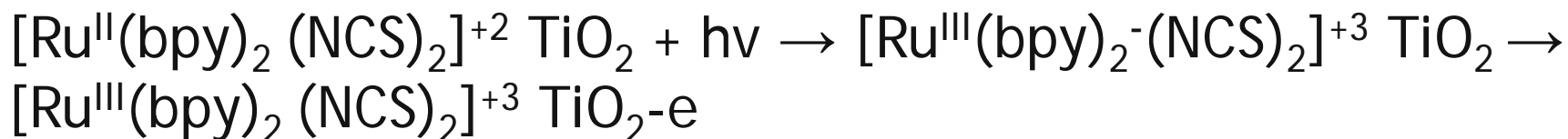
- Is this system energetically feasible;
- Can we control the singlet excited state lifetime to be long enough for e-injection?
- Does the triplet state have sufficient energy for e-injection?
- Are the linkers at right place for e-injection?
- Can the transient Cu(II) species be stable complex?
- Does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

# Interfacial Charge Transfer in Dye Sensitized Solar Cells



NCS: high electron withdrawing, strong interaction with Ru, less steric hindrance and strong  $\pi$ -backbonding result in shorter Ru-N(CS) bonds

dc bpy: highly sterically hindered due to binding to TiO<sub>2</sub>, cancellation between the two effects, 1) smaller ionic radius for Ru(III) than Ru(II) and 2) reduced bond order due to the addition of the anti-bonding electrons, increasing the repulsion.



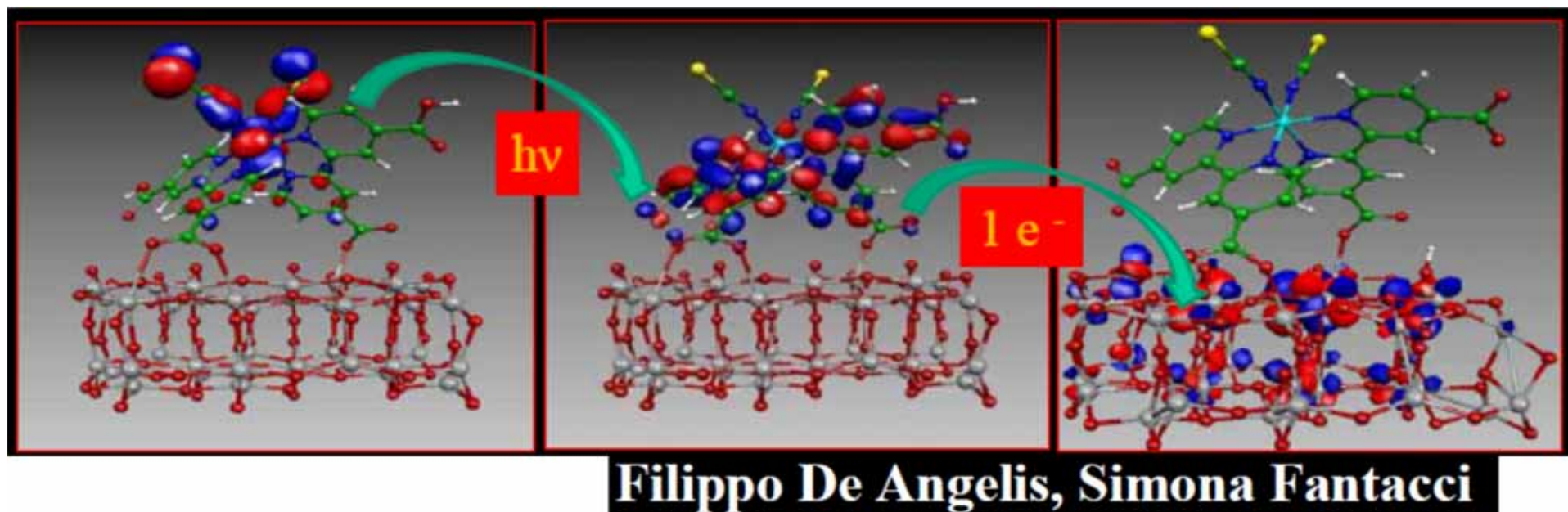
Ru-N on NCS lengthened by 0.05 Å  
 Ru-N on bpy not changed.  
 Structural changes from 100 ps to longer delays are observed.

**Table 1.** Structural parameters of RuN<sub>3</sub> adsorbed to TiO<sub>2</sub> nanoparticle surface extracted from XAS spectra.

Ru-N Bond	RuN <sub>3</sub>	RuN <sub>3</sub> <sup>+</sup>
Ru-N(dcbpy)	2.04 Å	2.05 Å
Ru-N(NCS)	2.05 Å	1.99 Å



# Interfacial Charge Transfer in Dye Sensitized Solar Cells



The results confirmed a step-wise mechanism:

1. Electron density locates at Ru-(NCS)<sub>2</sub> 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 TiO<sub>2</sub> lattice, causing the net loss of electron density in Ru-(NCS)<sub>2</sub> 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 TiO<sub>2</sub> while Ru-N(dcbpy) bonds unchanged after the electron injection;

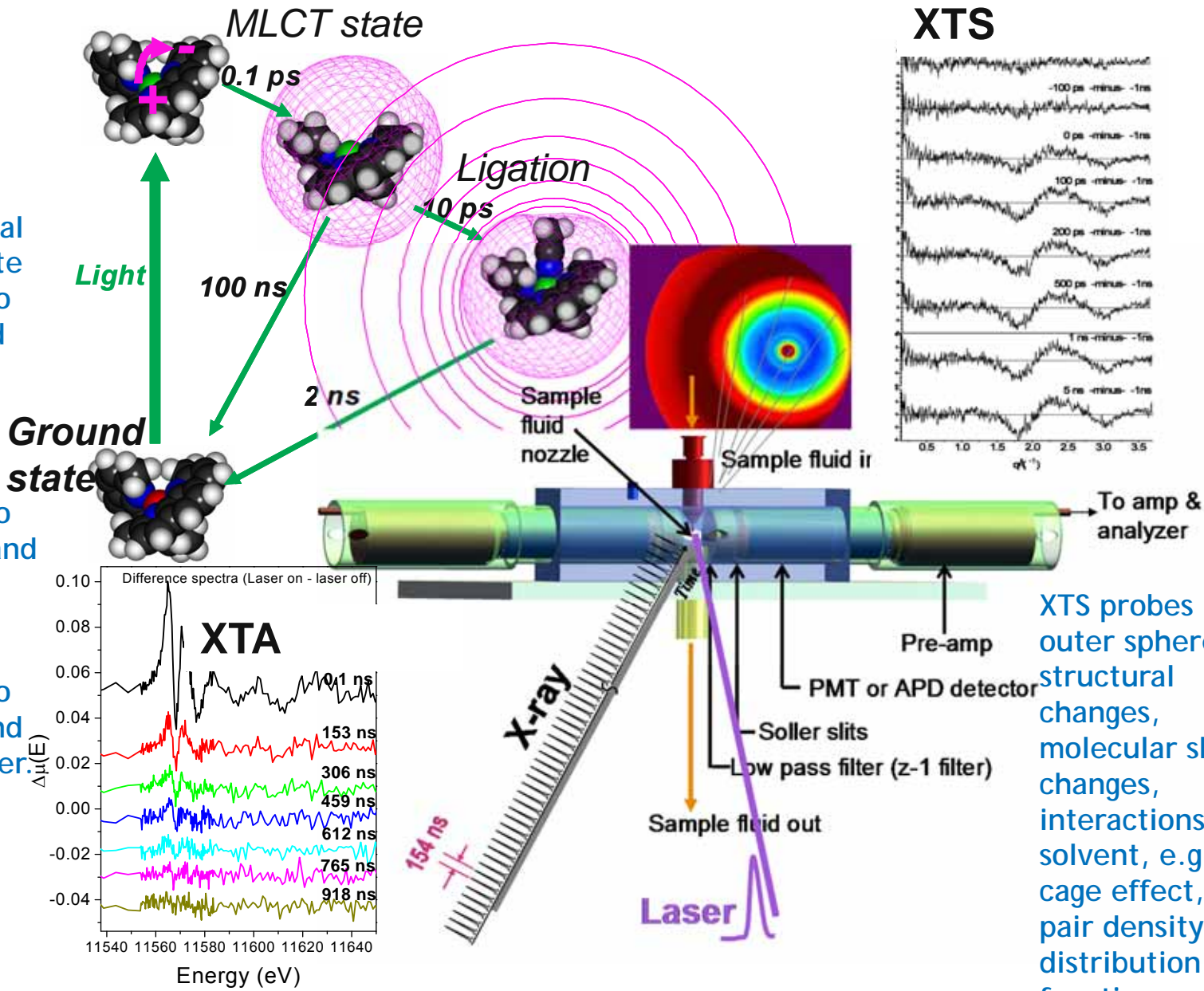
Ru-N(NCS) change with less hindrance.

## 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

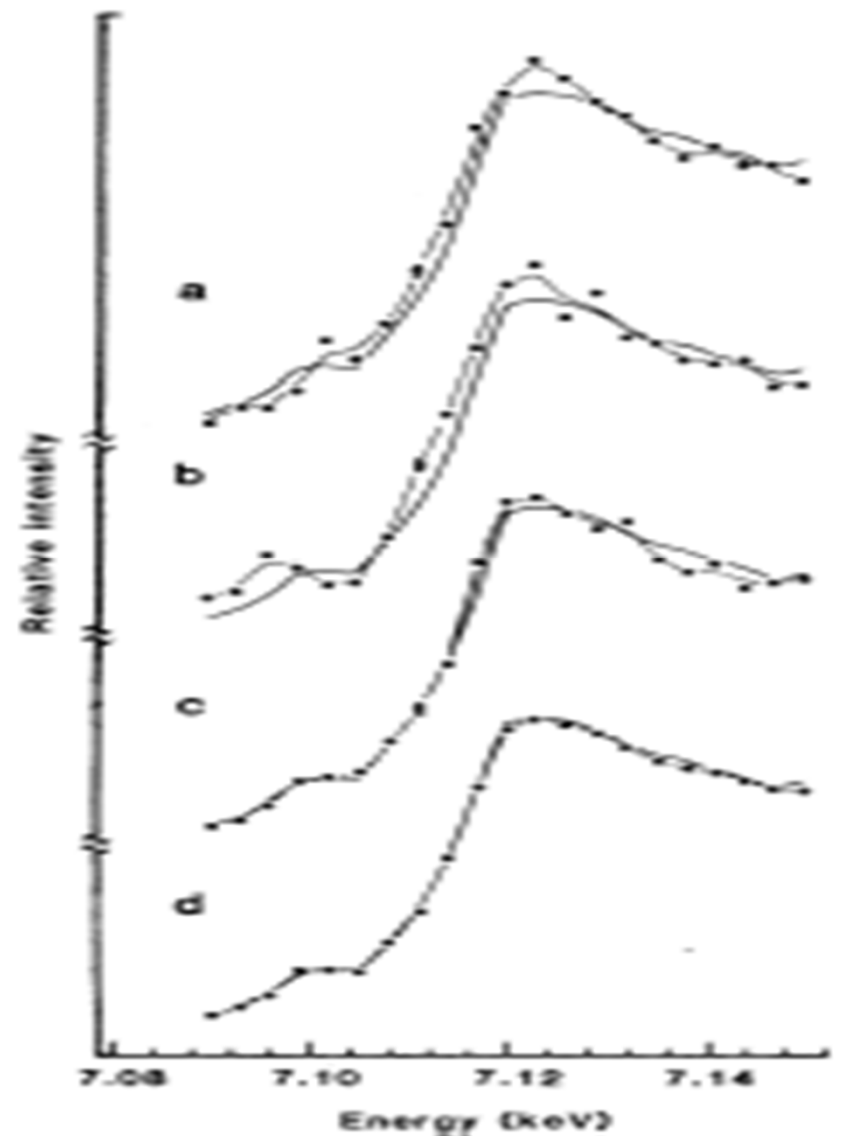
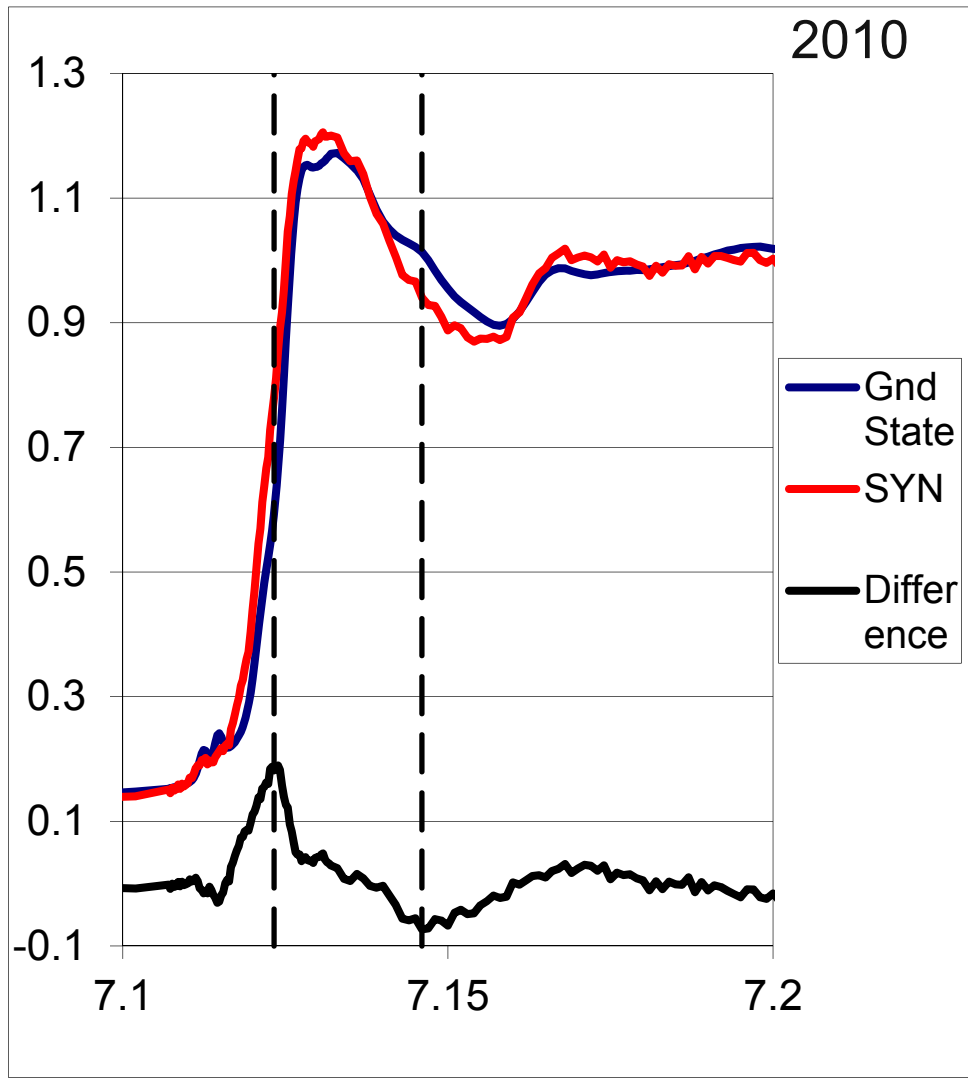
XTA probes inner sphere structural changes, metal oxidation state change due to photoinduced electron transfer, Coordination geometry change due to dissociation and ligation, and electronic structure change due to metal to ligand charge transfer.



XTS probes outer sphere structural changes, molecular shape changes, interactions with solvent, e.g. cage effect, and pair density distribution functions.

Science, (1984) 223 811-813

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



***Thank you.***