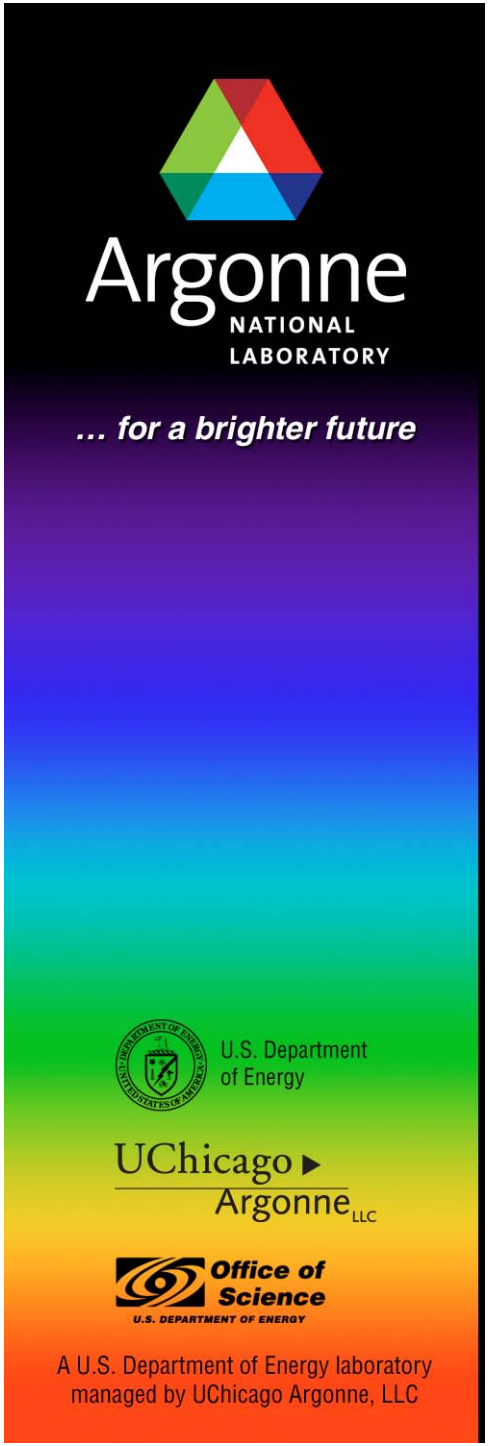


Short X-ray Pulse Workshop,
Argonne National Laboratory, February 15, 2008

Ultrafast Structural Dynamics and Reaction Control in Solar Energy Conversion Processes

Lin X. Chen, David M. Tiede, Klaus Attenkofer, Guy Jennings, Xiaoyi Zhang, Dijia Liu

Chemical Sciences and Engineering Division

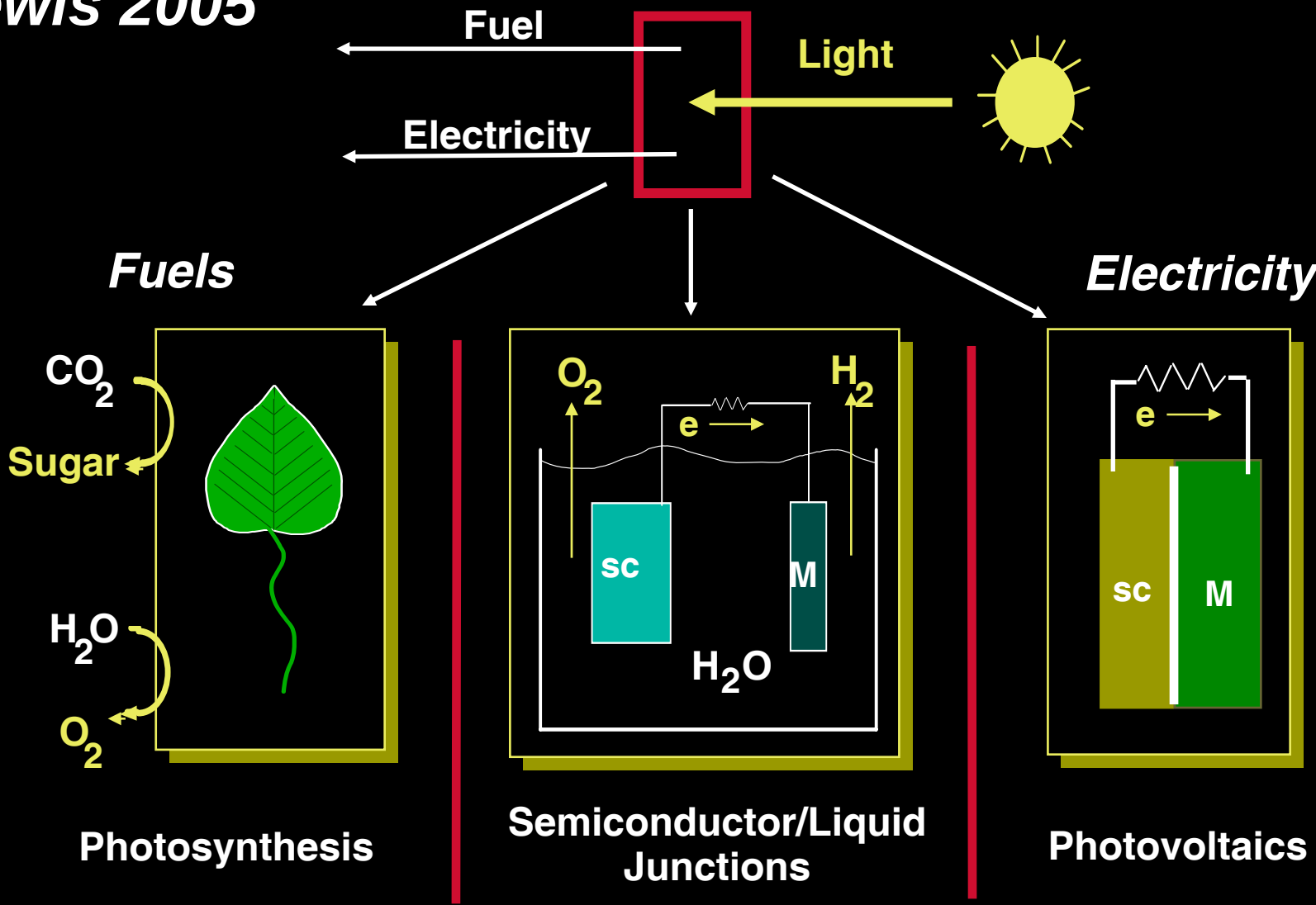
X-ray Science Division

Argonne National Laboratory

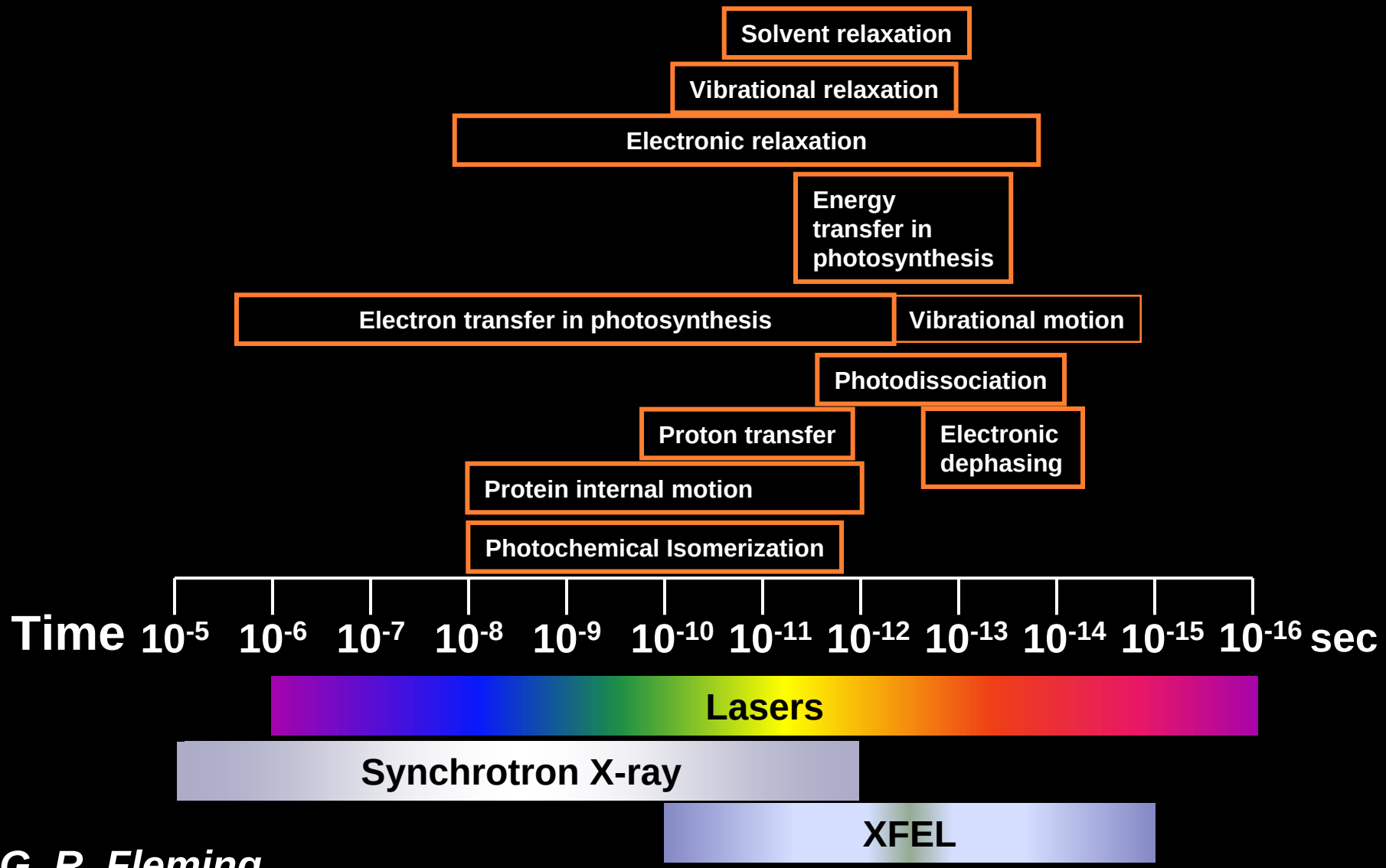
Department of Chemistry, Northwestern University

Energy Conversion Strategies

Lewis 2005



Multiple Temporal Scales in Solar Energy Conversion



G. R. Fleming
1986

Light harvesting protein array

B850→B850
100-200 fs

B800-B850
1.2 ps

LHI-RC
35 ps

LH-I

LH-II

LH-II

LH-II→LH-I
3-5 ps

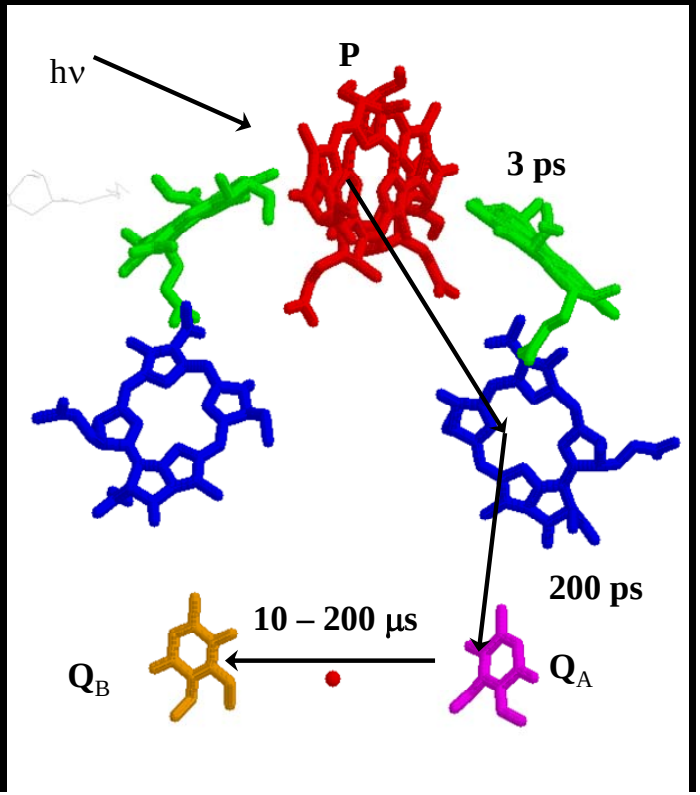
B800→B800
500 fs

LH-II

RC

Bacterial photosynthetic reaction center protein (RC)

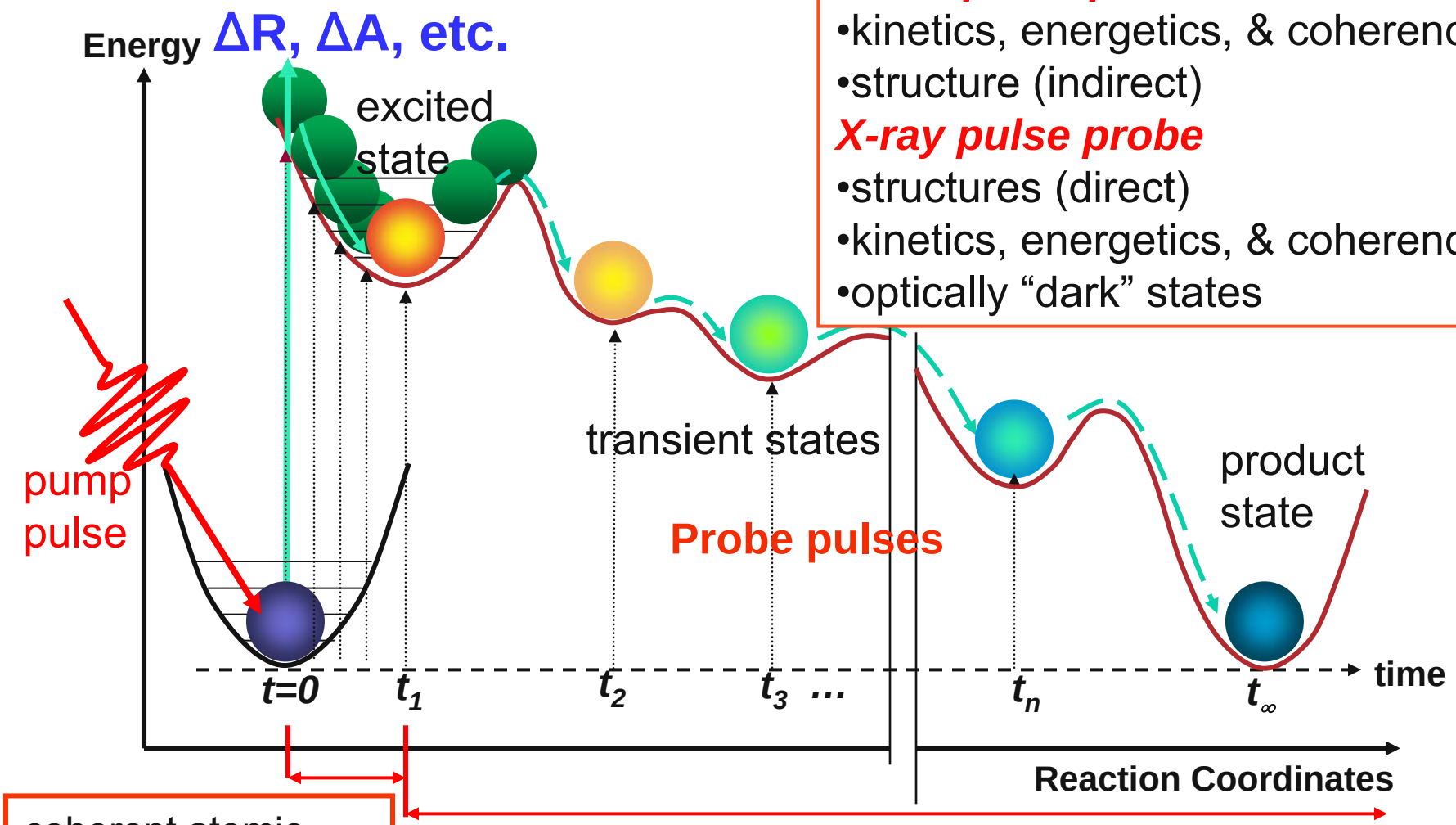
Photoinduced electron transfer cascade



The dream: "Seeing" molecules along reaction coordinates, and being able to understand and control reaction pathways.

Laser pulse probe
- kinetics, energetics, & coherence
- structure (indirect)

X-ray pulse probe
- structures (direct)
- kinetics, energetics, & coherence
- optically "dark" states



coherent atomic motions → "molecular movie"

incoherent atomic motions leading to discrete thermally equilibrated transient states → "molecular snapshots"

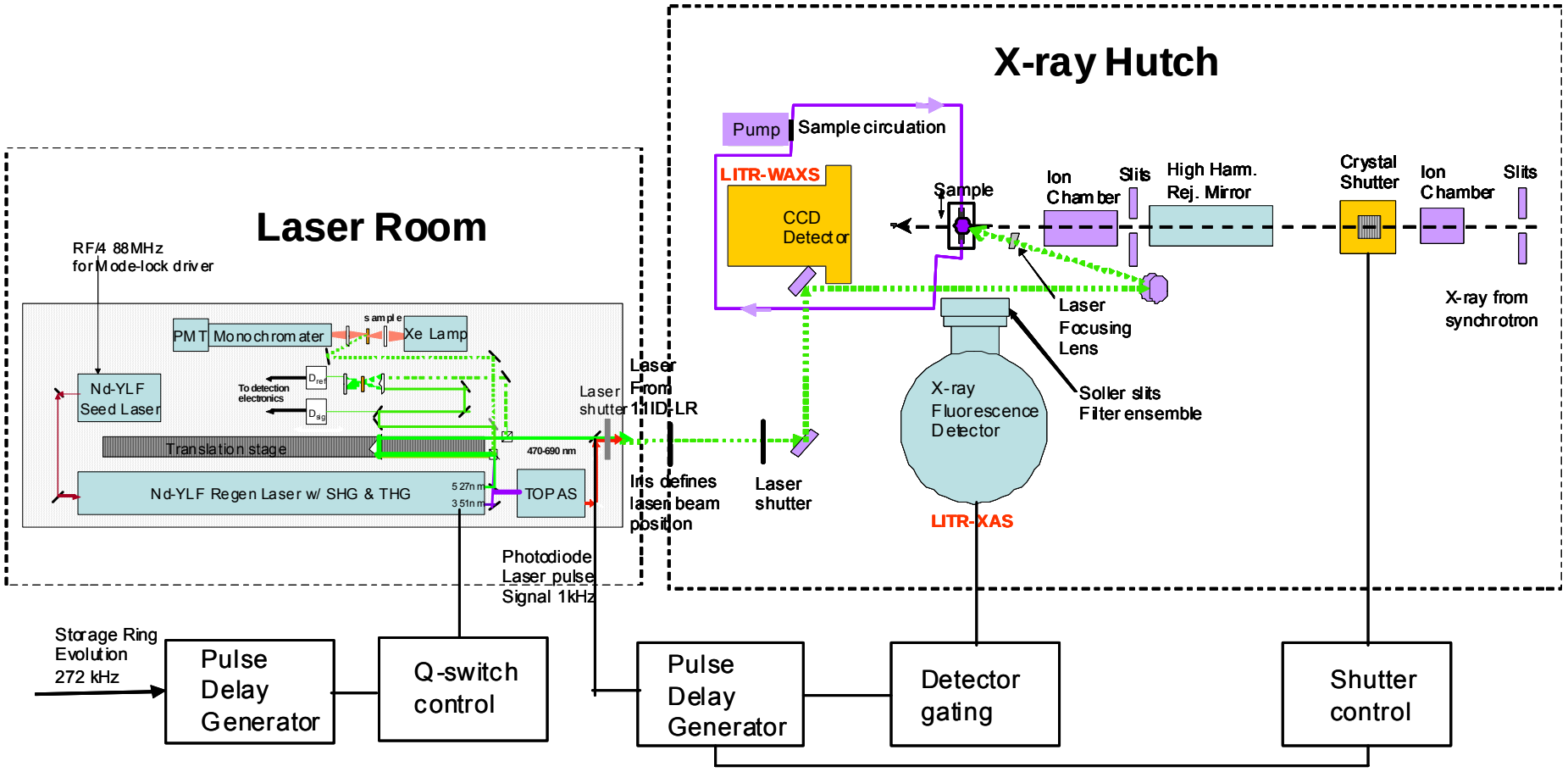


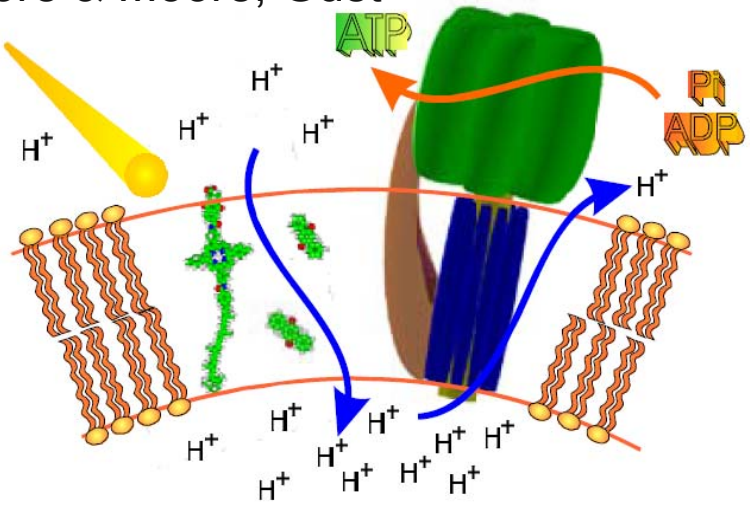
Fig. 3. Current XTA setups at Beamline 11-ID-D of the APS (LITR, laser-initiated time-resolved). The laser room (left) has three operating modes, 1) XAS/WAXS(wide-angle x-ray scattering), 2) nanosecond photolysis, and 3) picosecond pump-probe transient absorption, marked by a solid line, a thick dotted line and thin dotted line, respectively. The x-ray hutch (right) can host both XAS and WAXS experiments.

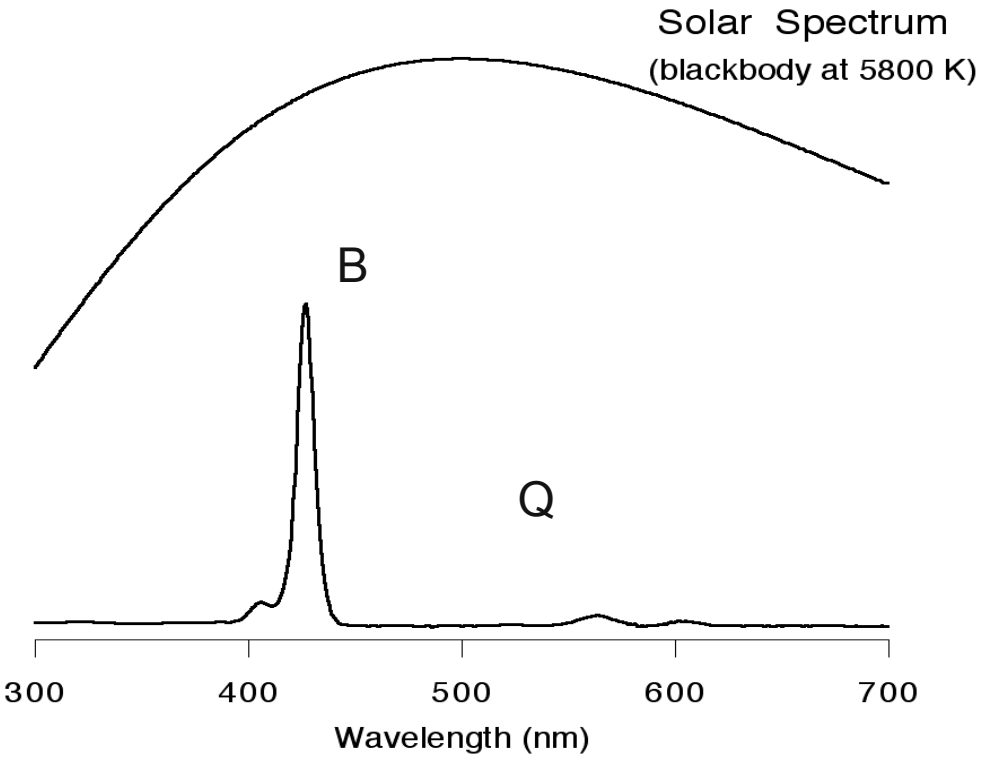
Outline

- ***Studying ultrafast structural dynamics with ultrafast lasers and x-rays***
- ***Light conversion by metal complexes***
- ***Light conversion at interfaces (New)***
- ***Light conversion in nanoscale organic photovoltaic materials (New)***
- ***Control reactions by light***
- ***Perspective***

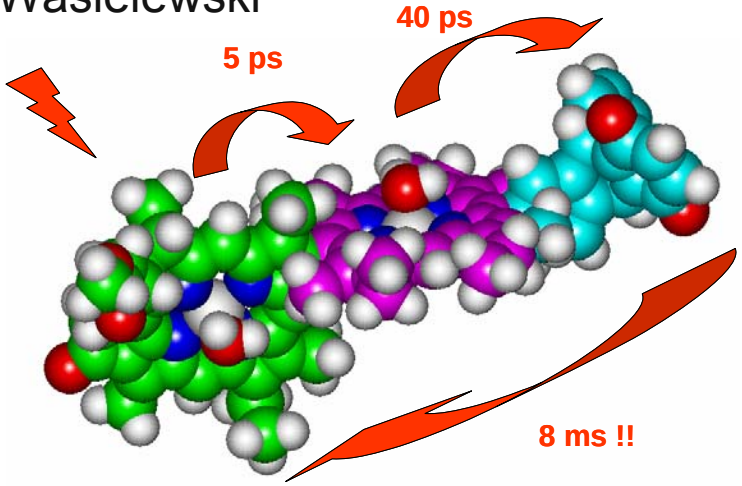
Light conversion by metalloporphyrins

Moore & Moore, Gust

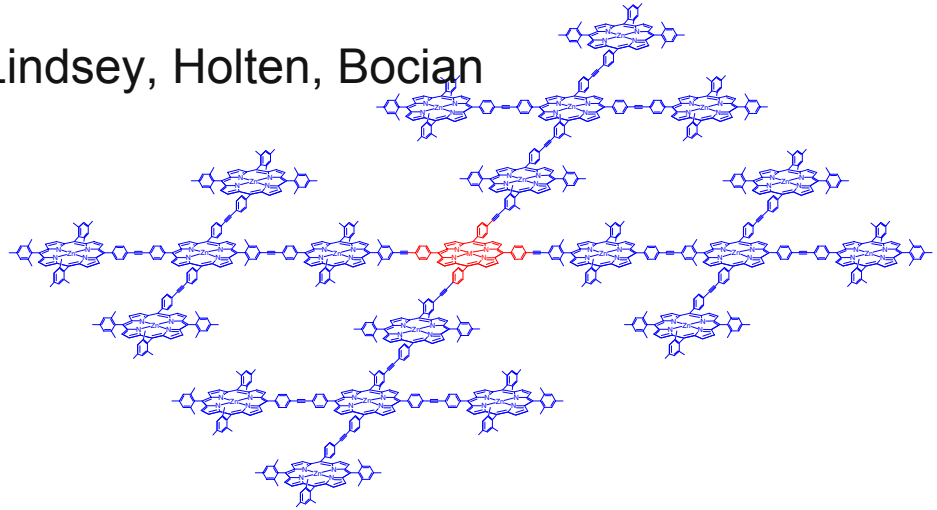




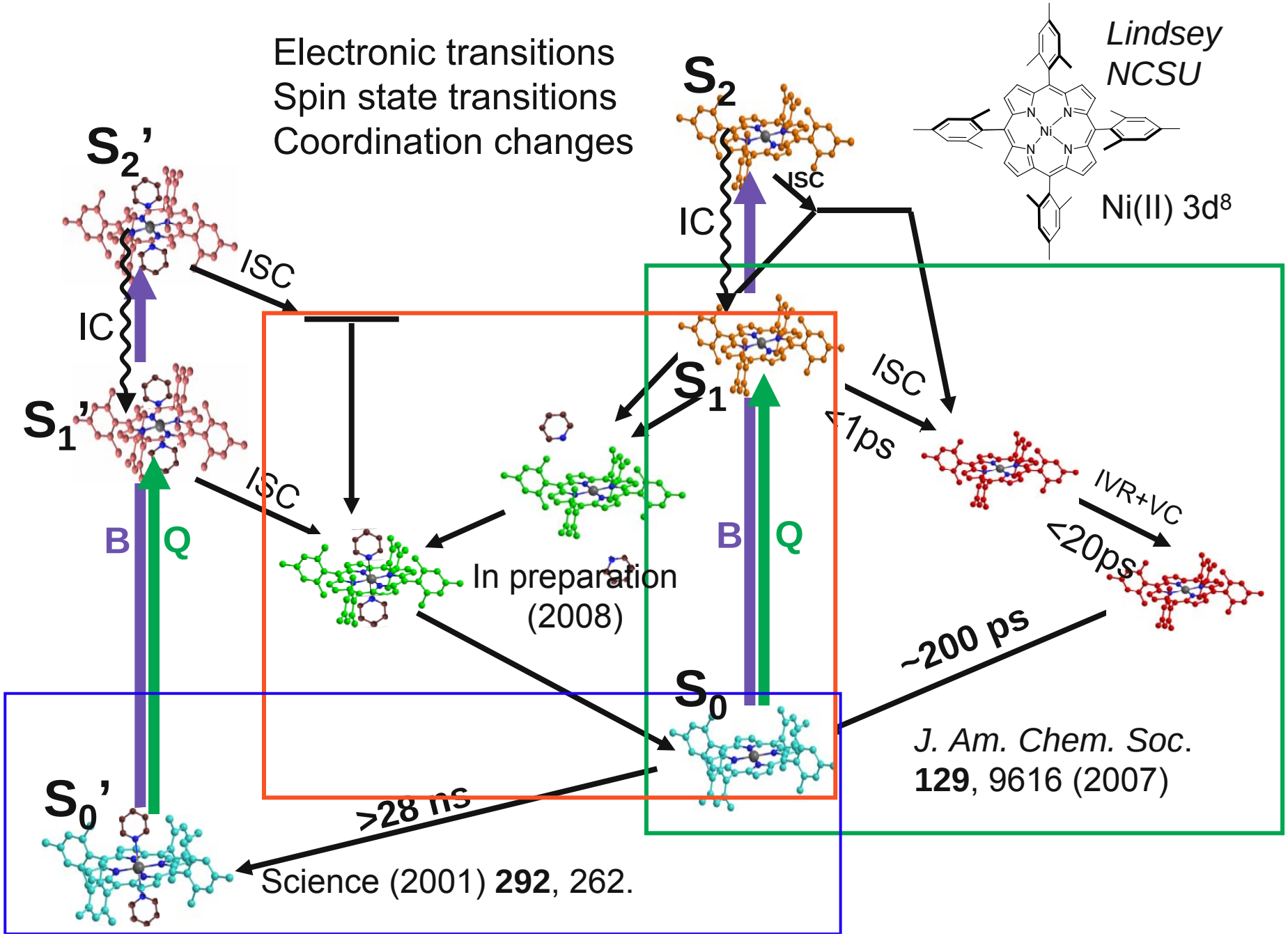
Wasielewski



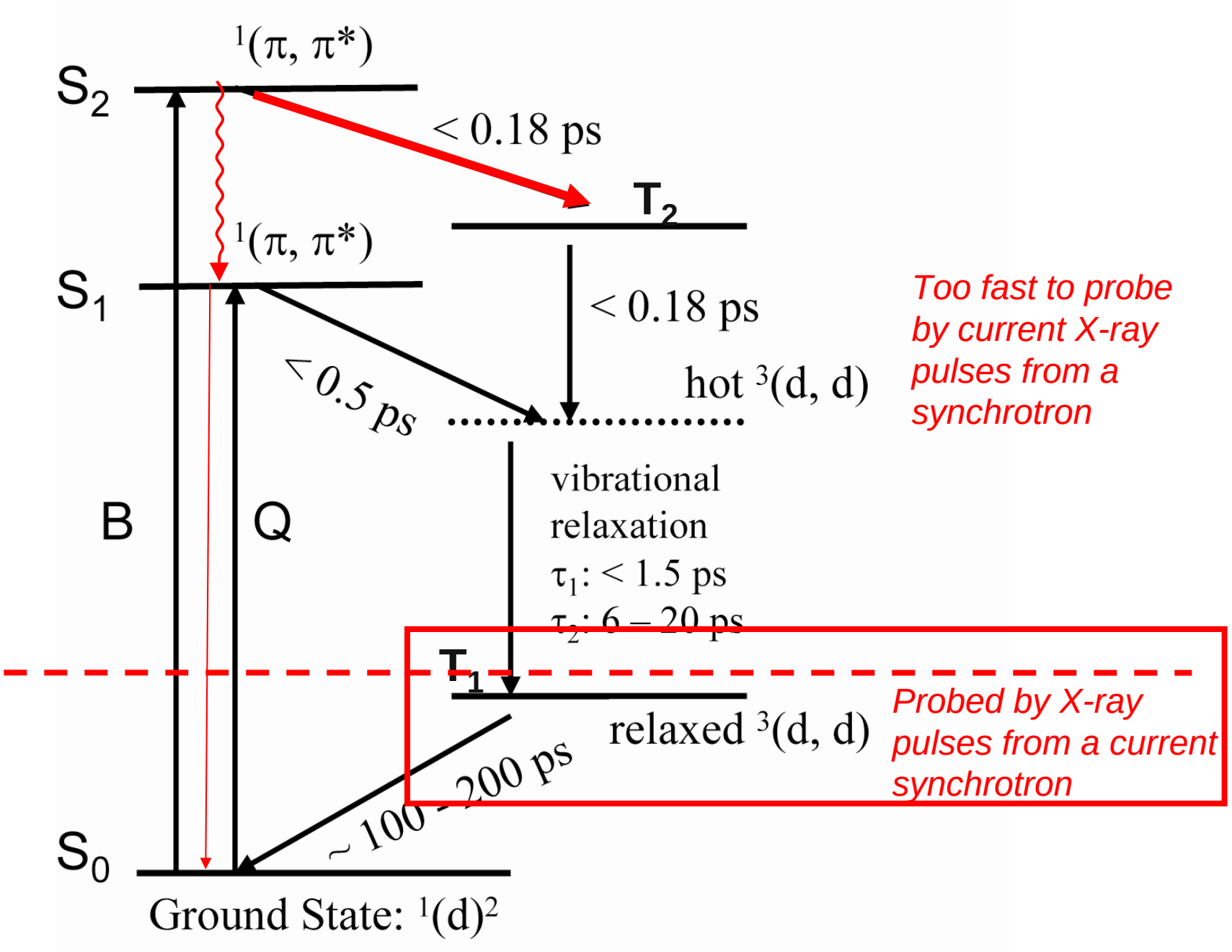
Lindsey, Holten, Bocian



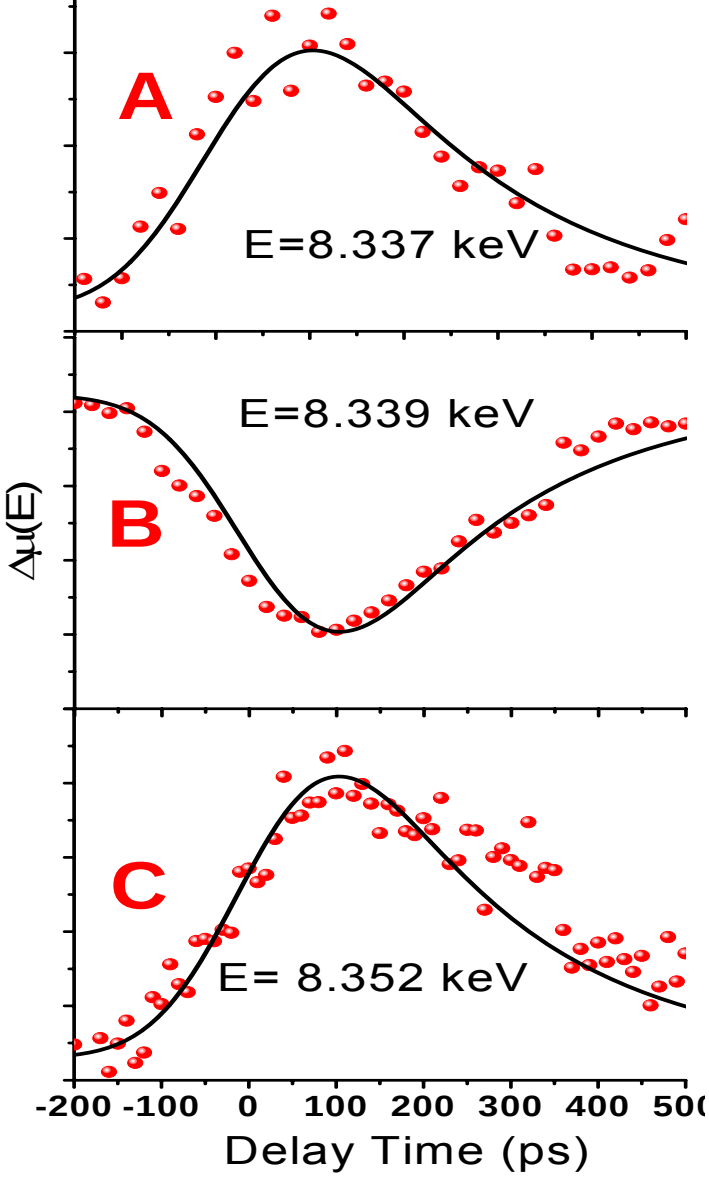
Light conversion by metalloporphyrins

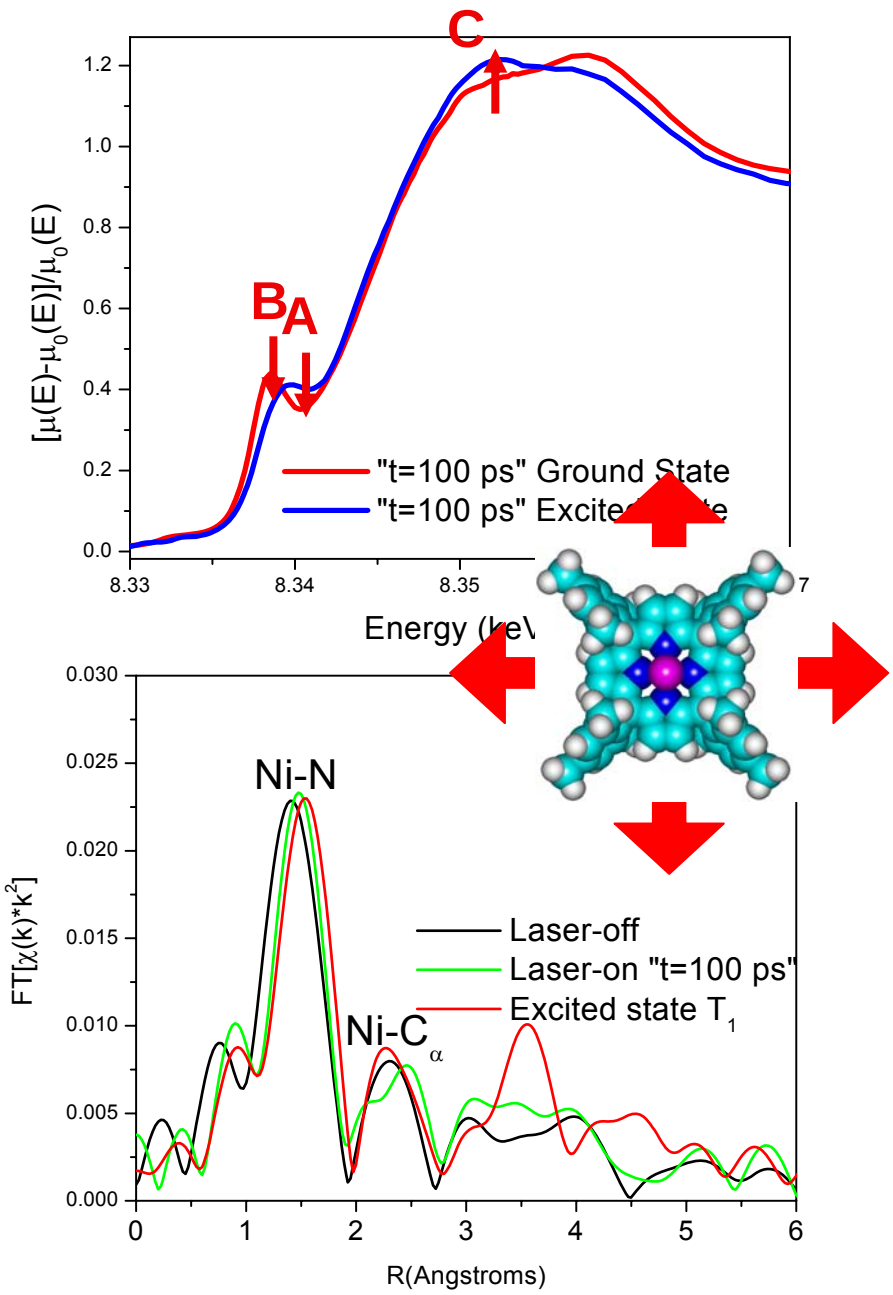


Light conversion by metalloporphyrins



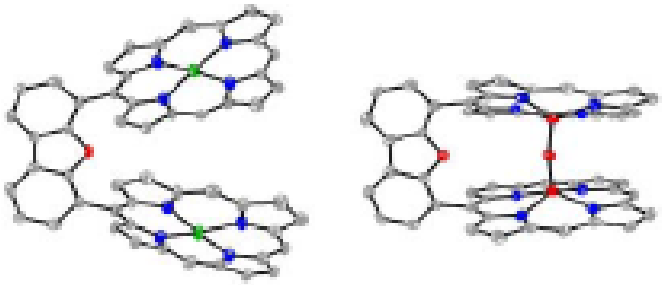
Light conversion by metalloporphyrins

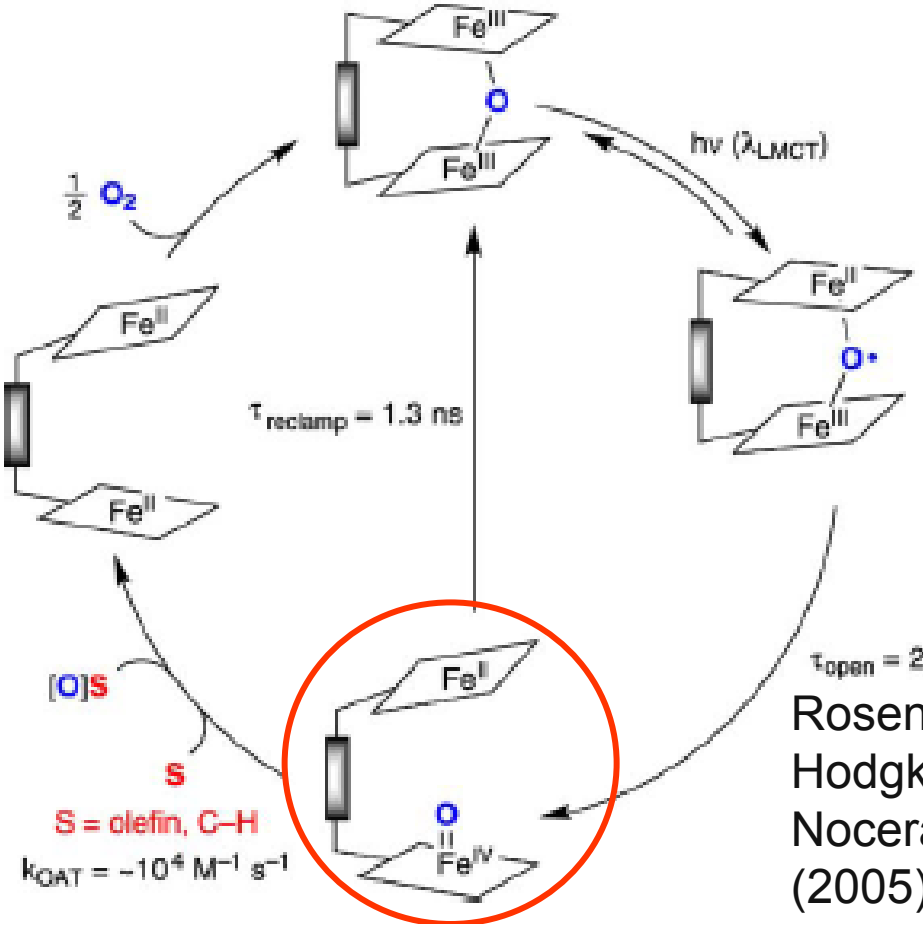




correlation/coherence studies using shorter X-ray pulses

Photocatalysis dynamics of Pacmanporphyrins





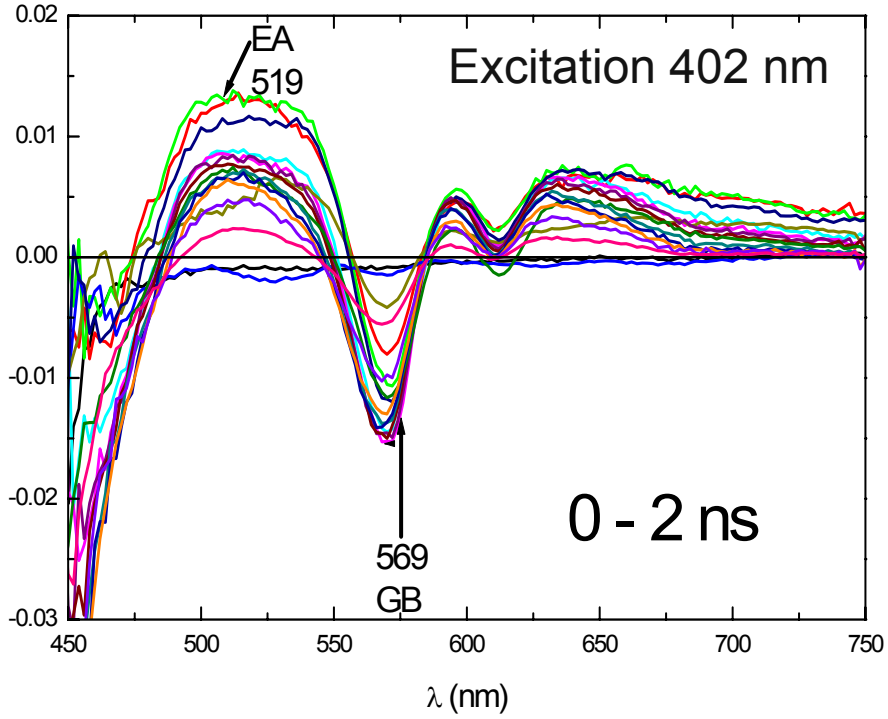
In the absence of the substrate*: Capturing high oxidation Fe(IV) (a key reactant in understanding the mechanism, implication in enzymatic reactions).*

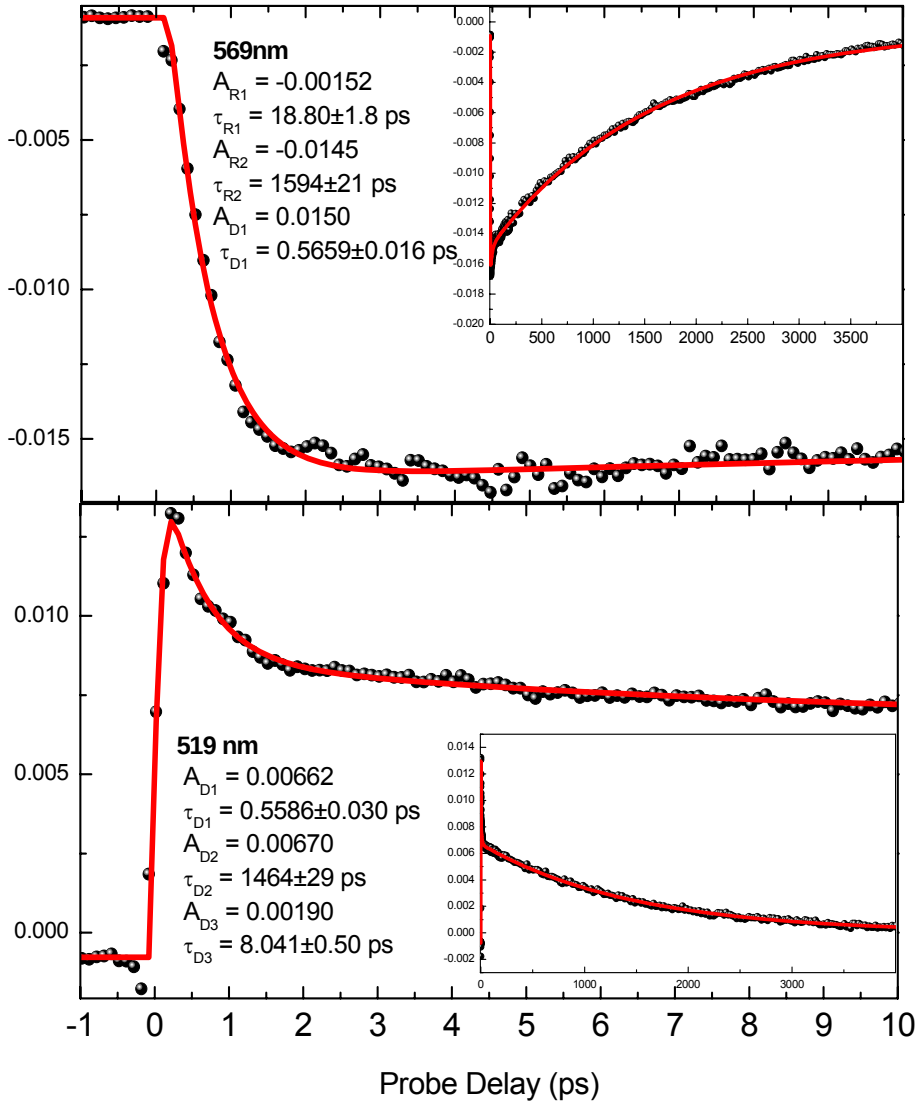
In the presence of the substrate*: Intermediate structure of the substrate/catalyst complex and recovery of the catalyst.*

Rosenthal, Bachman, Dempsey, Esswein, Gray, Hodgkiss, Manke, Luckett, Pistorio, Veige, Nocera, Coordination Chemistry Reviews 249 (2005) 1316–1326.

Photocatalysis dynamics of Pacmanporphyrins

Pacman photocatalysis and intermediate structures

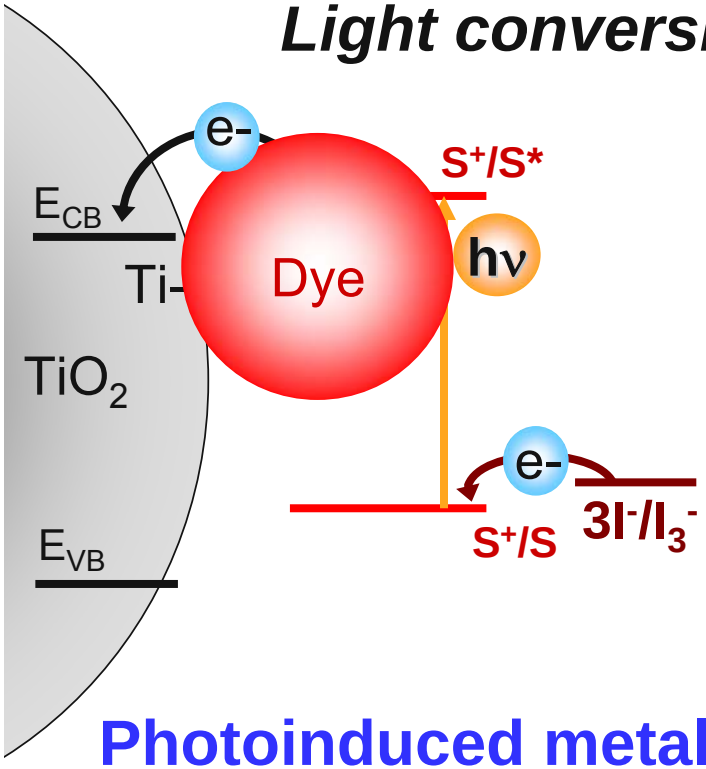


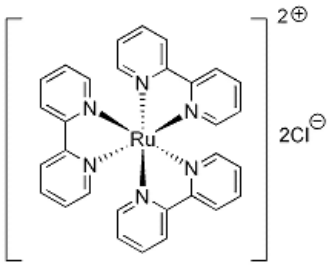


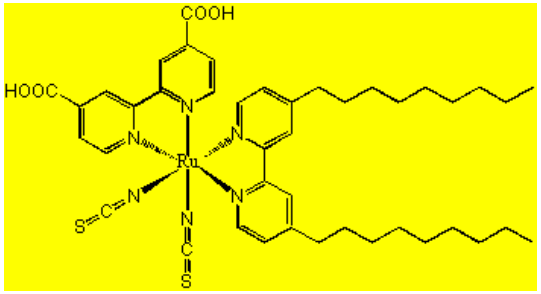
0.55 ps →LMCT
8-19 ps → Pacman opens
1.5 ns → Pacman closes

J. M. Hodgkiss, C. J. Chang, Bradford J. Pistorio, and Daniel G. Nocera, Inorg. Chem (2003)

Light conversion by transition metal complexes







M. Grätzel, Nature 2001, 414, 338–344.

B. O'Regan, M. Grätzel, Nature 1991, 353, 737–740

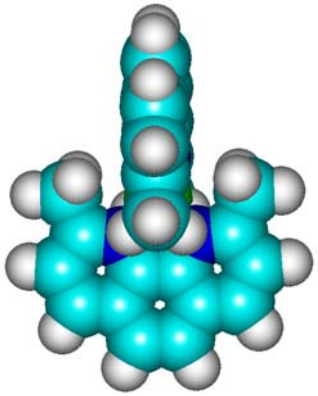
Photoinduced metal-to-ligand-charge-transfer (MLCT)

$$[Ru^{II}(bpy)_3]^{+2} \xrightarrow{h\upsilon} [Ru^{III}(bpy^-)(bpy)_2]^+$$ Expensive!

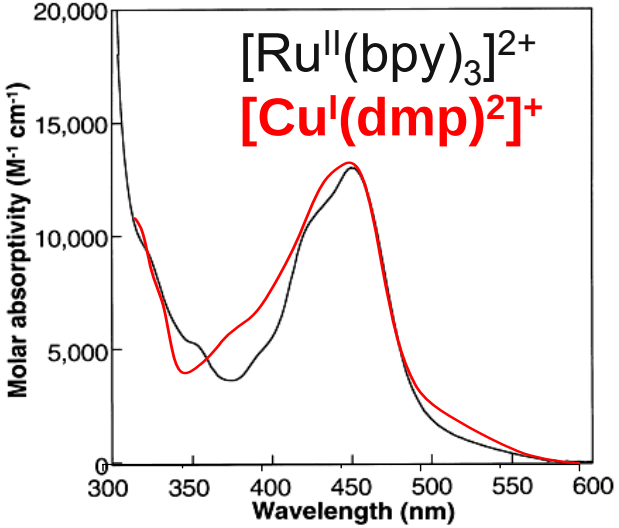
$$[Cu^{I}(dmp)_2]^{+} \xrightarrow{h\upsilon} [Cu^{II}(dmp^-)(dmp)]^+$$ Replacement?

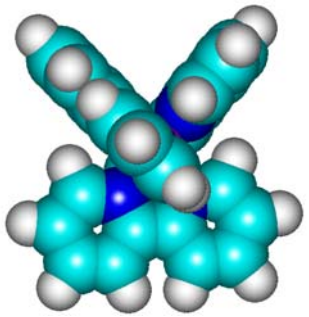
$3d^{10}$ $3d^{9}$

Light conversion by transition metal complexes

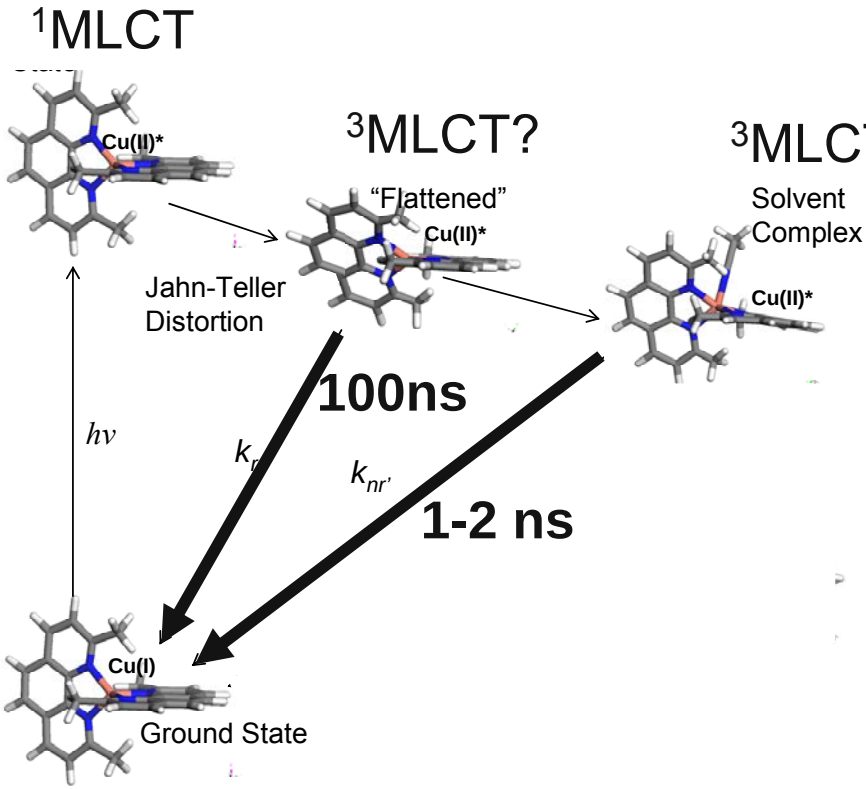


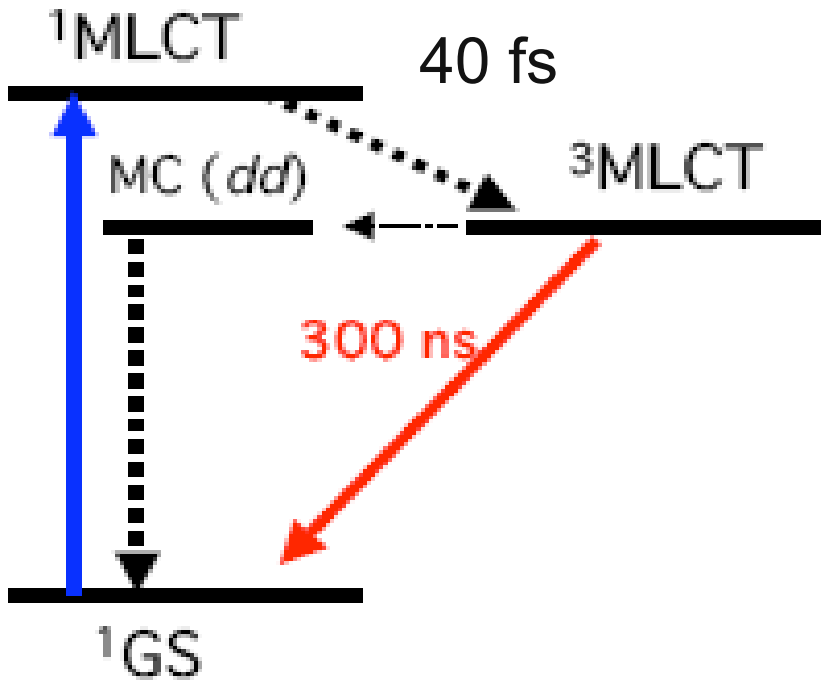
$[Cu^{I}(dmp)^{2}]^{+}$



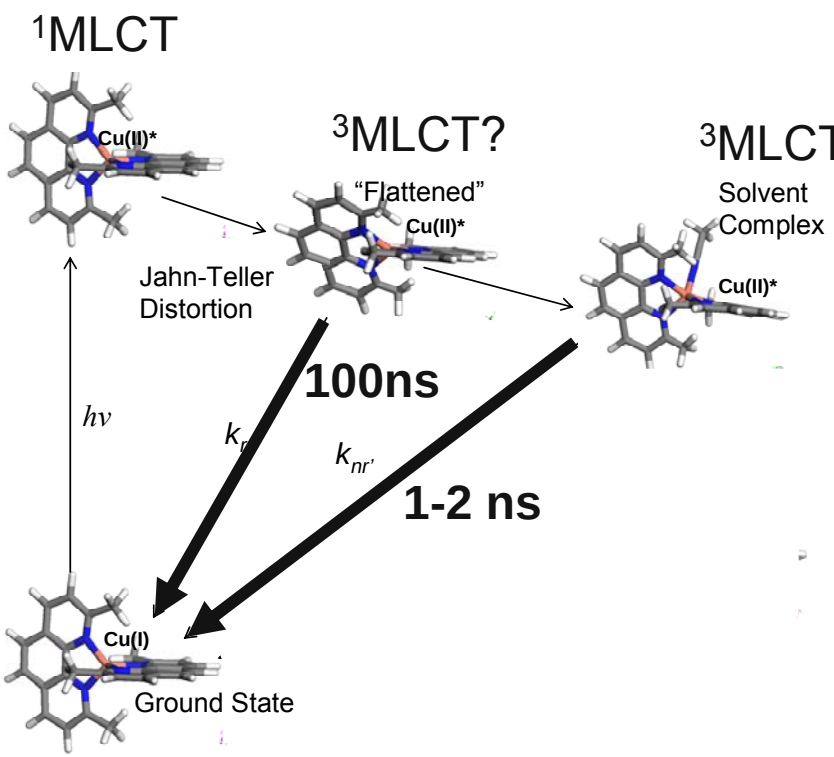


$[Ru^{II}(bpy)_3]^{2+}$

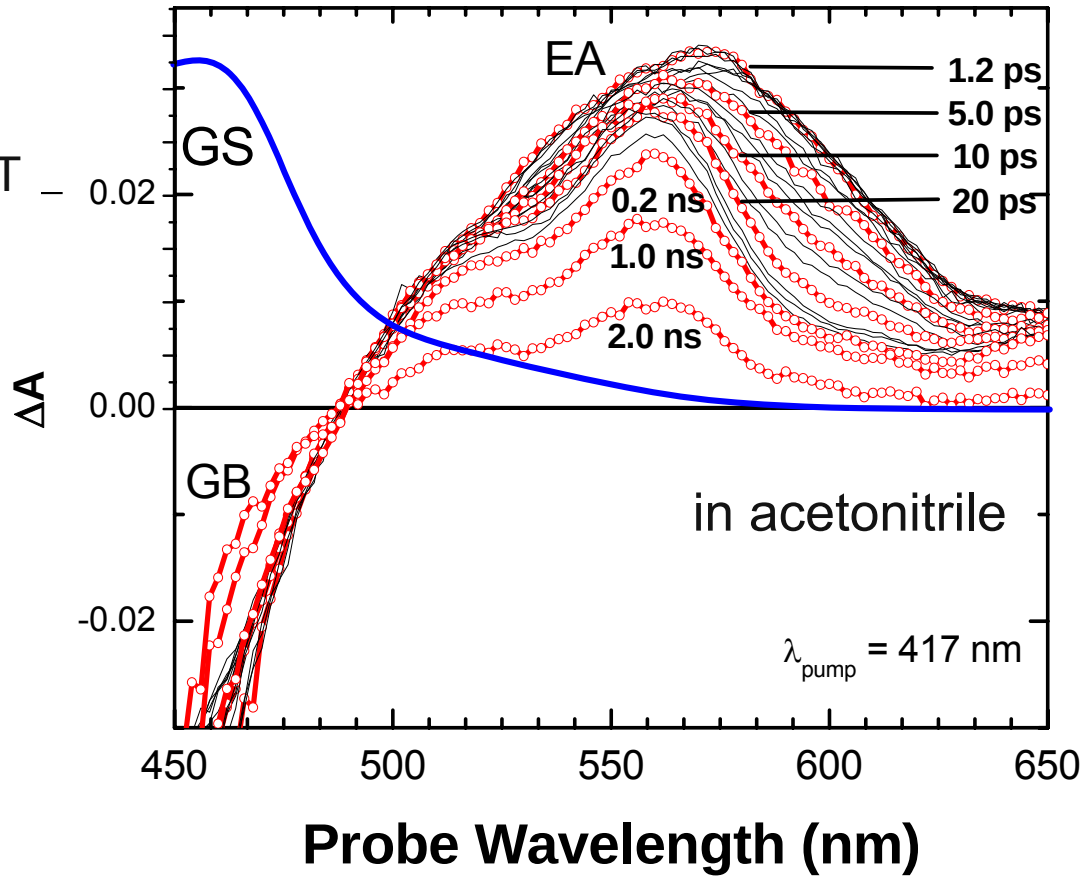




Light conversion by transition metal complexes



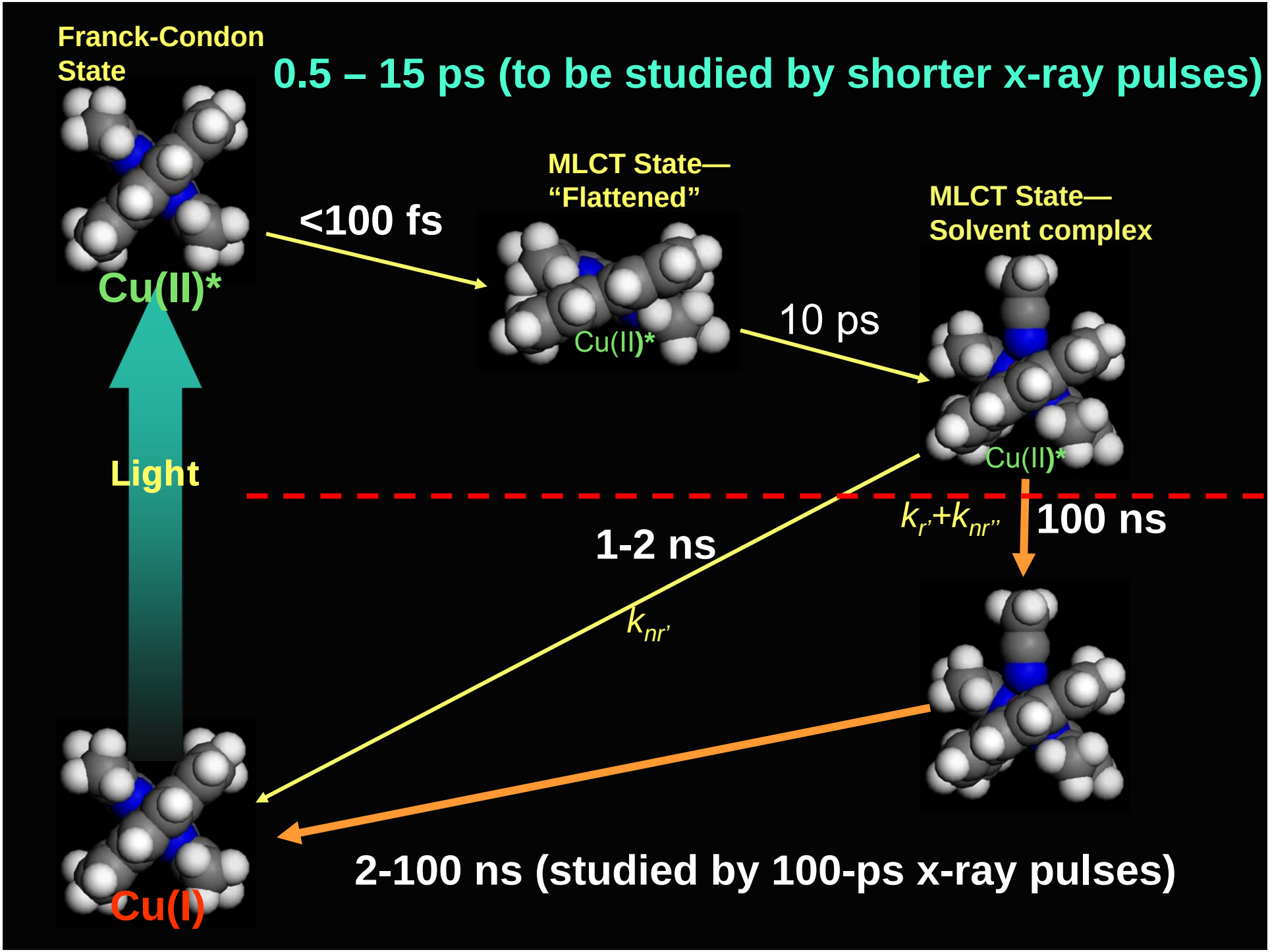
Ultrafast transient absorption of Cu(I)(dmp)$^{2+}$



***τ1* = 500 – 700 fs;**
EA rise, broad & featureless
Solvent independent
isc? (i.e. Ru(bpy)32+)

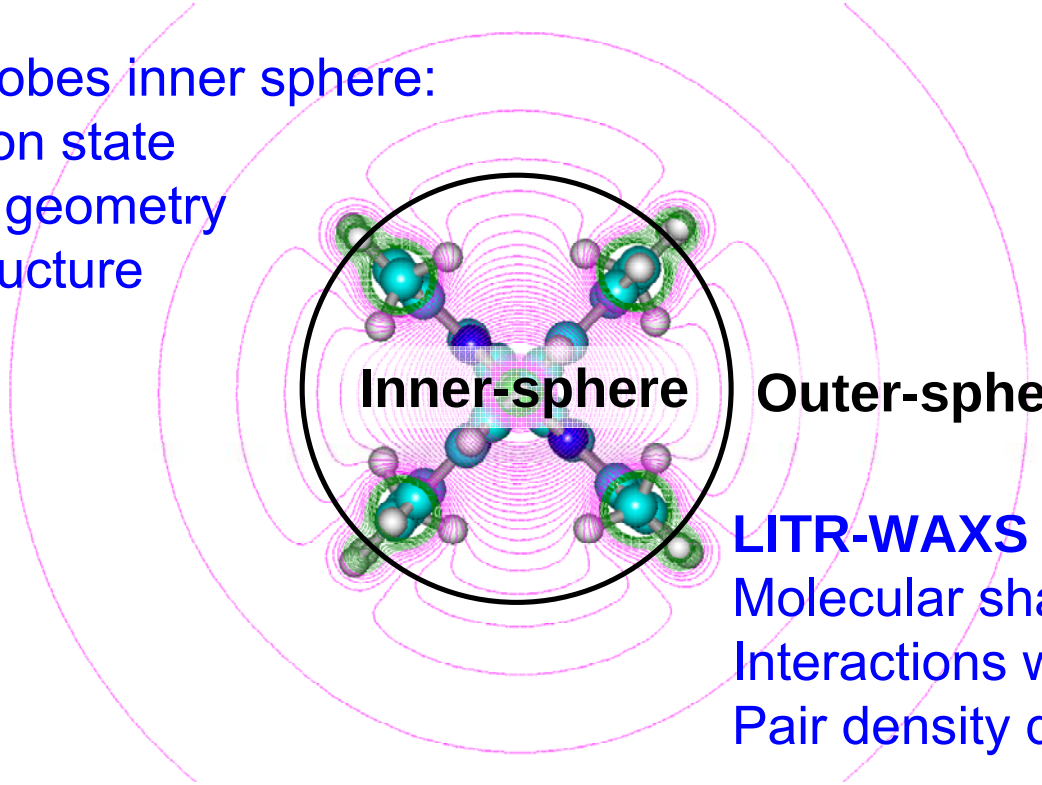
***τ2* = 10 – 15 ps**
EA blue-shift & narrowing
Solvent independent
Flattening?
Vibrational cooling?

τ3 = 2 -100 ns
Solvent dependent
ES population decay


Franck-Condon State
0.5 – 15 ps (to be studied by shorter x-ray pulses)
MLCT State—"Flattened"
MLCT State—Solvent complex
<100 fs
10 ps
Cu(II)*
Cu(II)*
Cu(II)*
Light
$k_{r'}+k_{nr''}$
100 ns
1-2 ns
$k_{nr'}$
Cu(I)
2-100 ns (studied by 100-ps x-ray pulses)

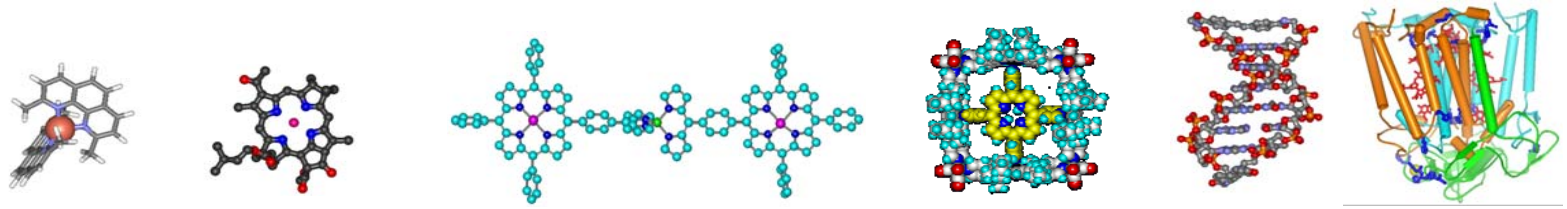
Solute-solvent interface structural dynamics

LITR-XAS probes inner sphere:
Metal oxidation state
Coordination geometry
Electronic structure

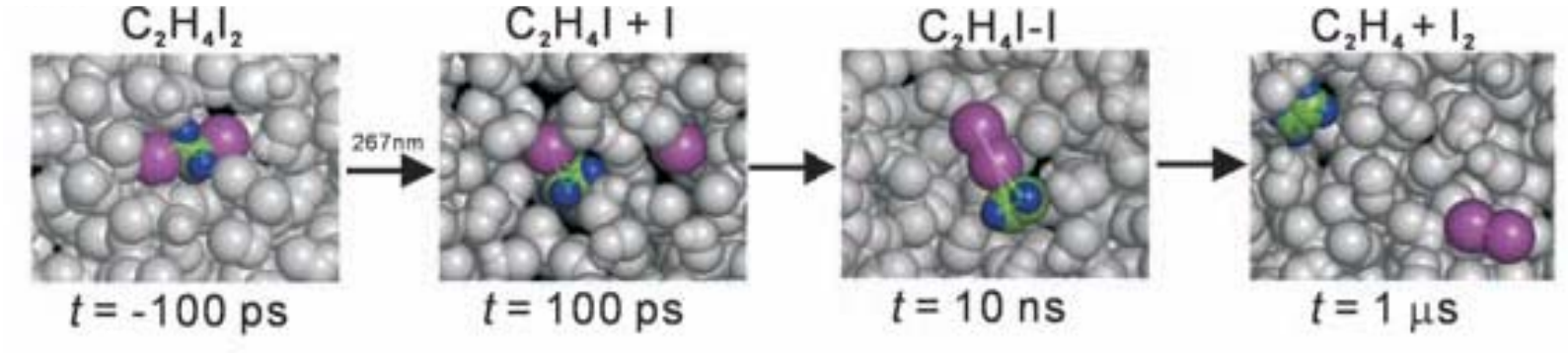


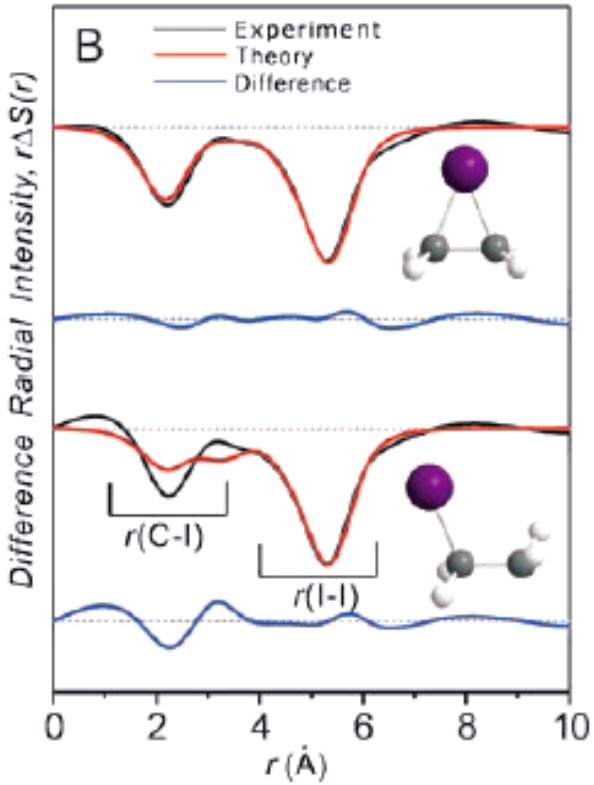
LITR-WAXS probes outer sphere:
Molecular shape
Interactions with solvent
Pair density distribution functions

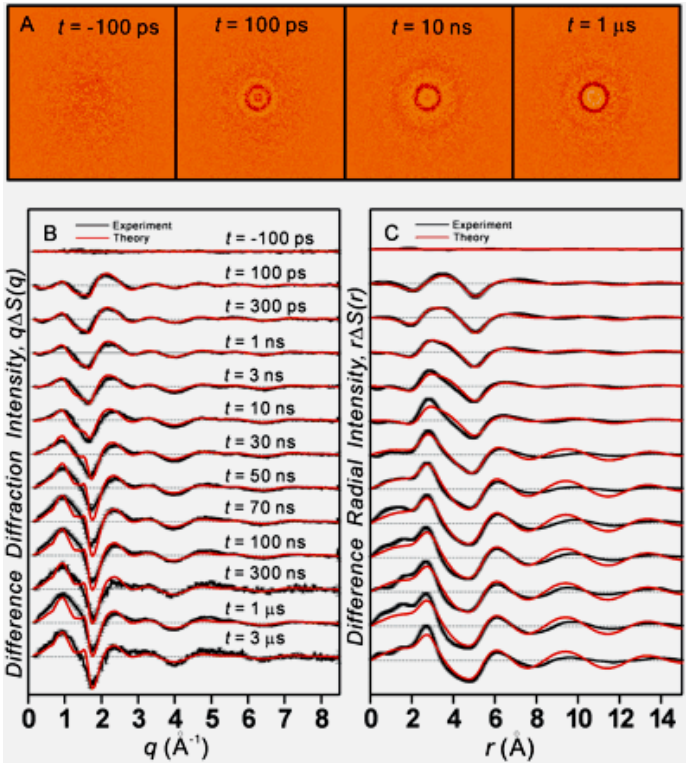
Combined LITR-XAS/WAXS with results of WAXS on $Cu(dmp)_2^+$(Tiede)



Solute-solvent interface structural dynamics

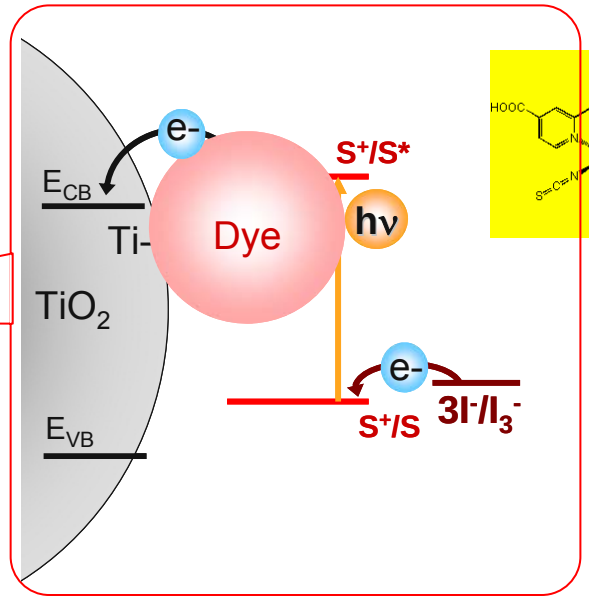


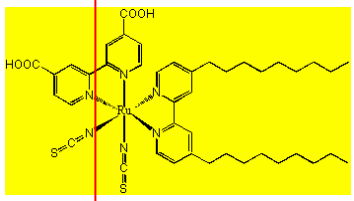


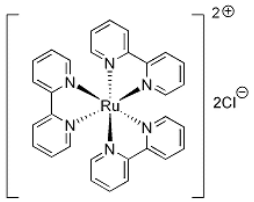


H. Ihee, M. Lorenc, T. K. Kim, Q. Y. Kong, M. Cammarata, J. H. Lee, S. Bratos, M. Wulff Science (2005) 309, 1223.*

Interfacial Structural Dynamics in Solar Electricity Generation

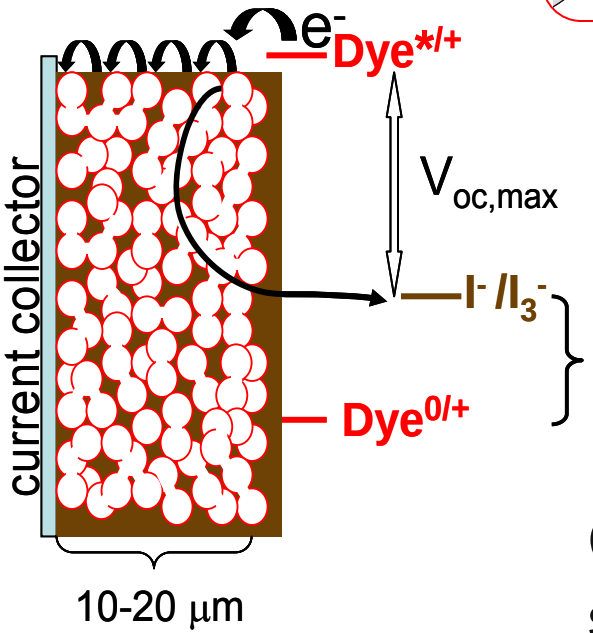






M. Grätzel, Nature 2001, 414, 338–344.

B. O'Regan, M. Grätzel, Nature 1991, 353, 737–740



Photoinduced metal-to-ligand-charge-transfer (MLCT)

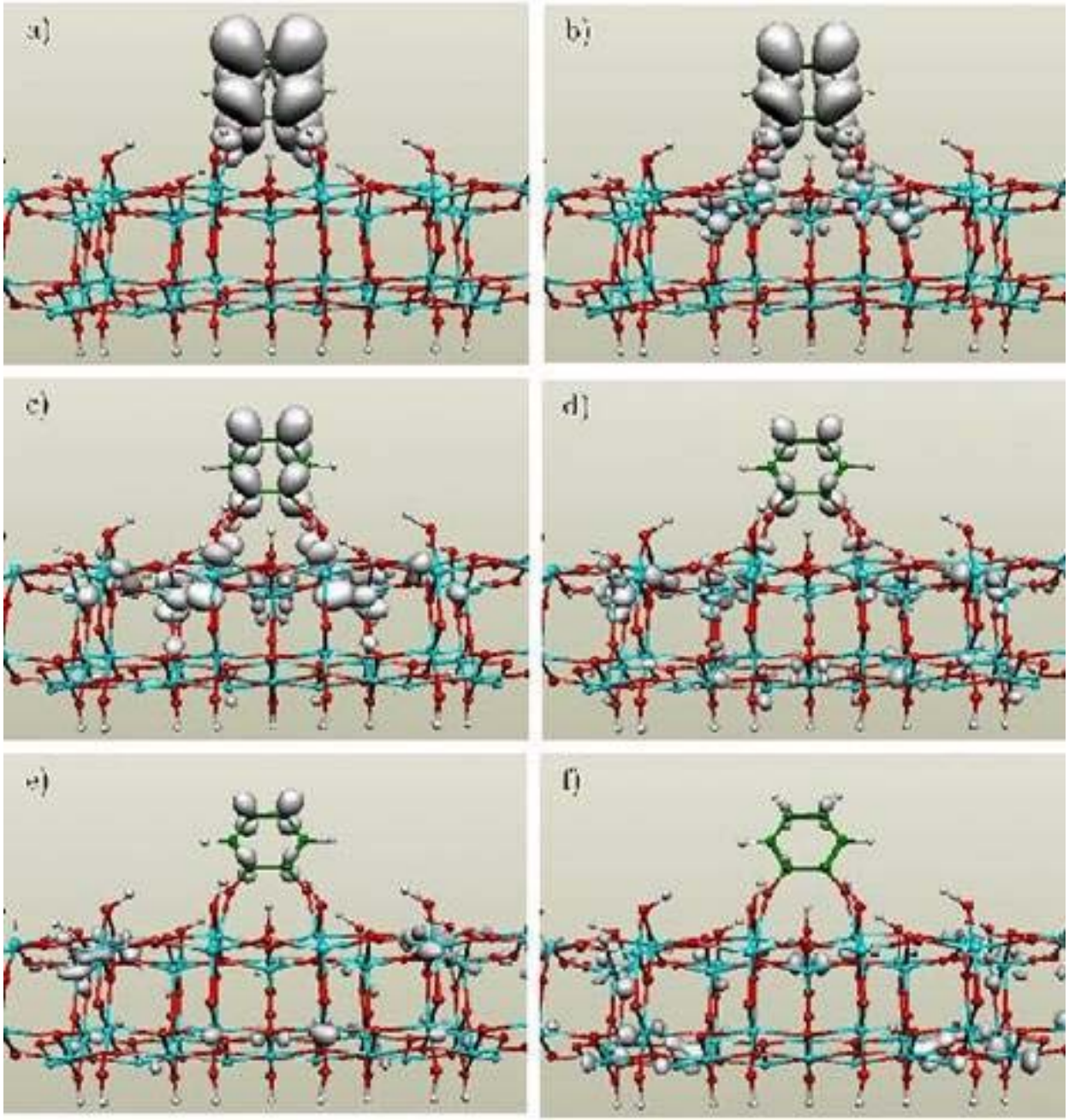
$$[Ru^{II}(bpy)_3]^{+2} \xrightarrow{h\upsilon} [Ru^{III}(bpy^-)(bpy)_2]^+$$

Expensive!

Change structures to optimize V_{oc}?

Low cost, more abundant replacement?

Interfacial Structural Dynamics in Solar Electricity Generation

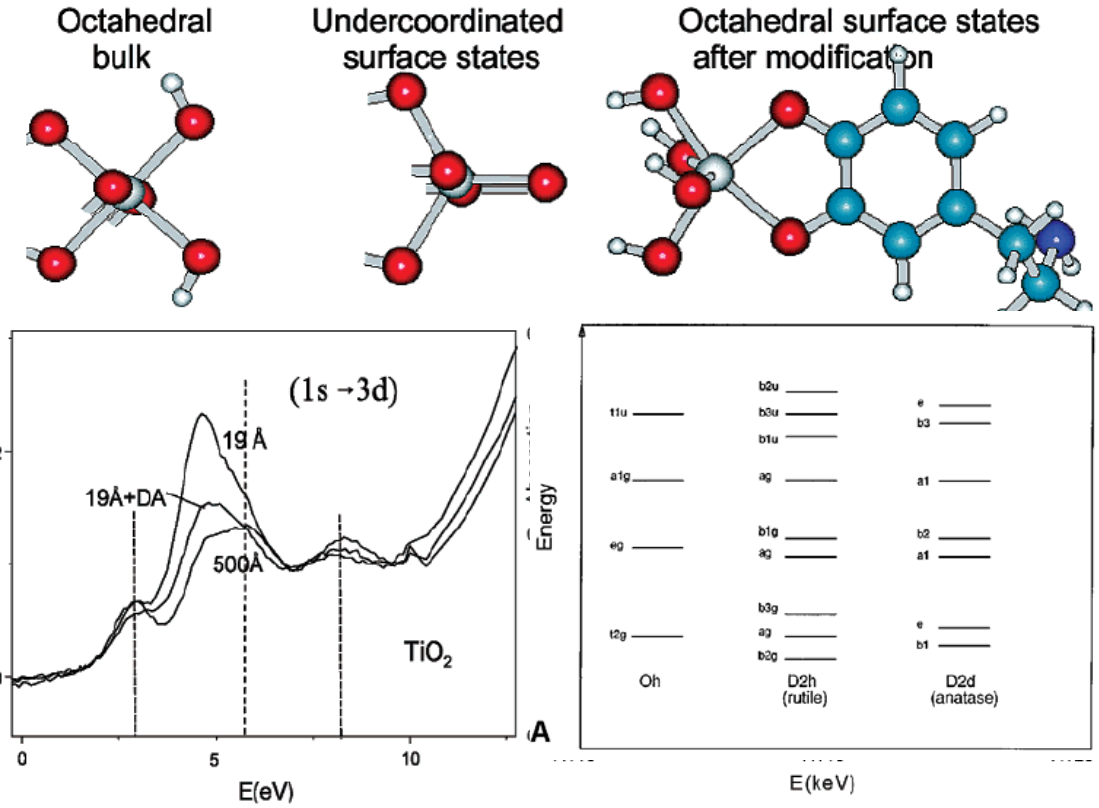


Photoinduced electron injection from a dye molecule at the organic-inorganic interface.

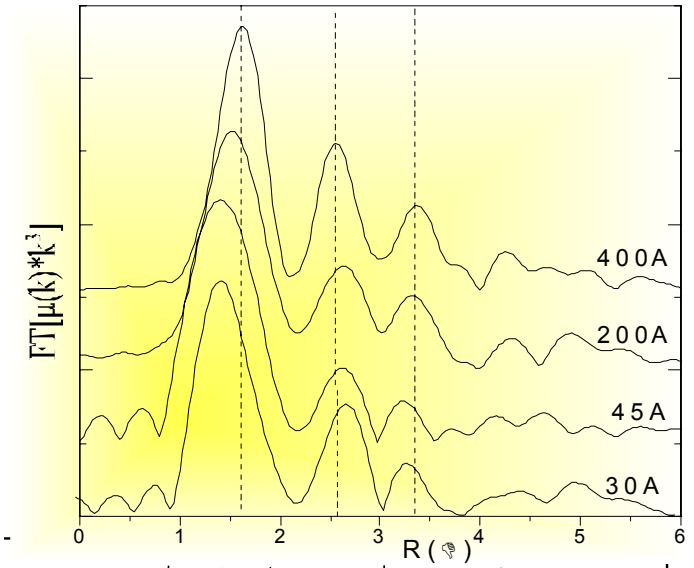
Prof. Victor S. Batista
Chemistry Department
Yale University

Calculated snapshots of the instantaneous electronic iso-density surface at intervals of 2.5 fs during the photo-induced interfatial electron transfer in a functionalized TiO2 semiconductor nanostructure.

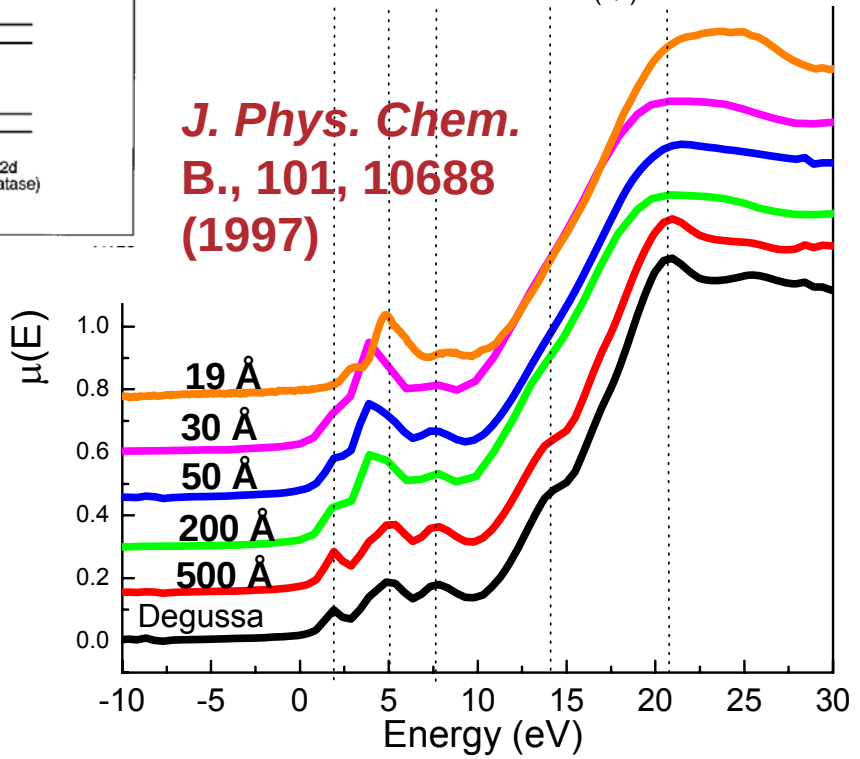
Interfacial Structural Dynamics in Solar Electricity Generation



J. Phys. Chem. B **106 10543 (2002).**



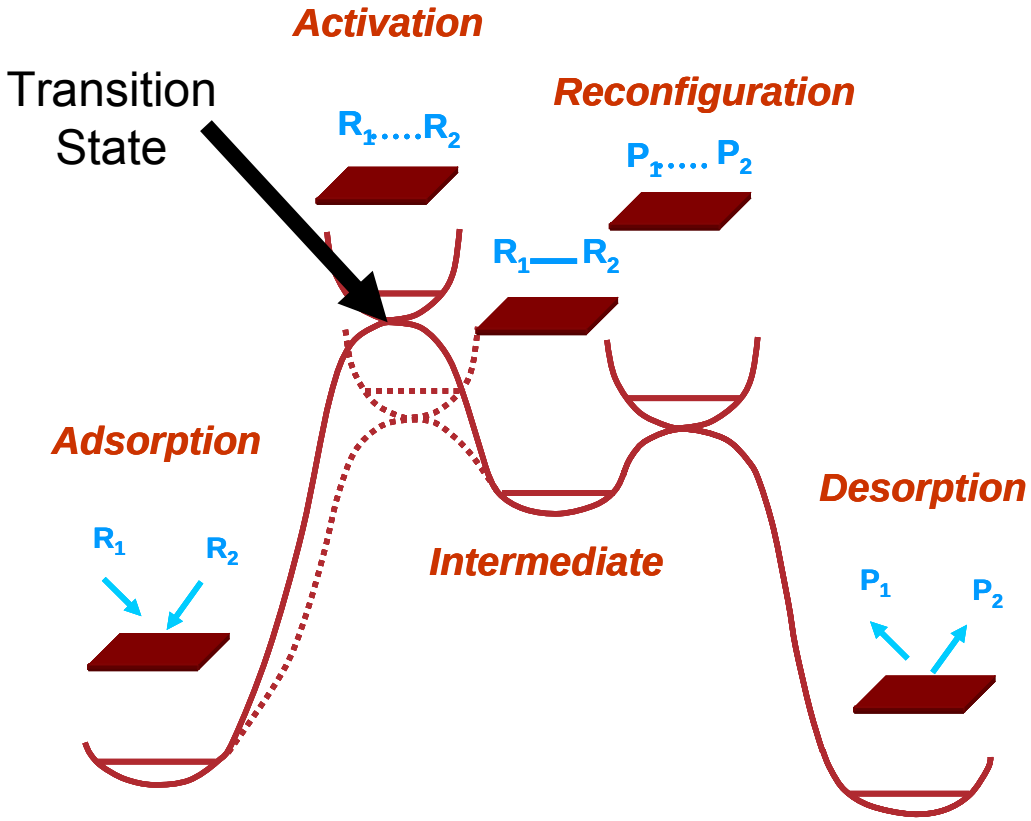
***J. Phys. Chem.* B., 101, 10688 (1997)**



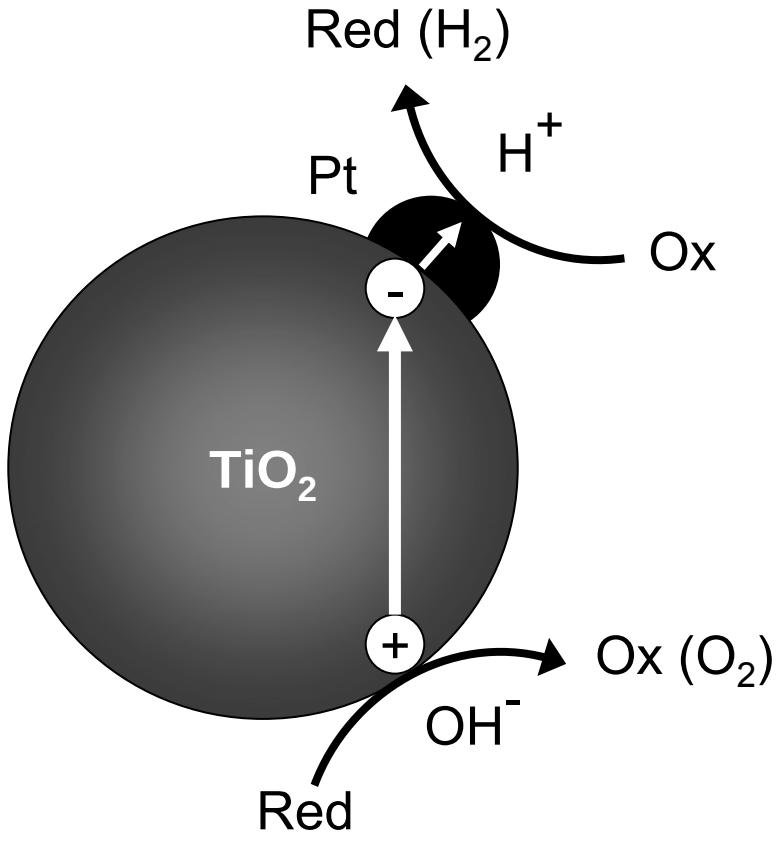
Surface defect sites are responsible for effective binding of surface modifiers and the fs structural dynamics will visualization of both electron and nuclear restructuring and gain insight into coherent control of electron injections by light.

Interfacial Structural Dynamics in Solar Electricity Generation

At Molecular Level…



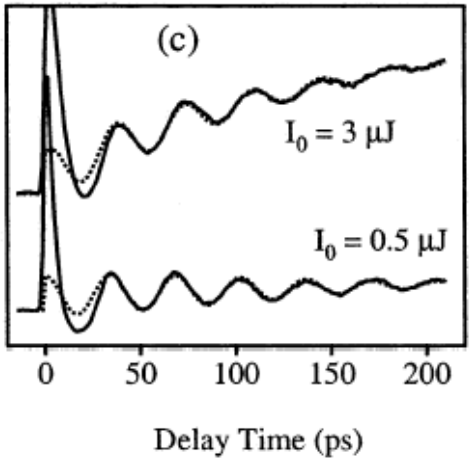
Heterogeneous Catalysis : Photocatalytic Reaction of H_2O Splitting over Pt/TiO_2



Energy Diagram along Catalysis Pathway

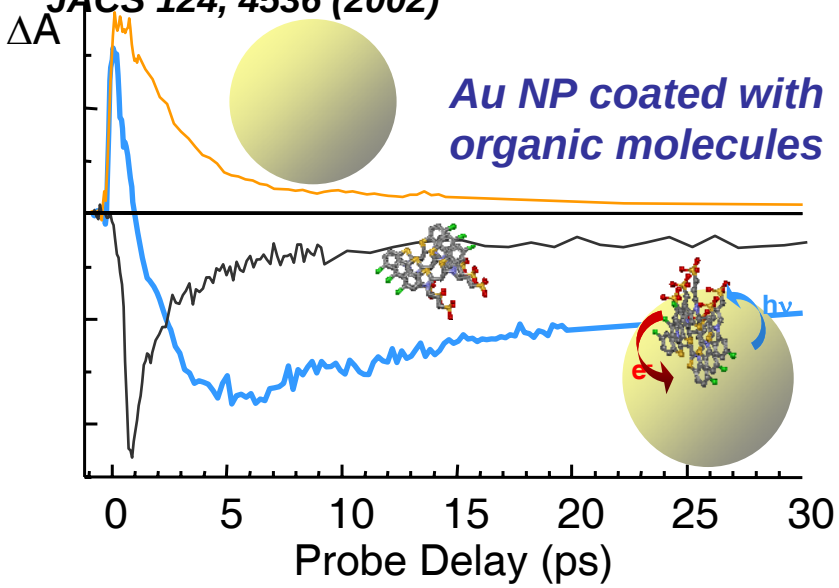
M. Anpo, *Bull. Chem. Soc. Jpn, 2004*

Interfacial Structural Dynamics in Solar Electricity Generation

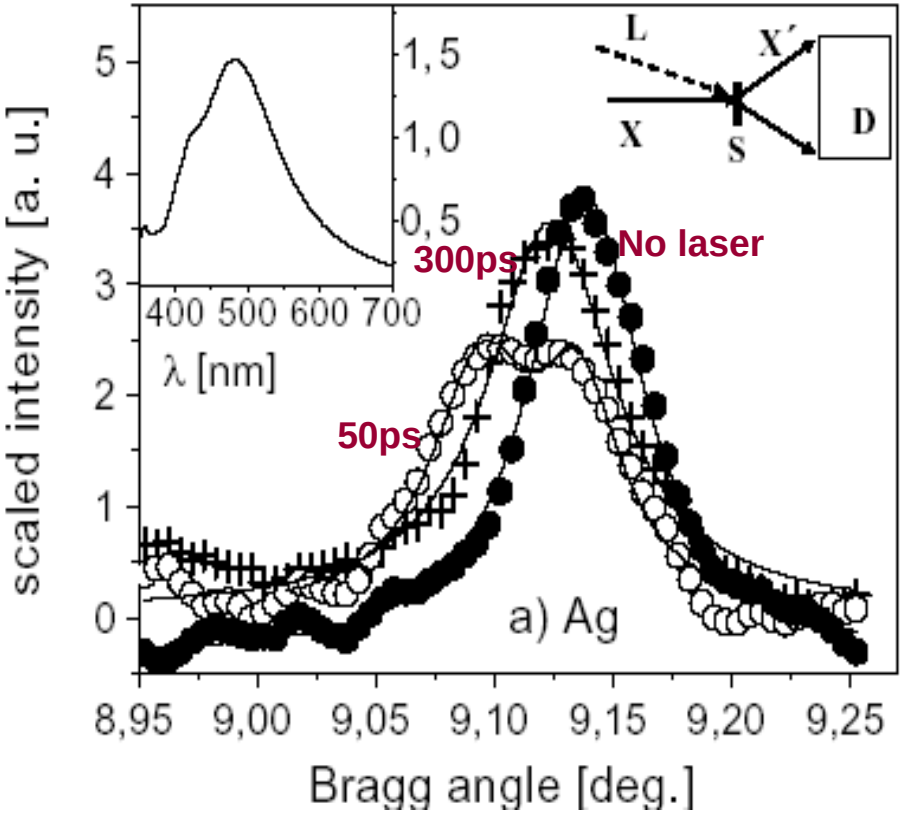


Au NP
G. Hartland
JPCB (2003)

Hranisavljevic, Dimitrijevic, Wurtz, Wiederrecht,
JACS 124, 4536 (2002)

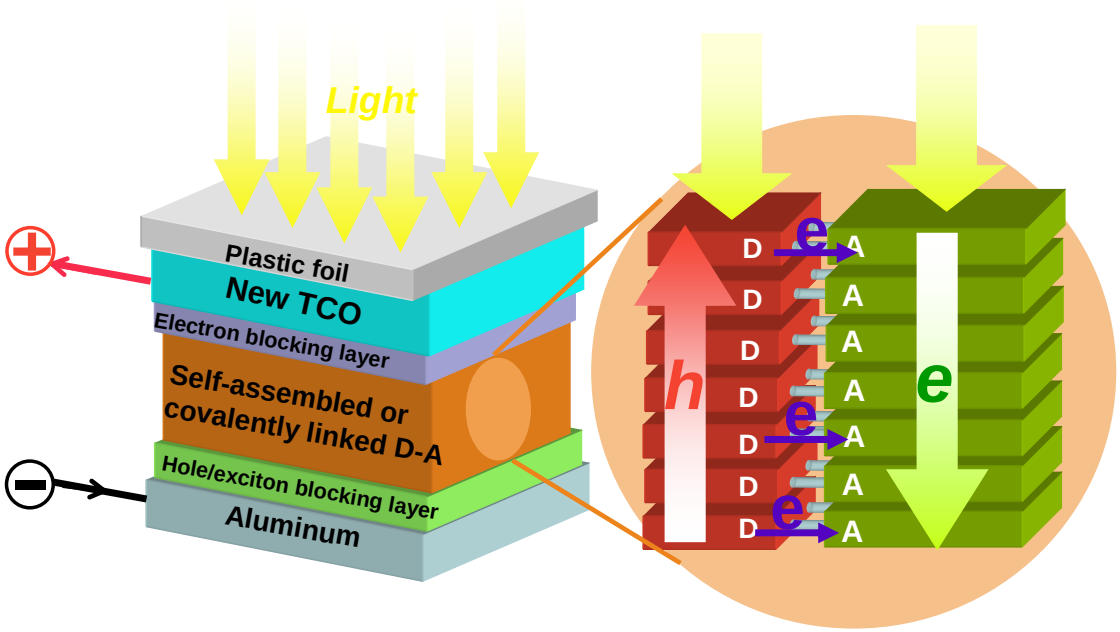


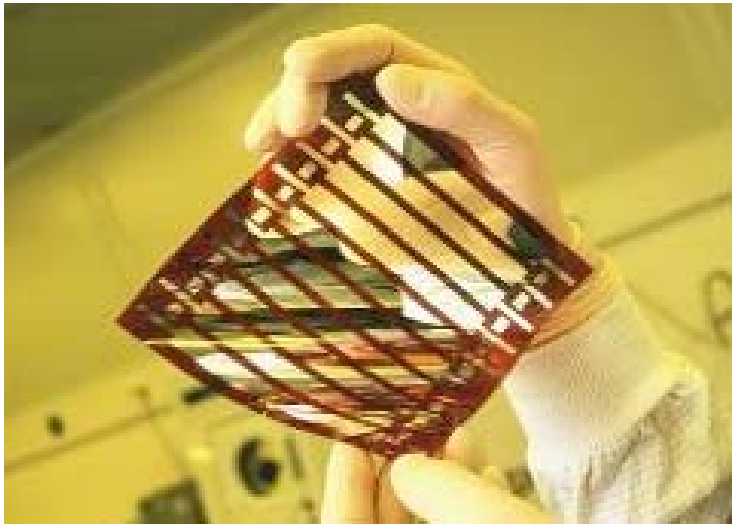
Plech et al. Eur. Phys. Lett. (2003)



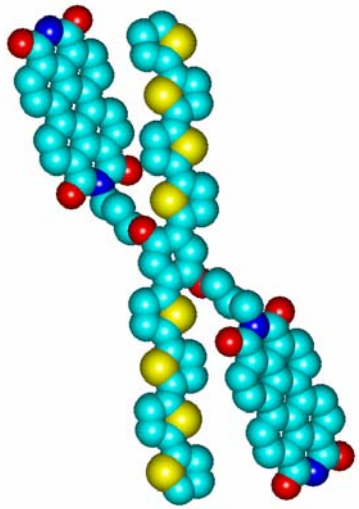
Searching for correlation between transient structures of metal NP and their properties and the influence of light induced phonons to chemical reactivities of molecules adsorbed on the metal NP.

Novel nanoscale organic photovoltaic materials



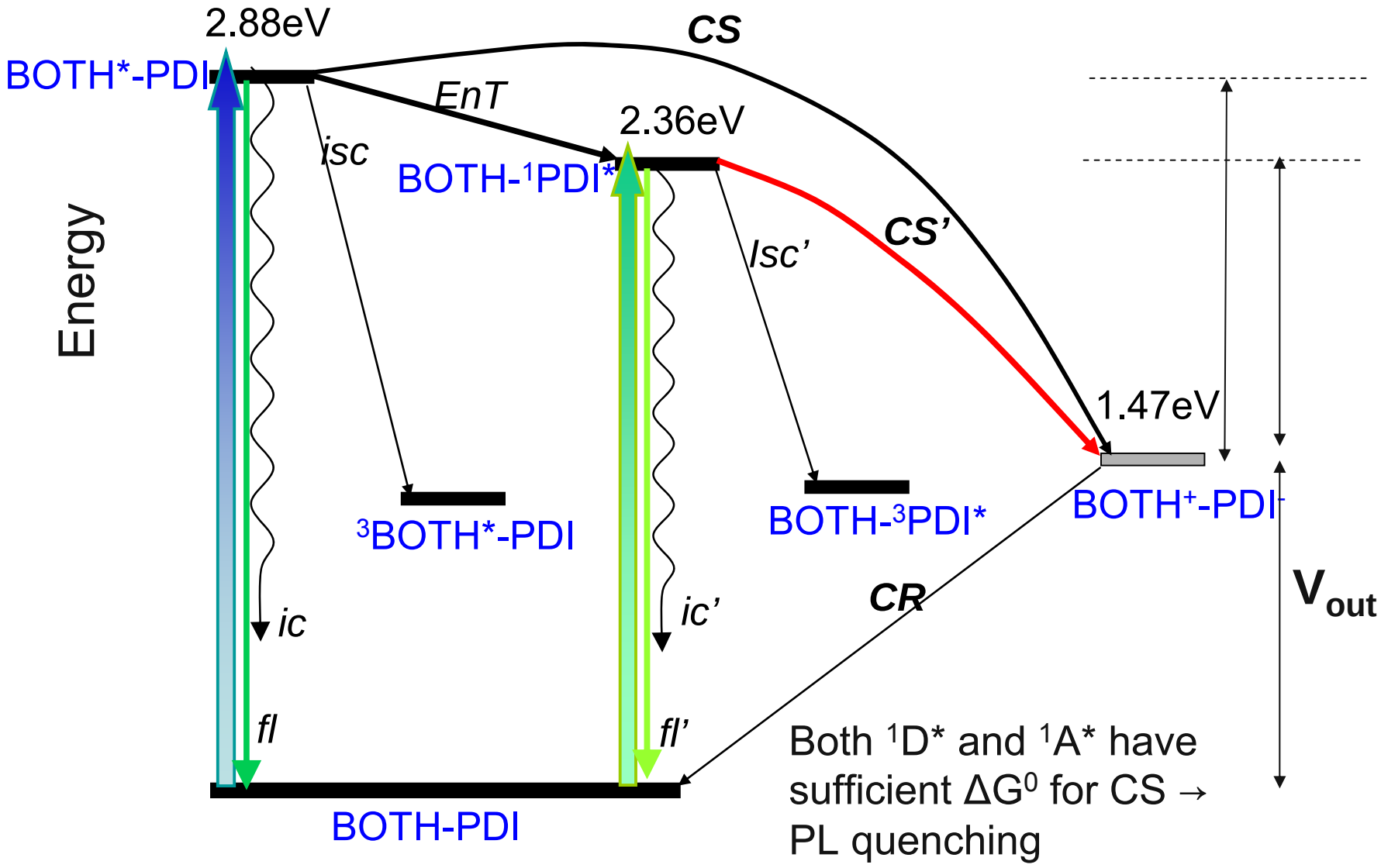


- **Light absorption by D and A;**
- **Charge separation within covalently linked D-A;**
- **Charge carrier hopping through the π-π stacked pile formed by SA;**
- **Charge collection though TCO electrodes;**
- **Prototype devices.**

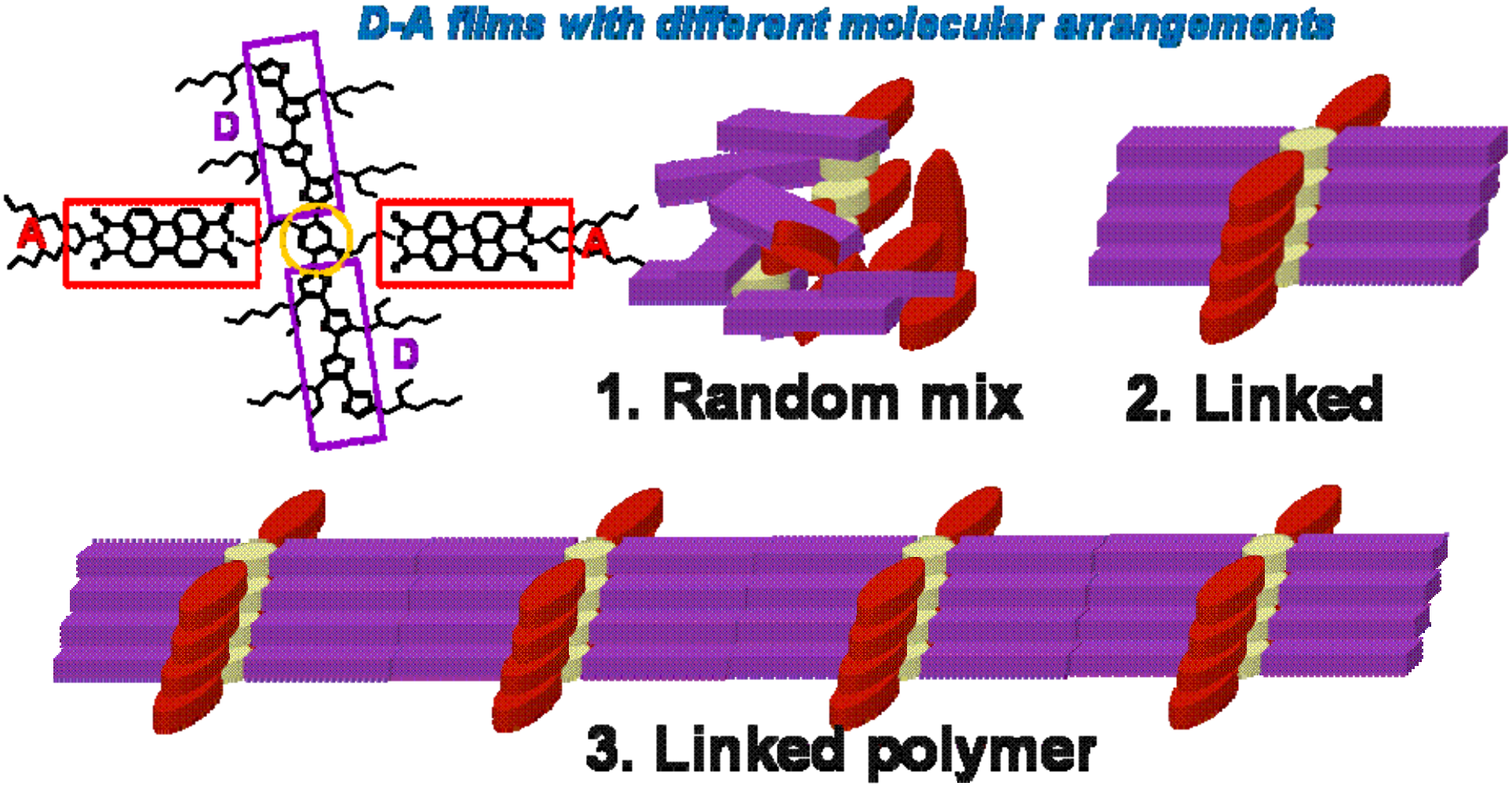


Novel nanoscale organic photovoltaic materials

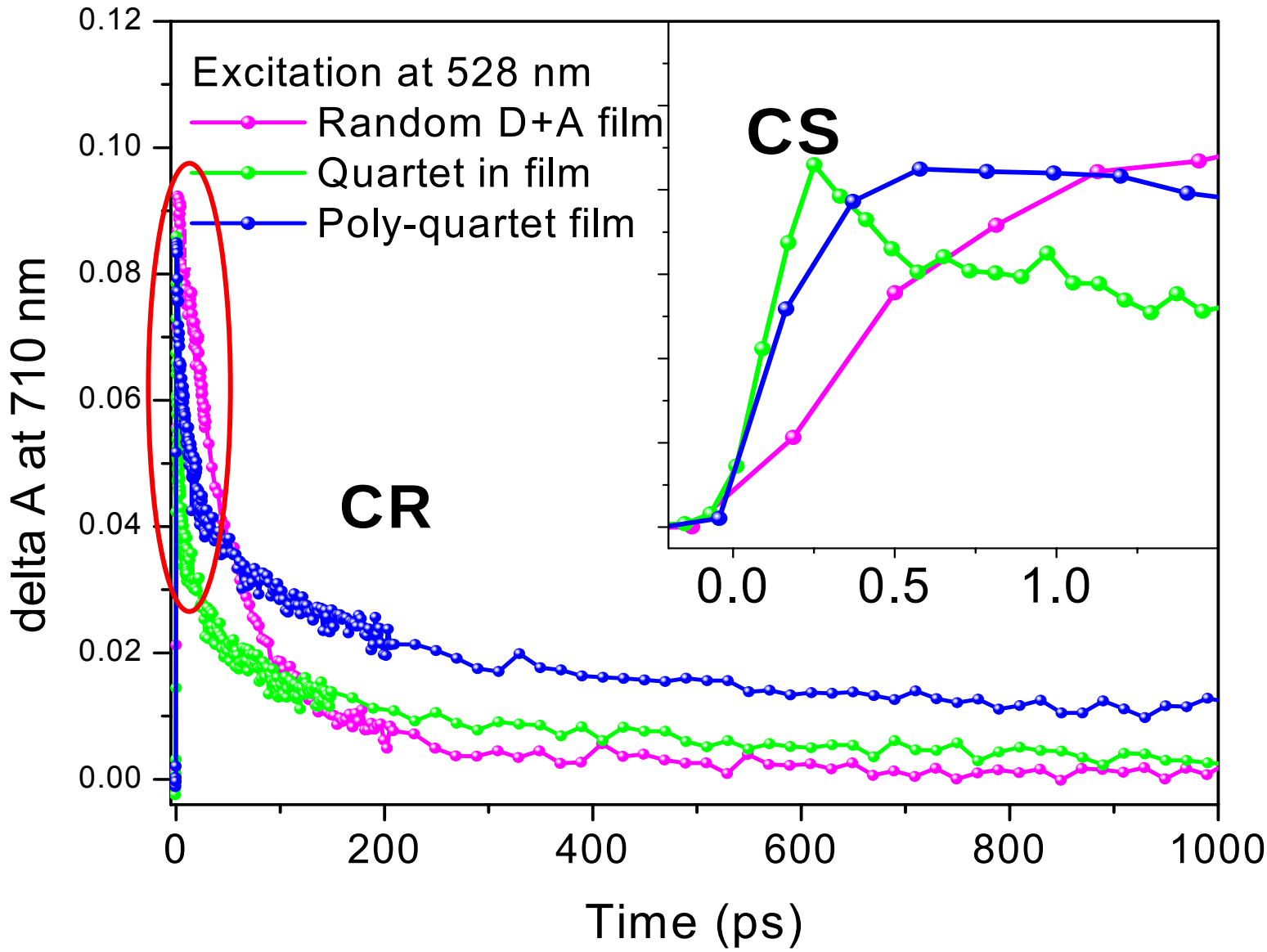
The quartet D-A in solution: Energy levels



Novel nanoscale organic photovoltaic materials

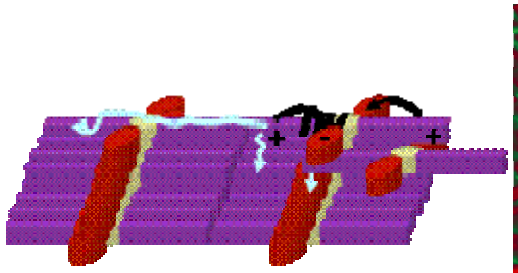


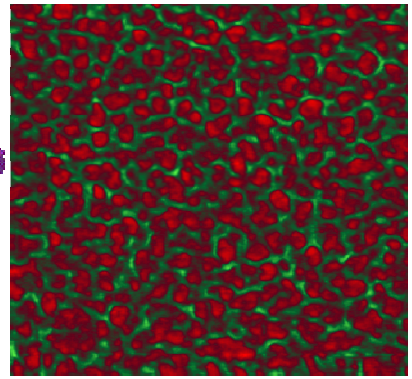
Novel nanoscale organic photovoltaic materials

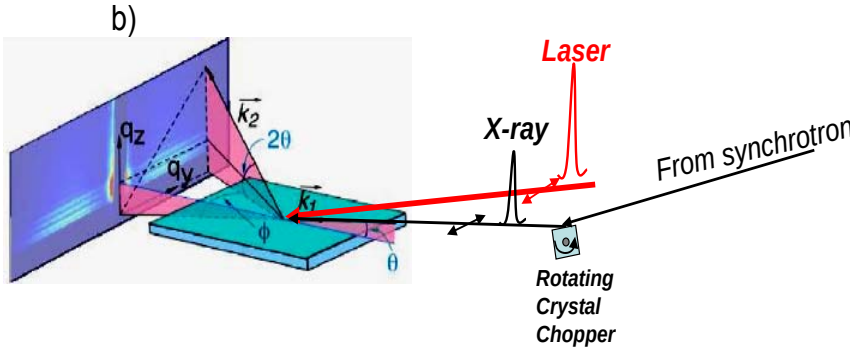


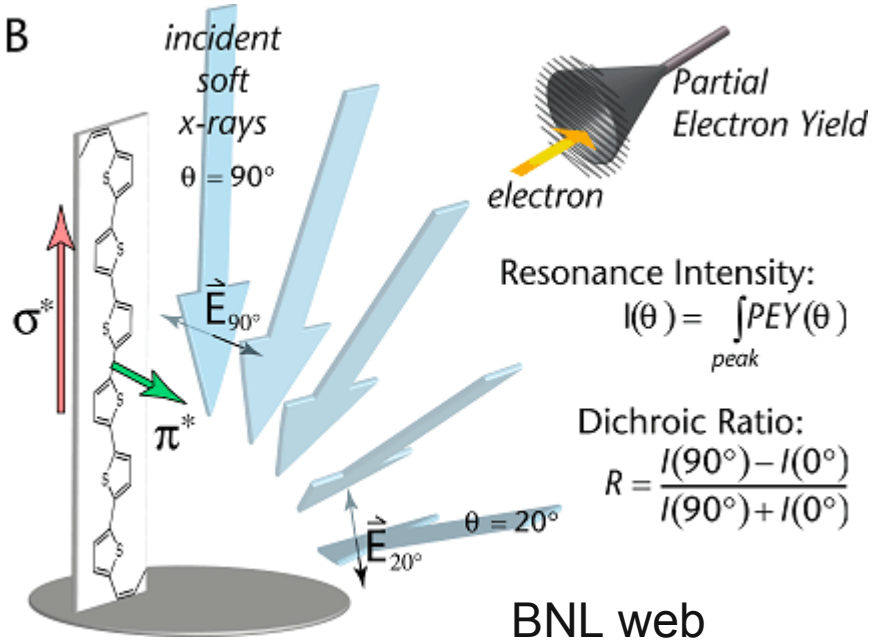
Interfacial Structural Dynamics in Solar Electricity Generation

Correlating domain, molecular packing and local molecular structure with energy and electron flow in organic and hybrid materials during PV function with steady-state and ultrafast pump-probe NEXAFS and WAXS/SAXS









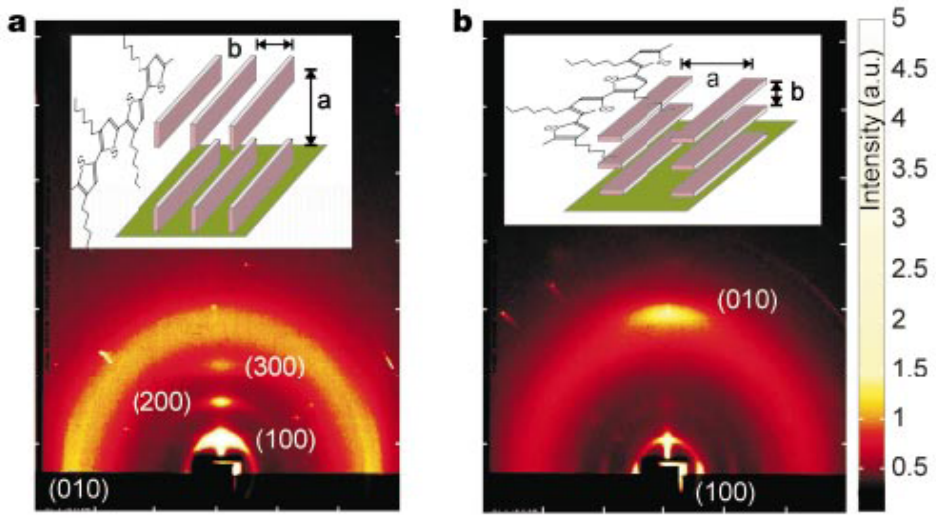
Resonance Intensity:

$$I(\theta) = \int_{peak} PEY(\theta)$$

Dichroic Ratio:

$$R = \frac{I(90°) - I(0°)}{I(90°) + I(0°)}$$

BNL web



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Perspective in Application of Short X-ray Pulses

- The short X-ray pulse generation will open up a new regime in studying solar energy conversion structural dynamics (i.e. vibrational relaxation) as well as fundamental photochemical and photophysical processes in general (Slicing+Compression???, kHz repetition rate)
- The short X-ray pulses will enable some coherent control and multipulse excitation experiments coupling laser and x-ray pulses to reveal structure/function correlations;
- The energy tunability is an unique advantage at the APS in comparison with XFEL sources in providing spectral coverage and resolution necessary in detecting electronic and nuclear geometry on ps time scale;
- Theoretical studies coupling the experimental studies are important;
- Synchronization scheme on ps scale is crucial;
- The capability of accommodating multiple users and much lower costs compared to building a new source need to be emphasized in the proposal.