

# Time-resolved X-ray Spectroscopy

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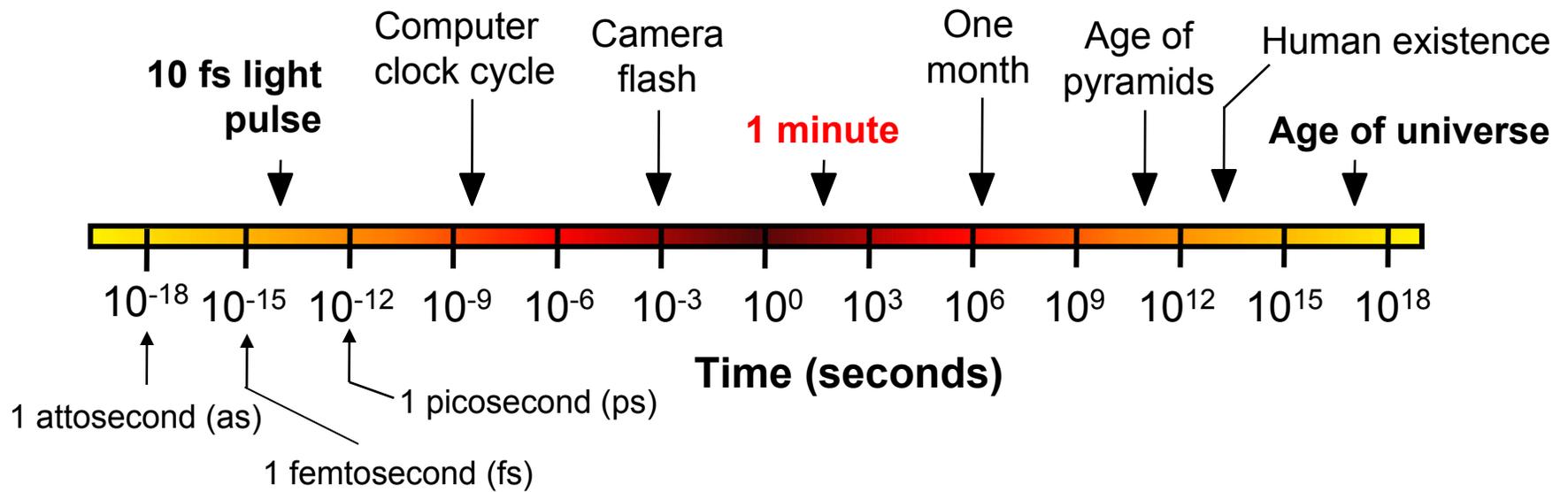


# Outline

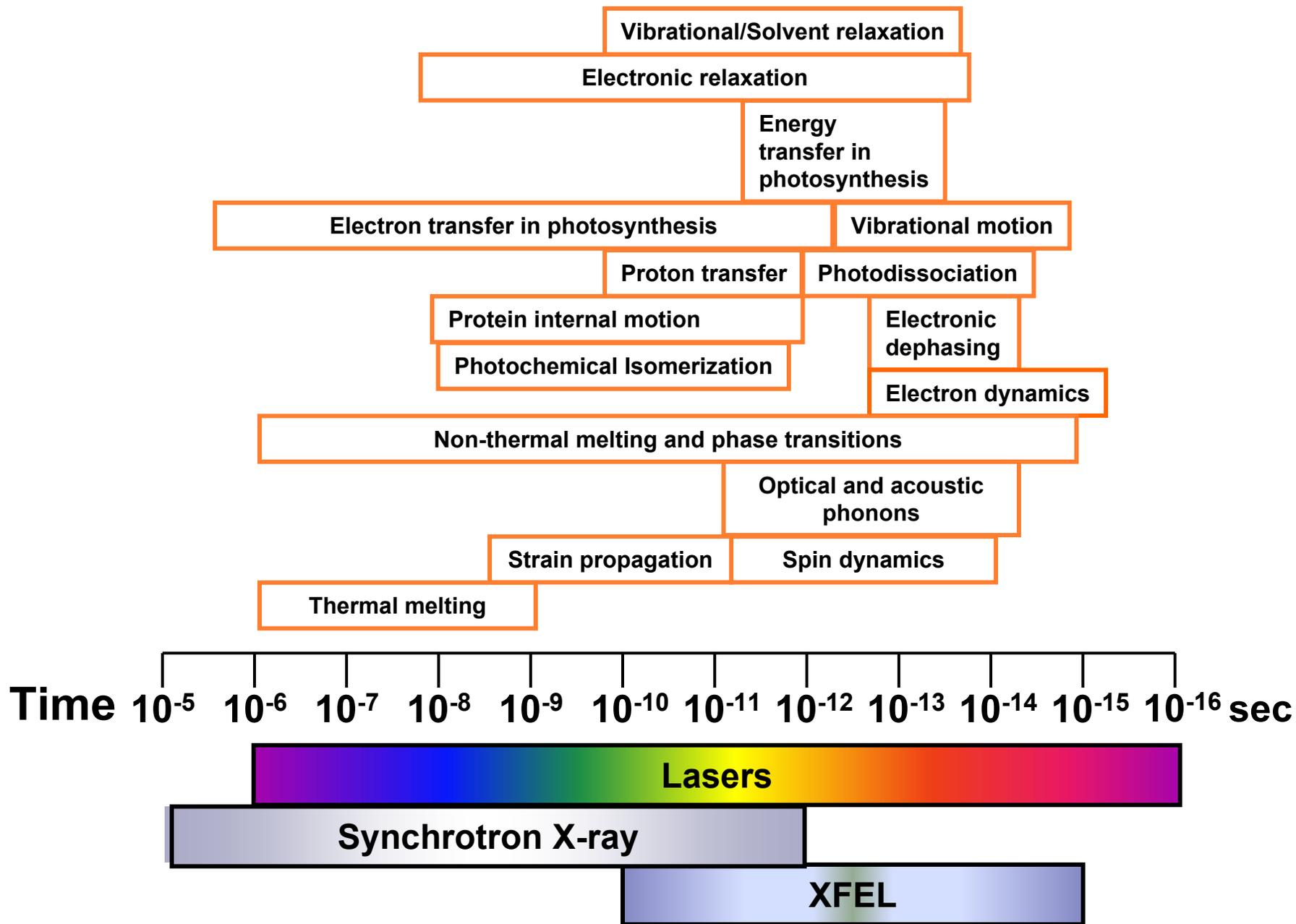
- **Introduction: Time scales and processes**
- **The principle of “pump-probe” transient spectroscopy**
- **Basic considerations and calculations in X-ray transient absorption spectroscopy**
- **Basic experimental setup**
- **XTA study examples**
- **Future studies**

# 1. Introduction

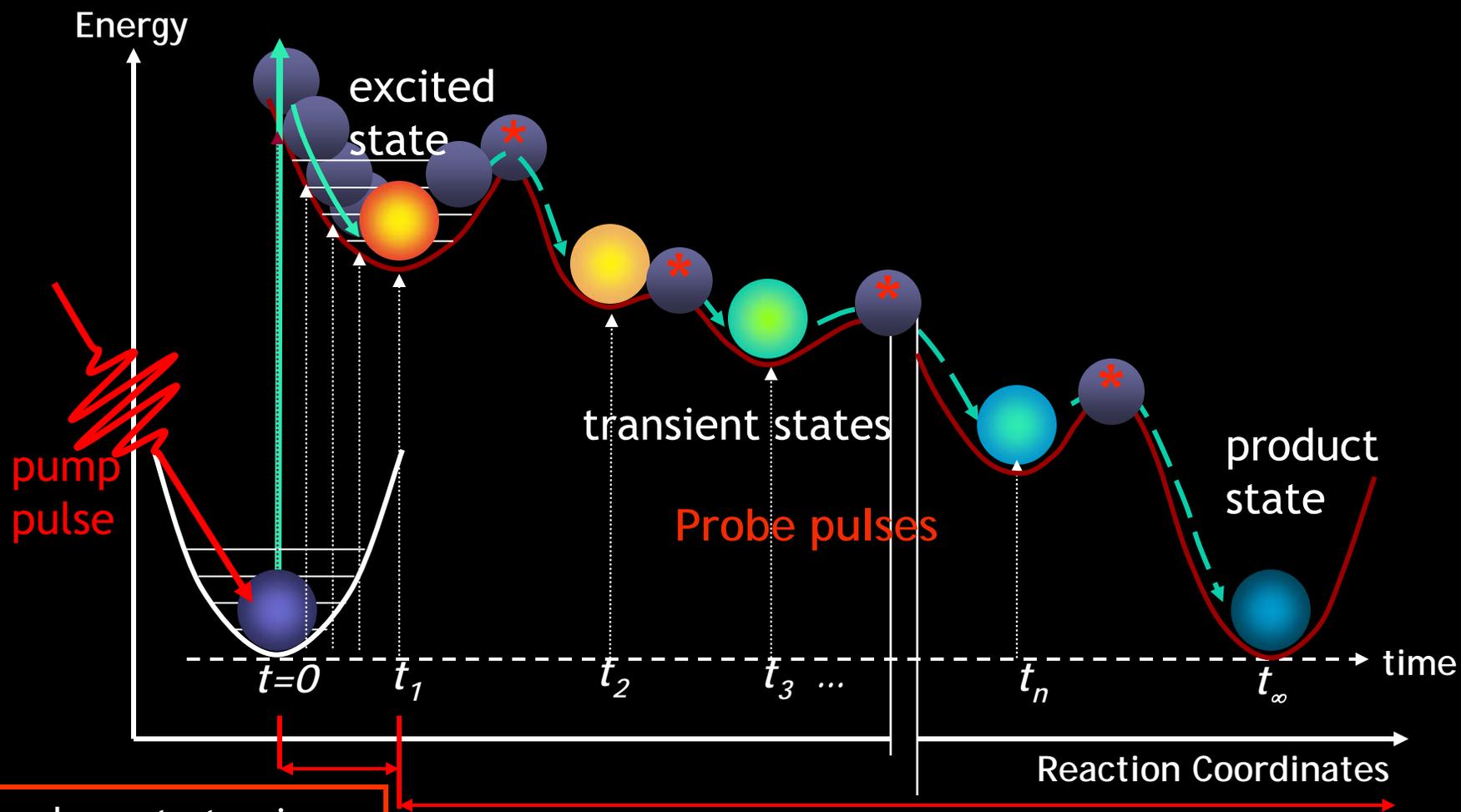
# Time scales



# Transient processes and their time scales



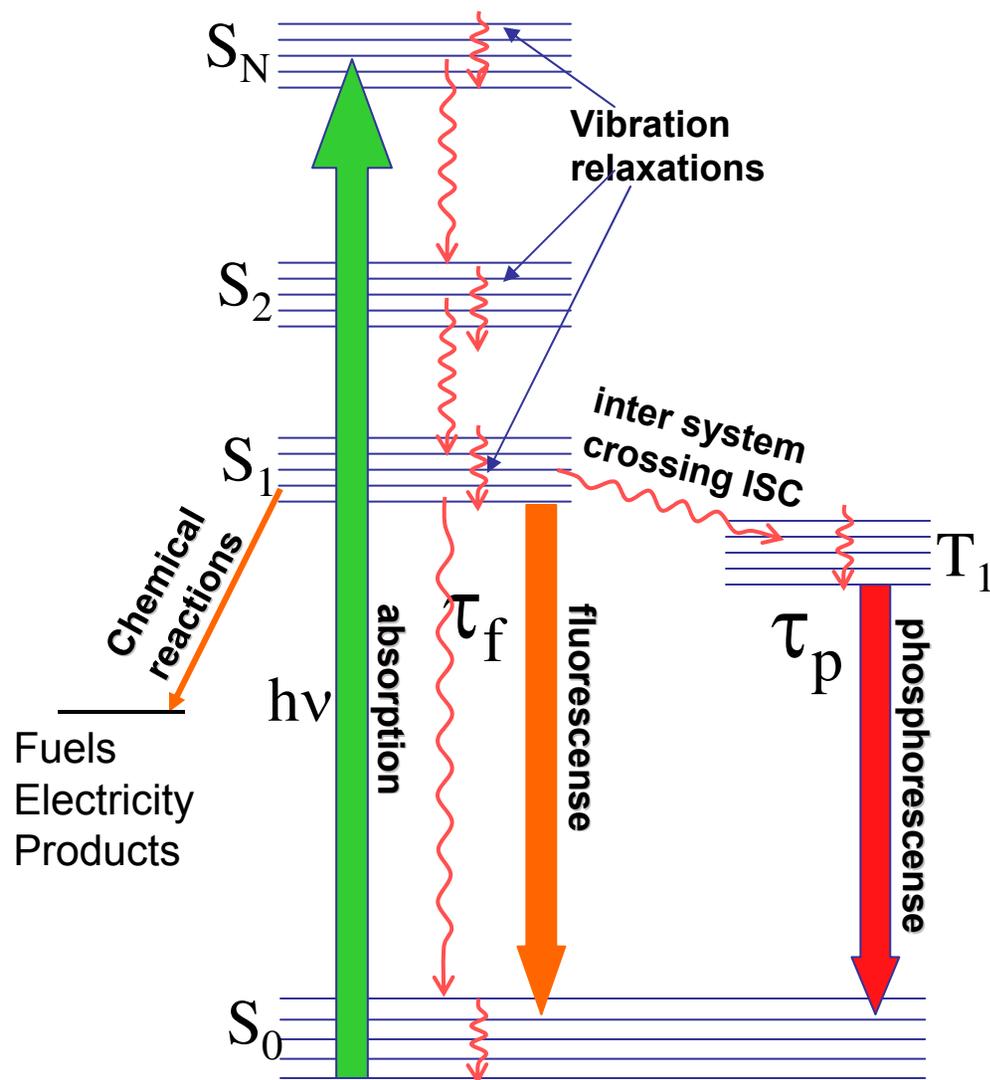
# X-ray snapshots and movies



coherent atomic motions →  
"molecular movie"

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

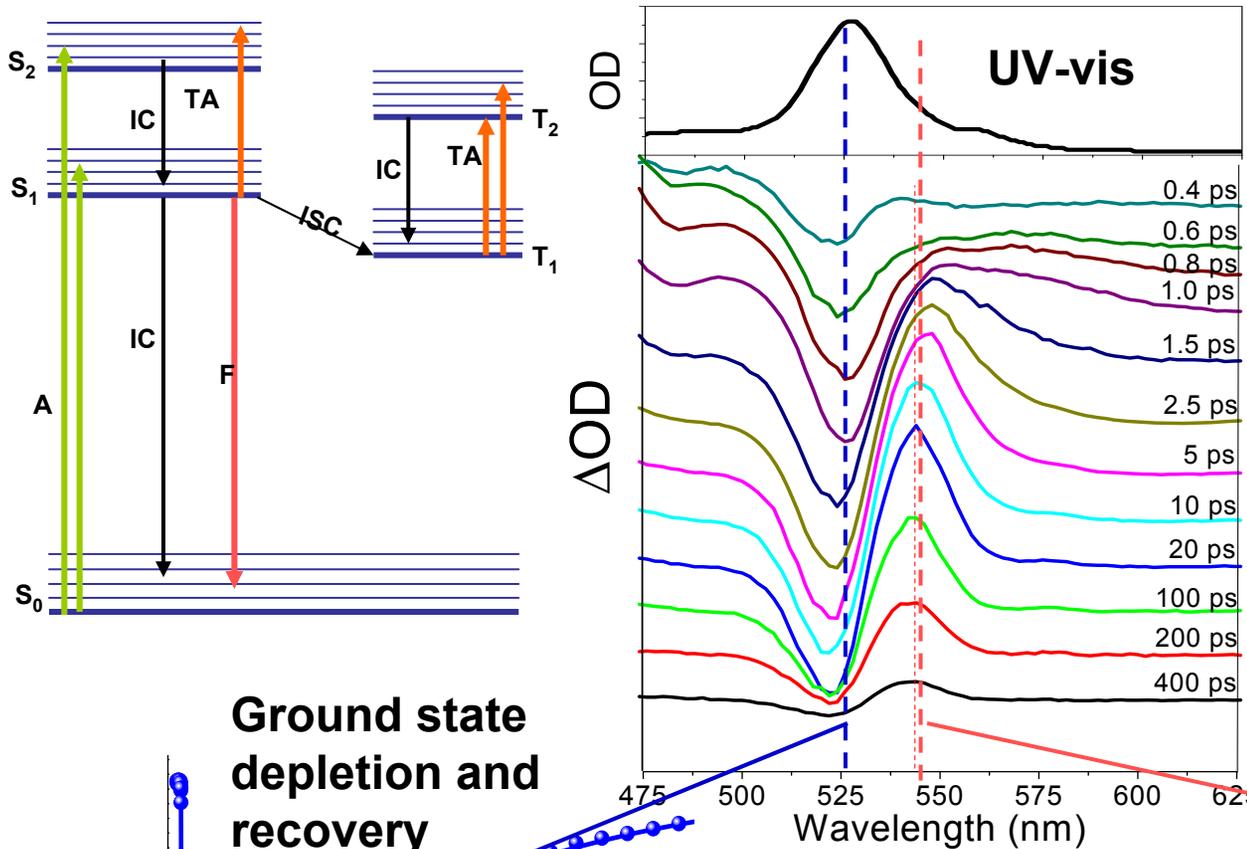
# Interactions of molecules with photons



Photons induce transitions to generate energetic species, the excited states that then proceed to many different processes.

By capturing the optical signatures of transient species, one can follow the reaction kinetics and mechanisms and identify the final products.

# Transient absorption spectroscopy



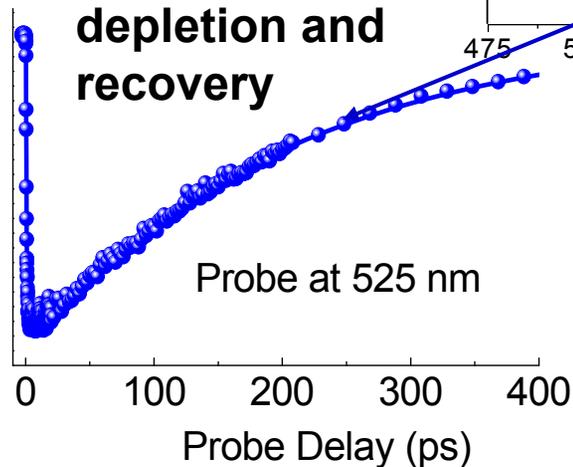
“Pump” laser pulse:

Single wavelength at a certain absorption feature of the UV-vis spectrum.

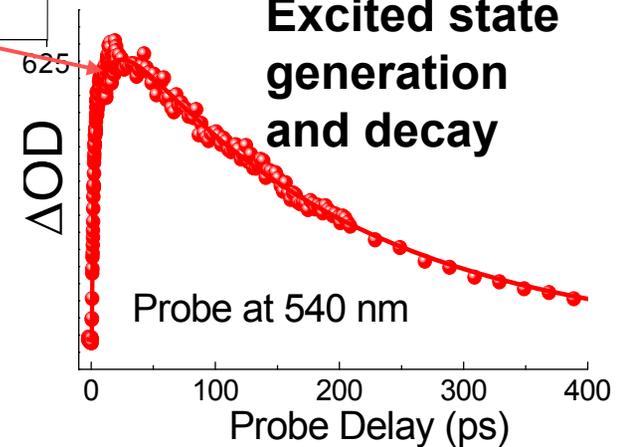
“Probe” laser pulse:

White light pulse with a variable optical path to set delay from the “pump” pulse.

**Ground state depletion and recovery**

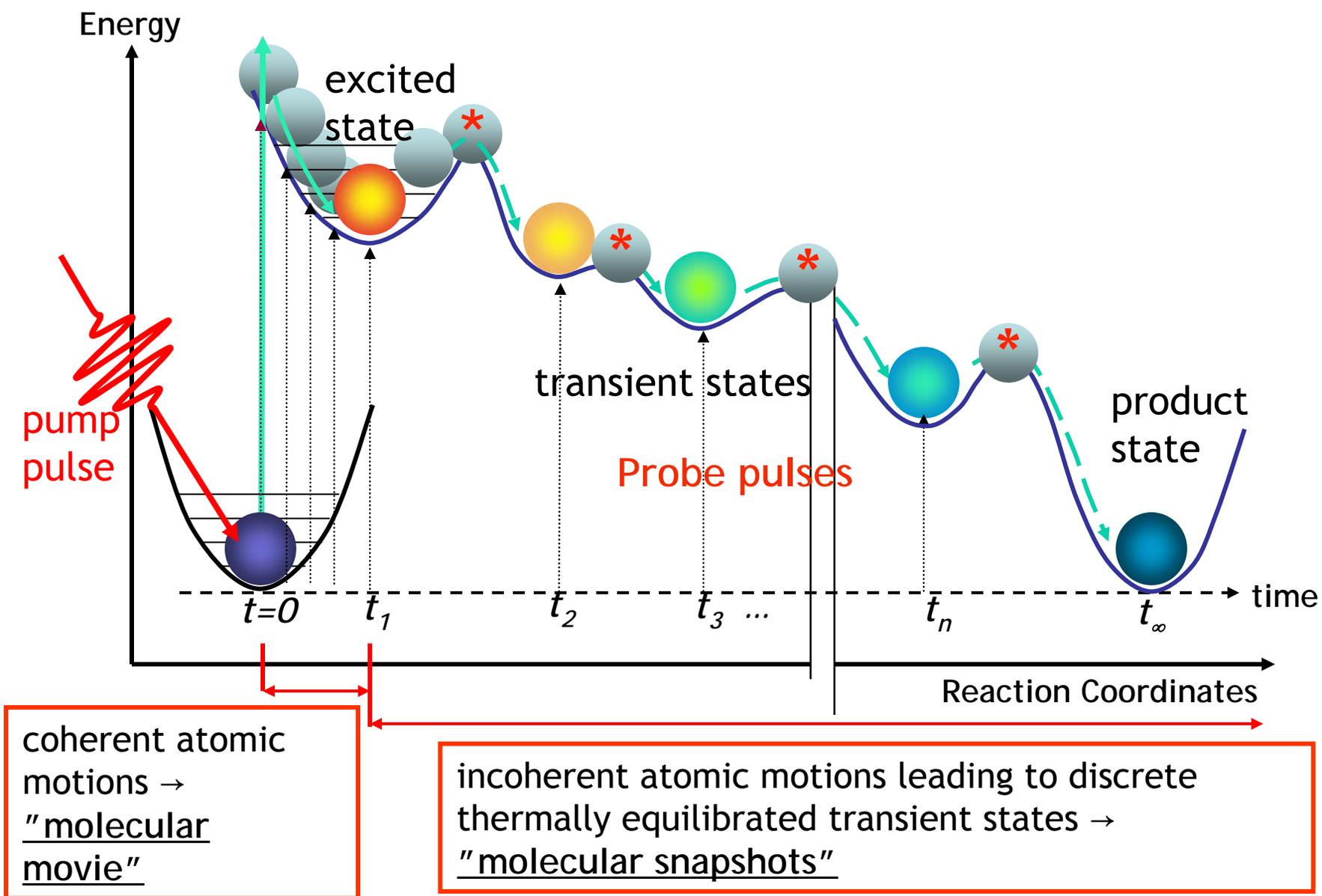


**Excited state generation and decay**

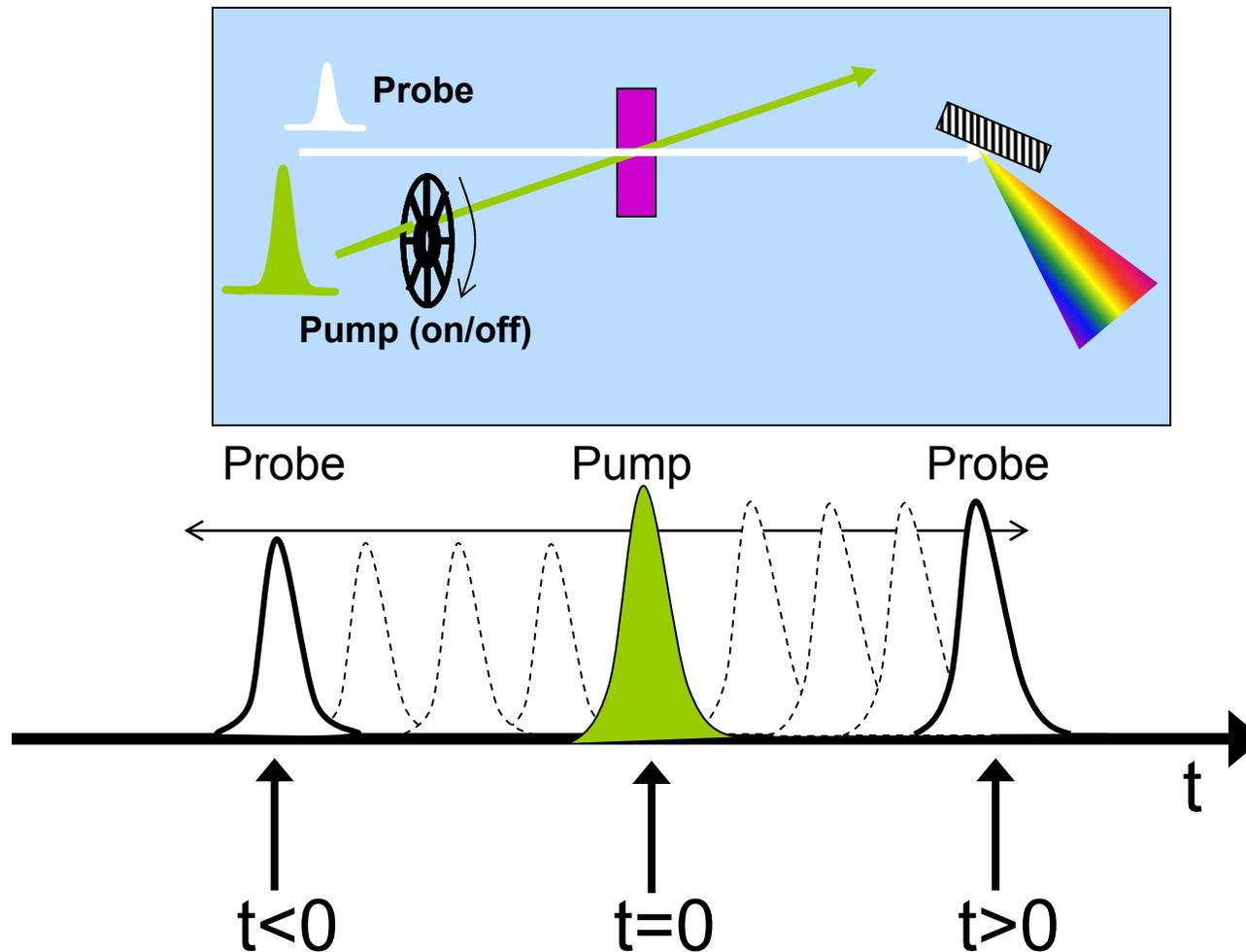


## **2. The principle of “pump-probe” transient spectroscopy**

# X-ray snapshots and movies



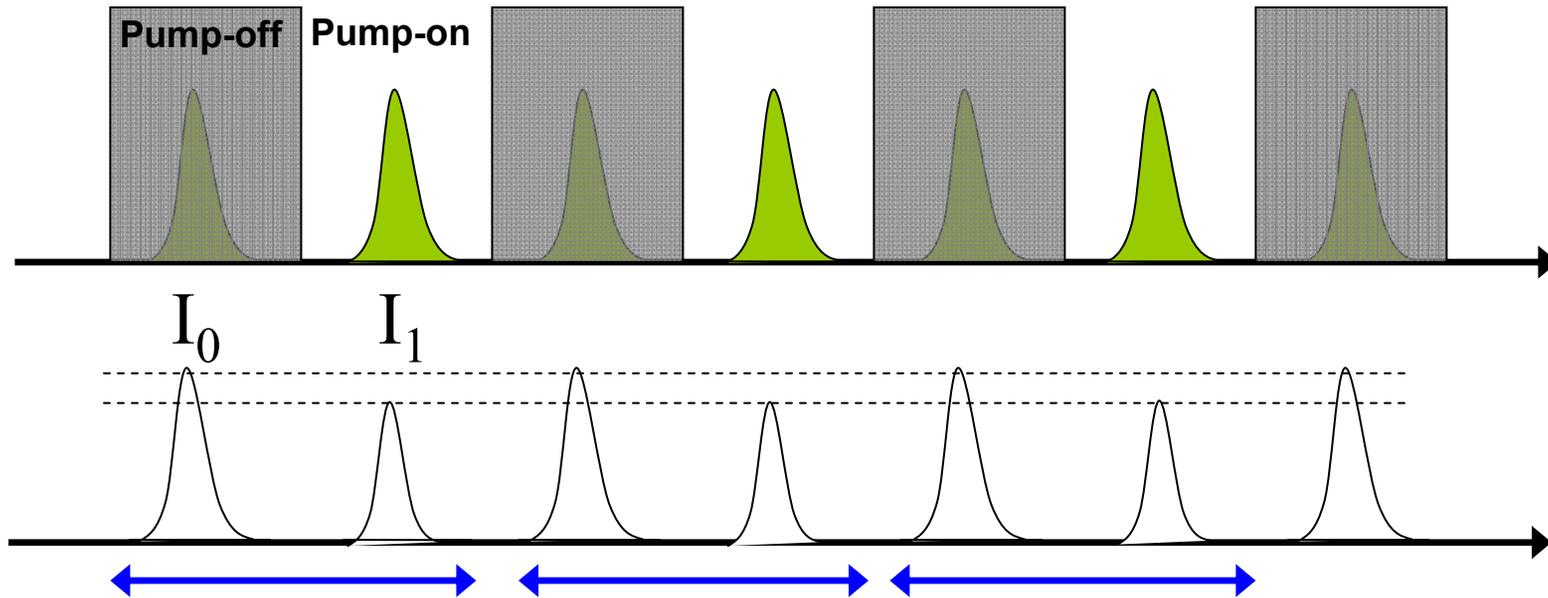
# Pump - probe concept



- At one delay time, many pump-probe cycles are collected for sufficient S/N level in the data;
- Changing the delay time step-by-step to cover the entire kinetics trace;
- Time resolution determined by the laser pulse duration ( $\sim 50$ - $100$  fs);
- Time window determined by the optical delay length (i.e. 1-6 ns).

# Pump - probe concept

The probe signal at one delay time,



The probe signal at any delay time  $t$ ,

$$\Delta OD(\lambda, t) = \log \frac{I(\lambda, t)_{pump-off}}{I(\lambda, t)_{pump-on}} = \log \frac{I_0(\lambda, t)}{I_1(\lambda, t)}$$
$$= \log \frac{\varepsilon_{GS} C_{GS}(\lambda, 0)}{[(\varepsilon_{GS} C_{GS}(\lambda, t) + \varepsilon_{ES} C_{ES}(\lambda, t))]}$$

# Pump excitation light sources

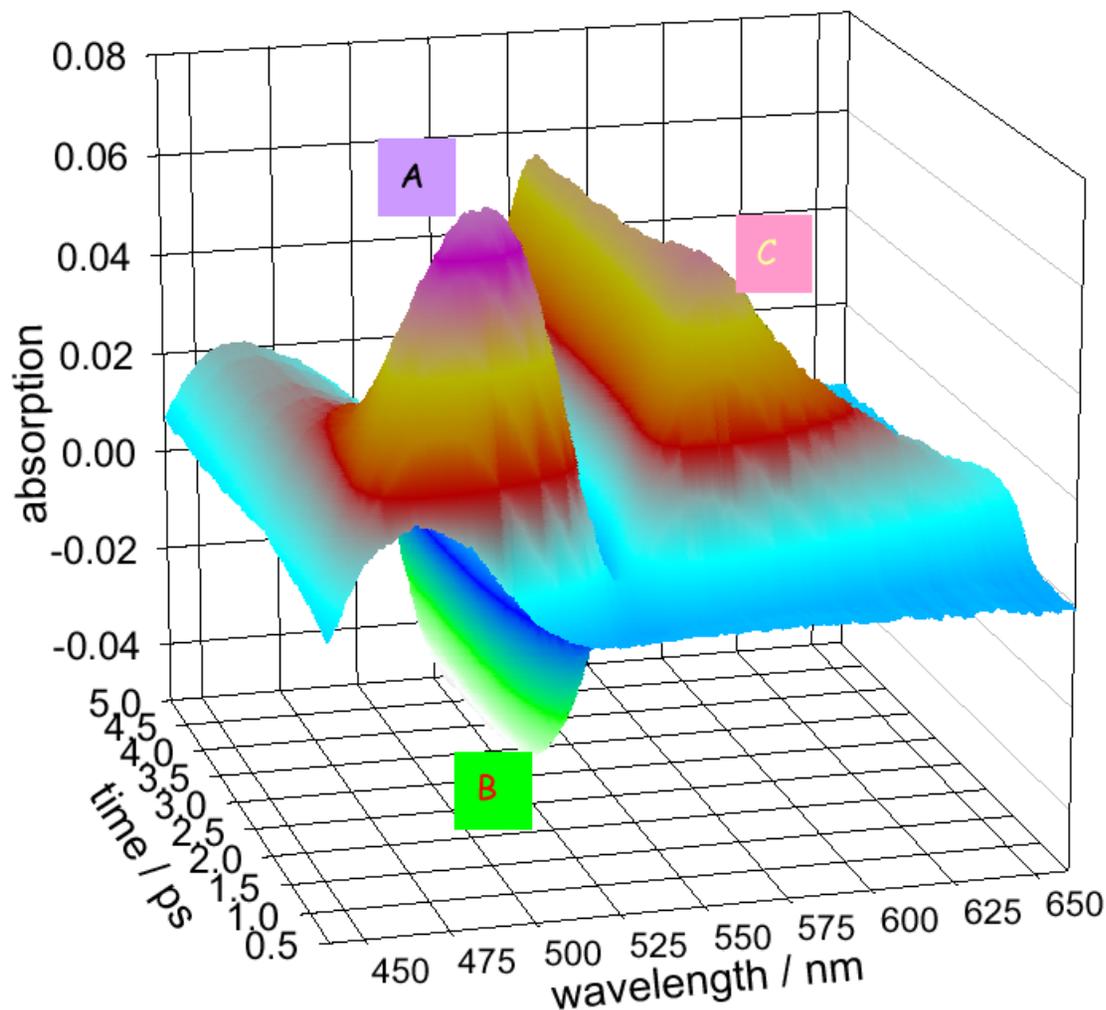
- Direct Ti-Sapphire laser output - 800 nm
- Harmonic generation - SHG 400 nm and THG 267 nm
- Optical parametric amplification - 250-12000 nm

# Laser probe light sources

- White light continuum generation
  - Advantage: Easy to use and All wavelengths are generated at once
  - Disadvantage: Somewhat limited spectral range 330-1000 nm
- Optical parametric amplification
  - Advantage: Broad spectral range 250-12000 nm
  - Disadvantage: Requires more sophisticated equipment; Only narrow spectrum range can be used – need to scan wavelength.

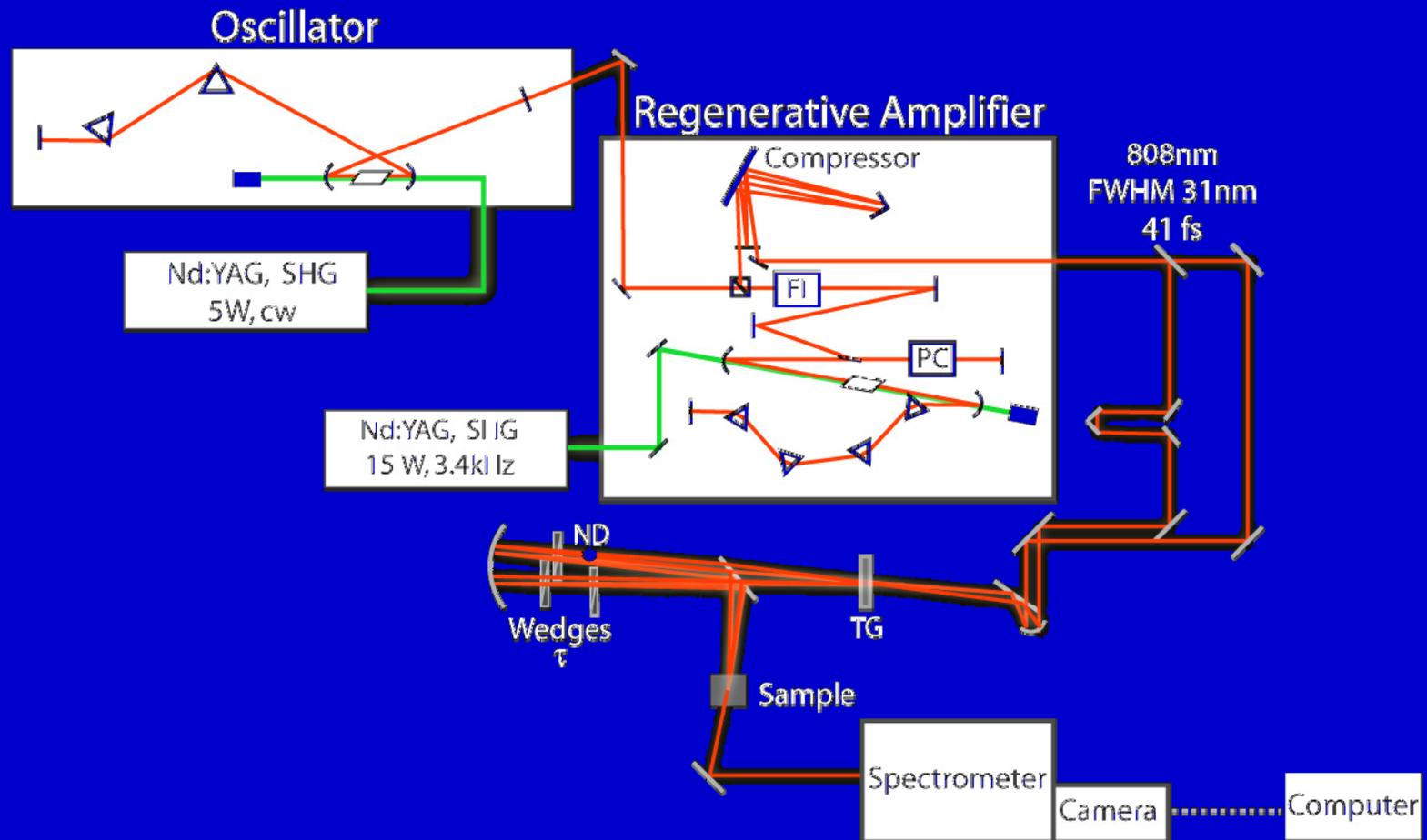
# The capability of optical transient absorption method

- Direct observation of a transient by monitoring a characteristic spectral signature
- Observation of the electronic and vibrational energy redistribution
- Probing broad spectral and temporal range in automated mode
- Observation of stimulated emission

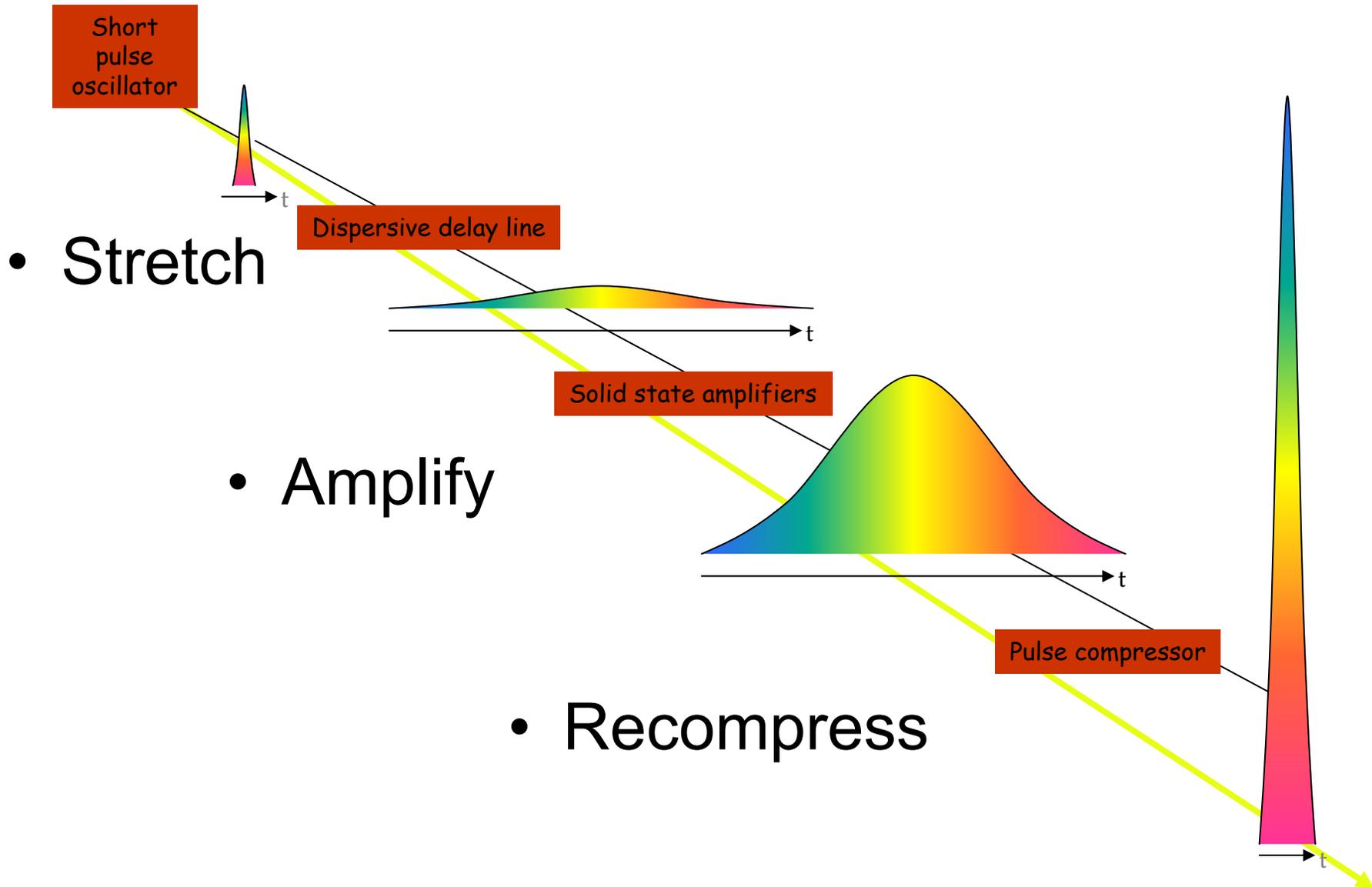


# Three main components of an ultrafast laser system

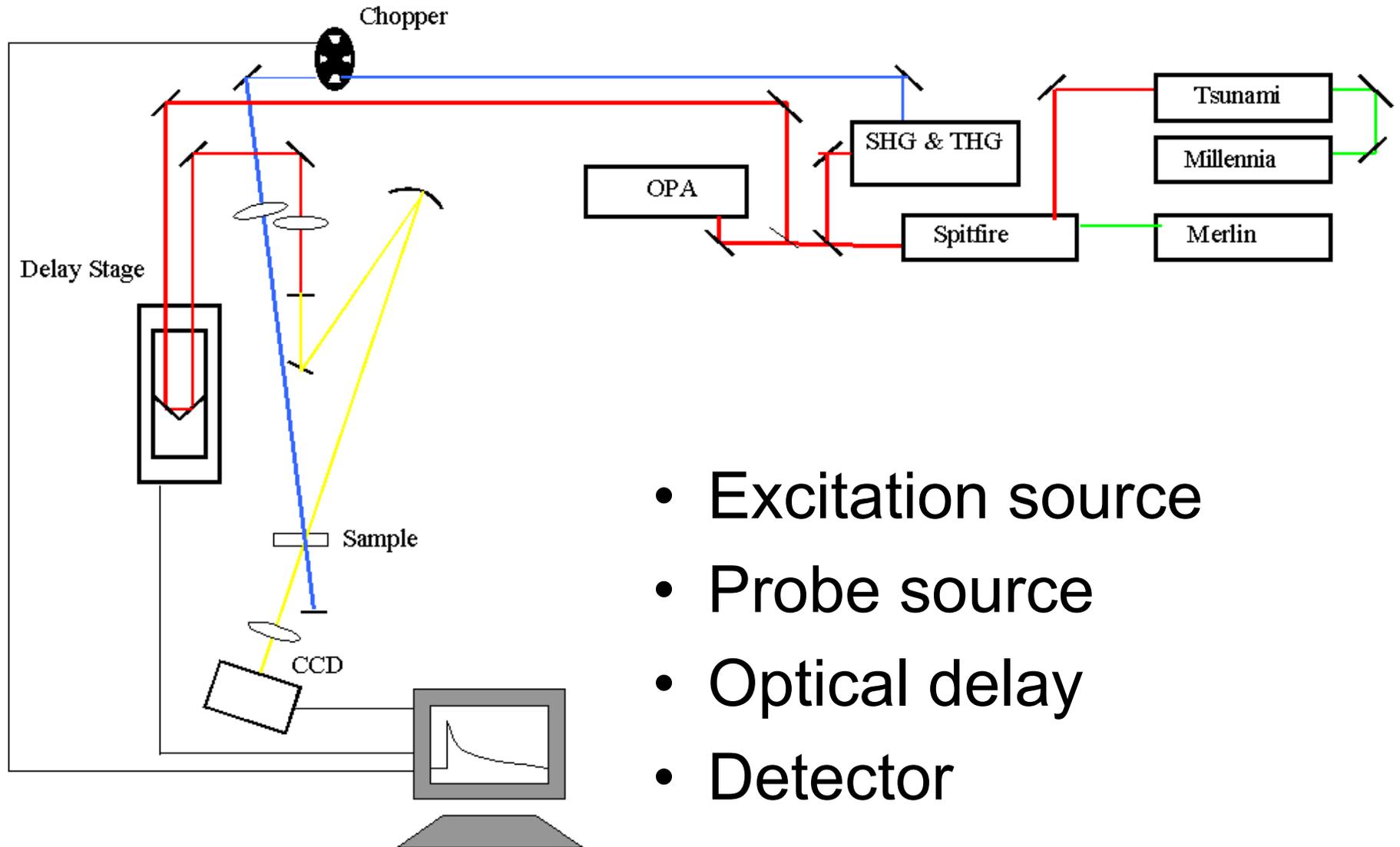
- Oscillator
- Regenerative Amplifier
- Tunable Parametric Amplifier



# Chirped Pulse Amplification



# Transient absorption setup



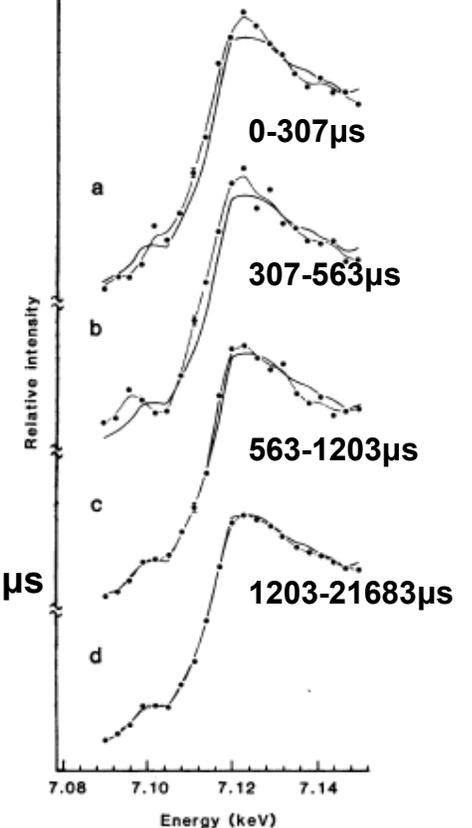
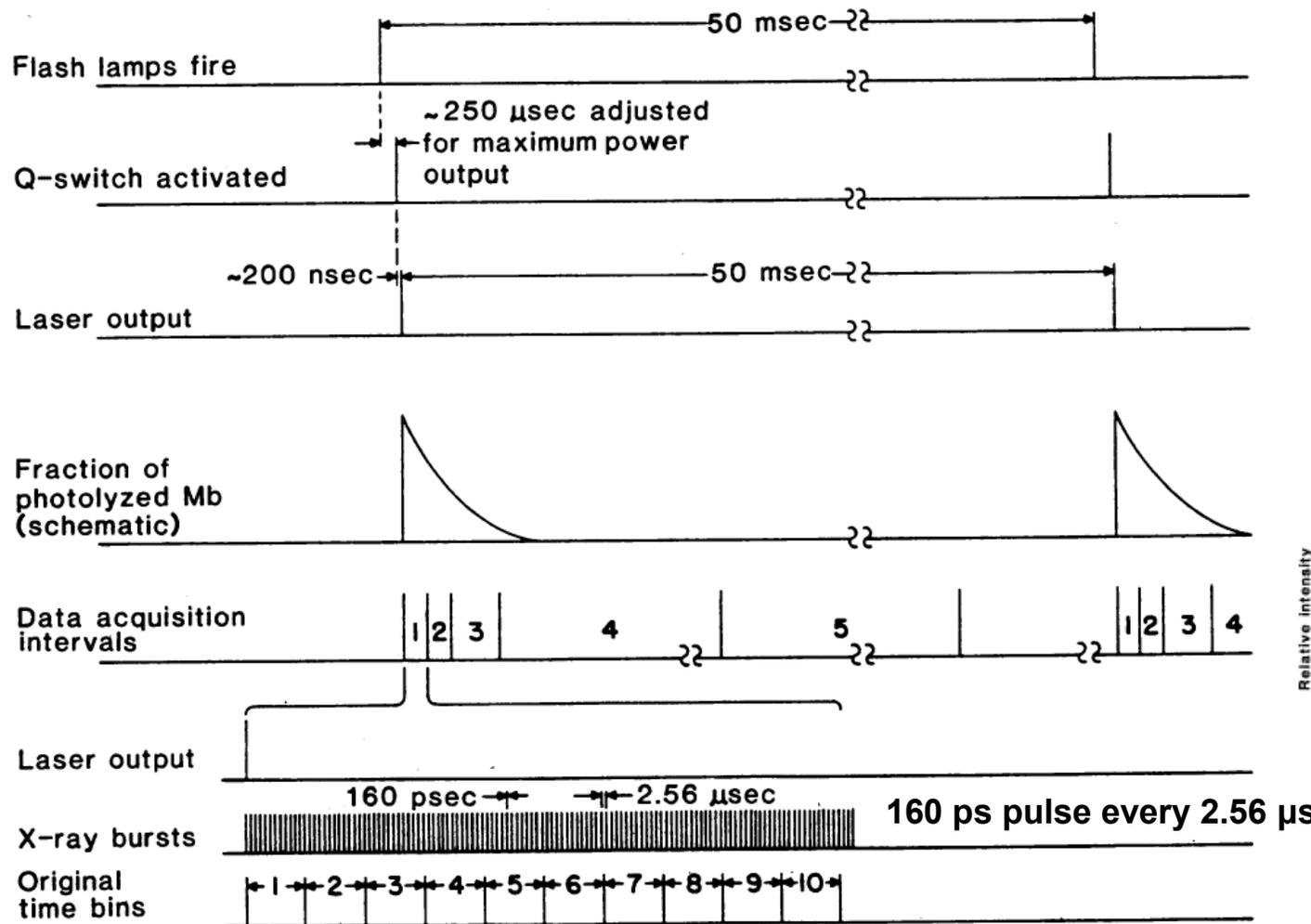
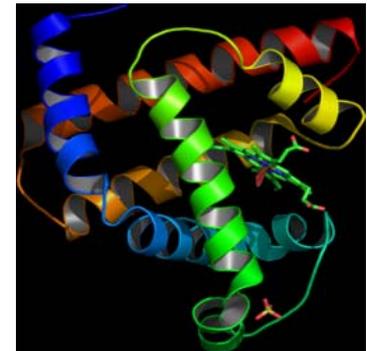
- Excitation source
- Probe source
- Optical delay
- Detector

### **3. Basic considerations and calculations in X-ray transient absorption (XTA) spectroscopy**

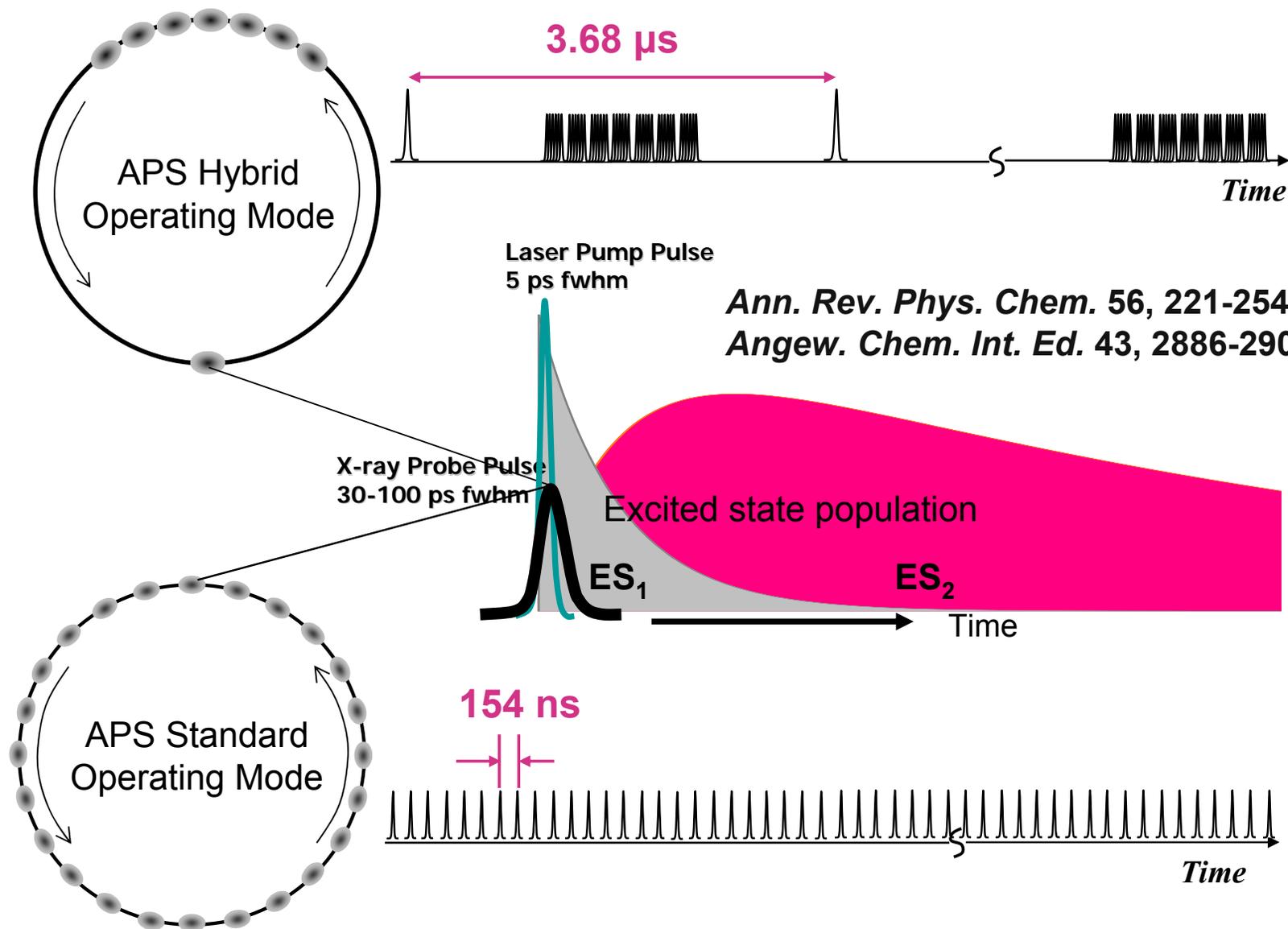
# A pioneering study from the second generation synchrotron source

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

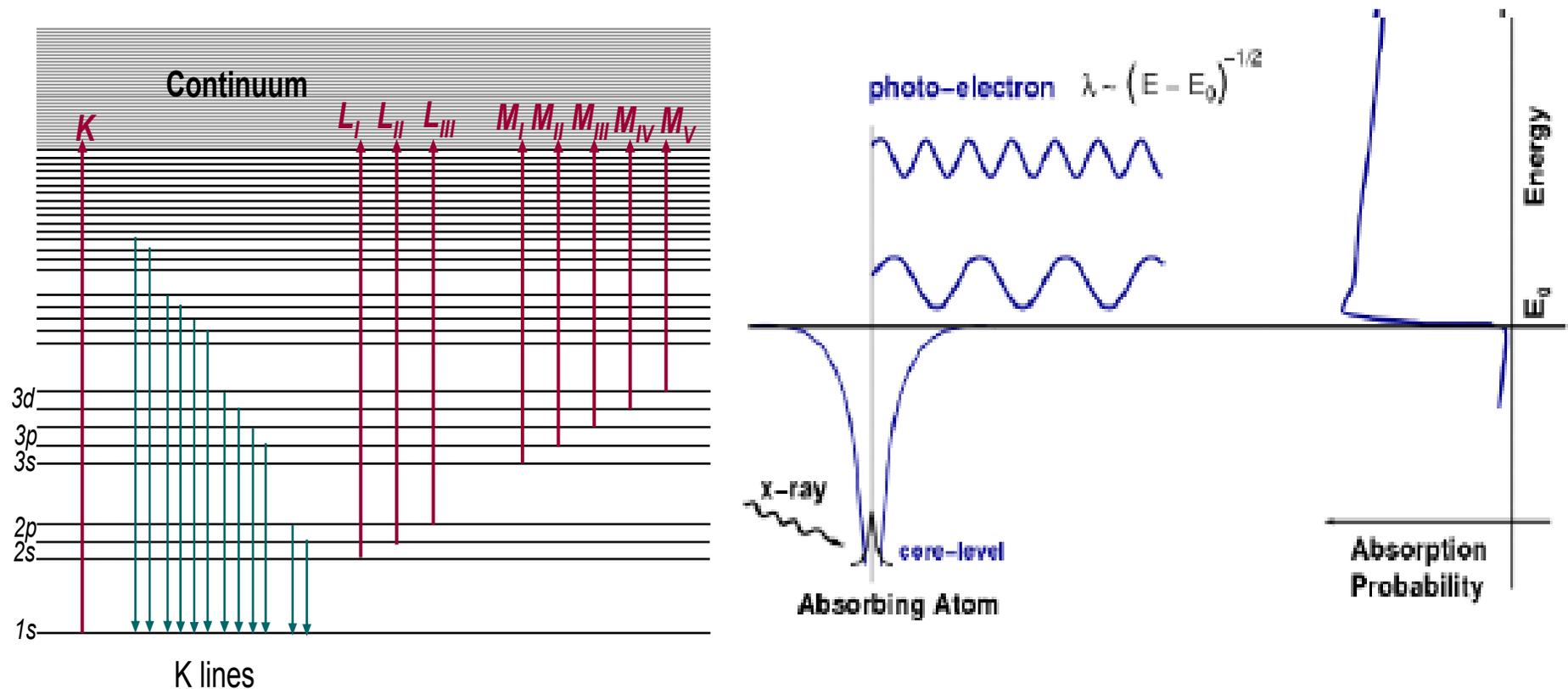
Mills et al., Science (1984)223, 812.



# X-ray transient absorption spectroscopy (XTA) at the APS with Delay time sequence and Operating Fill Patterns

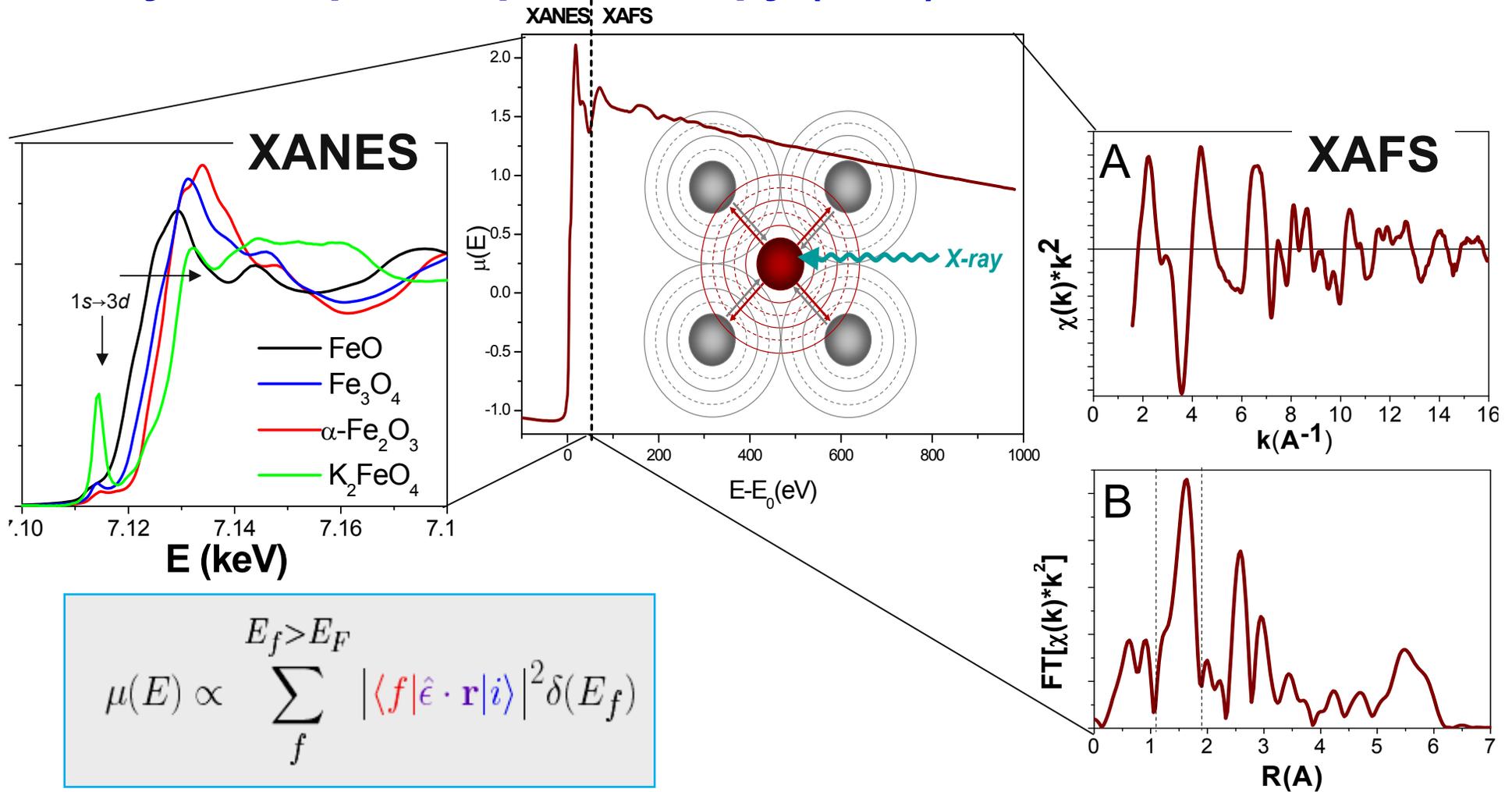


# X-ray Absorption Spectroscopy (XAS)



- Element specific;
- Precise local structure (0.02Å);
- No crystalline sample required (solution);
- Sensitive to oxidation state and coordination number & geometry.

# X-ray Absorption Spectroscopy (XAS)



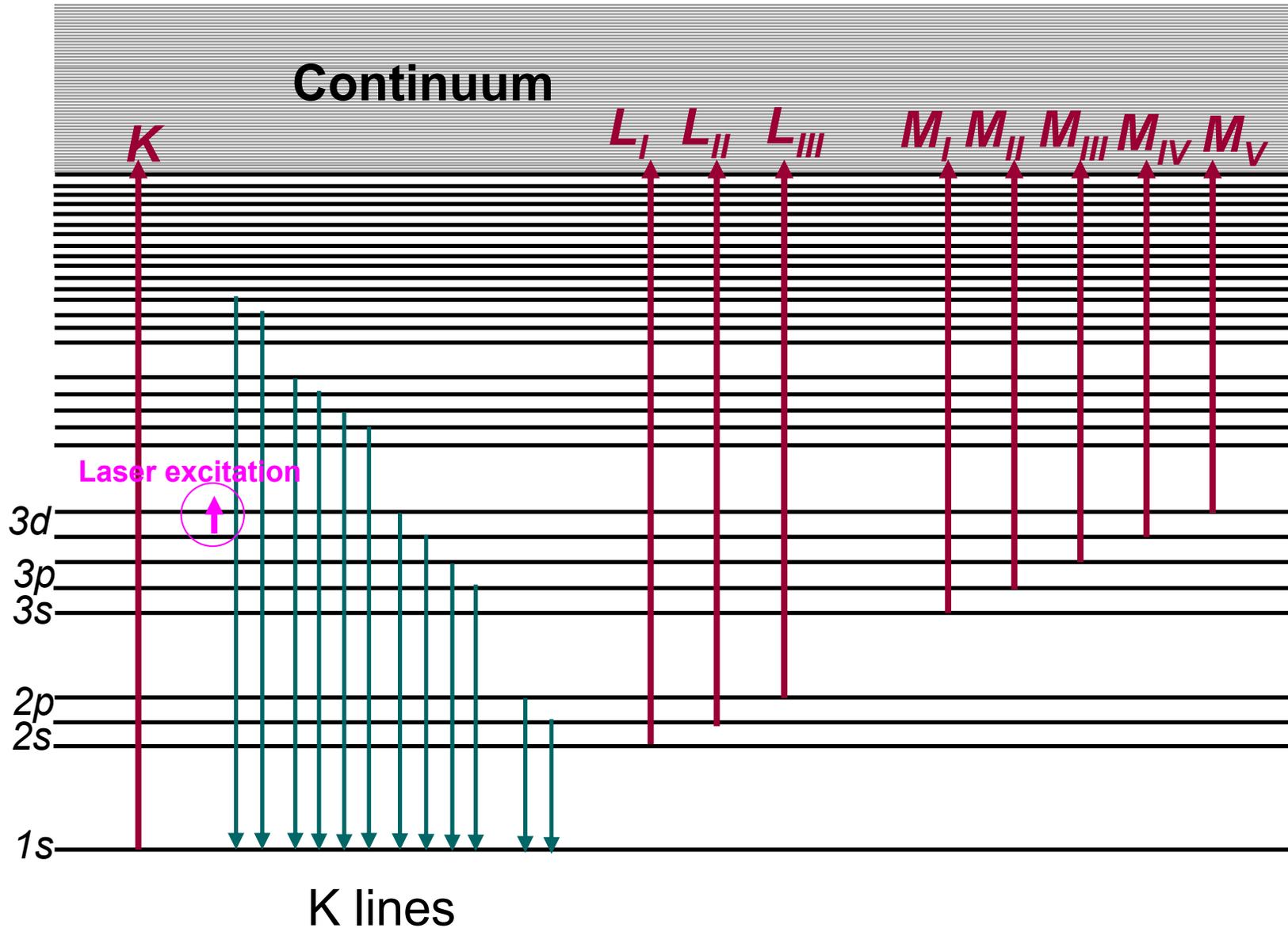
$$\mu(E) \propto \sum_f^{E_f > E_F} |\langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle|^2 \delta(E_f - E)$$

*Stern, Lytle and Sayers, 1970's*

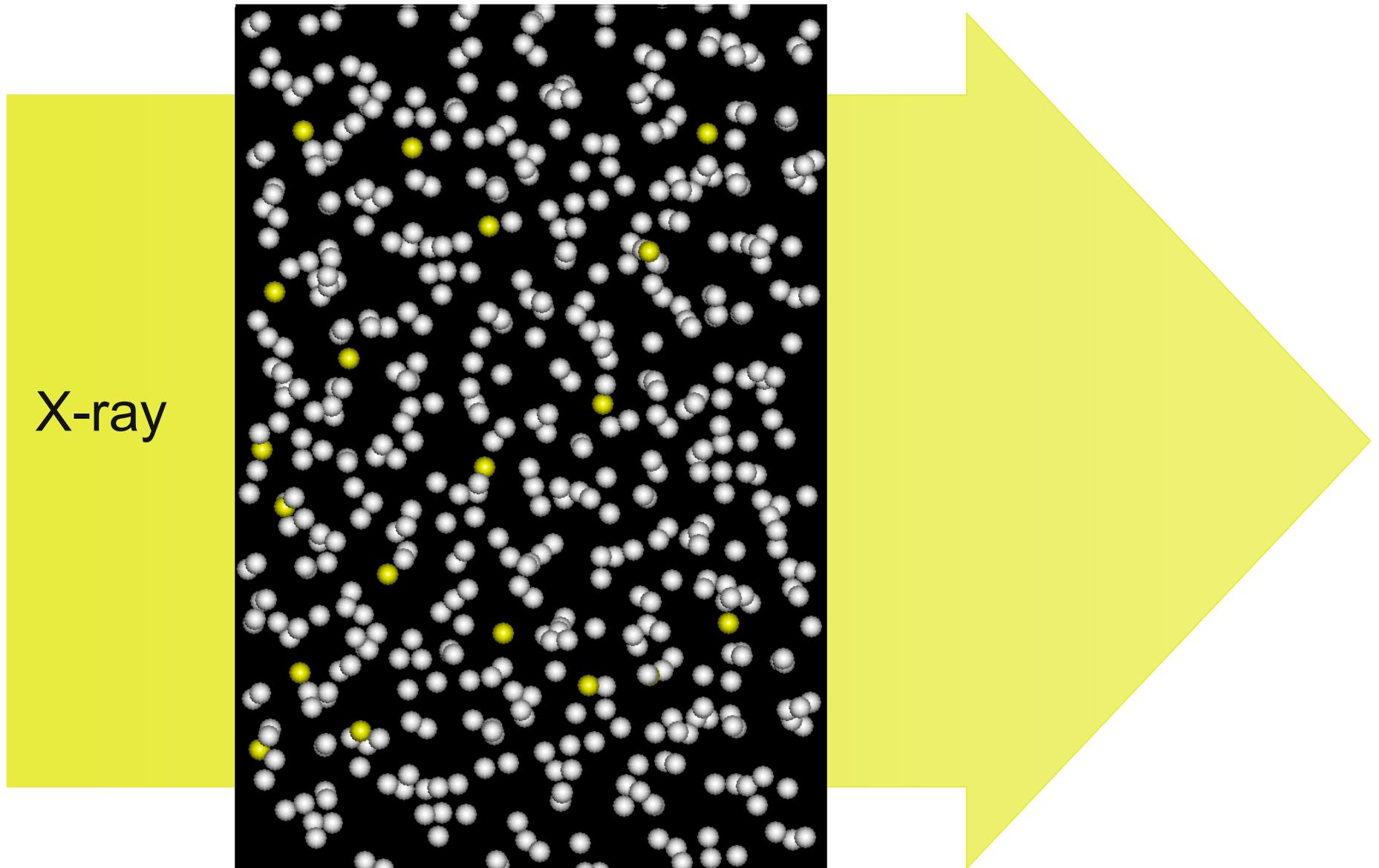
# X-ray Absorption Spectroscopy (XAS)

$$\chi(k) = \sum_j N_j F_j(k) e^{-2\sigma^2 k^2} e^{-\frac{2r_j}{\lambda_j(k)}} \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

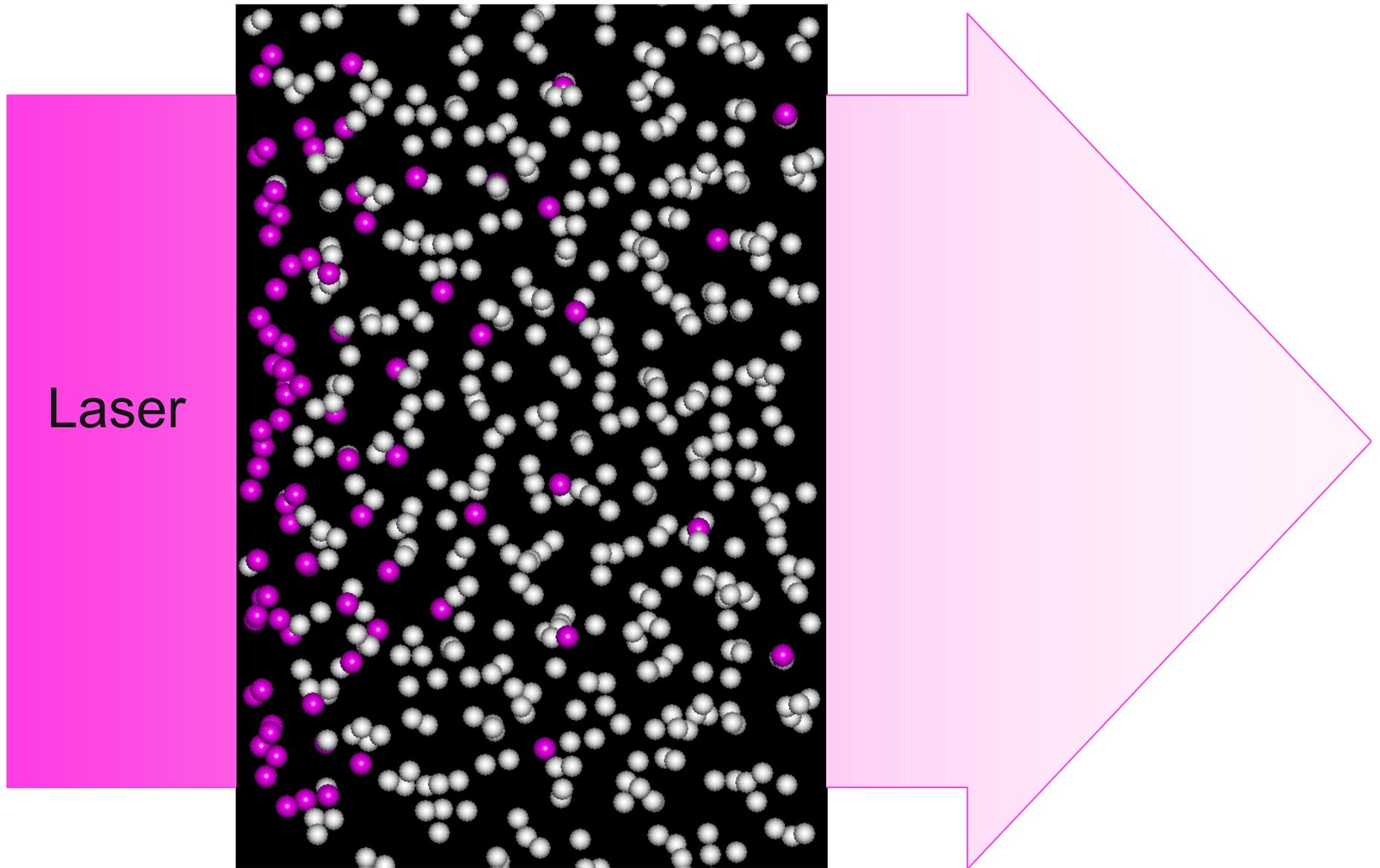
# Core level excitation (keV) vs. valence level (laser pump) excitation (eV)



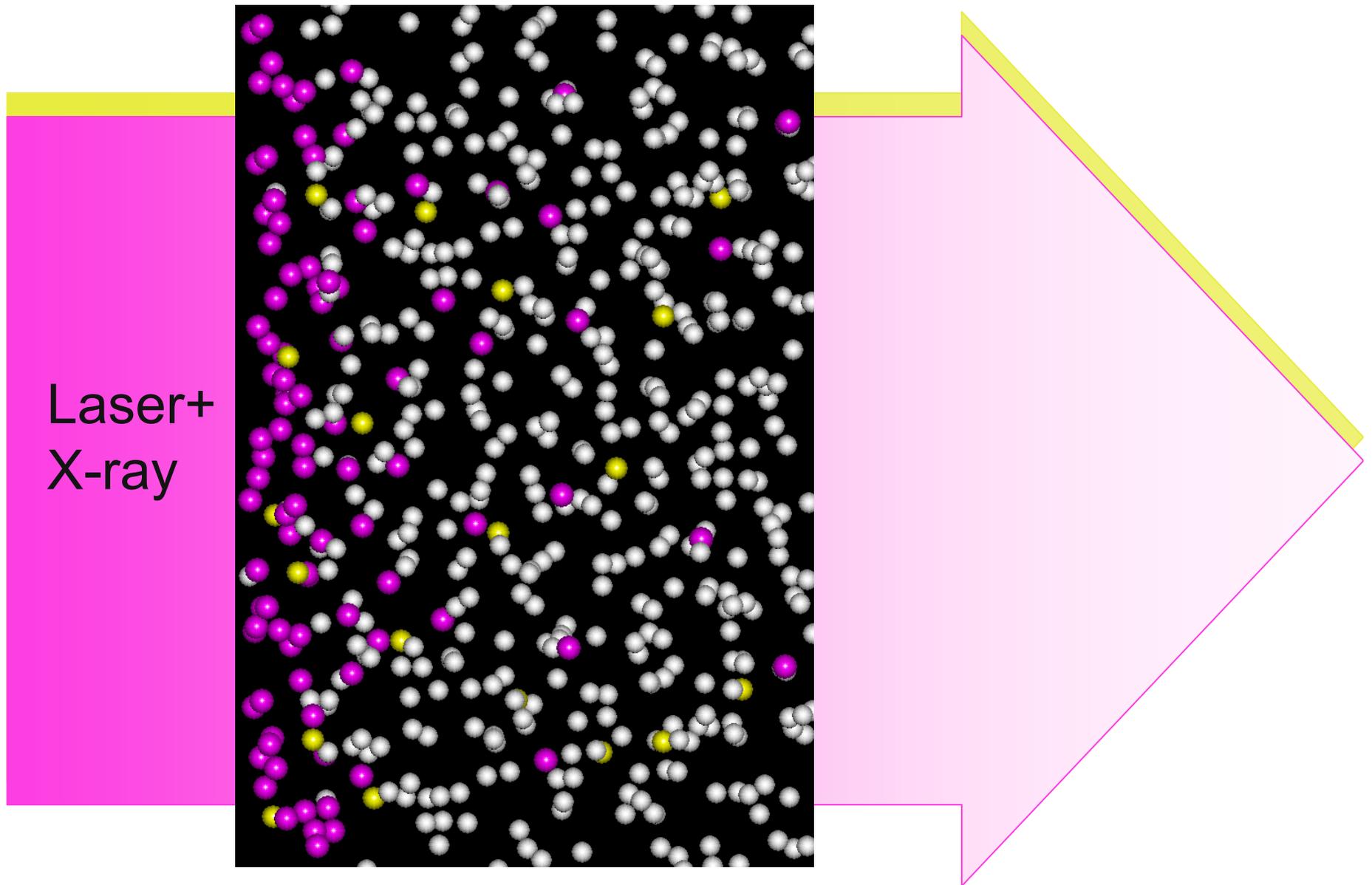
## X-ray and laser photon absorption cross sections



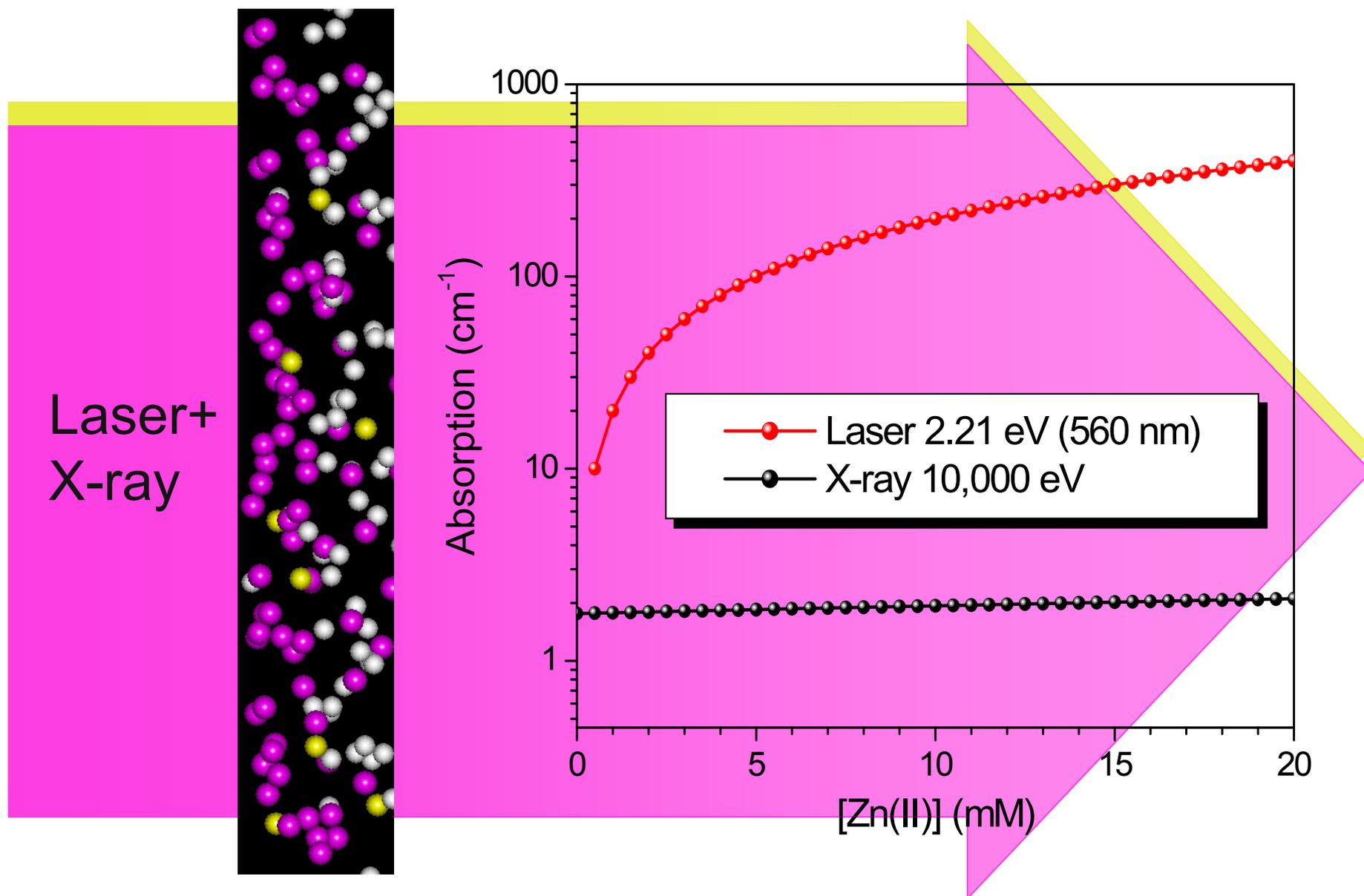
# X-ray and laser photon absorption cross sections



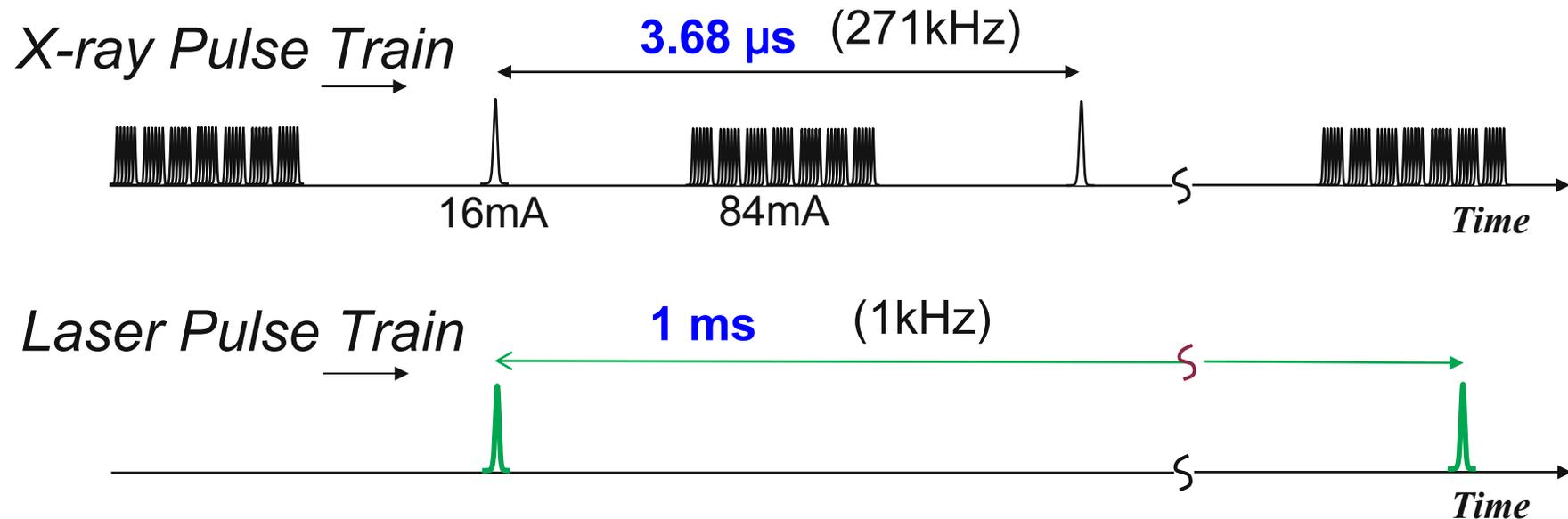
# X-ray and laser photon absorption cross sections



# X-ray and laser photon absorption cross sections



## X-ray and laser pulse repetition rates



A factor of 1,700 or more reduction of the x-ray photon flux!

- Long data acquisition hours
- Low signal/noise ratio

Solutions: Higher x-ray flux, higher repetition rate of laser.

## Extracting excited state (or transient state) spectrum from XTA

$$\begin{aligned}\chi(k, t) &= f_{GS}(t)\chi_{GS}(k, t) + f_{ES}(t)\chi_{ES}(k, t) \\ &= [1 - f_{ES}(t)]\chi_{GS}(k, t) + f_{ES}(t)\chi_{ES}(k, t) \\ &= \chi_{GS}(k, t) + f_{ES}(t)[\chi_{ES}(k, t) - \chi_{GS}(k, t)]\end{aligned}$$

Two unknowns and one equation  $\rightarrow$  need to find  $f_{ES}$  via other means

A, via calculation

$$f_{ex} = \frac{P \cdot e^{-kt} \cdot Q}{N \cdot h\nu} \cdot [1 - 10^{-\varepsilon(\lambda)lC(1-f_{ex}Q \cdot e^{-kt})}]$$

P, laser pulse energy (J);

k, rate const., ( $s^{-1}$ );

t, time, s;

$\varepsilon(\lambda)$ , absorption coeff. at laser wavelength  $\lambda$  ( $M^{-1}cm^{-1}$ );

l, thickness (cm);

C, concentration (M);

N, total number of molecules illuminated by the laser.

## Extracting excited state (or transient state) spectrum from XTA

B. via optical transient absorption (e.g. two state system)

*From laser pump, laser probe transient absorption spectroscopy in a two-state example, where the total concentration of excited and ground states remain to be the starting ground state concentration  $C_{GS}(\lambda, t=0)$ :*

$$\begin{aligned}\Delta OD(\lambda, t) &= \log \frac{\varepsilon_{GS}(\lambda) C_{GS}(\lambda, 0)}{[(\varepsilon_{GS}(\lambda) C_{GS}(\lambda, t) + \varepsilon_{ES}(\lambda) C_{ES}(\lambda, t))]} \\ &= \log \frac{\varepsilon_{GS} C_{GS}(\lambda, 0)}{\{(\varepsilon_{GS}(\lambda) C_{GS}(\lambda, 0)[1 - f_{ES}(t)] + \varepsilon_{ES}(\lambda) C_{GS}(\lambda, 0) f_{ES}(t)\}} \\ &= \log \frac{\varepsilon_{GS}(\lambda)}{\{(\varepsilon_{GS}(\lambda)[1 - f_{ES}(t)] + \varepsilon_{ES}(\lambda) f_{ES}(t)\}}\end{aligned}$$

*If the extinction coefficient for the excited state at a particular detection wavelength  $\lambda$ ,  $\varepsilon_{ES}(\lambda) = 0$ ,*

$$\Delta OD(\lambda, t) = \log \frac{\varepsilon_{GS}(\lambda)}{(\varepsilon_{GS}(\lambda)[1 - f_{ES}(t)]} = \log \frac{1}{[1 - f_{ES}(t)]} = -\log[1 - f_{ES}(t)]$$

$$[1 - f_{ES}(t)] = e^{\Delta OD} \rightarrow f_{ES}(t) = 1 - e^{\Delta OD}$$

# Extracting excited state (or transient state) spectrum from XTA

C. via calculation (one example by Grigory Smolentsev et al.)

## Multidimensional interpolation

Interpolated  
spectrum

Calculated  
spectrum

Calculated  
coefficients

$$\mu_i(E, p_1 + \delta p_1, \dots, p_n + \delta p_n) = \mu(E, p_1, \dots, p_n) + \sum_n A_n(E) \delta p_n + \sum_{m,n} B_{m,n}(E) \delta p_m \delta p_n + \dots$$

Starting  
values

Small  
deviations

## Non-muffin-tin FDMNES or FEFF8

Comparison of spectra:

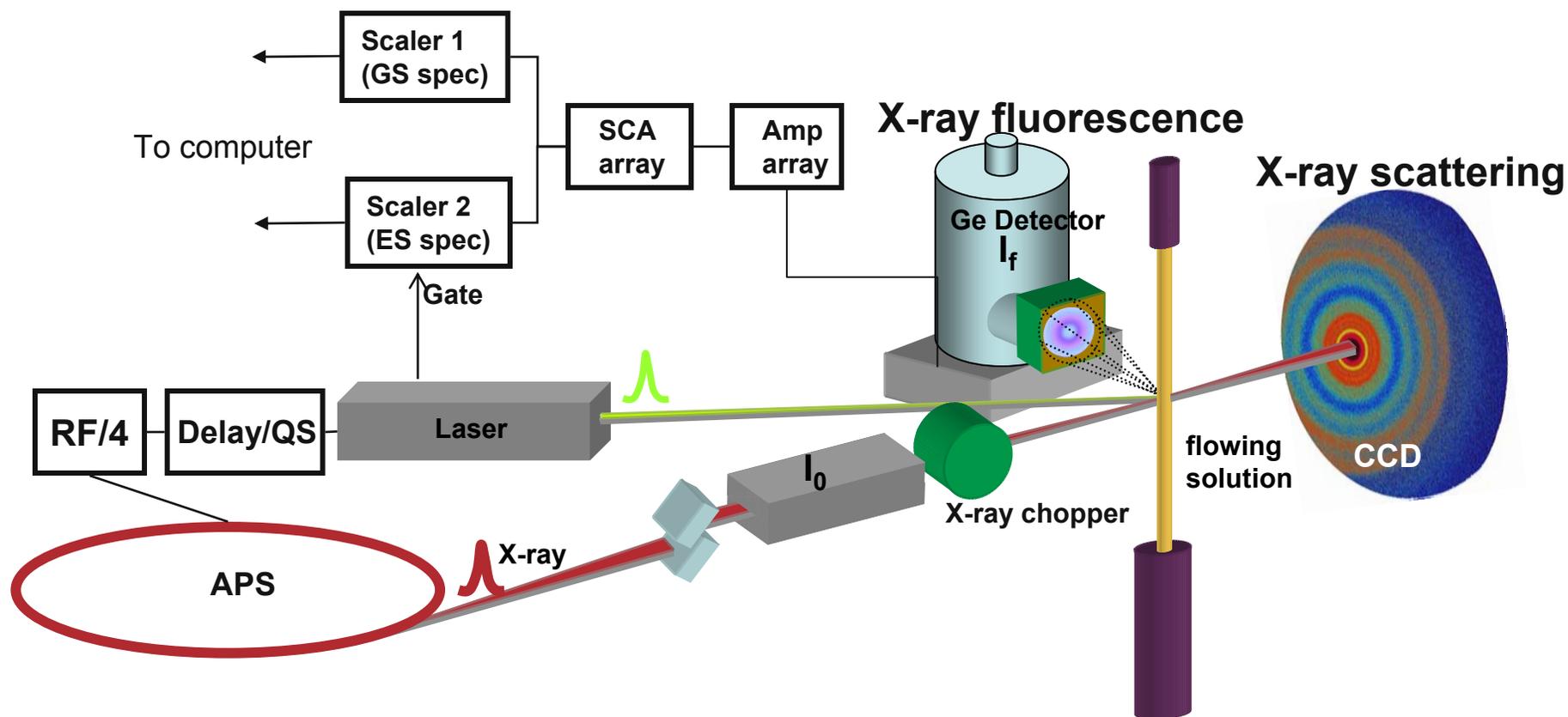
$$\min\left(\frac{1}{E_2 - E_1} \int_{E_1}^{E_2} \left[ \left( \mu_{\text{exp}}^{\text{laser-on}} - \mu_{\text{exp}}^{\text{laser-off}} \right) - Y \left( \mu_{\text{theor}}^{\text{es}}(\delta p_1, \delta p_2) - \mu_{\text{theor}}^{\text{gs}} \right) \right]^2 dE \right)$$

## Principal component analysis

Smolentsev, G.; Soldatov, A. *Journal of Synchrotron Radiation* **2006**, 13, 19-29.  
Smolentsev, G.; Soldatov, A. V. *Computational Materials Science* **2007**, 39, 569-574.

## **4. Basic experimental setup**

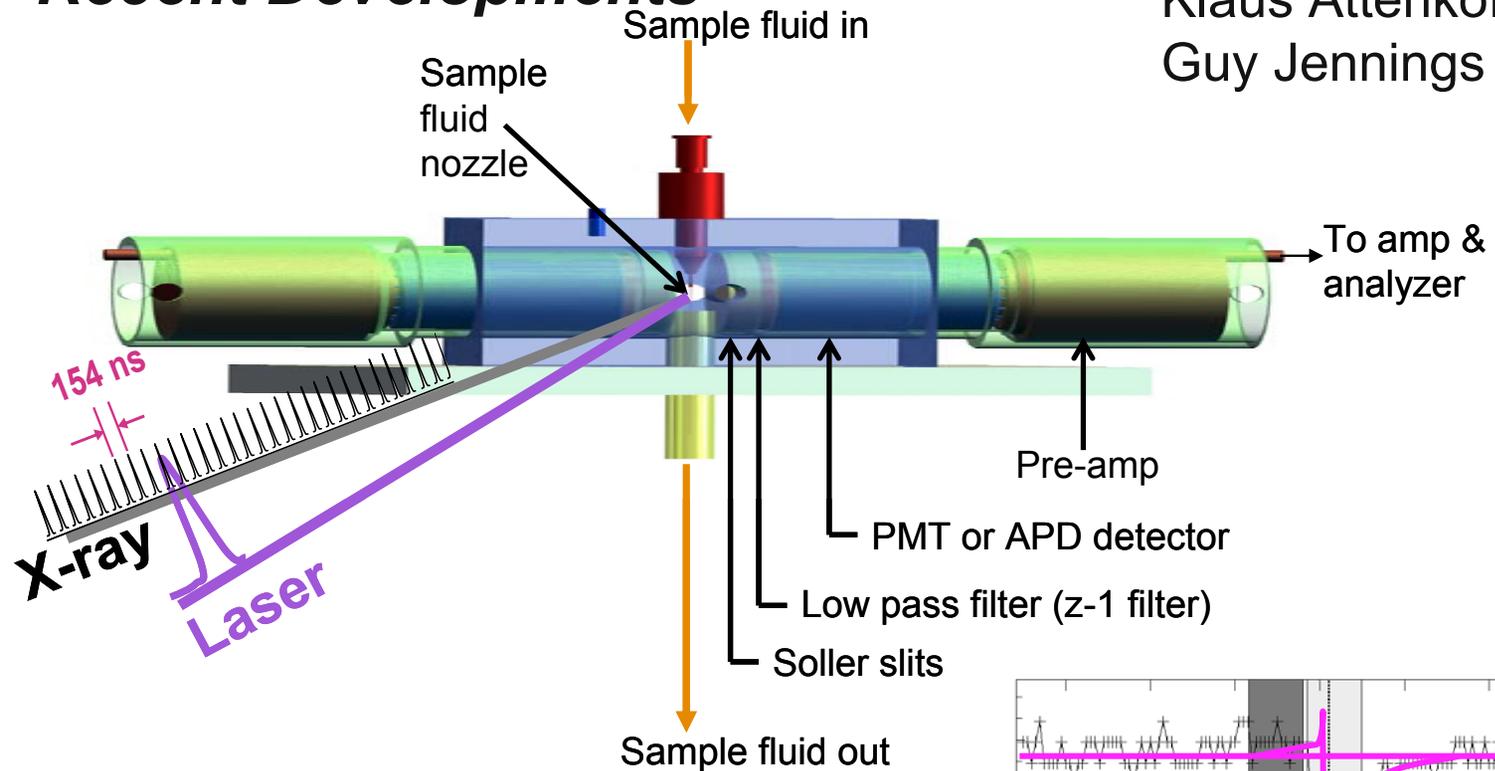
# Experimental Setup for X-ray Transient Absorption/Scattering at 11-ID-D, APS



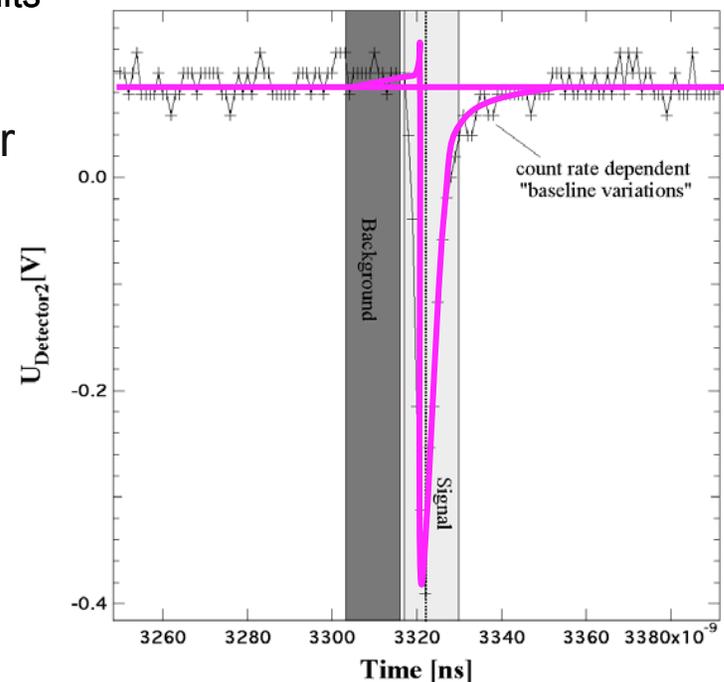
*Ann. Rev. Phys. Chem.* **56**, 221-254 (2005)  
*Angew. Chemie.* **43**, 2886-2905 (2004).

# XTA — Recent Developments

Klaus Attenkofer  
Guy Jennings

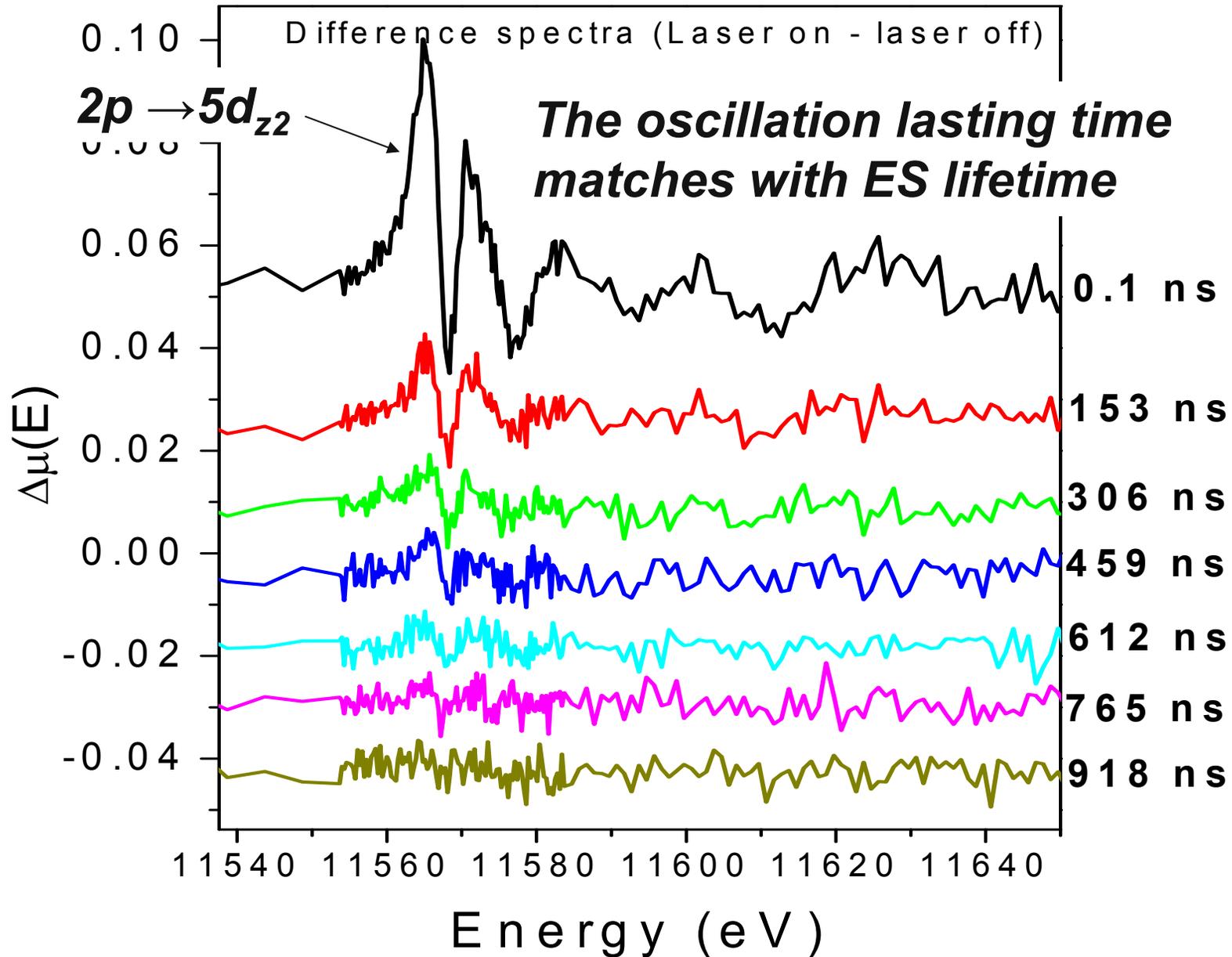


- Compact and integrated sample/detector chamber for air sensitive samples to ensure large solid detection angle, elastic scattering removal for dilute solution samples;
- In-situ curve fitting for data acquisition
- Current mode detection with fast digitizer/signal averaging allows large dynamic range;
- Fast detector system allow bunch to bunch resolution for all x-ray bunches in the pulse chain.



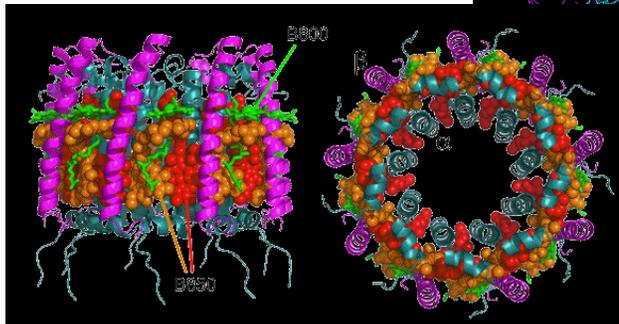
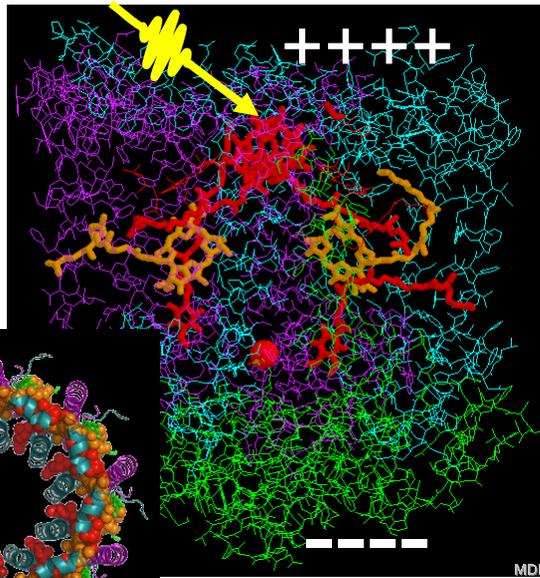
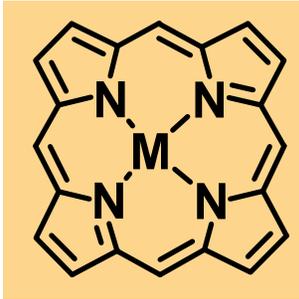
# ***XTA — Method Development***

***Difference XTA spectra at Pt  $L_{III}$ -edge for  $[Pt(ppy)(\mu-R_2pz)]_2$***



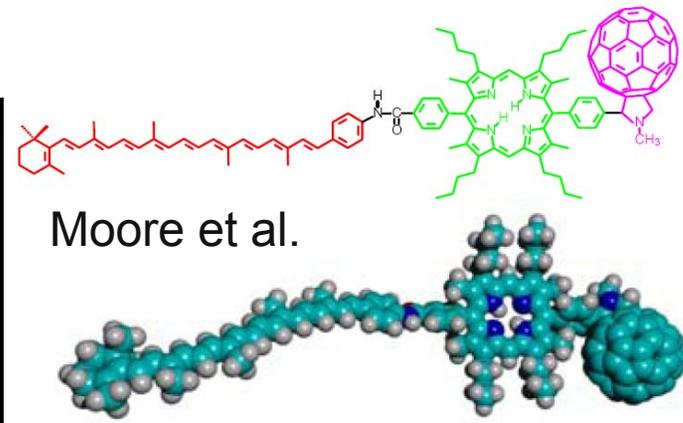
## **5. XTA study examples**

# Metalloporphyrins are important building blocks for solar energy conversion and life

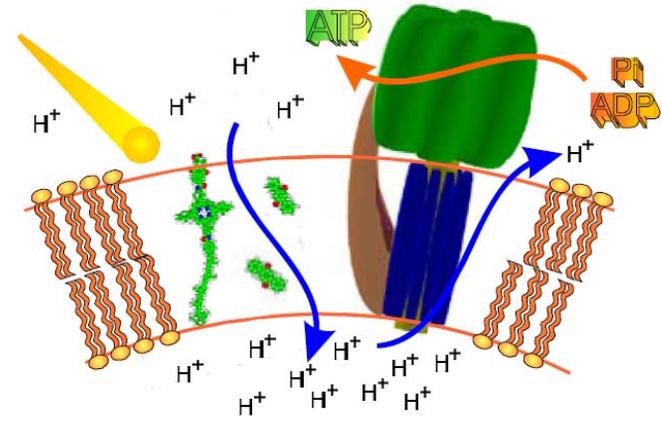


**Photosynthetic bacterial light harvesting protein**

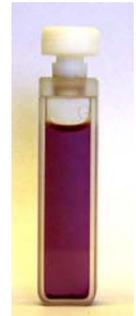
**Photosynthetic bacterial reaction center protein**



Moore et al.



**Chlorophyll a**

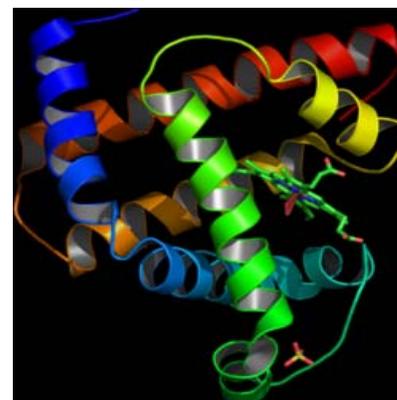


**$\beta$ -Porphyrin**



**Zn-Phthalocyanine**

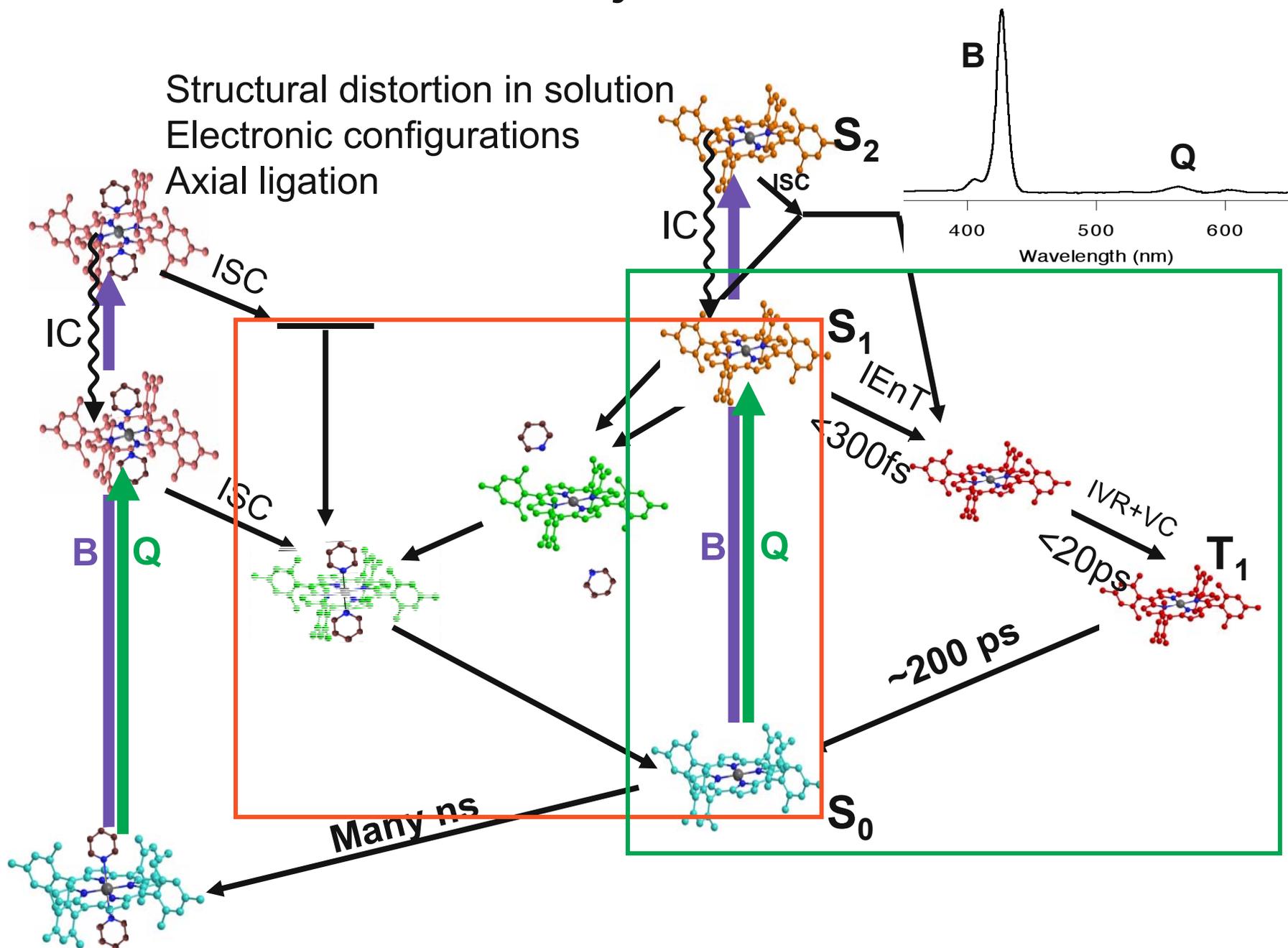
(J. S. Lindsey)



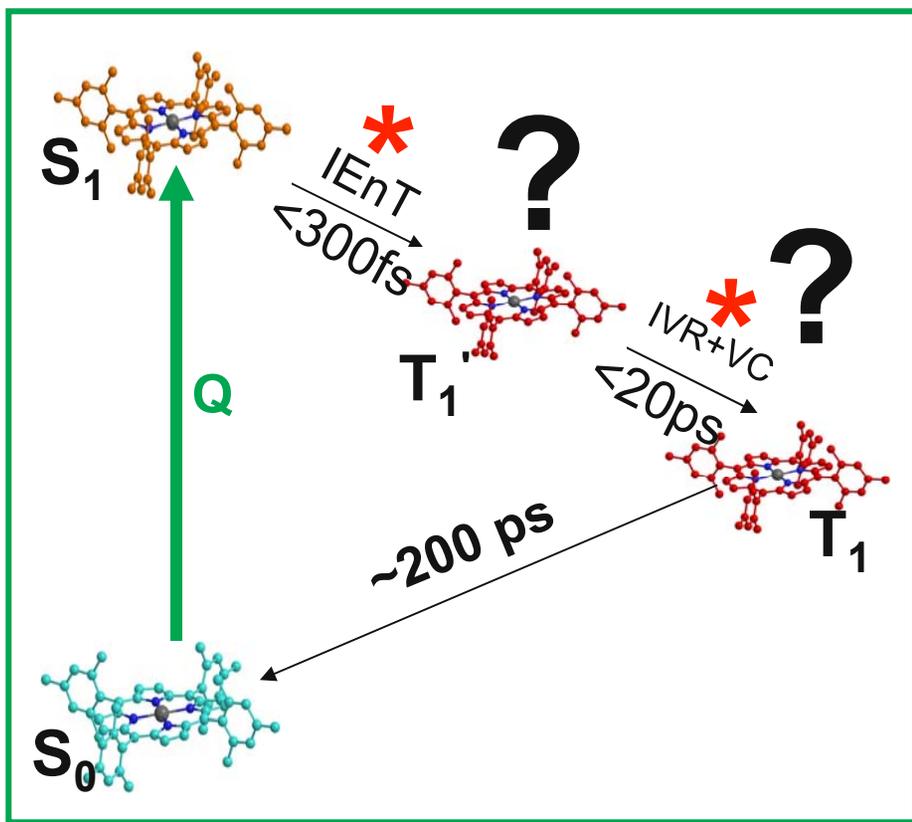
**Myoglobin**

Excited states of metalloporphyrins are: electron donors or acceptors, light harvesting pigments, photocatalysis, functional site analogs of heme proteins, photovoltaic materials.

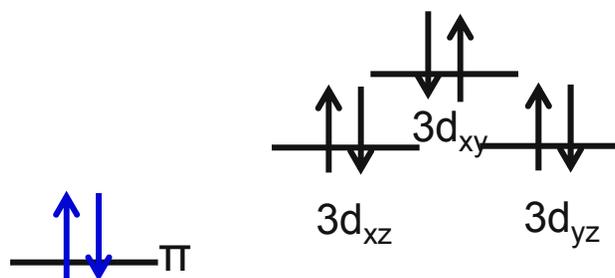
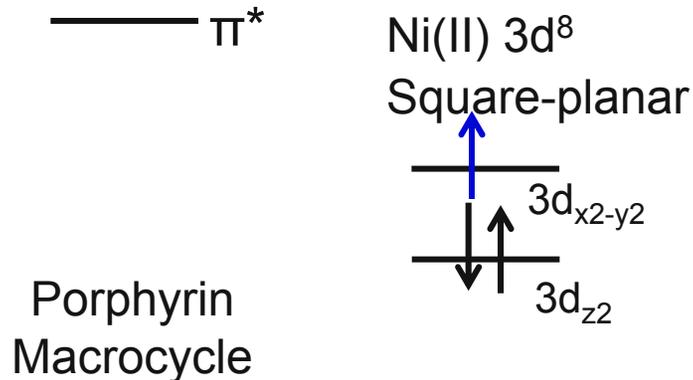
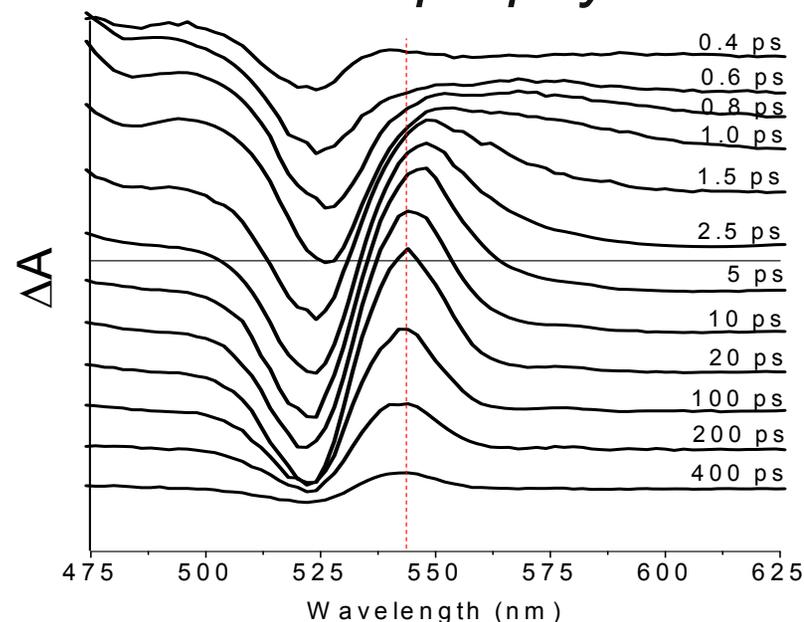
# Excited state structural dynamics of nickelporphyrins



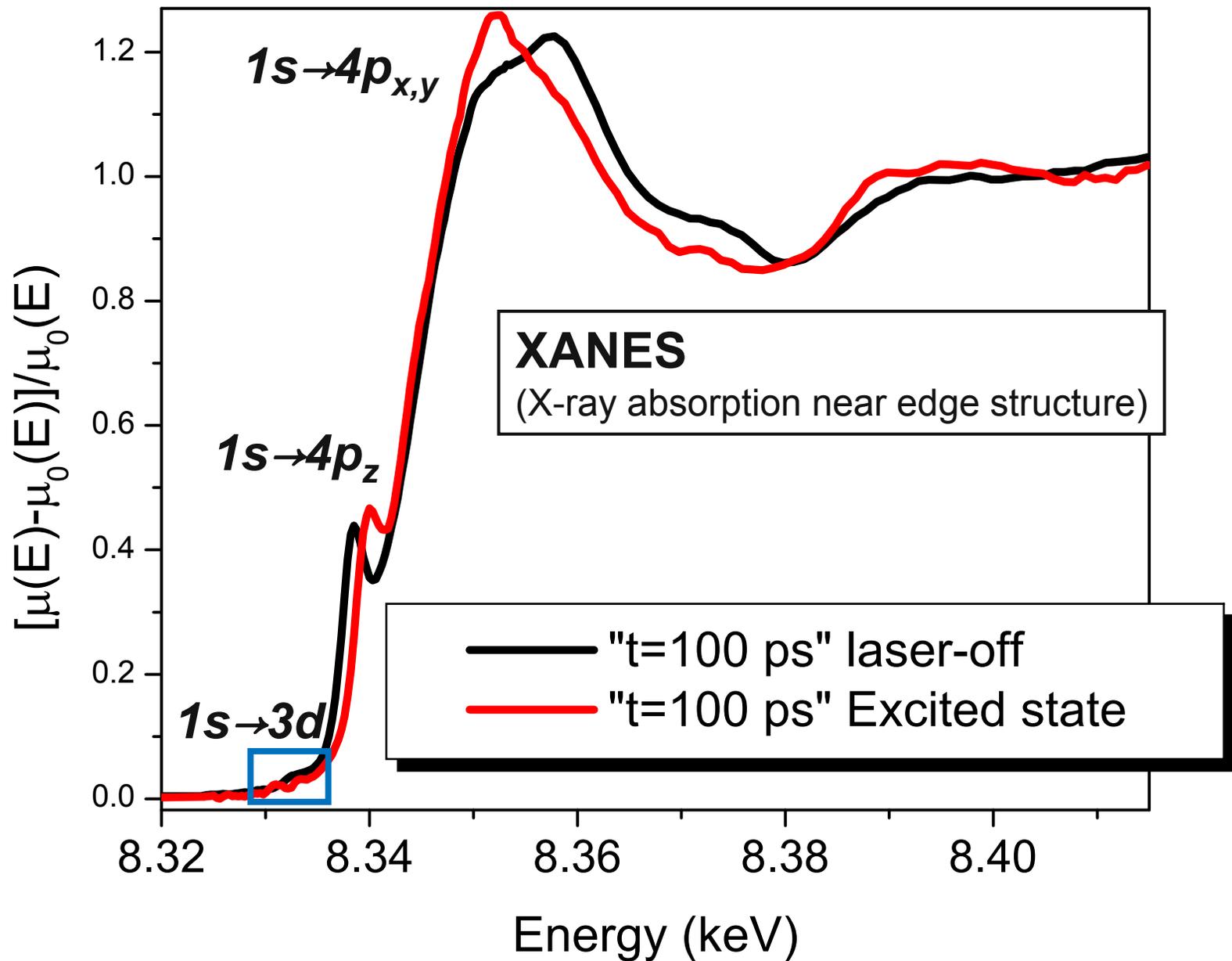
# Ultrafast excited state structural dynamics of nickelporphyrins



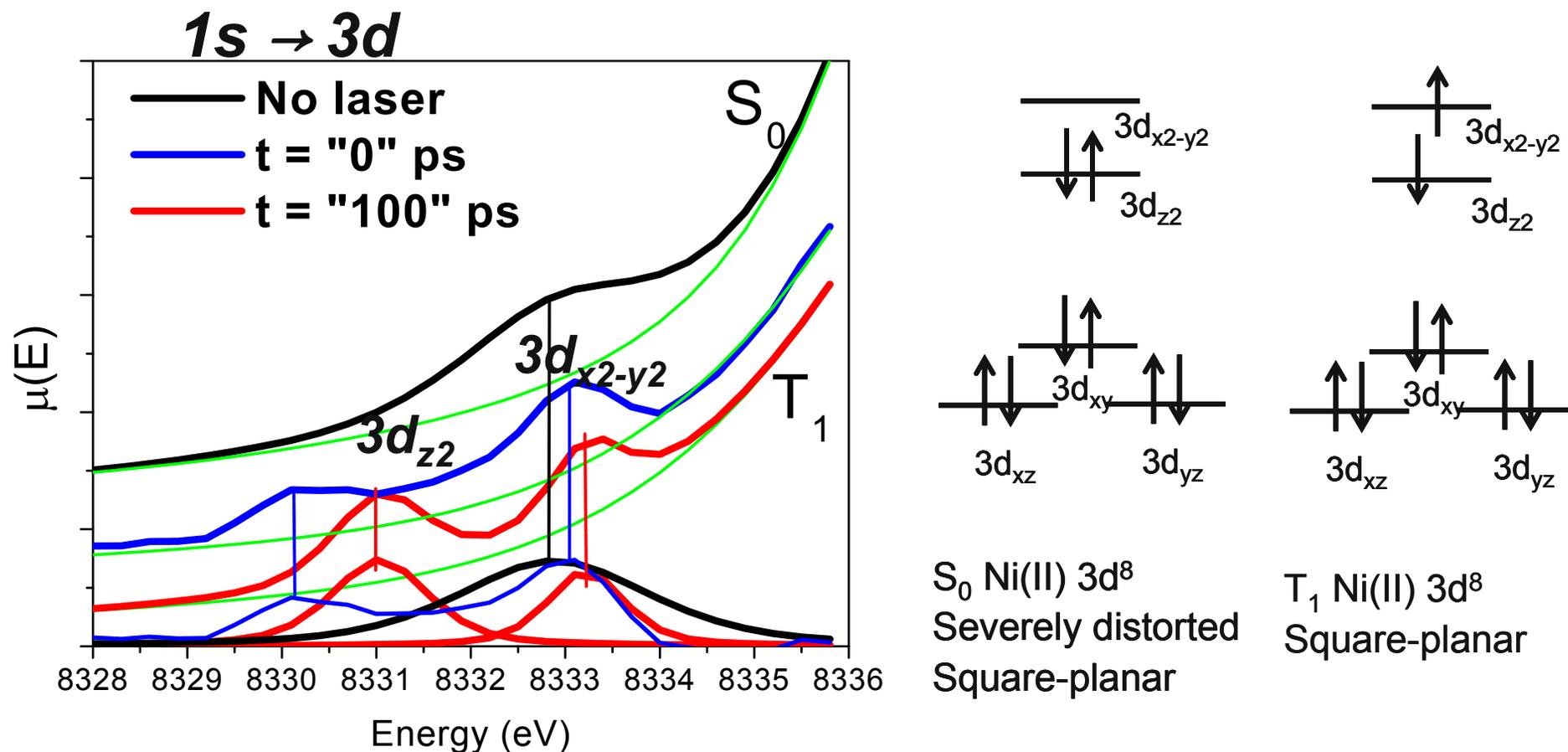
- $(\pi, \pi^*) \rightarrow (d, d,)$  conversion mechanism;
- Correlated structural change and energy transfer;
- MO energy levels;
- Role of the solvent and ligation;
- Transient oxidation state of Ni.



# Ultrafast excited state structural dynamics of nickelporphyrins



# Ultrafast excited state structural dynamics of nickelporphyrins

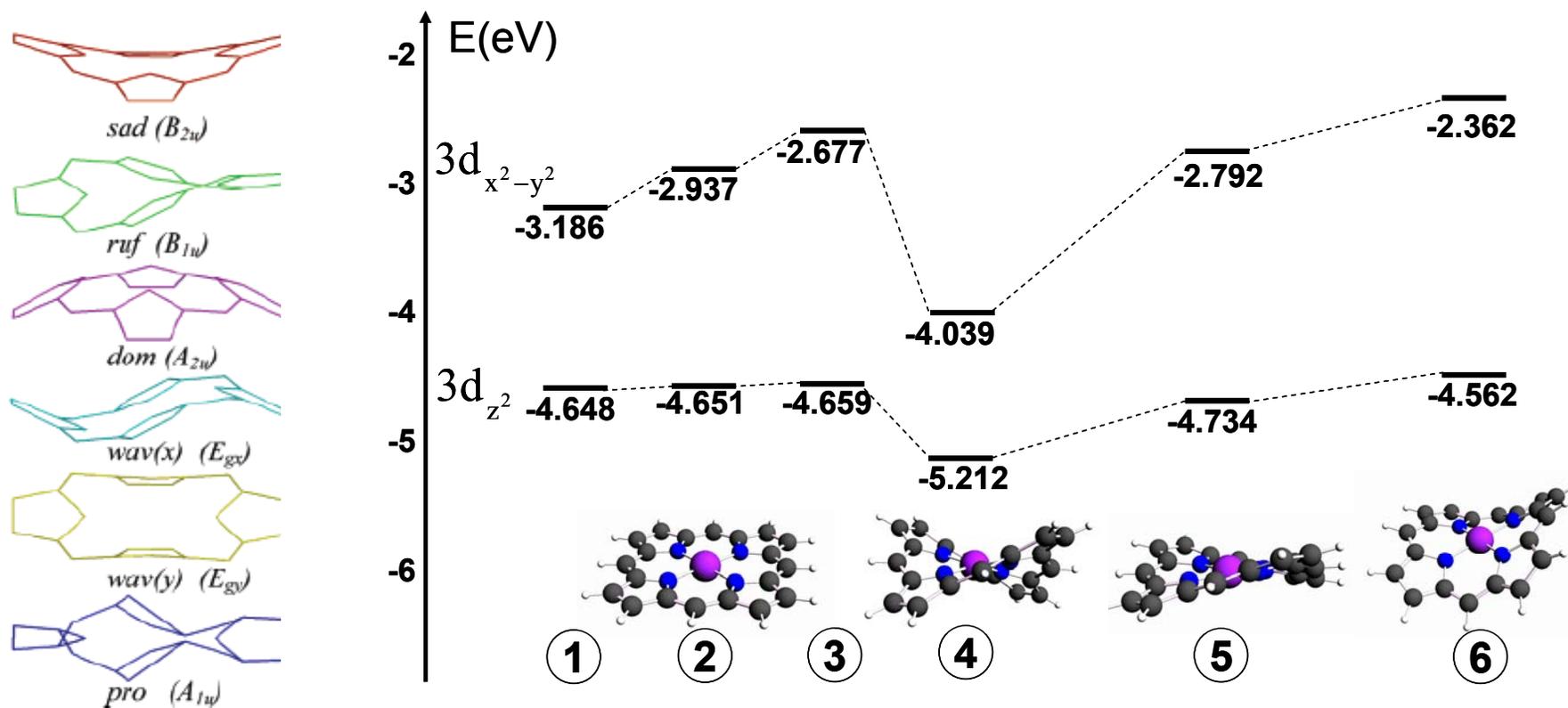


- 1) Singly occupied  $3d_{z^2}$  and  $3d_{x^2-y^2}$  MO in the  $T_1$  state:
- 2) Wider bandwidth for  $1s \rightarrow 3d_{x^2-y^2}$  transition in the  $S_1$  state than  $T_1$  state;
- 3) The d-d splitting evolves faster than one can currently resolve.

How fast is the intra-molecular electron shift and its correlation with nuclear geometry change?

# Ultrafast excited state structural dynamics of nickelporphyrins

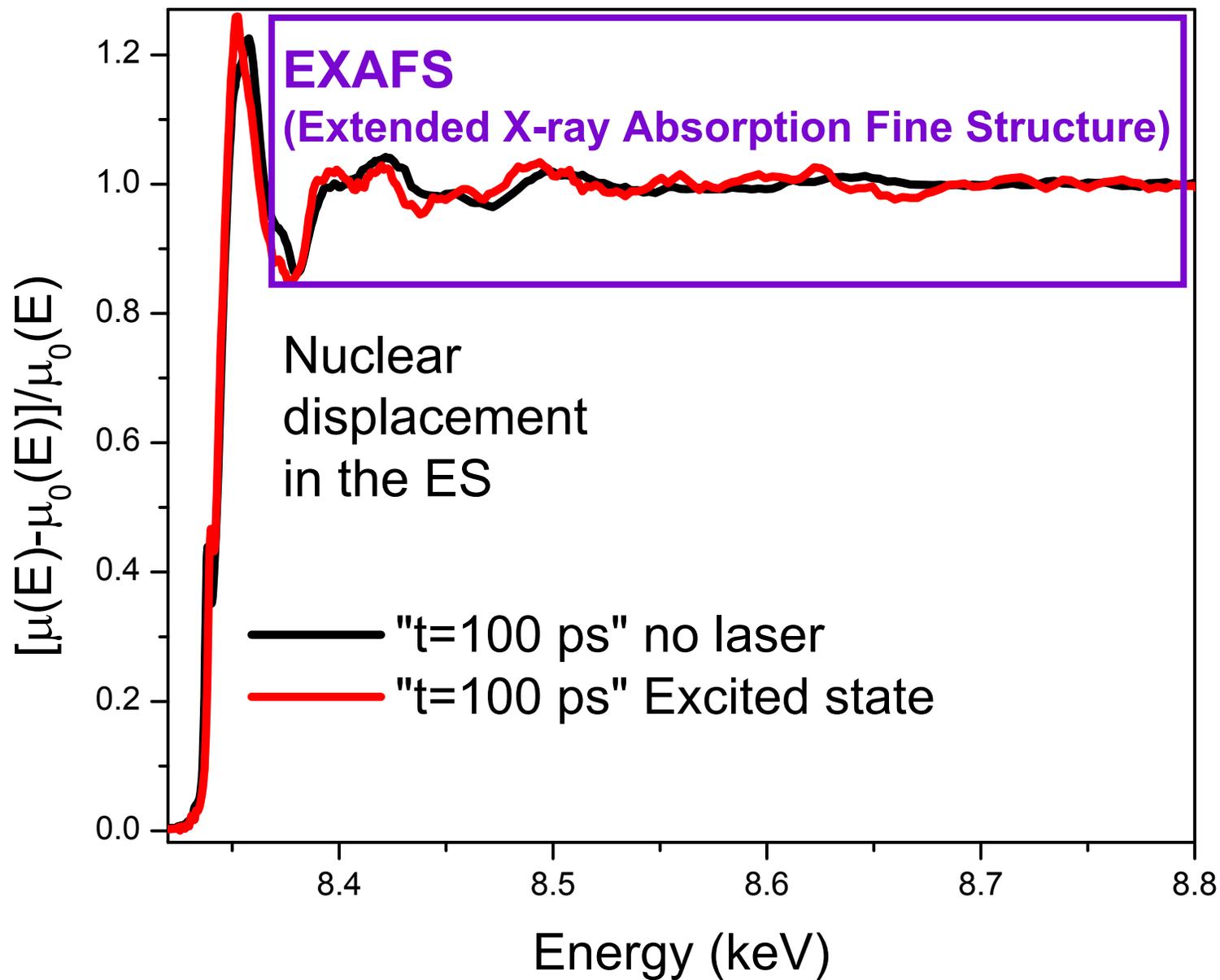
Why does the  $1s \rightarrow 3d_{x^2-y^2}$  transition band so broad (i.e.  $> 1.4$  eV)?



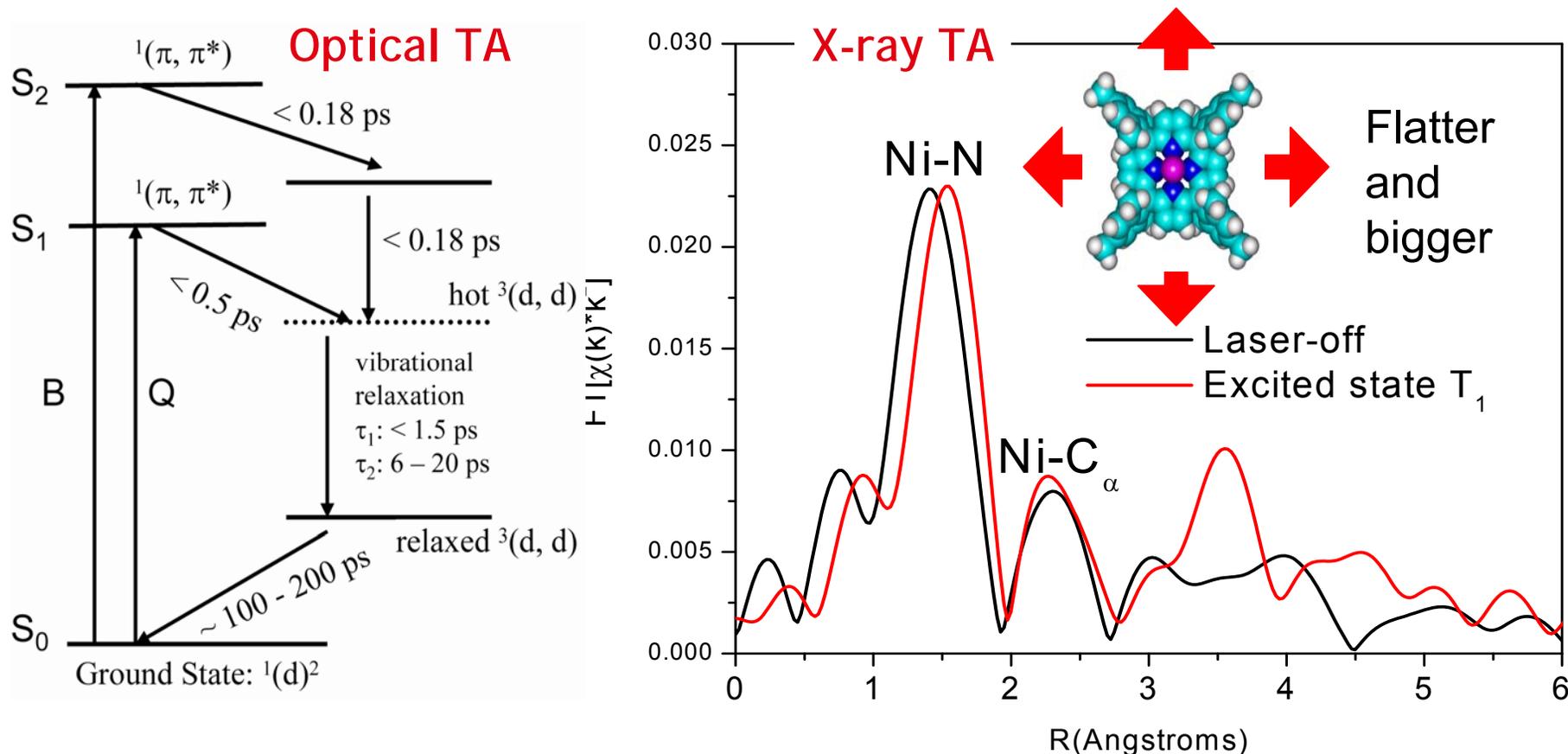
G. Smolentsev

Conformation dependence of 3d energy levels

# Ultrafast excited state structural dynamics of nickelporphyrins



# Ultrafast excited state structural dynamics of nickelporphyrins

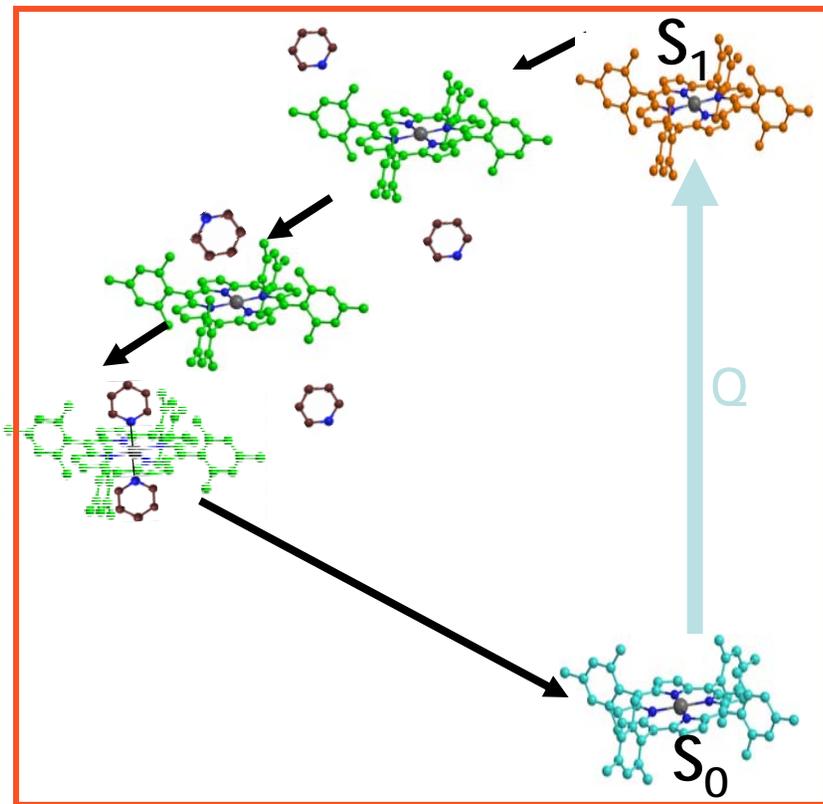


## Geometric changes in the excited state NiTMP

The Ni-N and Ni-C<sub>α</sub> distances both increase at the T<sub>1</sub> state.

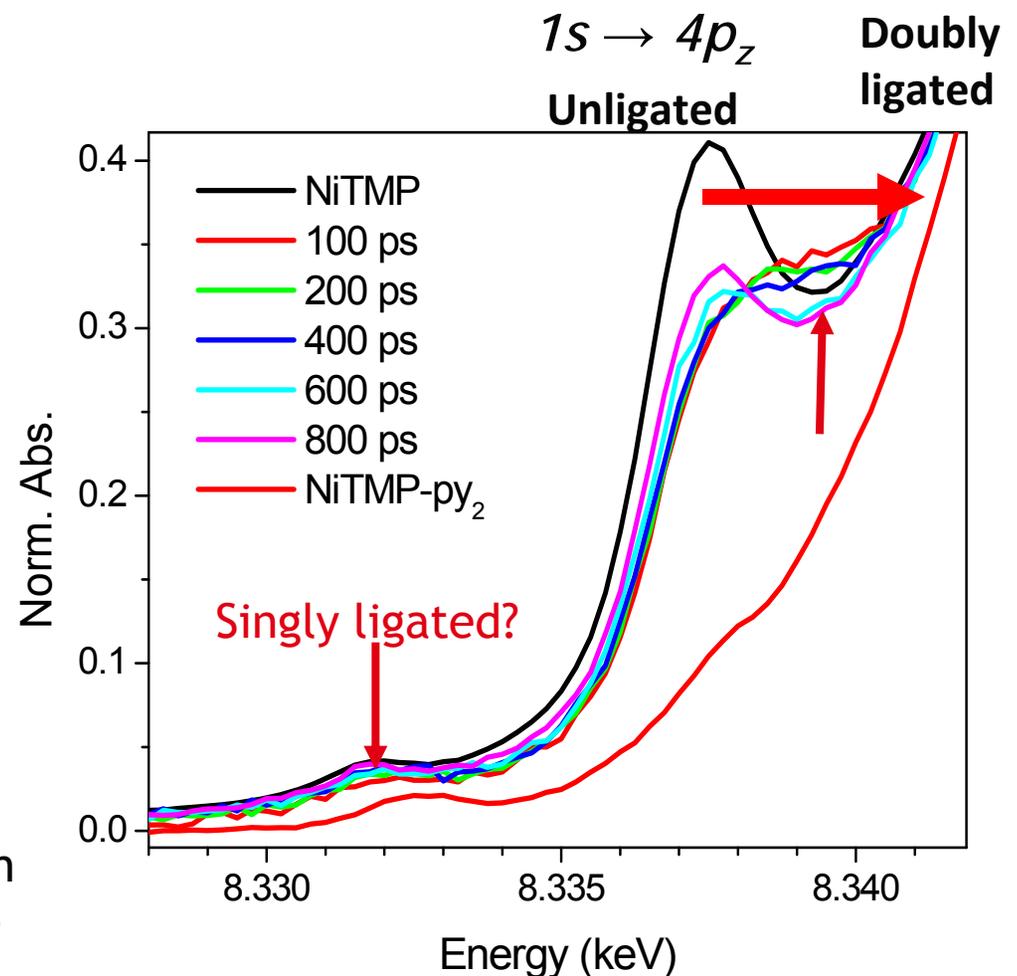
The x-ray pulses are too long to resolve the timing and time scale for the macrocycle expansion as well as the correlations with electronic transitions.

# Following photoinduced ligation of nickelporphyrins



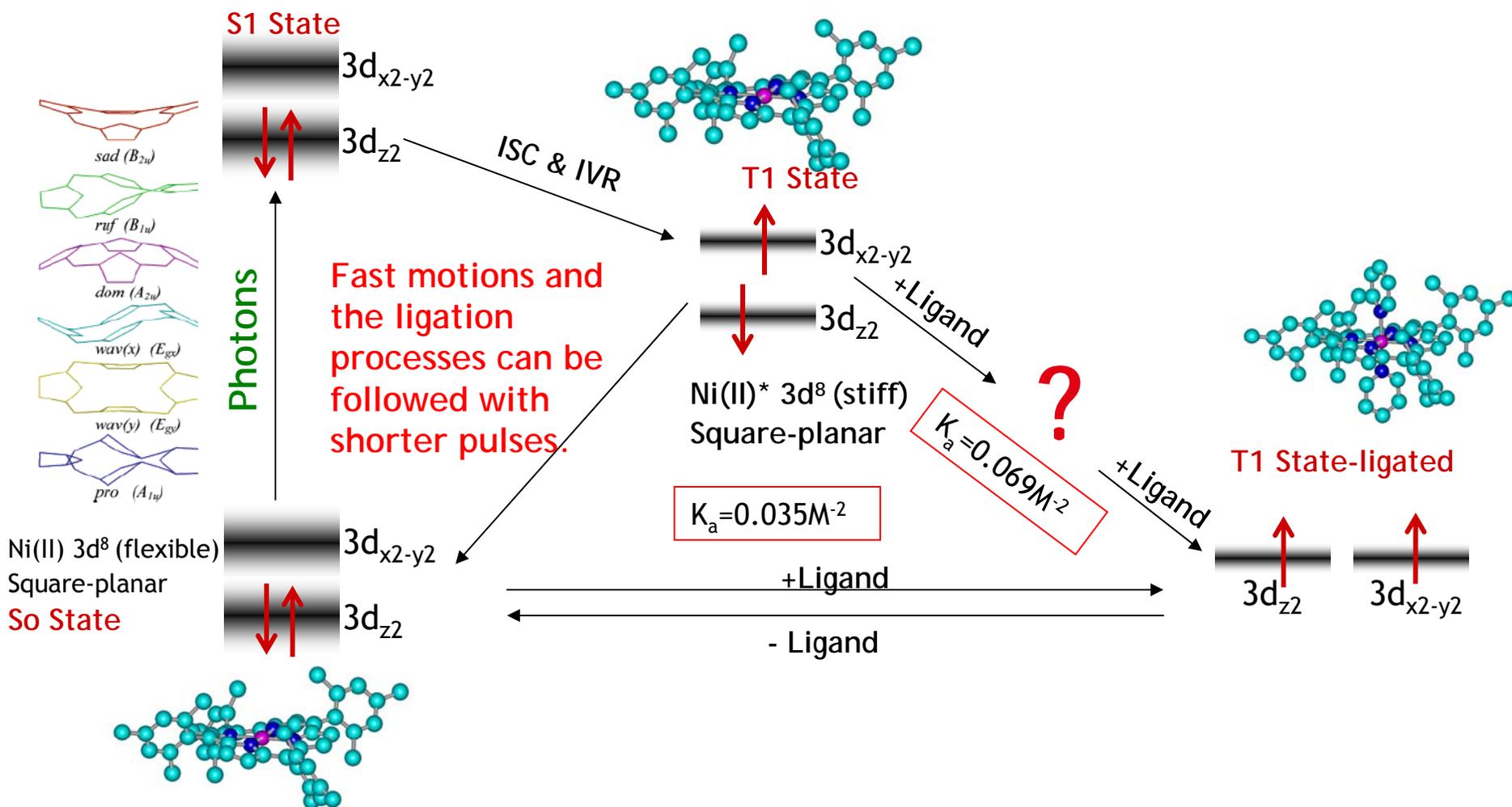
Time sequence in photoinduced ligation

- Generate  $S_1$  state,  $< 100$  ps to create vacancy at  $3d_{z^2}$ ;
- Pyridine solvation or singly ligated NiTMP\*,  $< 600$  ps;
- Pyridine double ligation,  $< 800$  ps.



*Absence of double peak  $\rightarrow$  py surrounding changes conformation to have degenerate  $3d_{z^2}$  and  $3d_{x^2-y^2}$*

# A unified mechanism for axial ligation of nickelporphyrins



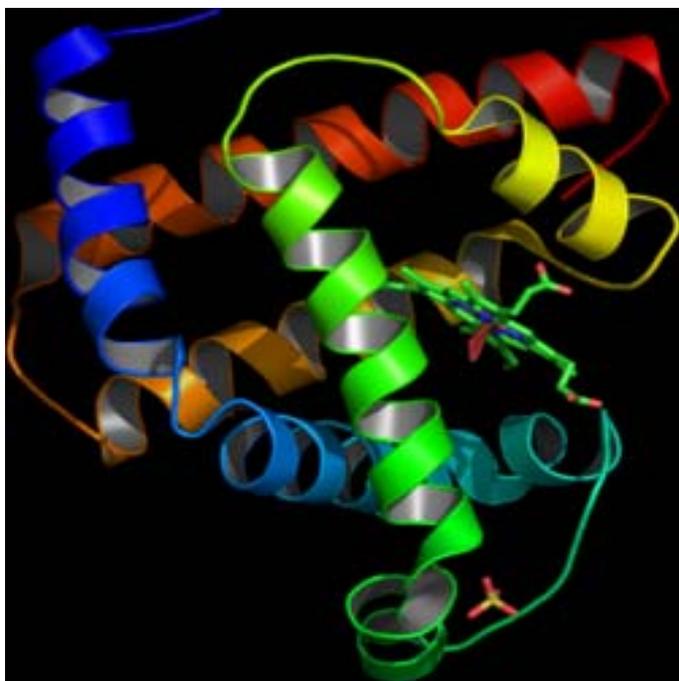
# Time-Resolved X-ray Absorption Spectroscopy of Carbon Monoxide-Myoglobin Recombination After Laser Photolysis

D. M. MILLS

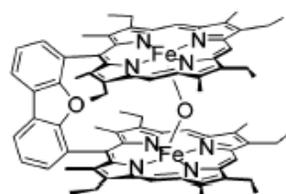
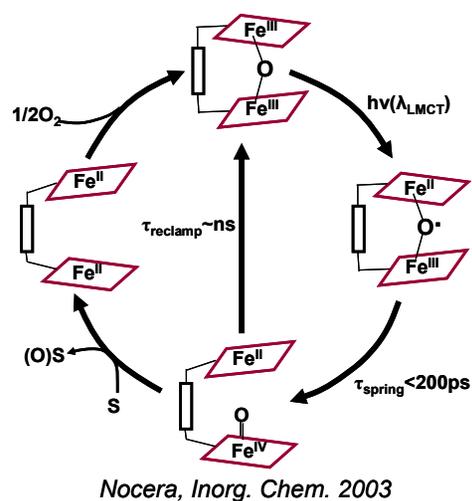
Cornell High Energy Synchrotron  
Source, Cornell University,  
Ithaca, New York 14853

A. LEWIS  
A. HAROOTUNIAN  
J. HUANG  
B. SMITH

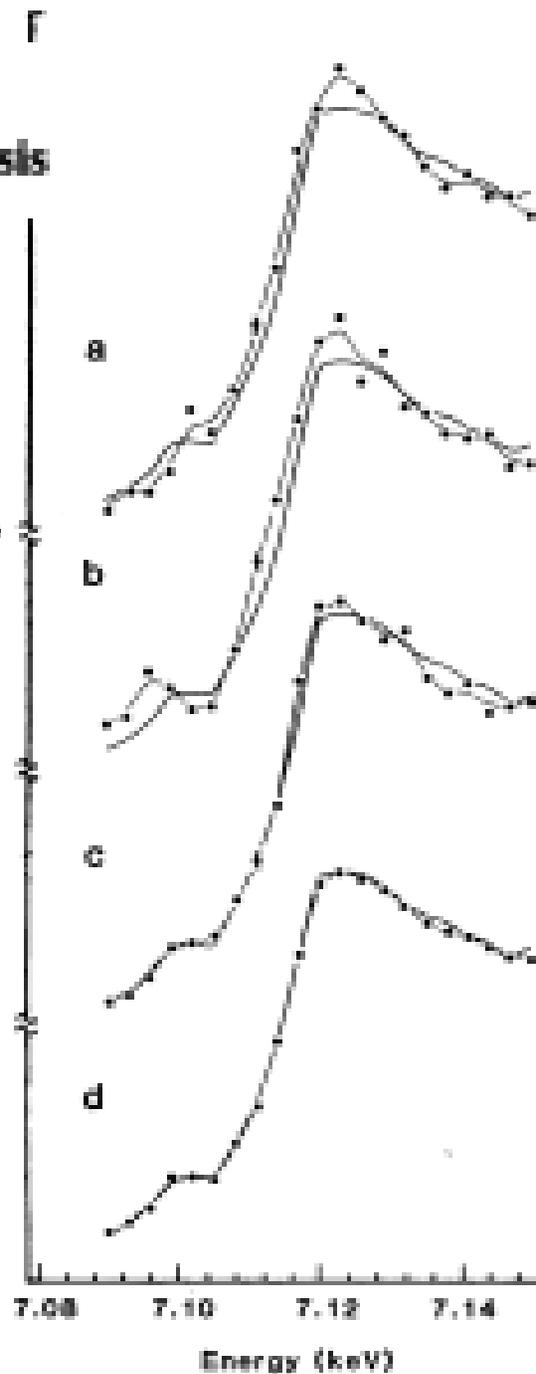
School of Applied and Engineering  
Physics, Cornell University



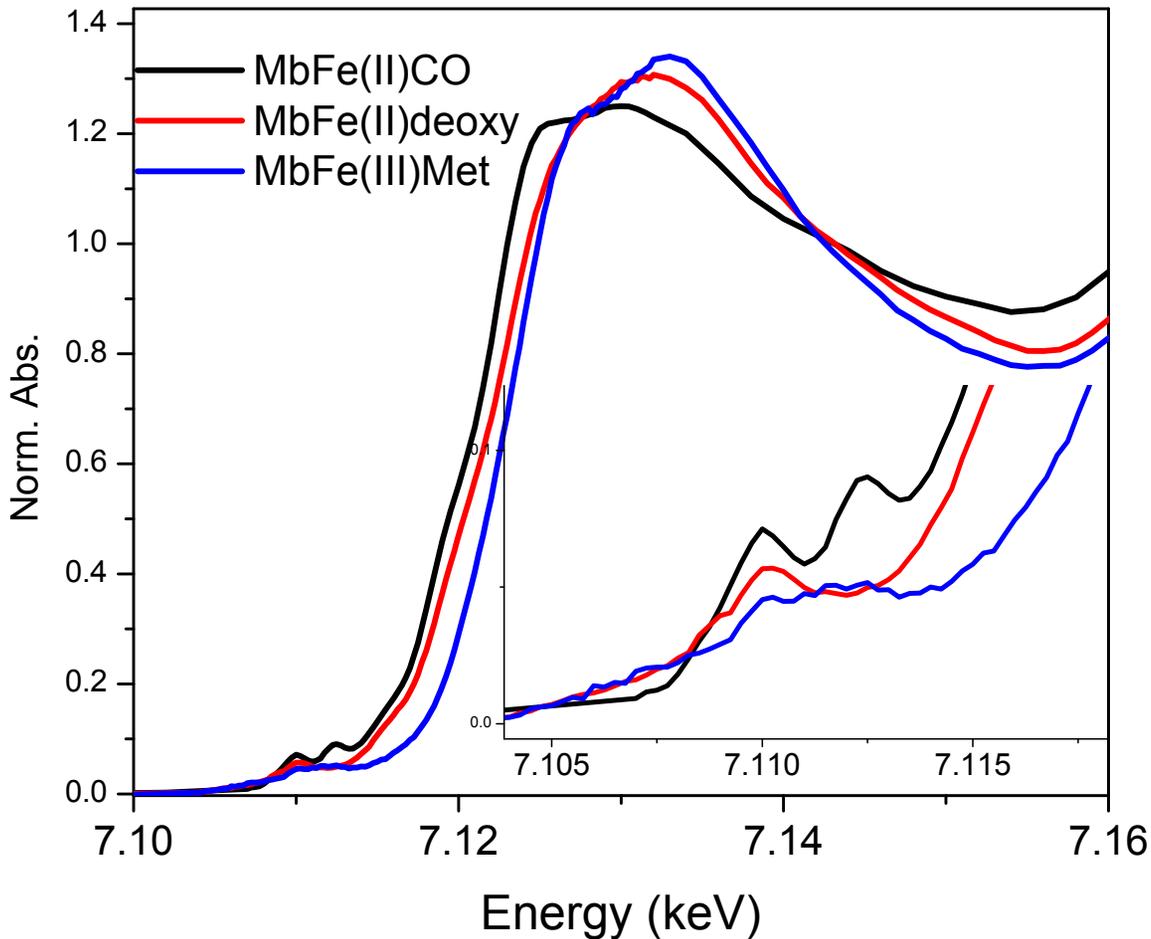
Science (1984)  
223, 812.



Nocera



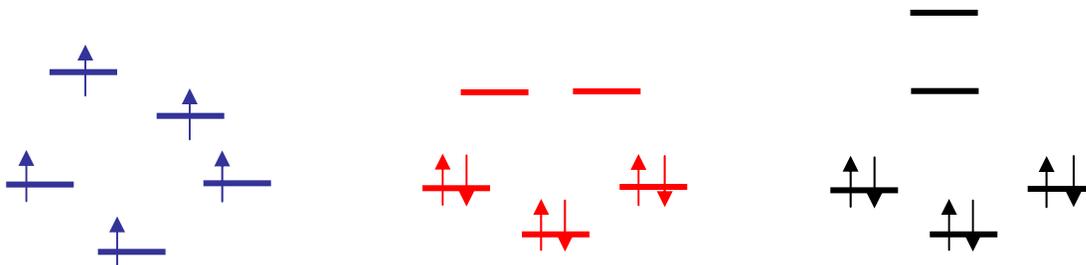
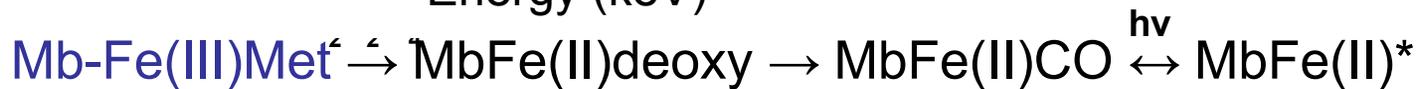
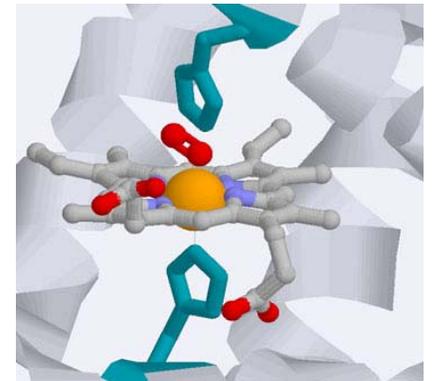
# Preliminary results for photodissociation of CO from heme in myoglobin



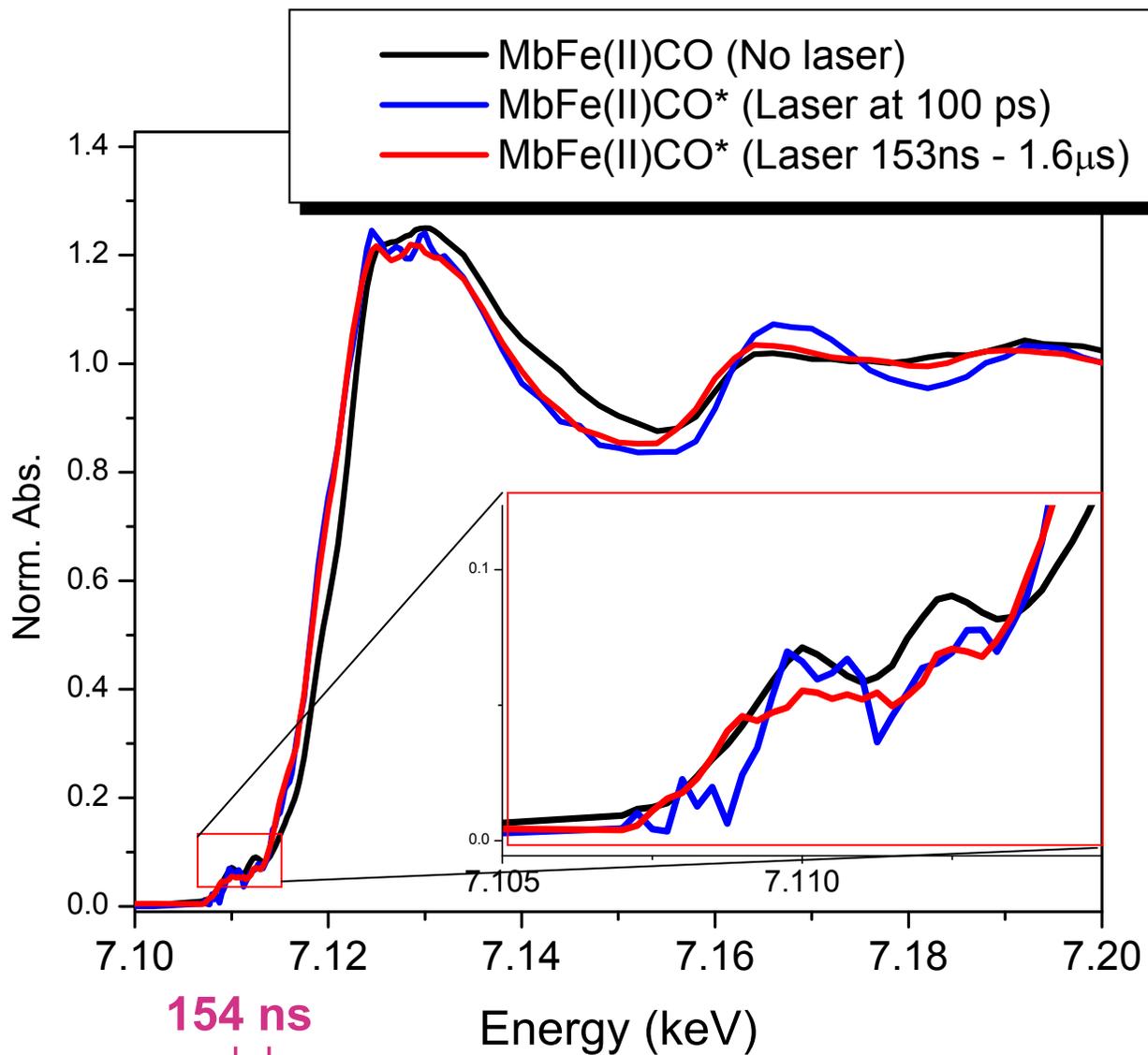
Direct electronic configuration change of Fe(II) center from LS to HS;

Time evolution from 0 - 1 ms are captured in a single experiment.

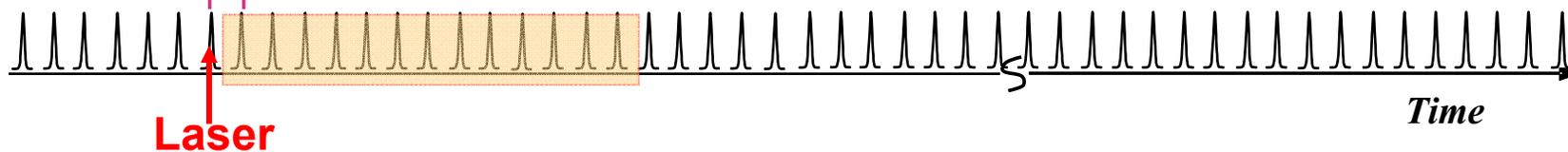
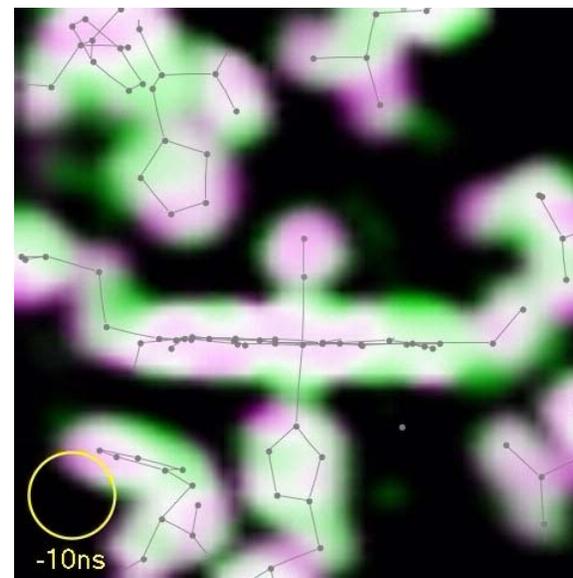
Fast structural dynamics can be investigated with fs x-ray pulses with caution of x-ray damage.



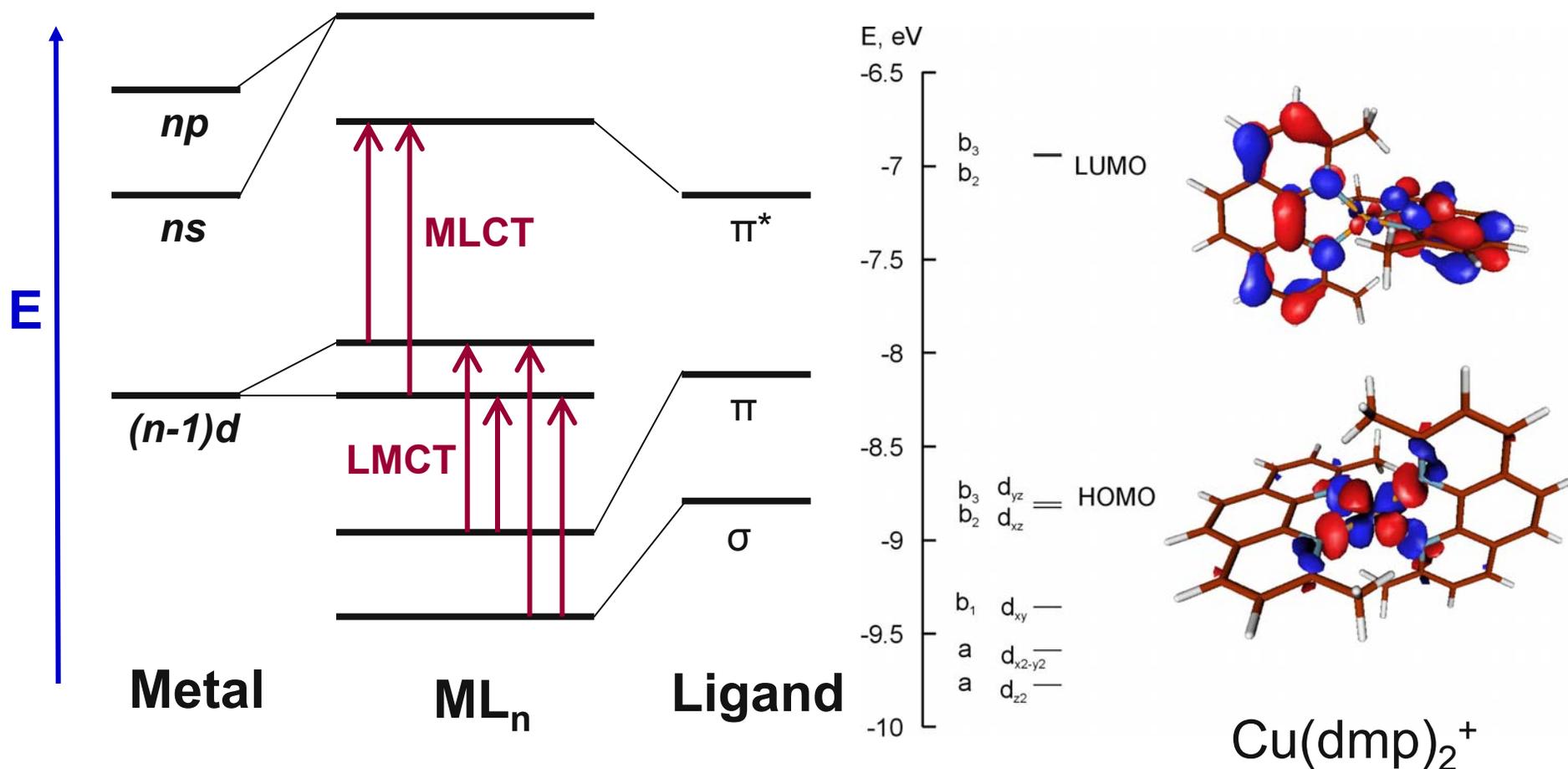
# Preliminary results for photodissociation of CO from heme in myoglobin



Anfinrud et al..

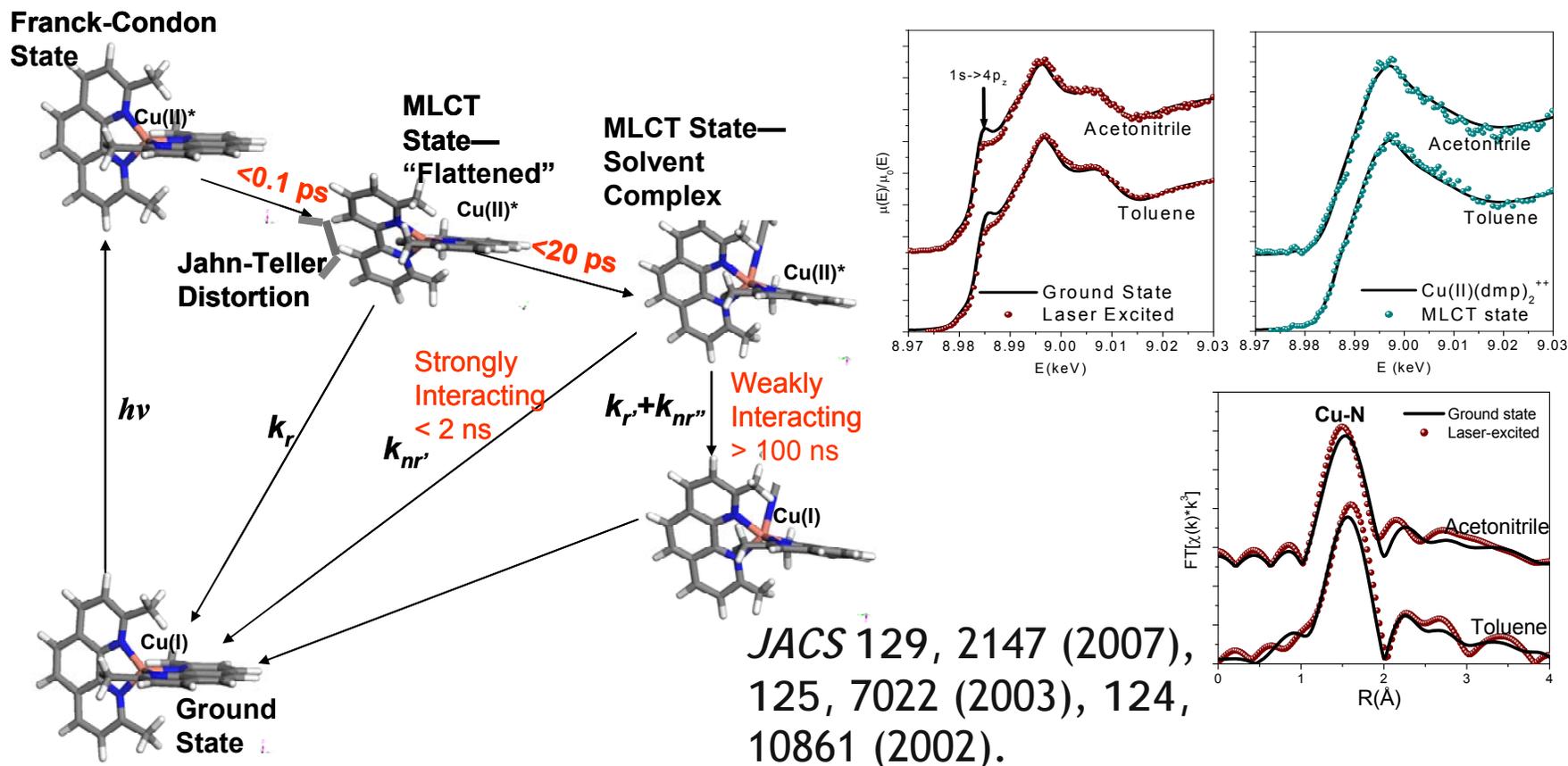


## The metal-to-ligand-charge-transfer (MLCT) states



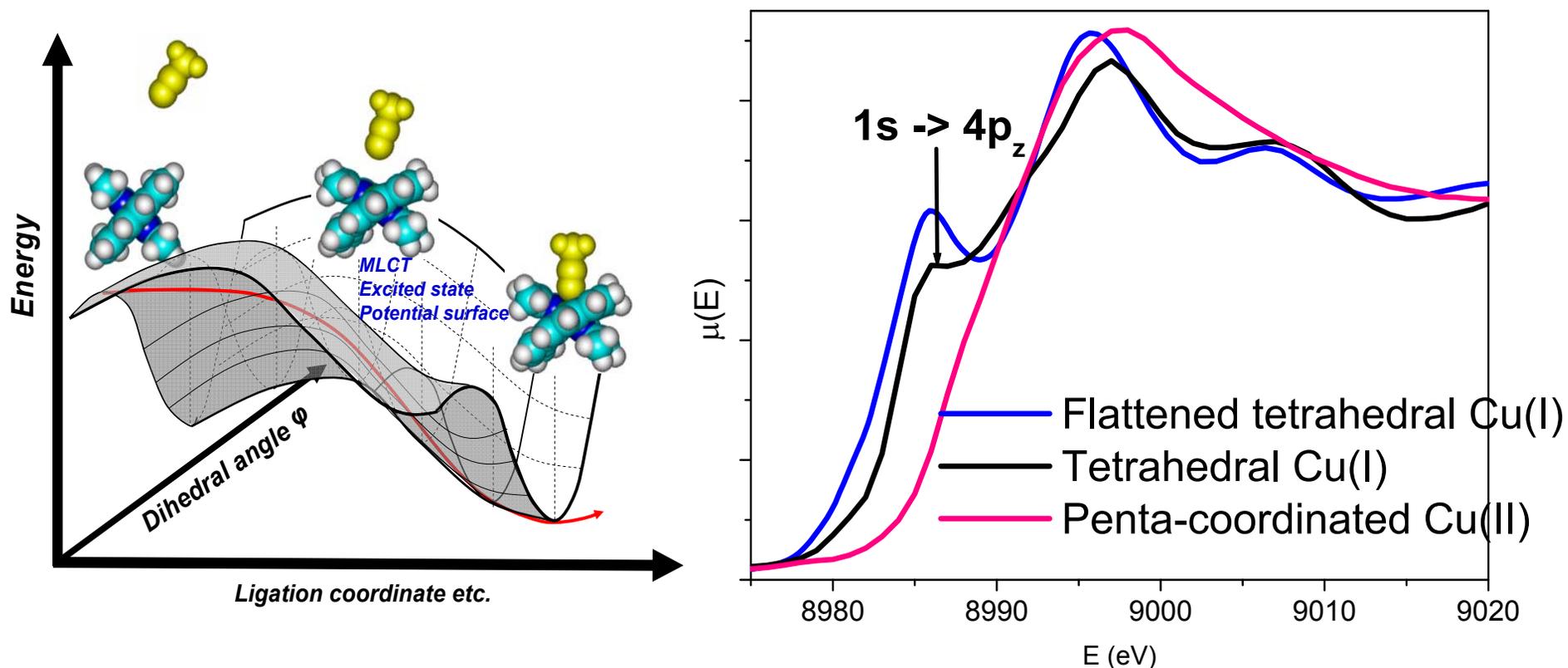
**MLCT transitions are often origins for transition metal complexes to be used in solar energy conversion initiated by electron density shifts between the metal and the ligands. Examples are DSSC, photocatalysis, etc.**

# Structural Dynamics of the MLCT state of Cu(I) complexes



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.

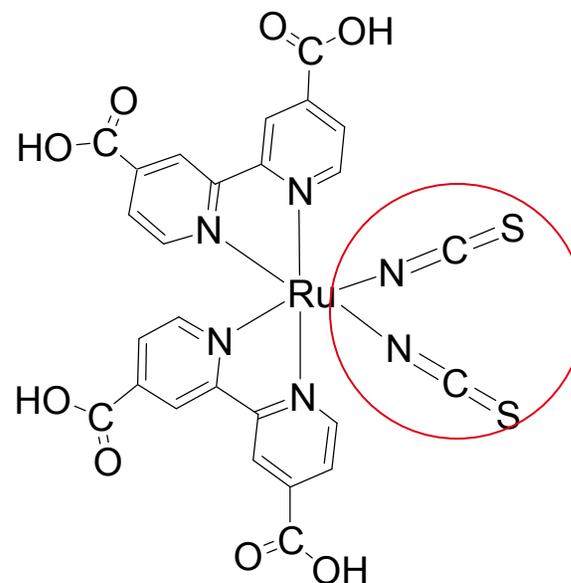
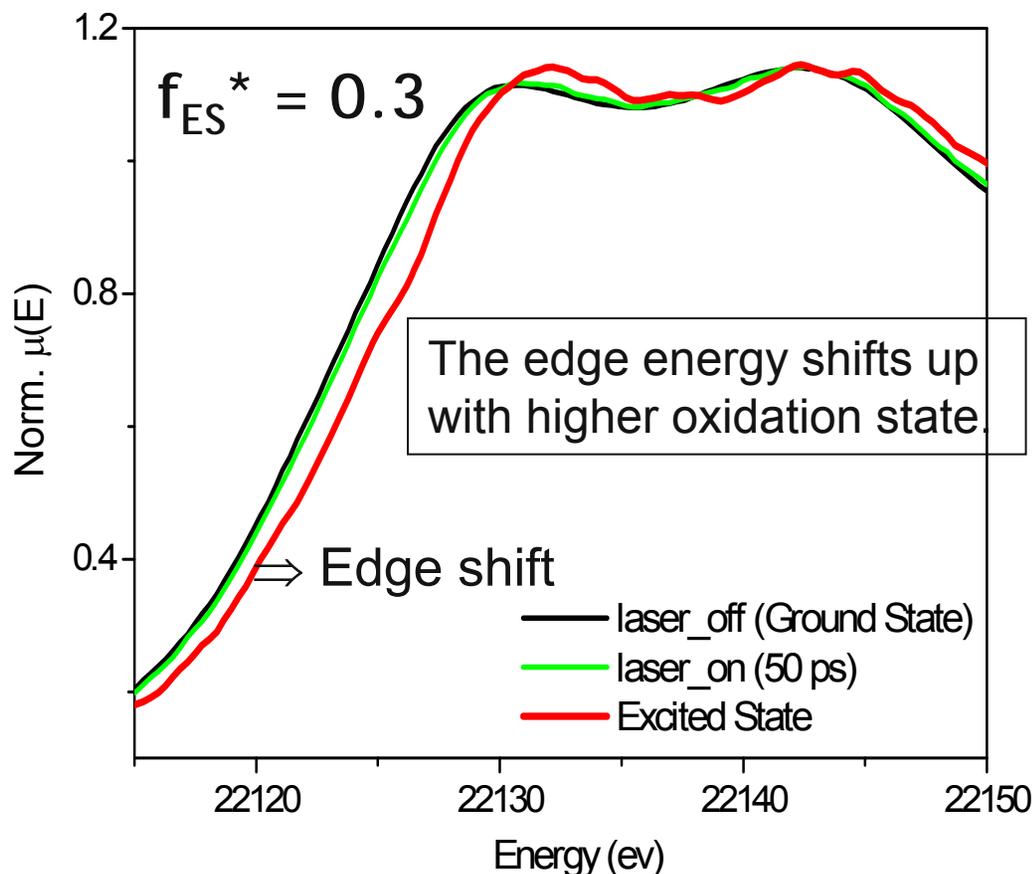
# Following flattening dynamics with fs X-rays at LCLS



- Two major structural factors for controlling the excited state properties: dihedral angle between two ligand planes, and space for the ligation.
- The structural dependent XANES provide the dynamics for flattening and ligation on 100-fs time scale. Proposal submitted to LCLS for coming experiments with  $< 100$  fs time resolution.

# Transition States at Hybrid interface: RuN<sub>3</sub> anchored to TiO<sub>2</sub> nanoparticles

*XANES spectra of RuN<sub>3</sub> on TiO<sub>2</sub> at Ru K-edge*

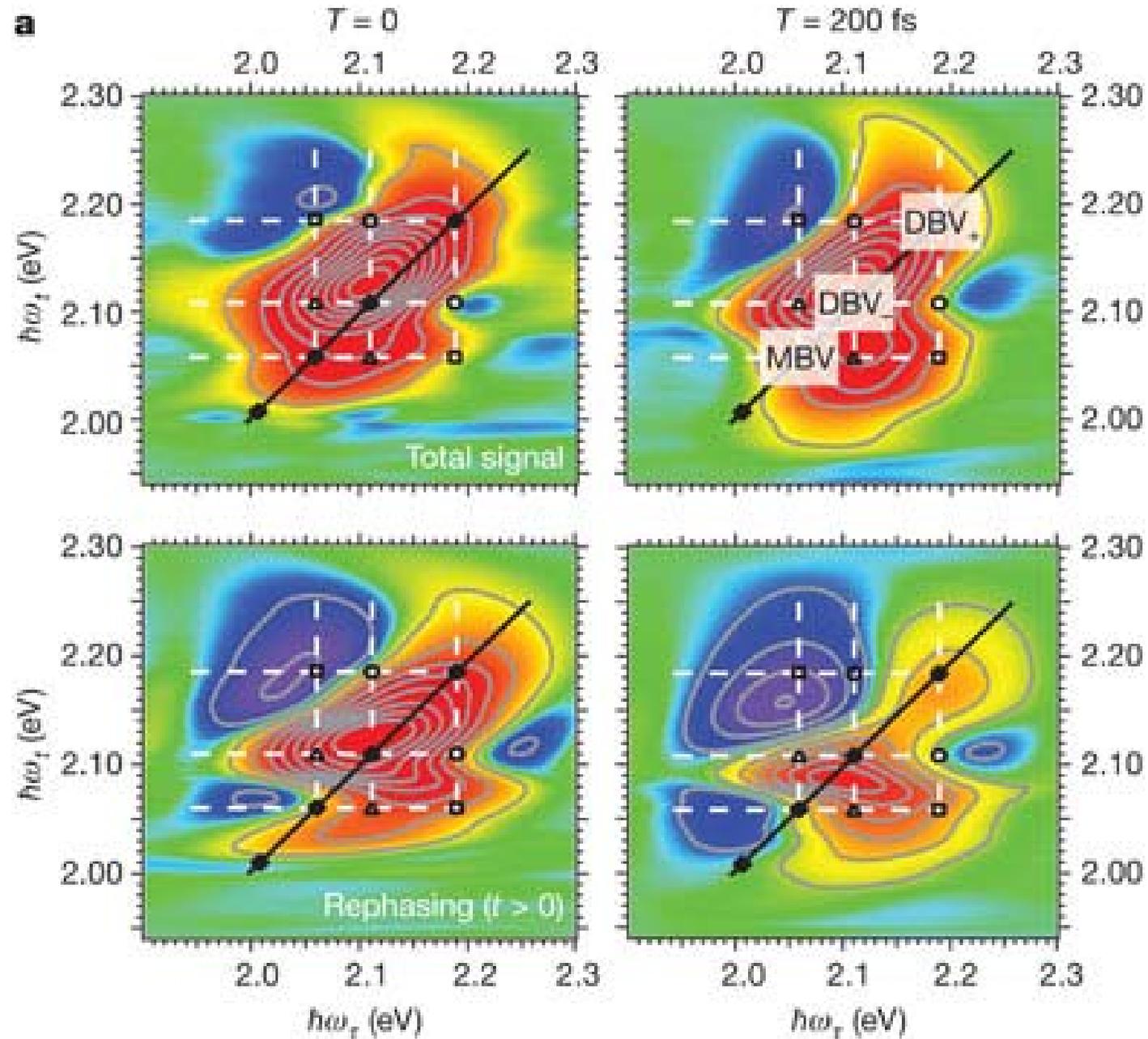


Preliminary analysis shows that Ru-N on NCS ligands are preferentially lengthened by 0.05 Å while the Ru-N distances on bpy ligands are not changed. Structural changes from 100 ps to longer delays are observed.

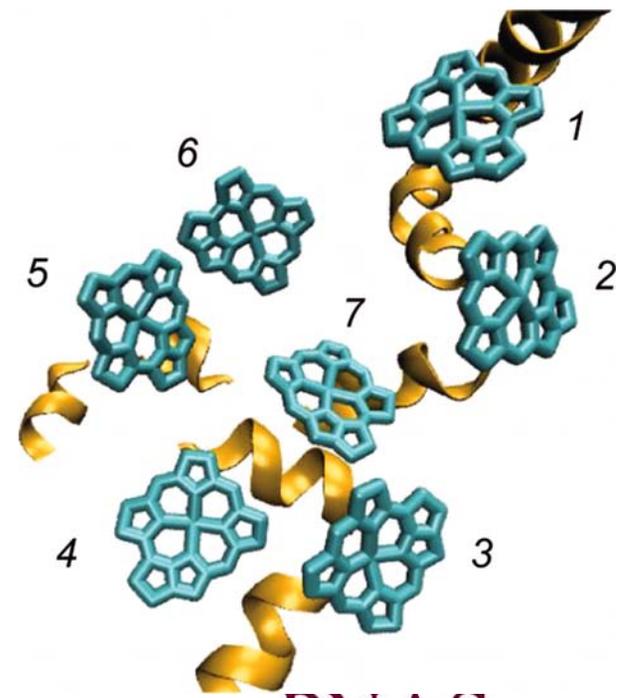
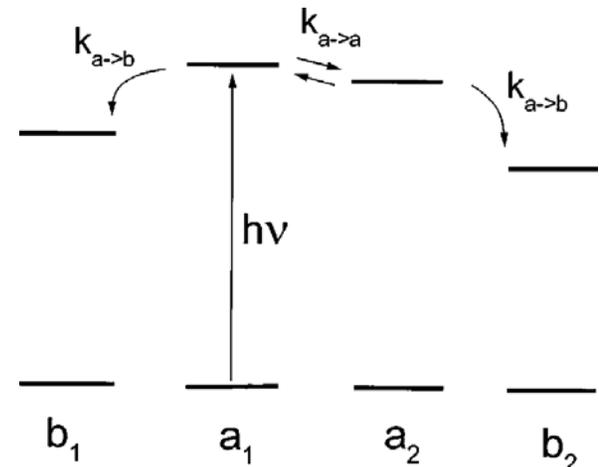
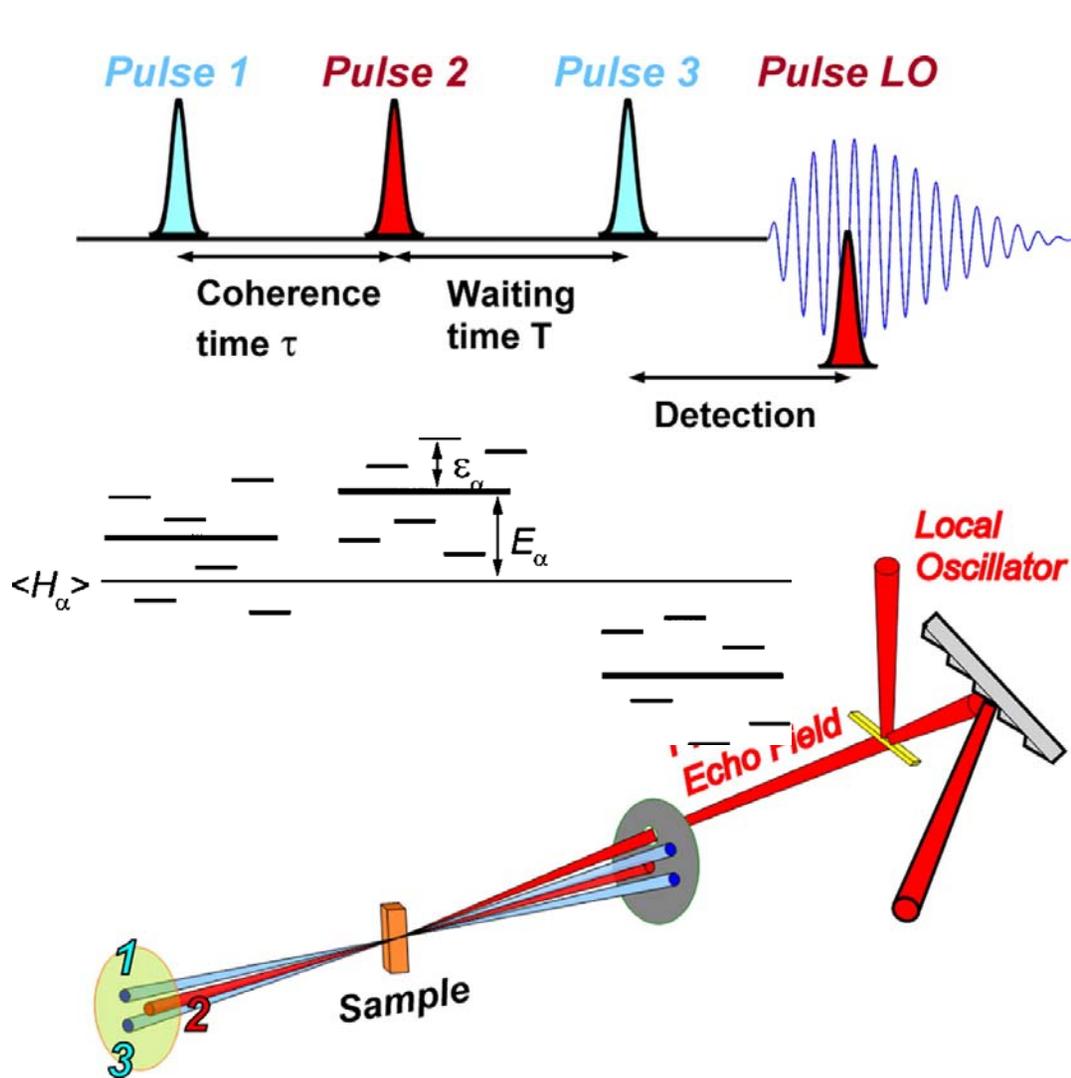


## **6. Future studies**

# 2D Transient optical spectroscopy



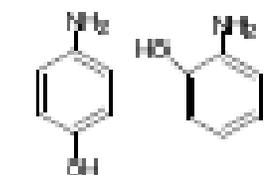
# 2D Transient optical spectroscopy



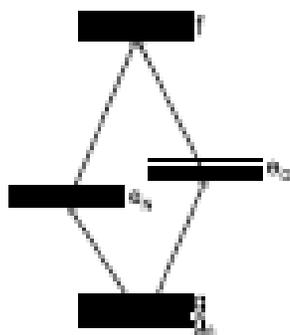
Hochstrasser R M PNAS 2007;104:14190-14196

# New frontiers in x-ray nonlinear spectroscopy

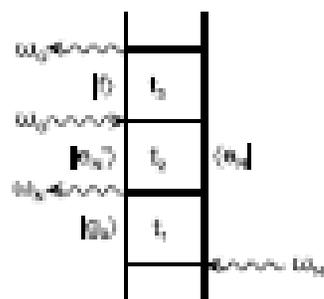
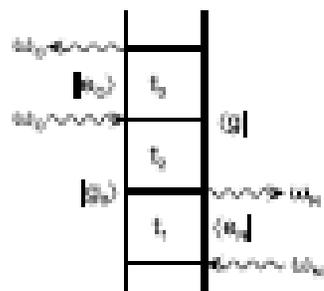
$$S_I^{(2)}(\Omega_3, t_3, \Omega_1) \equiv \iint_0^\infty dt_1 dt_2 S_I^{(2)}(t_3, t_2, t_1) e^{i\Omega_3 t_3} e^{i\Omega_1 t_1}.$$



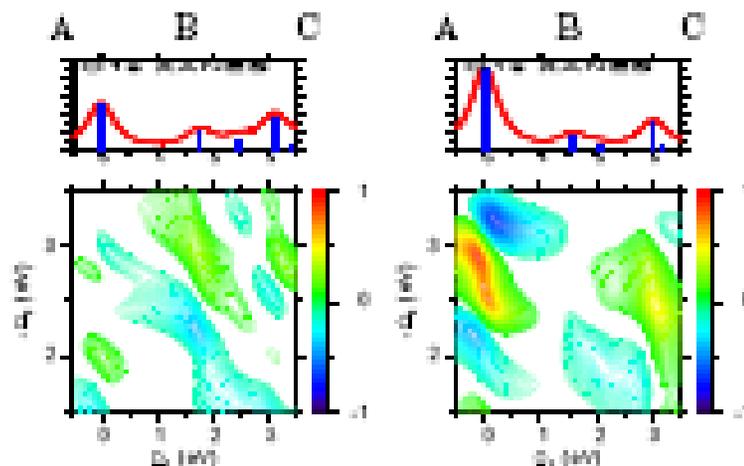
(a)



(b)

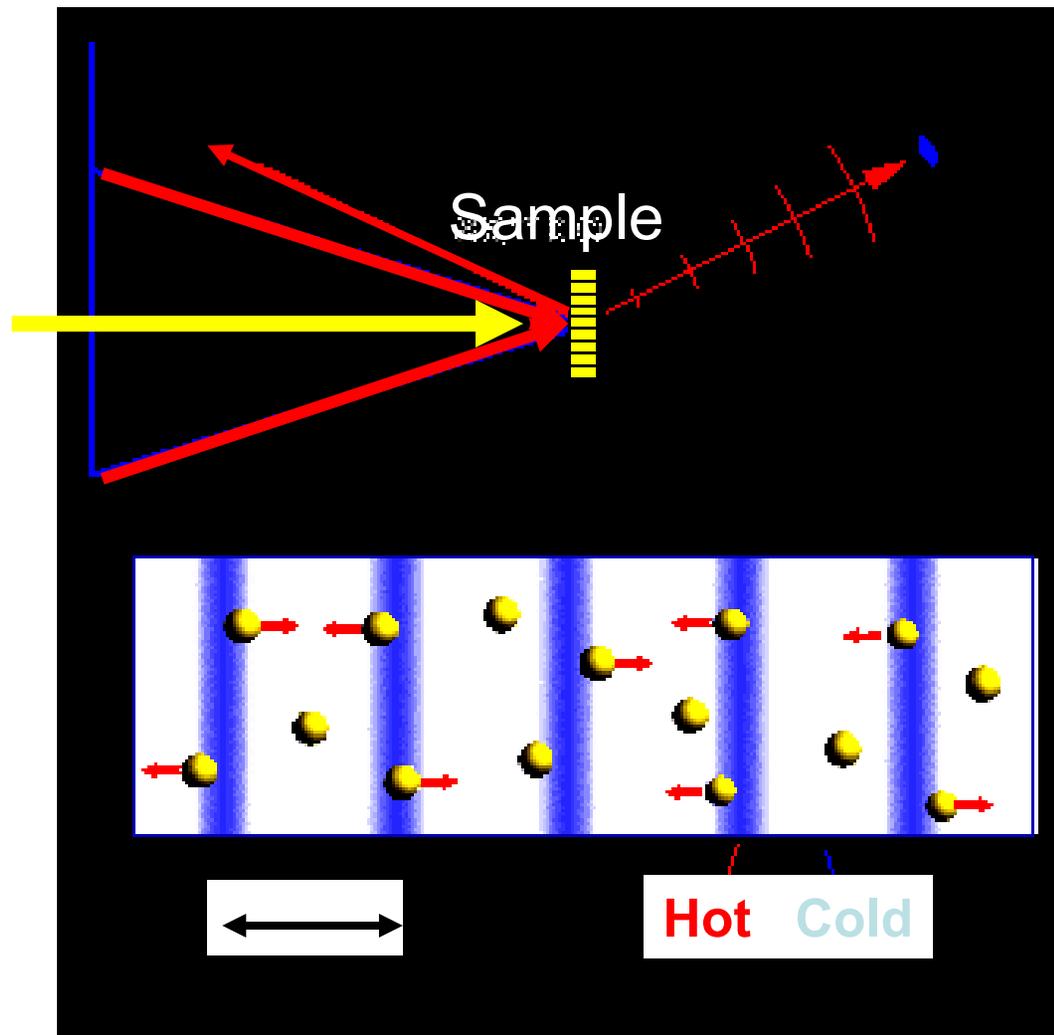


(c)



Coherent ultrafast core-hole correlation spectroscopy; x-ray analogues of multidimensional NMR, Igor V. Schweigert and Shaul Mukamel  
 Department of Chemistry, University of California, Irvine, California 92697-2025

# New frontiers in x-ray nonlinear spectroscopy

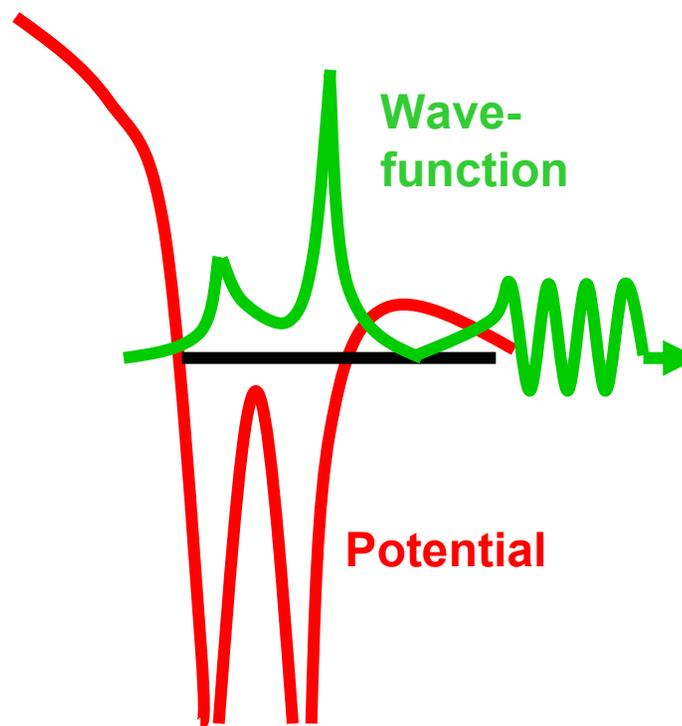
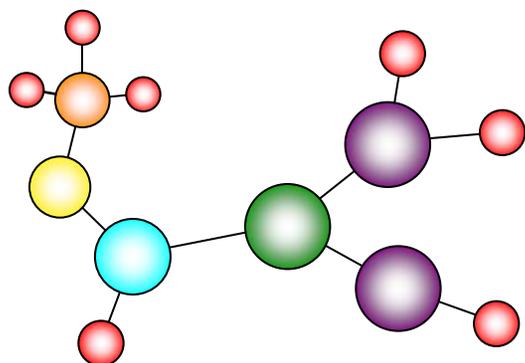


Observation of charge carrier dynamics in molecular crystals, conducting polymer films and solutions on nm length scale and fs time scale.

Need to explore

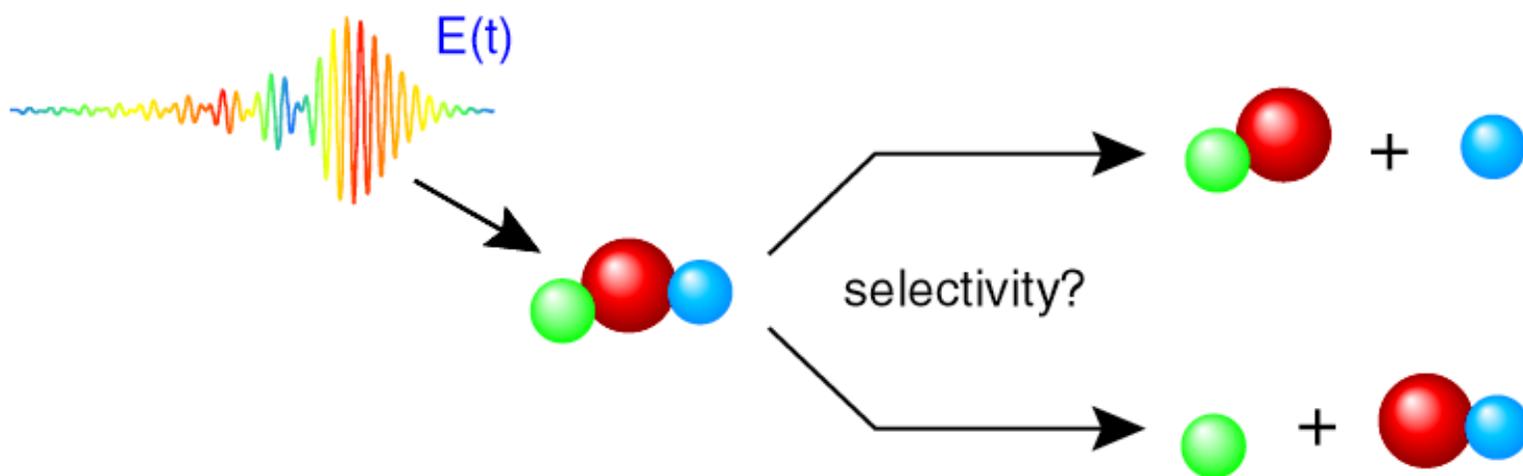
# Coherent Control of Chemical Reactions

- Coherent Control attempts to control a chemical reaction with light, usually a cleverly shaped ultrashort laser pulse.
- Using shaped pulses and an iterative approach.



# Coherent control: Using shaped ultrashort pulses to control the reaction

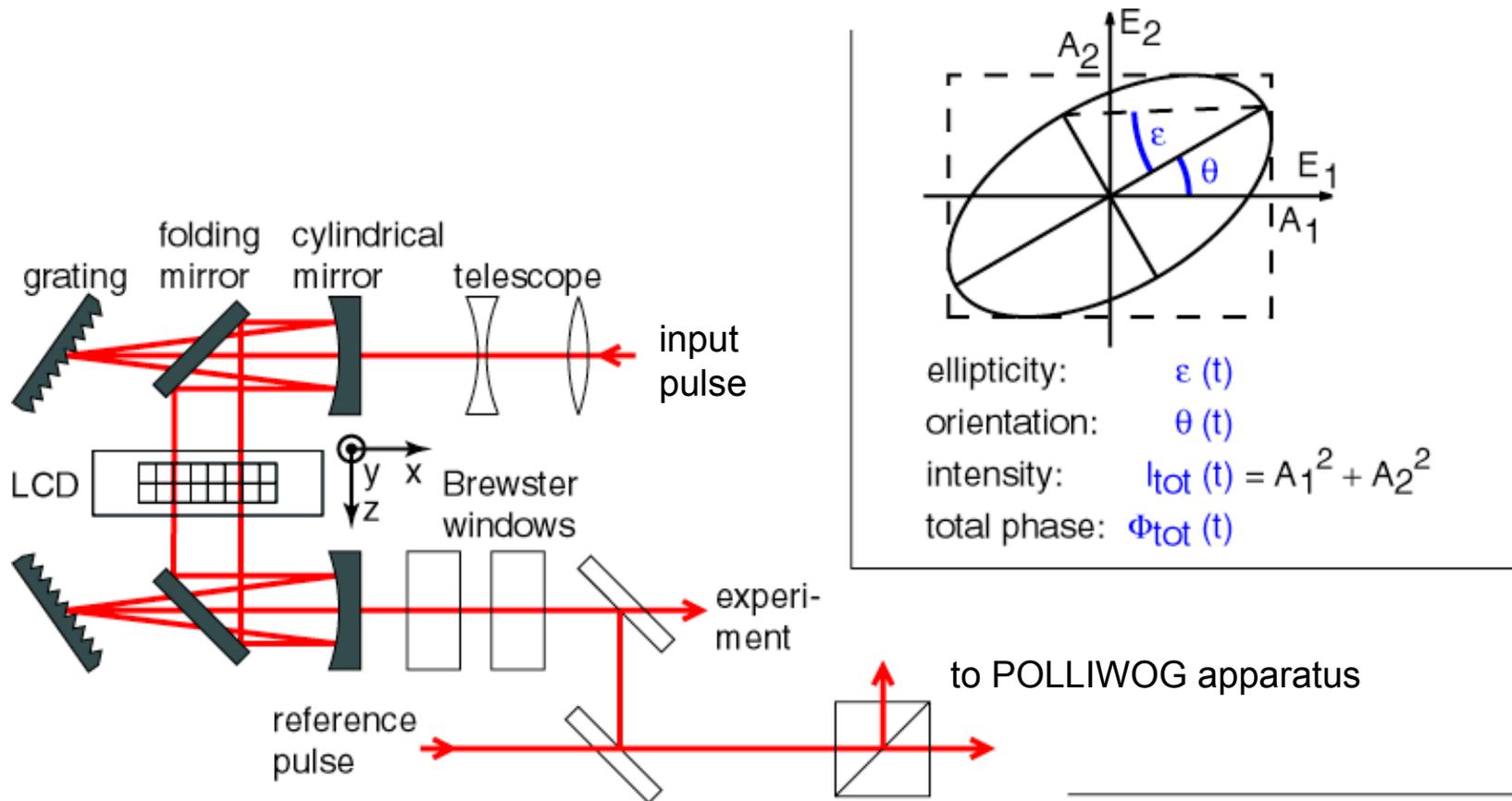
Can an ultrashort pulse cause a molecule to vibrate in such a way as to break the bond of our choice?



electric control field  $E(t)$ :

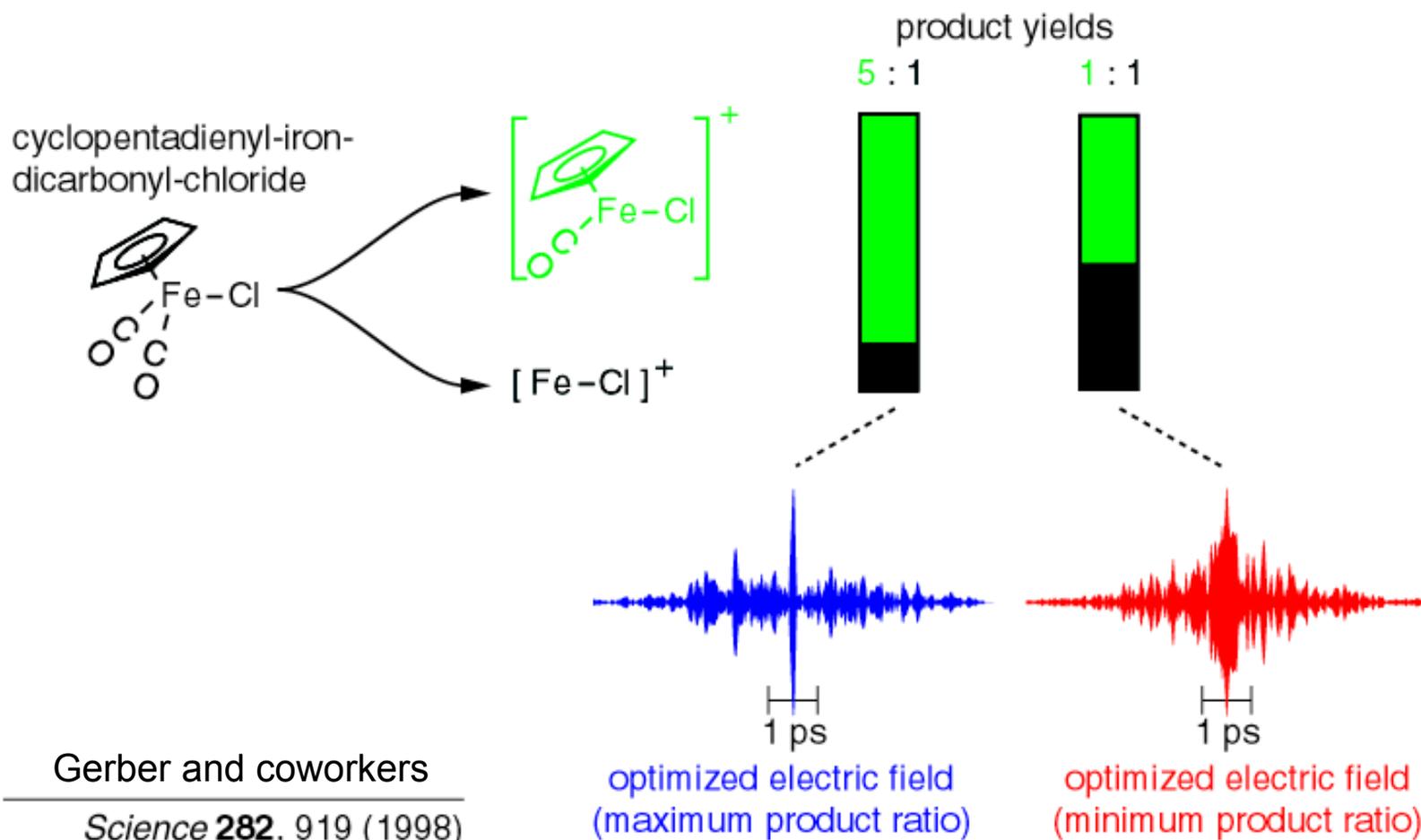
which one to use?  
how to generate it?

# Molecules are not isotropic, so pulse polarization shaping is important.



T. Brixner and G. Gerber:  
*Opt. Lett.* **26**, 557 (2001)

# Coherent polarization control of a complex molecule in the gas phase



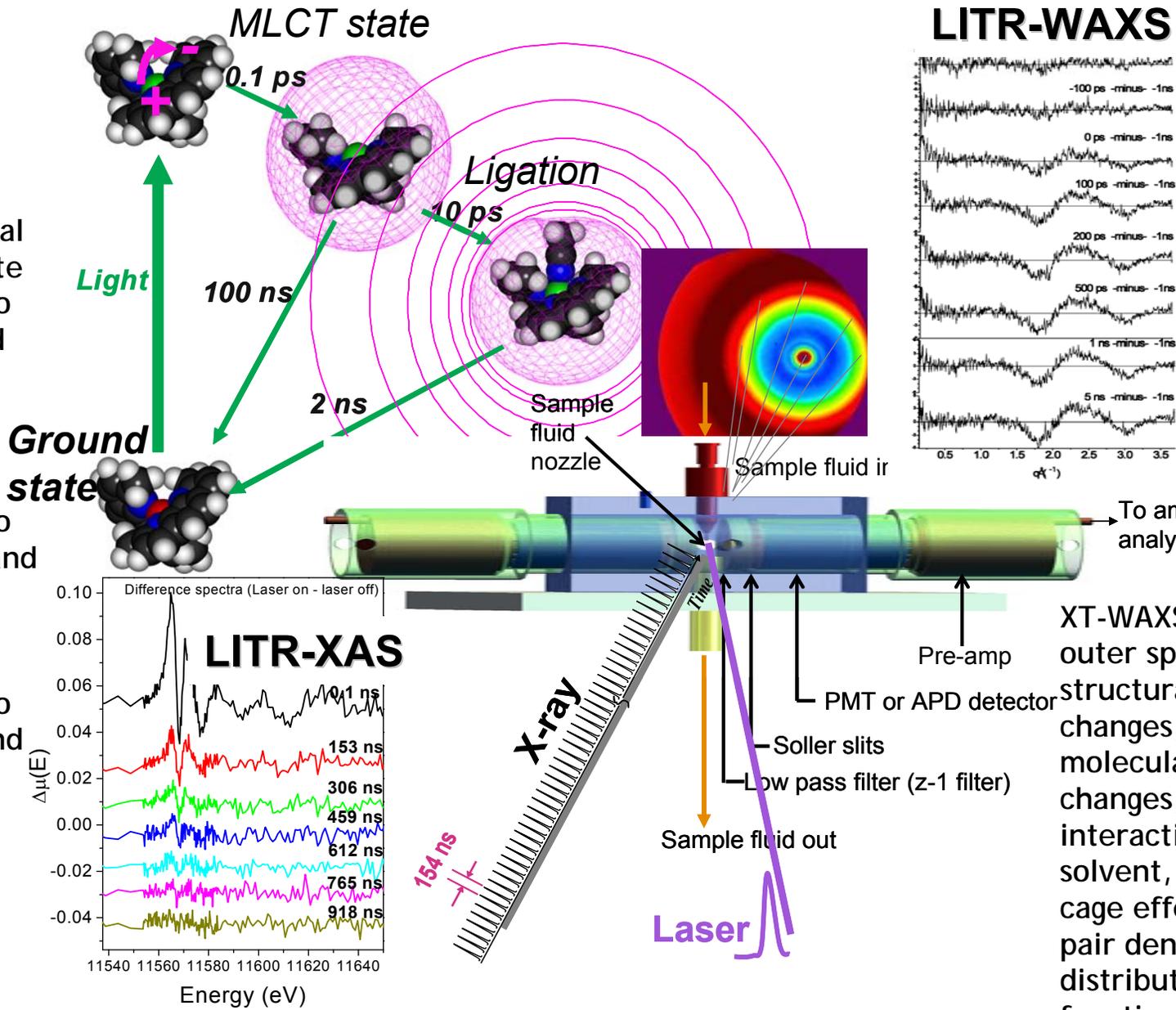
Gerber and coworkers

*Science* **282**, 919 (1998)

*Chem. Phys.* **267**, 241 (2001)

# Future Studies: 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.



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

Thank you