

**19th National School on Neutron and X-ray
Scattering Summer School**



X-RAY TRANSIENT ABSORPTION SPECTROSCOPY

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Department of Chemistry, Northwestern University**

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X-ray Transient Absorption Spectroscopy

Taking Snapshots of Photoexcited Molecular Structures in Disordered Media Using Pulsed X-rays, Lin X. Chen, *Angew. Chemie. Intl. Ed.*, 43, 2886-2905 (2004).

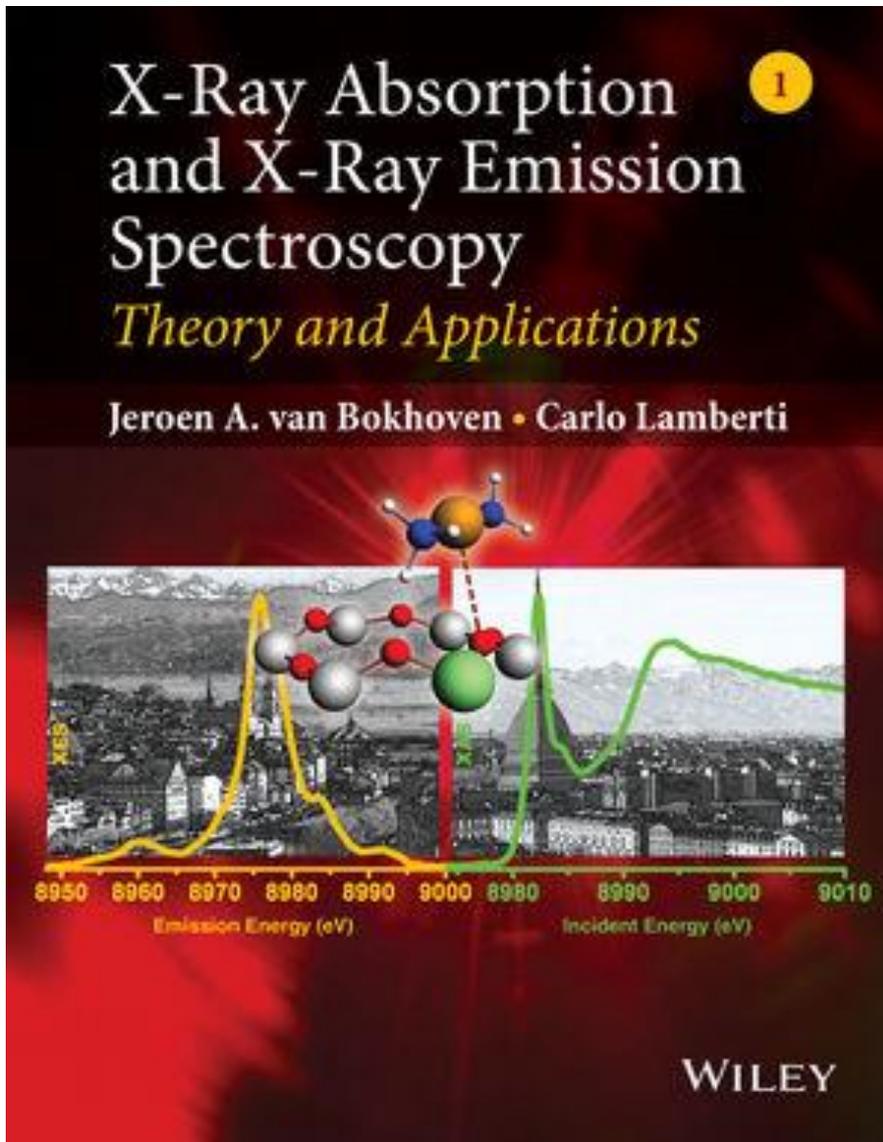
Ultrafast X-ray absorption spectroscopy, C. Bressler and M. Chergui, *Chem Rev.* (2004)104,1781-812

Probing Excited State Structures and Dynamics of Metal Complexes Using Time-resolved X-rays, Lin X. Chen, *Ann. Rev. Phys. Chem.* 56, 221-254 (2005).

Molecular Structural Dynamics Probed by Ultrafast X-ray Absorption Spectroscopy, C. Bressler and M. Chergui, *Annu. Rev. Phys. Chem.* (2010) 61: 263-82.

Photochemical Processes Revealed by X-ray Transient Absorption Spectroscopy, Lin X. Chen, Xiaoyi Zhang, *J. Phys. Chem. Lett.* 4, 4000–4013 (2013).

Today's lecture is based on Chapter 9 of the book entitled "X-ray transient absorption spectroscopy" by Lin X. Chen



Two-volume book published 2015

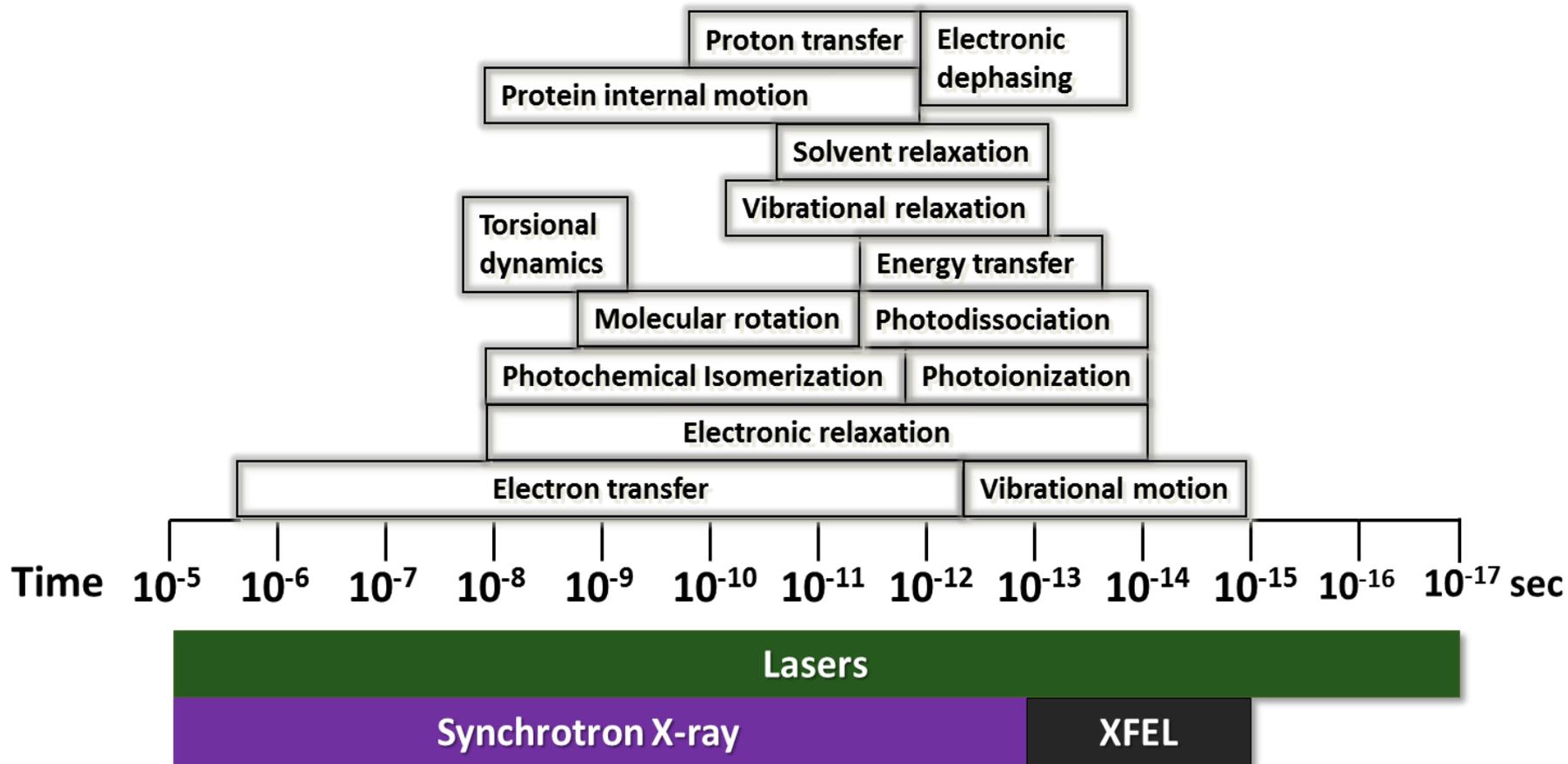
- Combines the theory, instrumentation and applications of x-ray absorption and emission spectroscopies which offer unique diagnostics to study almost any object in the Universe.
- Is the go-to reference book in the subject for all researchers across multi-disciplines since intense beams from modern sources have revolutionized x-ray science in recent years
- Is relevant to students, postdocurates and researchers working on x-rays and related synchrotron sources and applications in materials, physics, medicine, environment/geology, and biomedical materials.

Outline of today's lecture

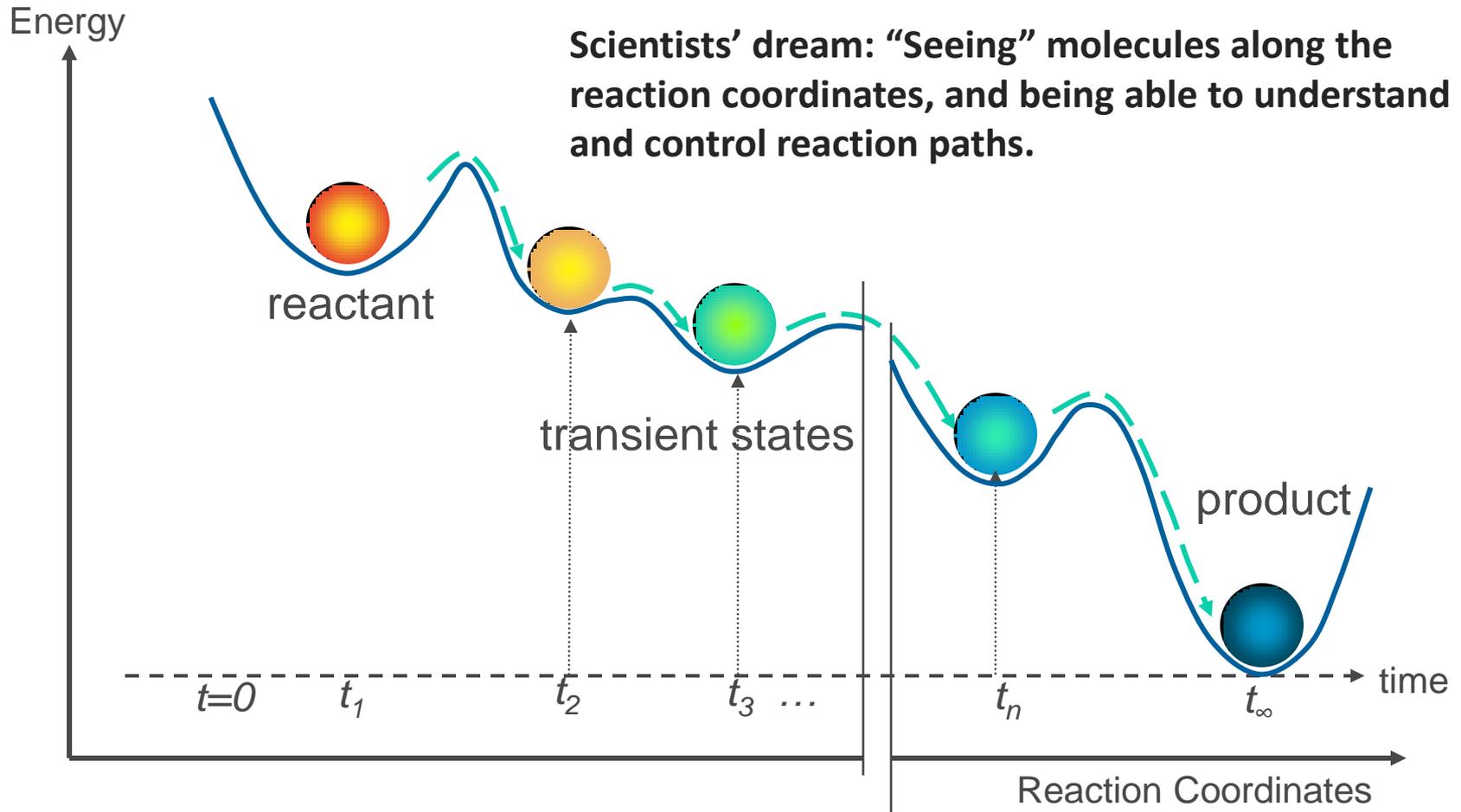
1. Pump-probe spectroscopy
2. Experimental Considerations
 - 2.1 XTA at a Synchrotron Source
 - 2.2 XTA at an X-ray Free Electron Laser Sources
3. Transient Structural Information Investigated by XTA
 - 3.1 Metal center oxidation state
 - 3.2 Electron configuration and orbital energies of X-ray absorbing atoms
 - 3.3 Transient coordination geometry of the metal center
4. X-ray pump-probe absorption spectroscopy, Examples
 - 4.1 Excited state dynamics of transition metal complexes (TMCs)
 - 4.2. Interfacial charge transfer in hybrid systems
 - 4.3 XTA Studies of Metal Center Active Site Structures in Metalloproteins
 - 4.4 XTA using the X-ray Free Electron Lasers
 - 4.5 Other XTA Application Examples
5. Perspective of Pump-probe X-ray spectroscopy

1. Pump-probe spectroscopy

Time scales of fundamental dynamic processes

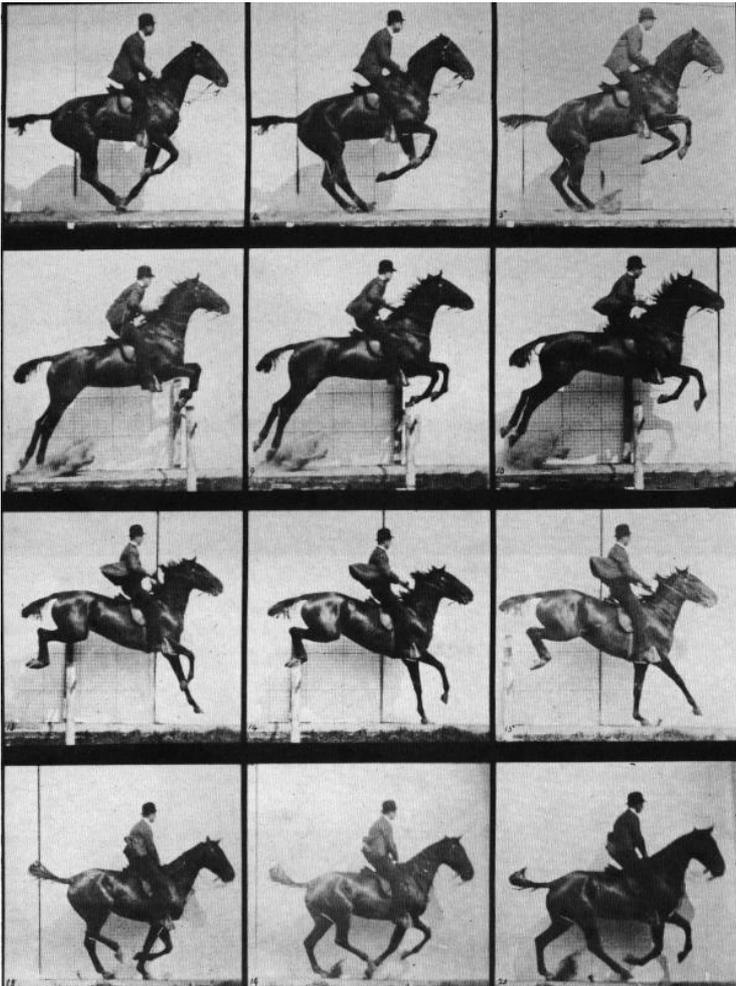


Molecular snapshots and reaction control



Molecular snapshots and reaction control

How can we follow a molecule in an ensemble of N_A ?

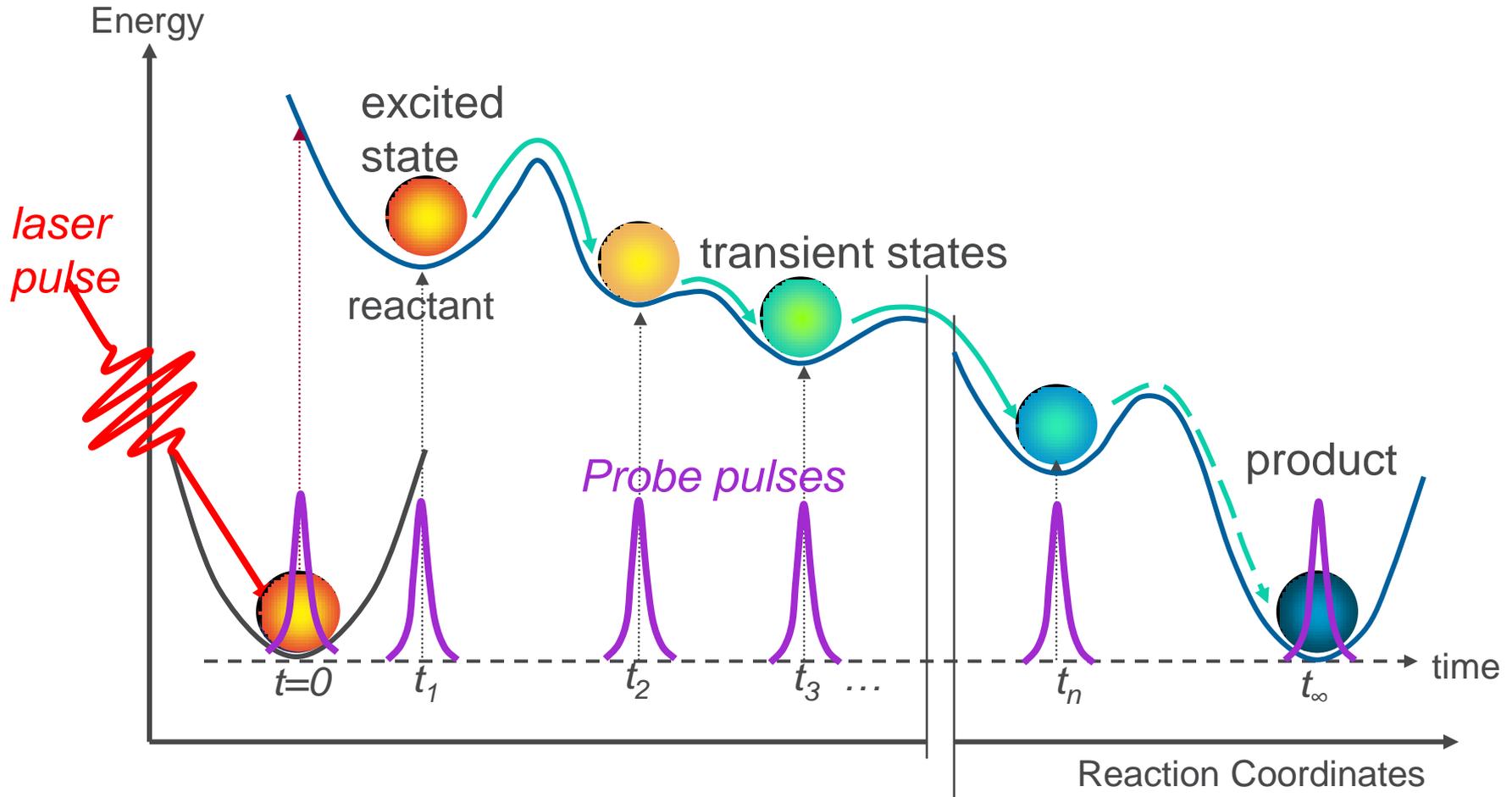


Single molecule (by Muybridge)



Ensemble of molecules

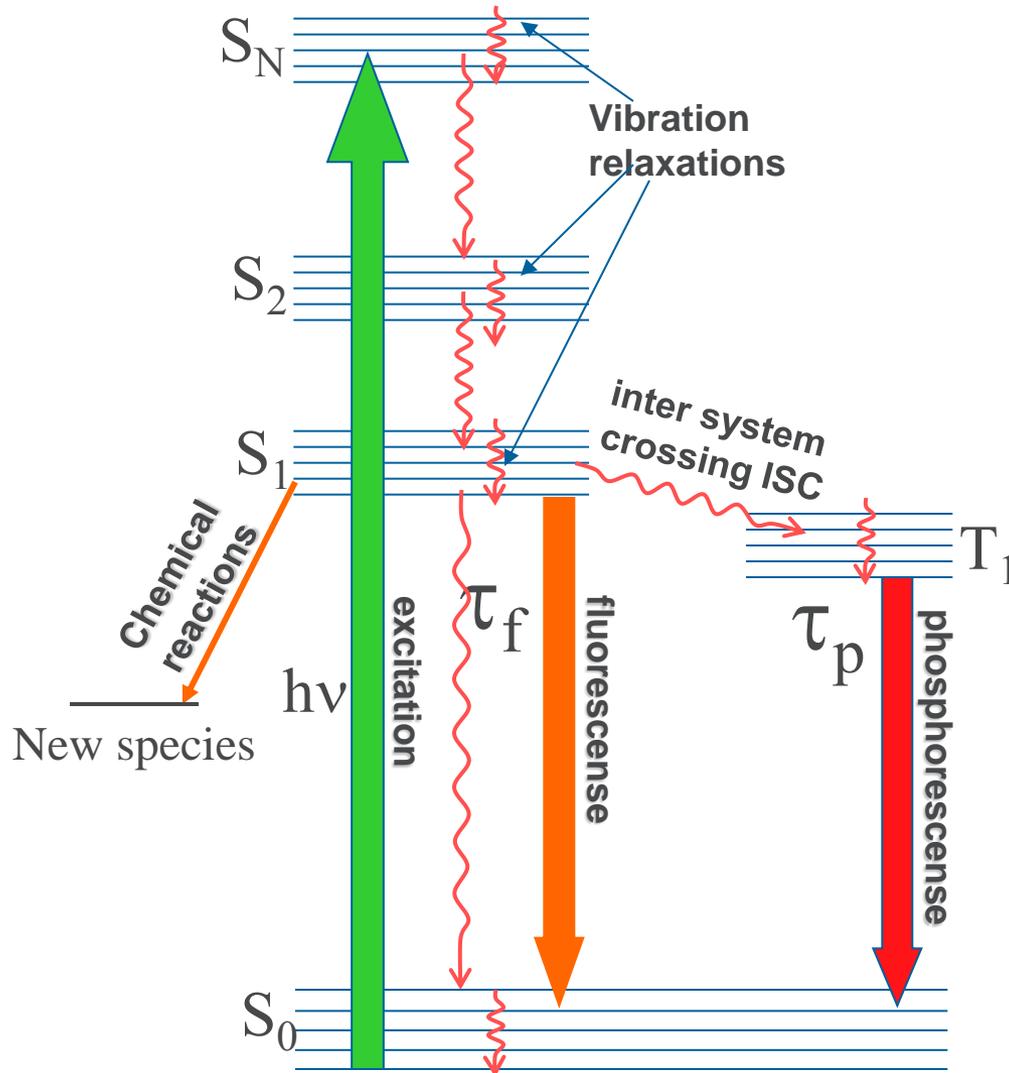
Molecular snapshots and reaction control



Femtosecond (10^{-15}) laser pulses trigger chemical events synchronously for N_A molecules ensemble, allowing snapshots to be taken.

1. Pump-probe spectroscopy

photoinduced processes to be investigated



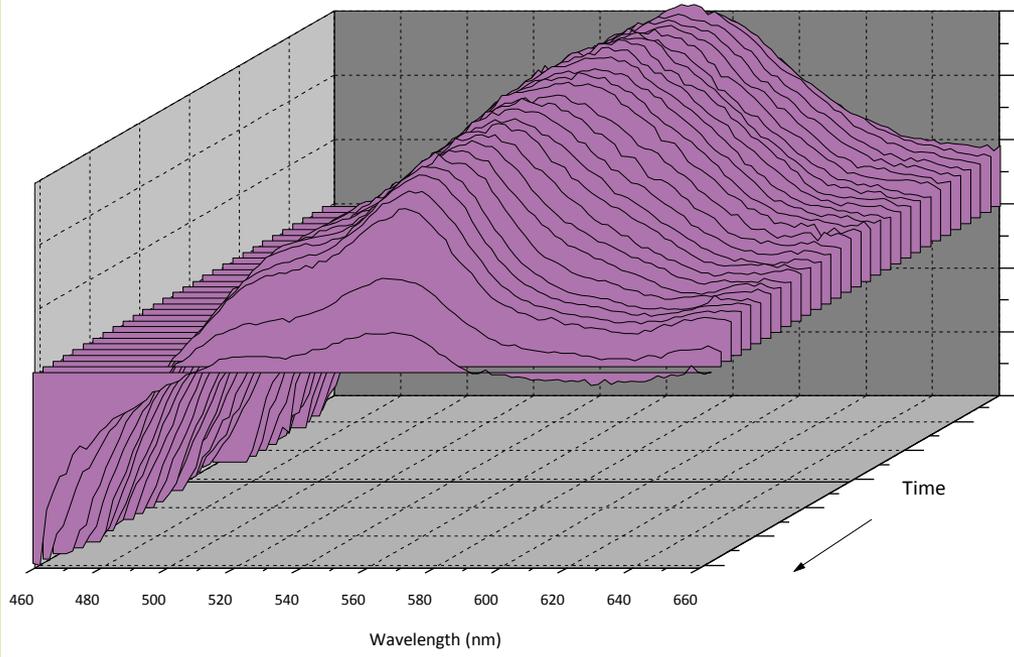
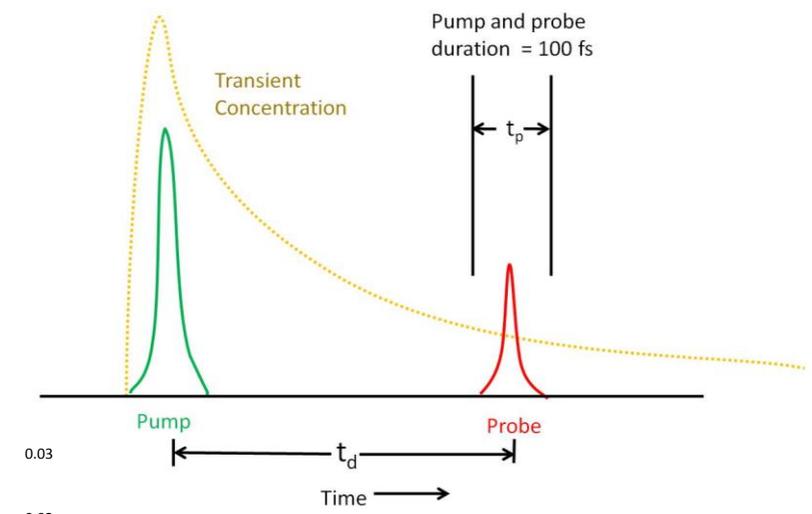
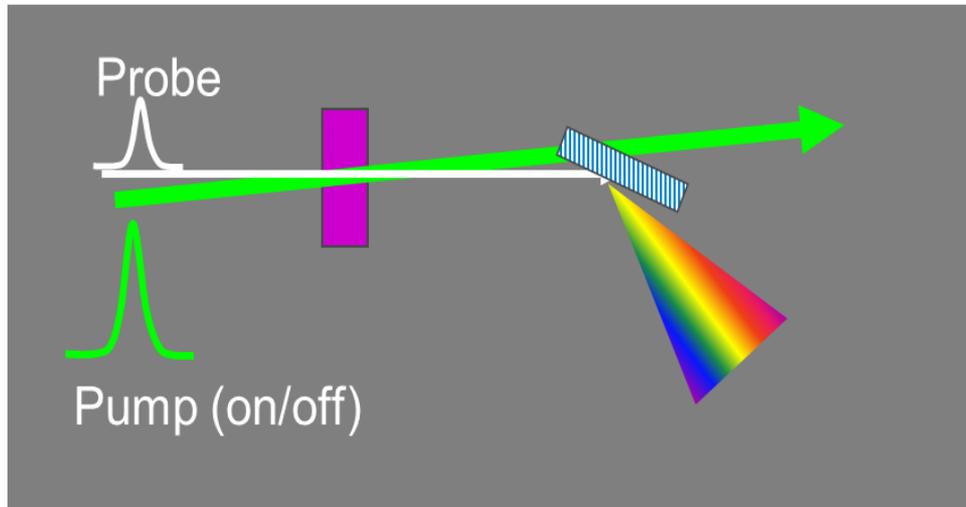
Photons induce transitions to **synchronously** generate energetic species, the excited states that then proceed to many different processes.

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

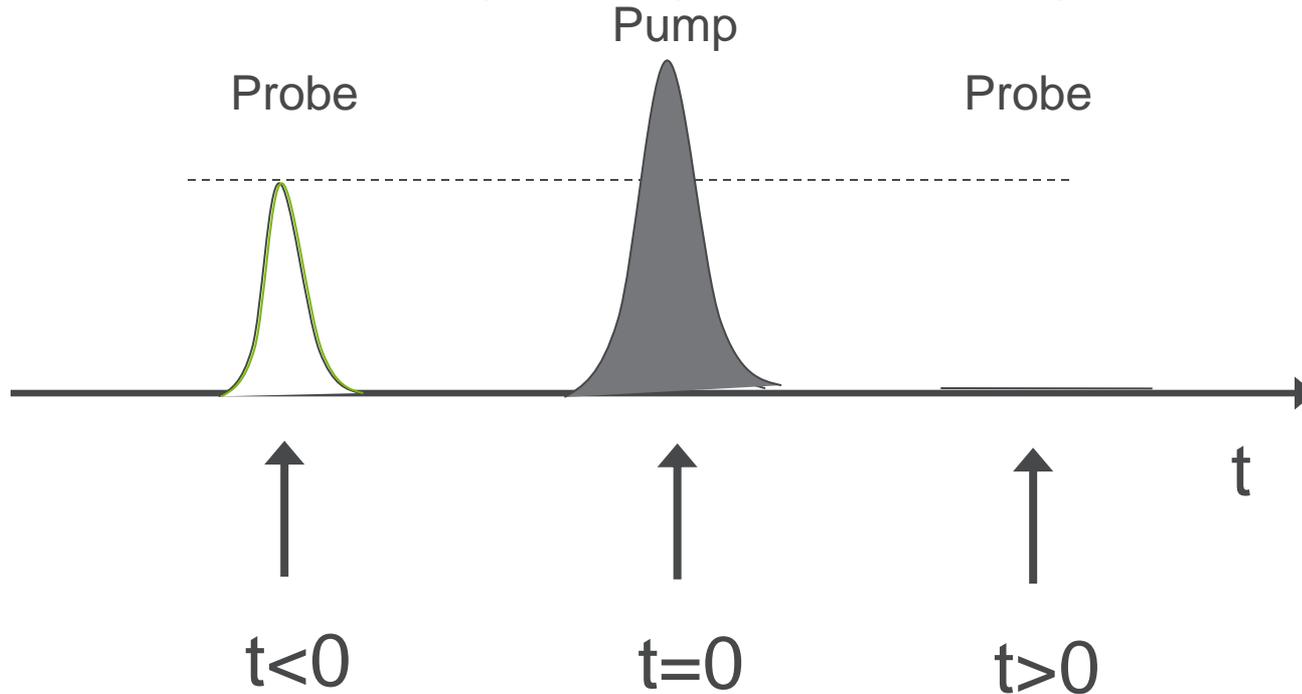
Discussions: other processes?

1. Pump-probe spectroscopy

Snapshots for molecules: Transient absorption spectroscopy (TA)



Pump and probe concept



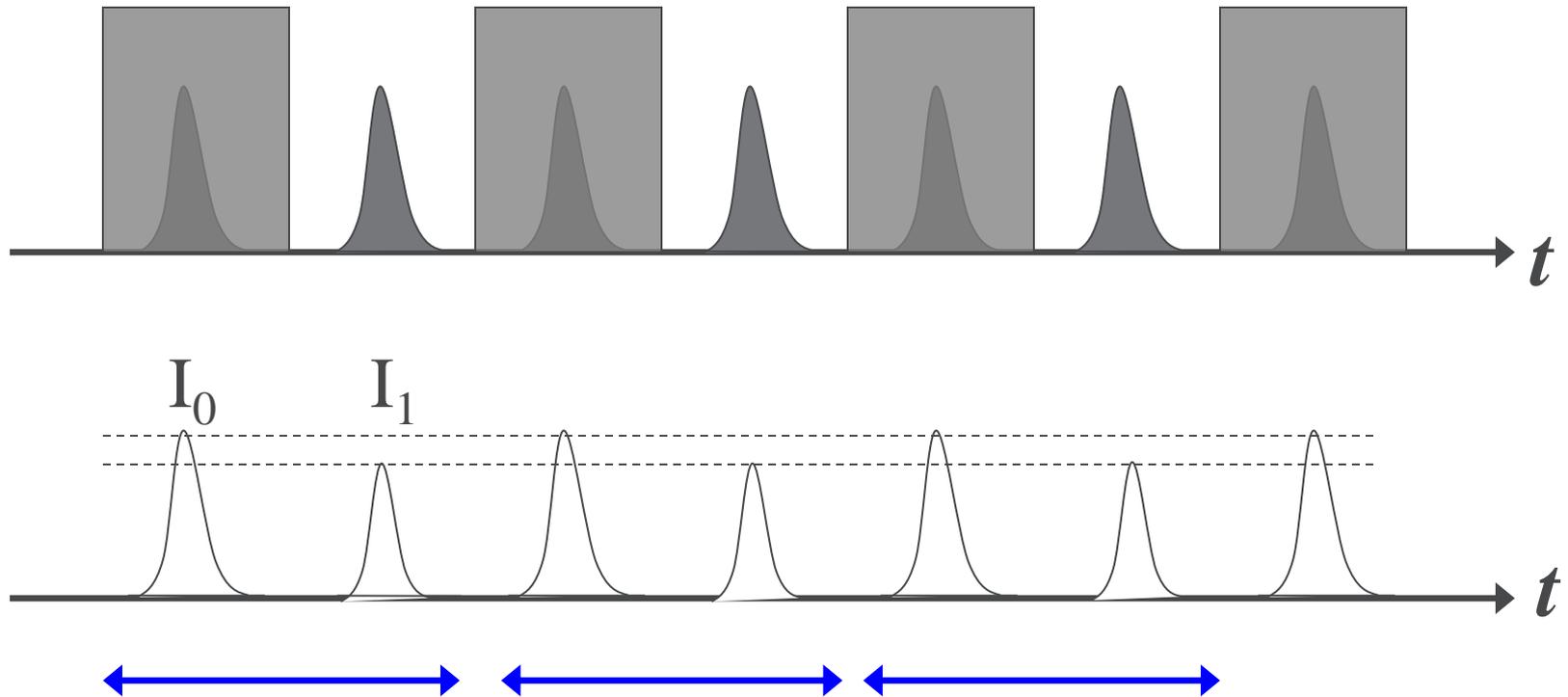
At one delay time, many pump-probe cycles are collected for sufficient S/N level in the data;

Changing the delay time step-by-step to cover the entire kinetics trace;

Time resolution determined by the laser pulse duration (i.e., $\sim 10\text{-}100$ fs);

Time window determined by the optical delay length (i.e. $0\text{-}6$ ns).

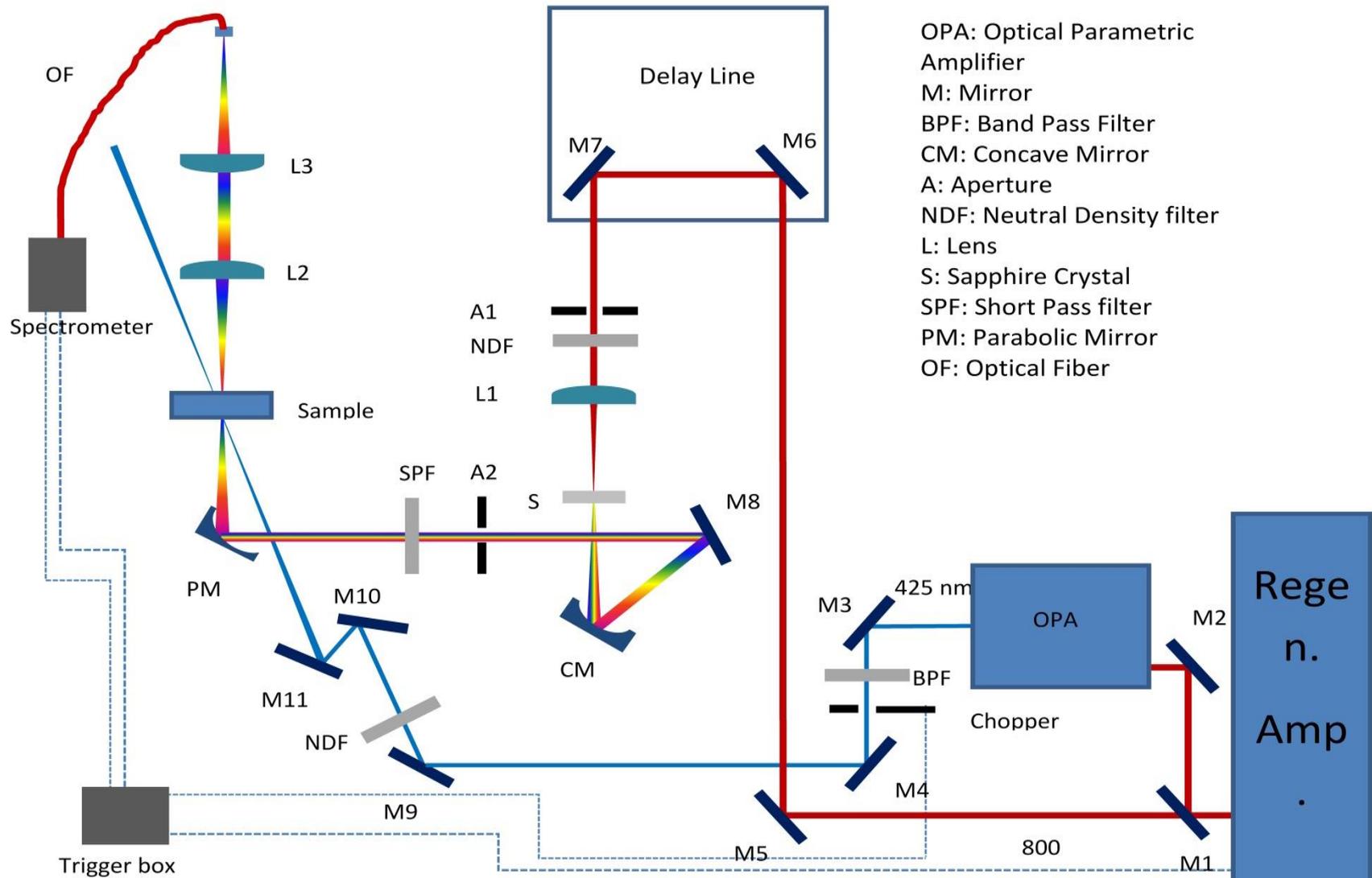
Pump and probe concept



$$\Delta OD(\lambda, t) = \log \frac{I(\lambda, t)_{pump - off}}{I(\lambda, t)_{pump - on}} = \log \frac{I_0}{I_1}$$

1. Pump-probe spectroscopy

Ultrafast Transient Absorption Spectroscopy Setup



Pump excitation light sources

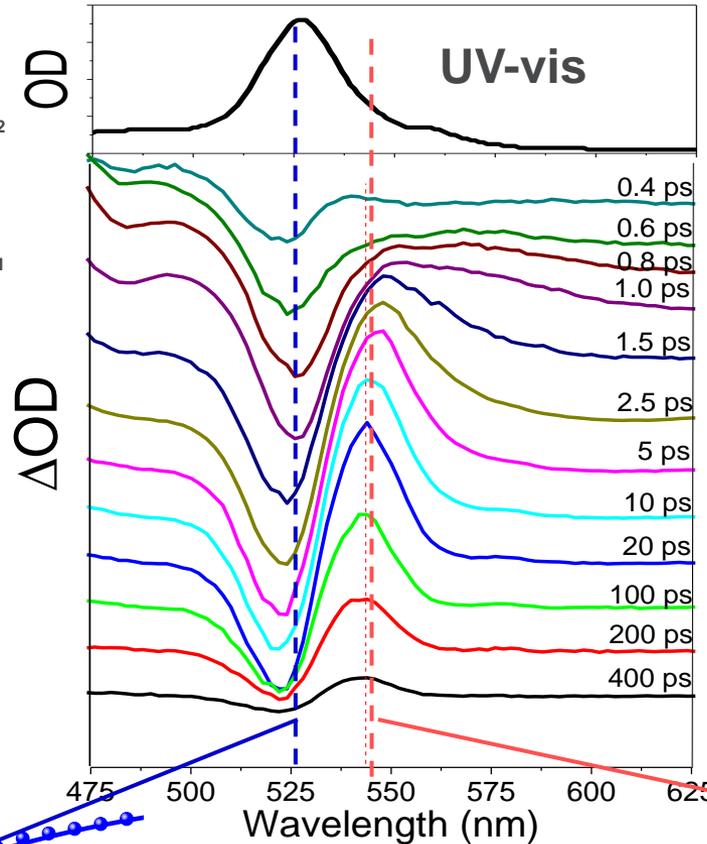
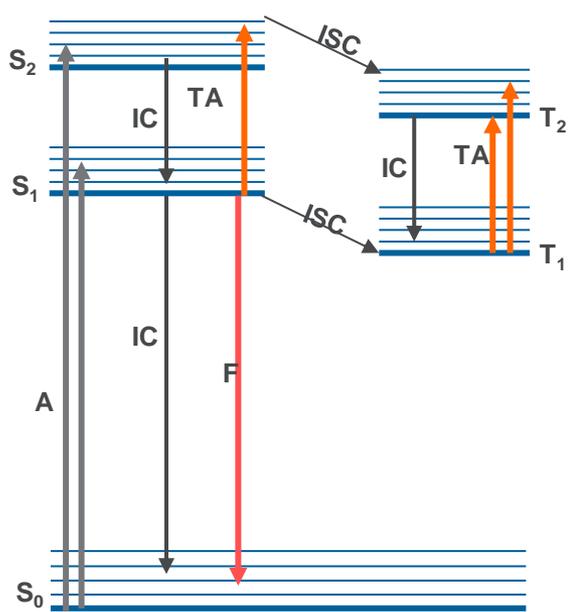
- Direct Ti-Sapphire laser output - 800 nm
- Harmonic generation - SHG 400 nm and THG 267 nm
- Optical parametric amplification - 250-12000 nm

Laser probe light sources

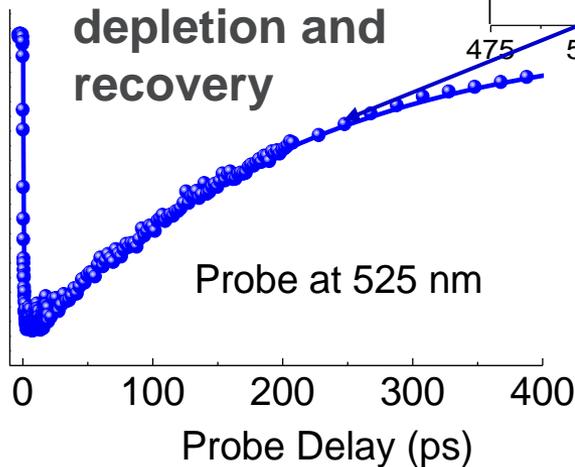
- White light continuum generation
 - Advantage: Easy to use and All wavelengths are generated at once
 - Disadvantage: Somewhat limited spectral range 330-1000 nm
- Optical parametric amplification
 - Advantage: Broad spectral range 250-12000 nm
 - Disadvantage: Requires more sophisticated equipment;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

1. Pump-probe spectroscopy

Optical transient absorption spectroscopy



Ground state depletion and recovery



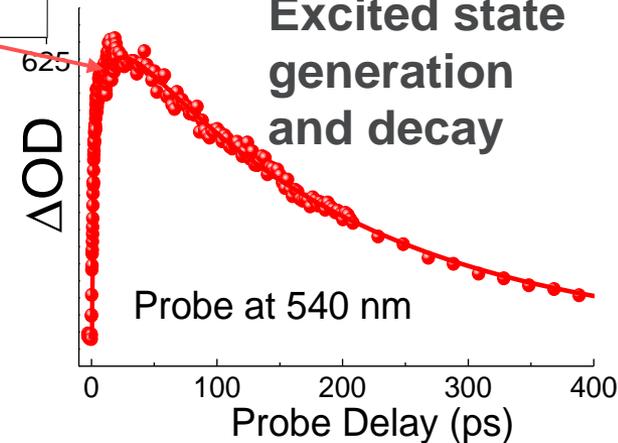
“Pump” laser pulse:

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.

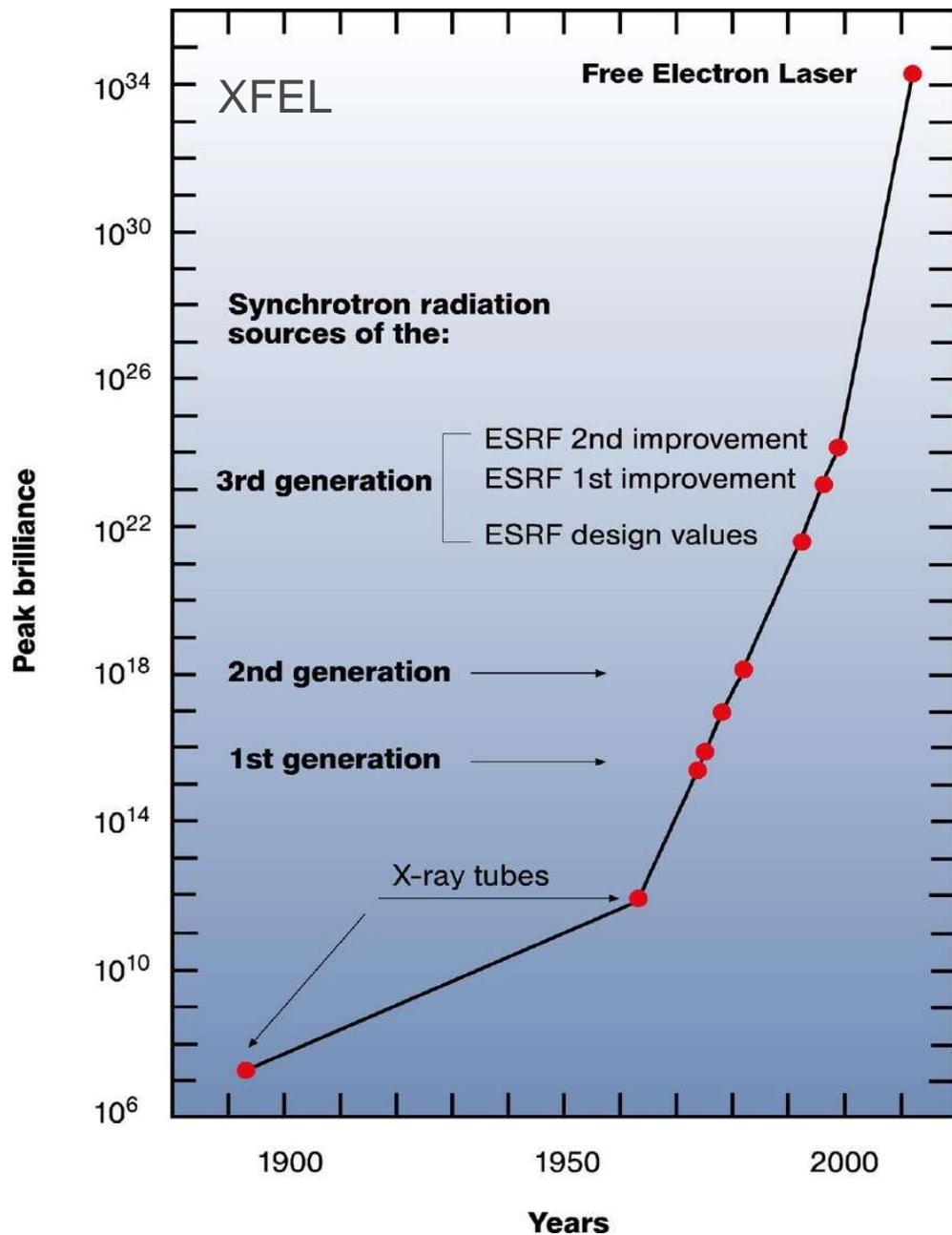
Excited state generation and decay



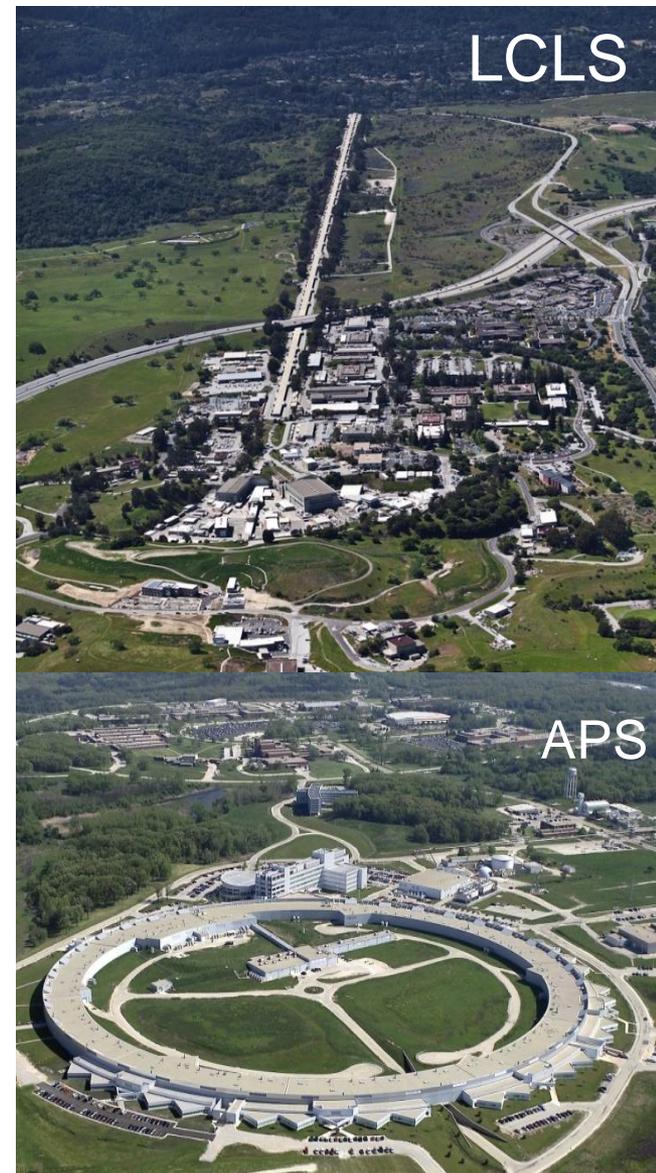
2. Experimental Considerations

- **Light sources for pump and probe pulses;**
- **Photon energy differences;**
- **Timing structure (synchronization of laser with X-ray pulses);**
- **Samples (absorption coefficients, concentration, lifetimes, stability);**
- **Detection scheme**
- **Capability of optical vs. X-ray transient absorption spectroscopy**

X-ray photon flux evolution in sources



2. Experimental Considerations



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

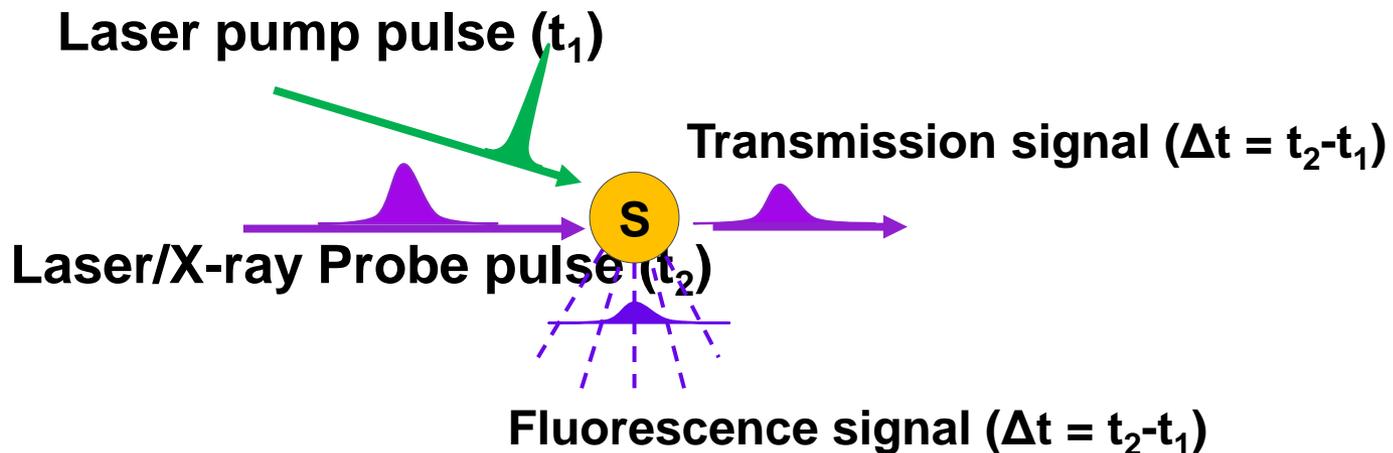
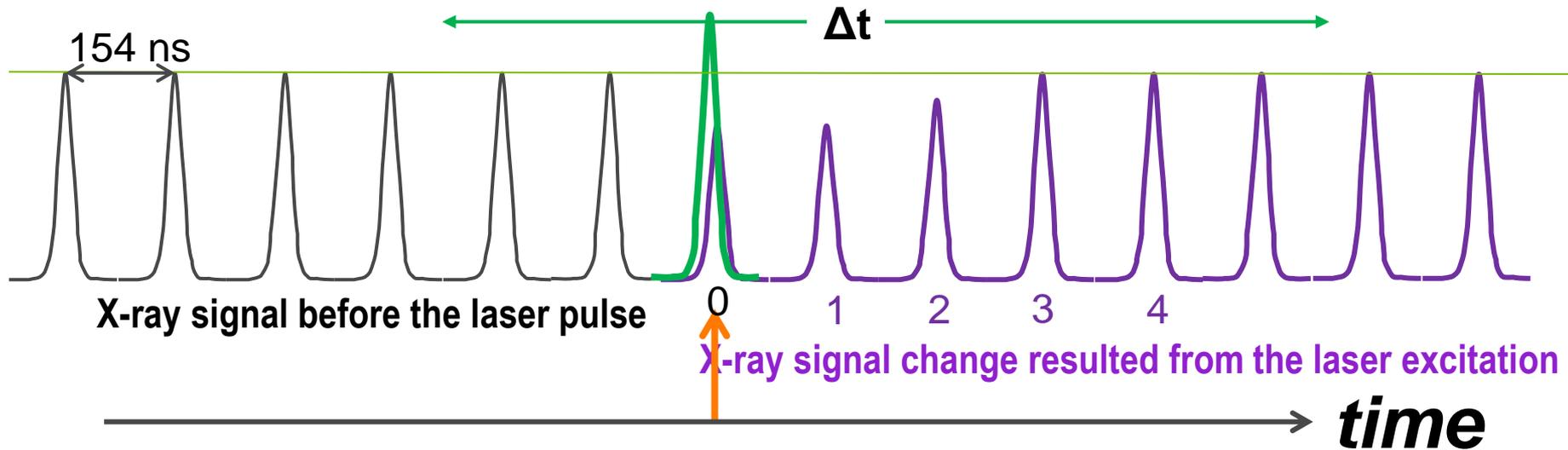
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X-ray probe light sources

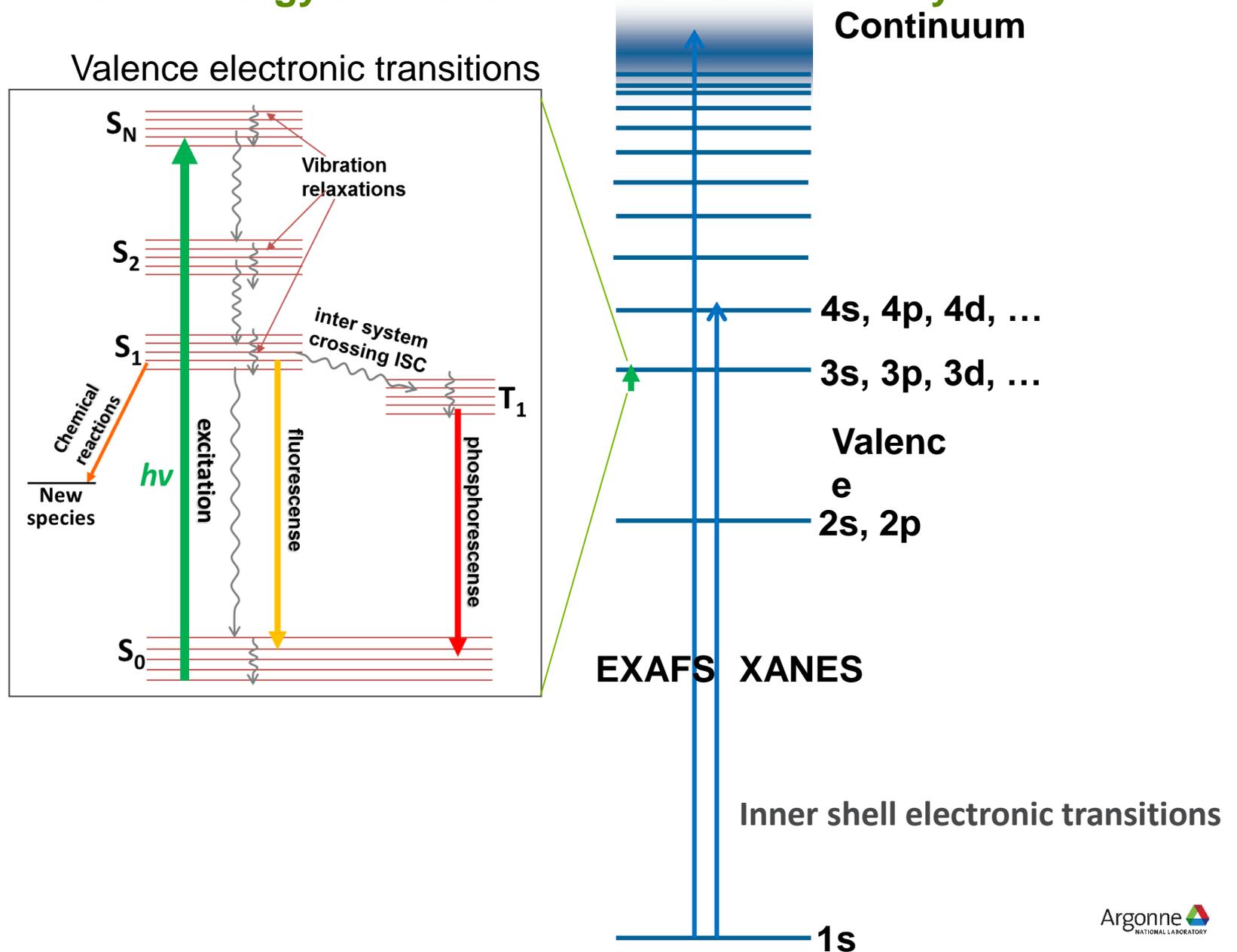
- Third generation synchrotron sources
- Table top laser driven fs pulsed x-ray pulses
- High harmonic generation
- X-ray free electron lasers

X-ray transient absorption spectroscopy (XTA)

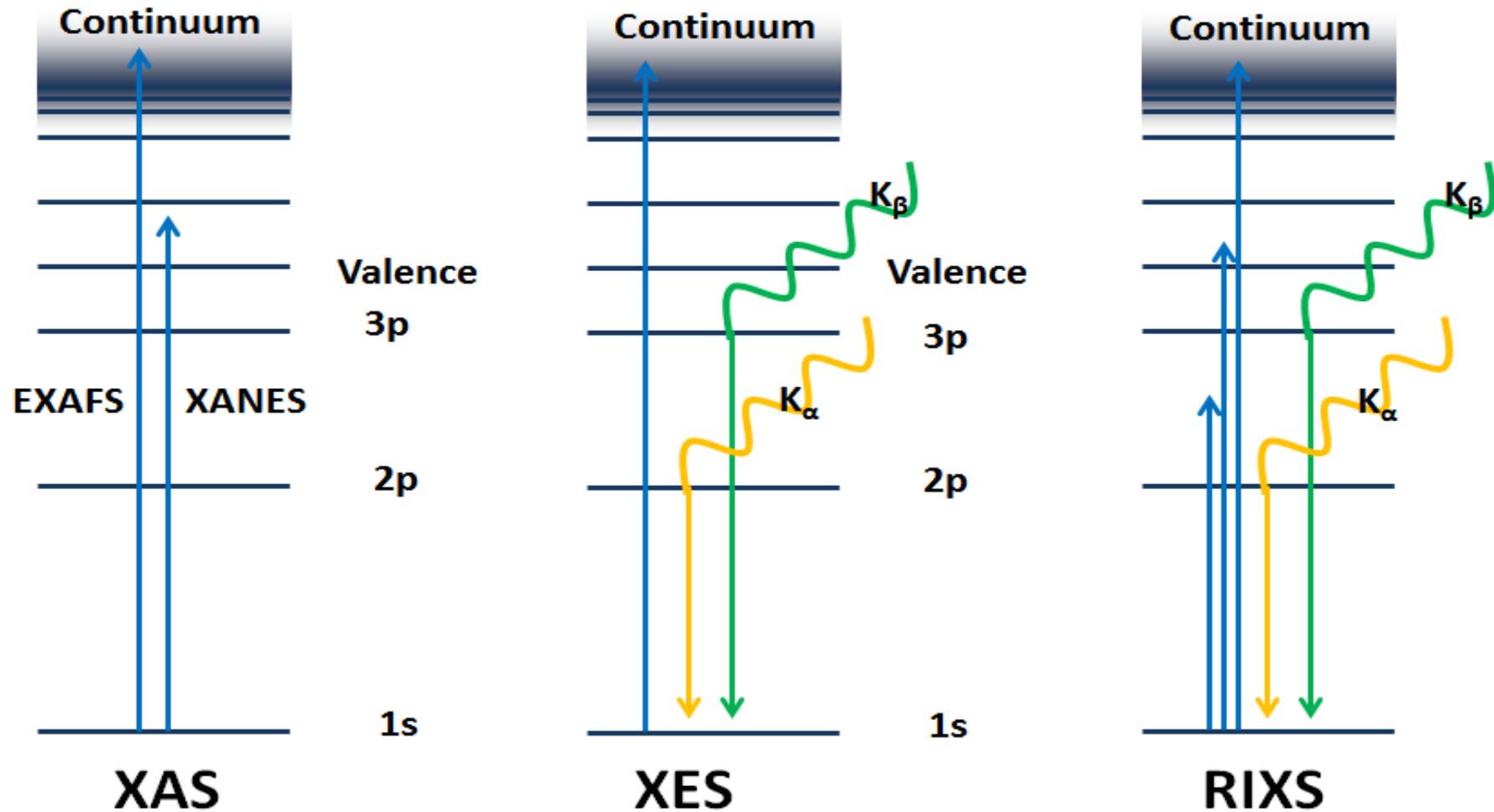
Synchronization of laser pump pulse with x-ray probe pulse through synchrotron RF signal



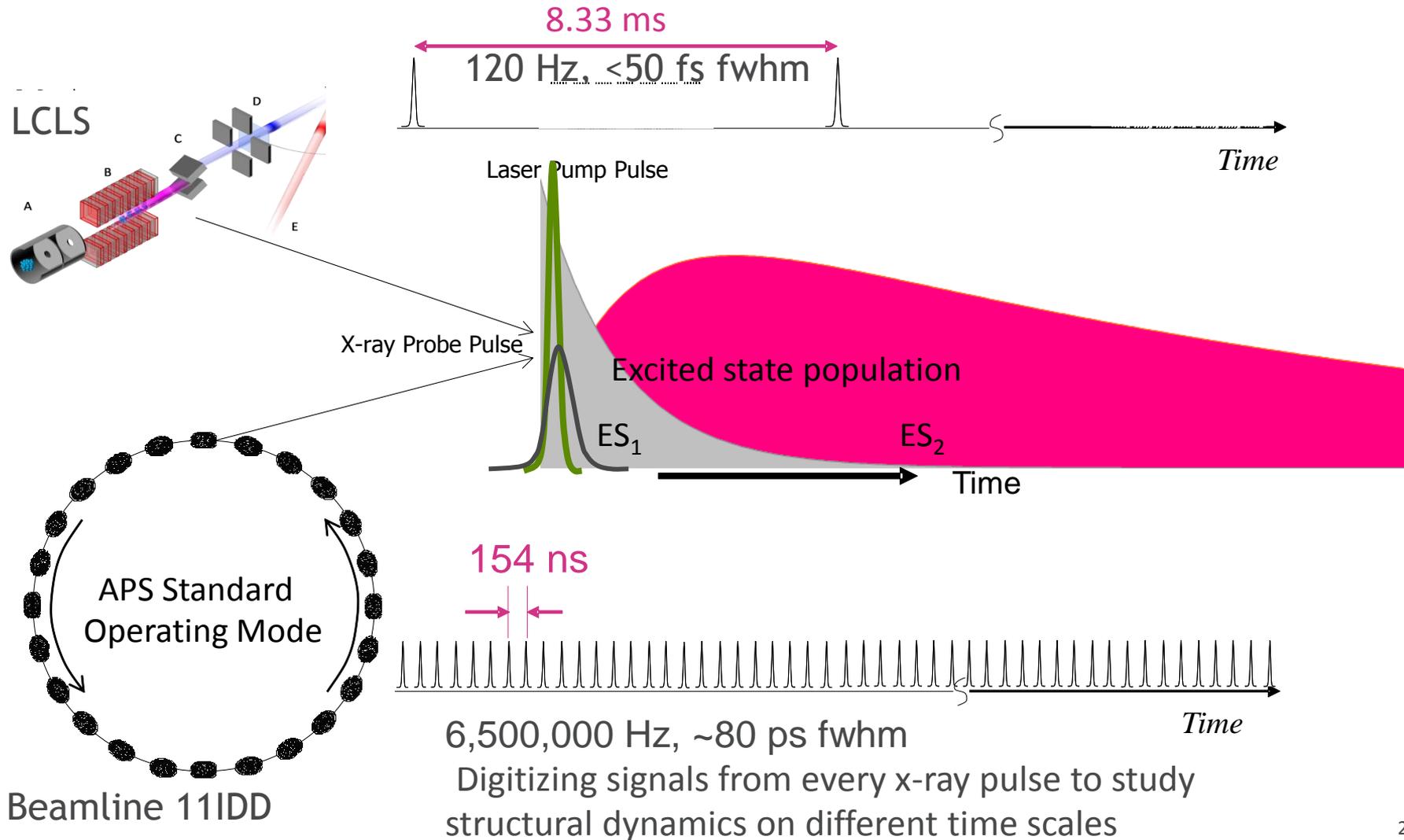
Photon energy difference: visible vs. hard X-ray



Photon energy difference: visible vs. hard X-ray

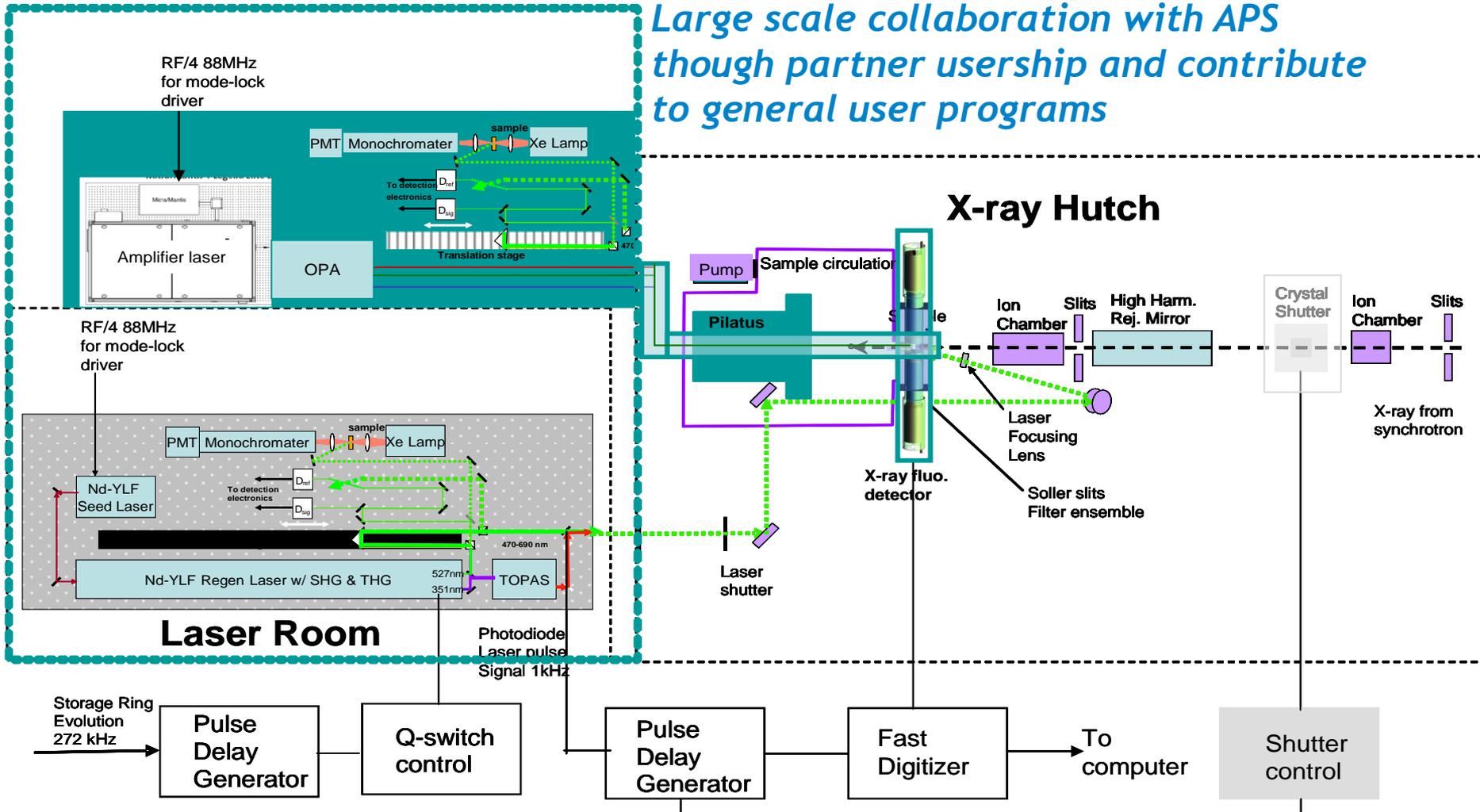


Timing structures of laser and X-ray pulses



Synchrotronization of laser pulses with X-ray pulses at the APS

Large scale collaboration with APS though partner usership and contribute to general user programs

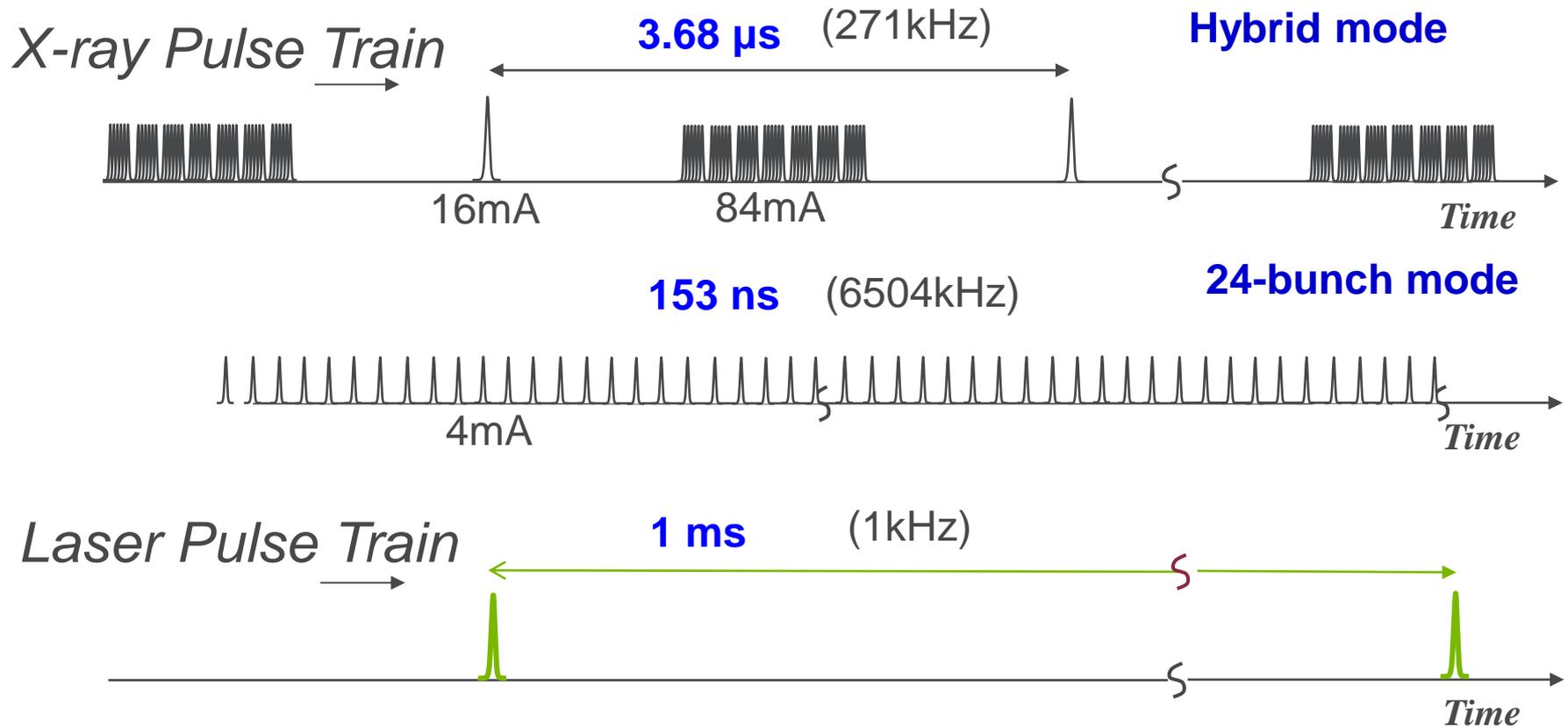


Time-resolved x-ray facility at 11IDD

Sample requirements

- Lifetime of the transient structure $>$ x-ray pulse duration (e.g. 100 ps) and less the x-ray pulse separation;
- Absorption coefficient or extinction coefficient at the excitation laser wavelength sufficiently high to ensure effective excitation;
- Concentration of the x-ray absorbing atoms sufficiently high for either transmission or fluorescence detection;
- Stability of the sample sufficiently high under illumination of the laser and x-ray pulses;
- Sample quantity sufficiently large to ensure necessary refresh of the sample during the data acquisition period;
- Meaningful samples.

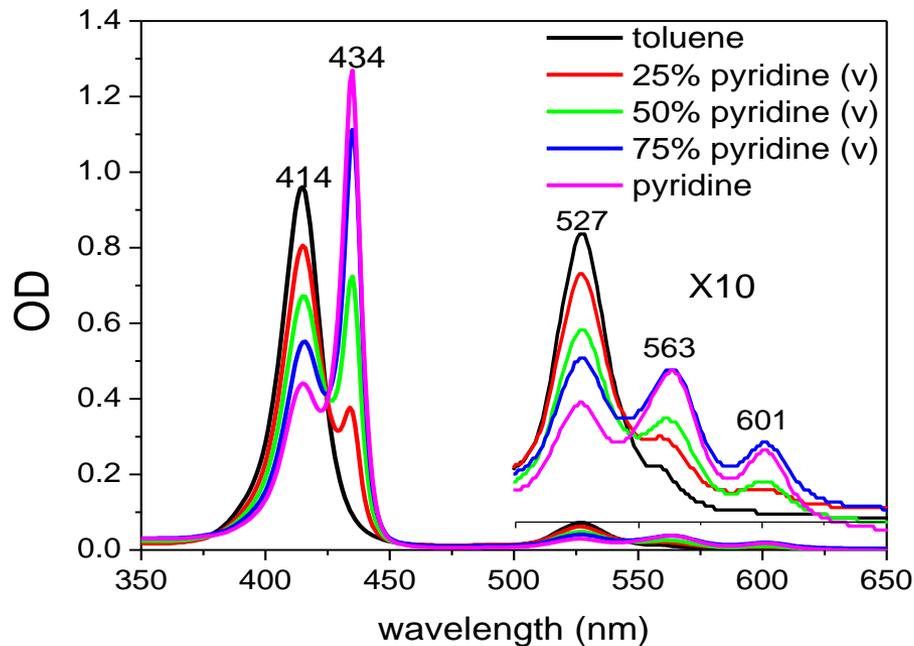
Sample requirements: X-ray and laser pulse repetition rates



For example, the pump-probe cycle repeats at 1 kHz due to the laser pulse repetition rate resulting in a factor of $\sim 1,700$ or $6,500$ reduction of the x-ray photon flux!

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

Sample requirements: The ground state absorption of laser photons



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

P , laser pulse energy (J);

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

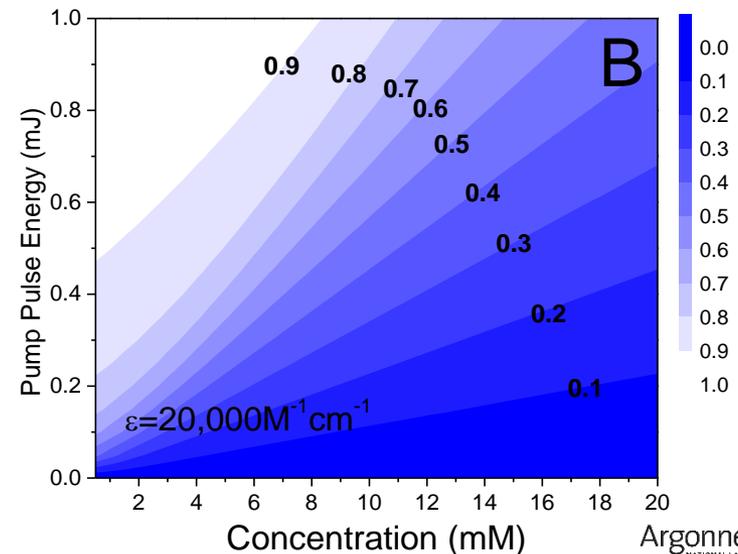
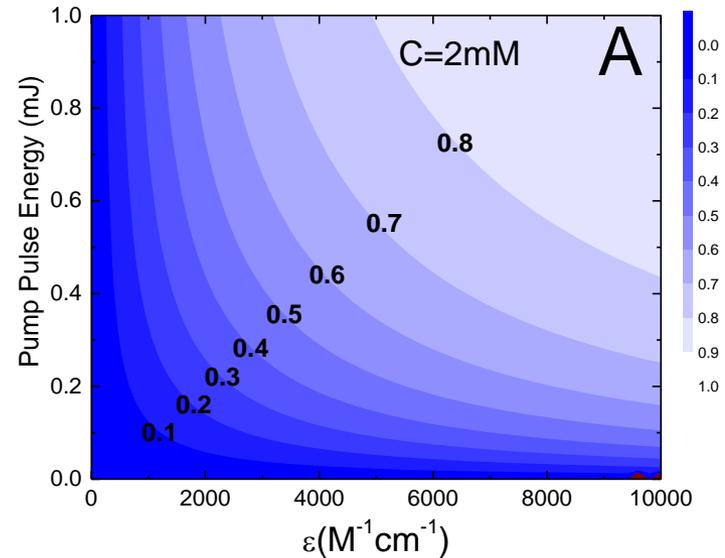
t , time, s;

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

l , thickness (cm);

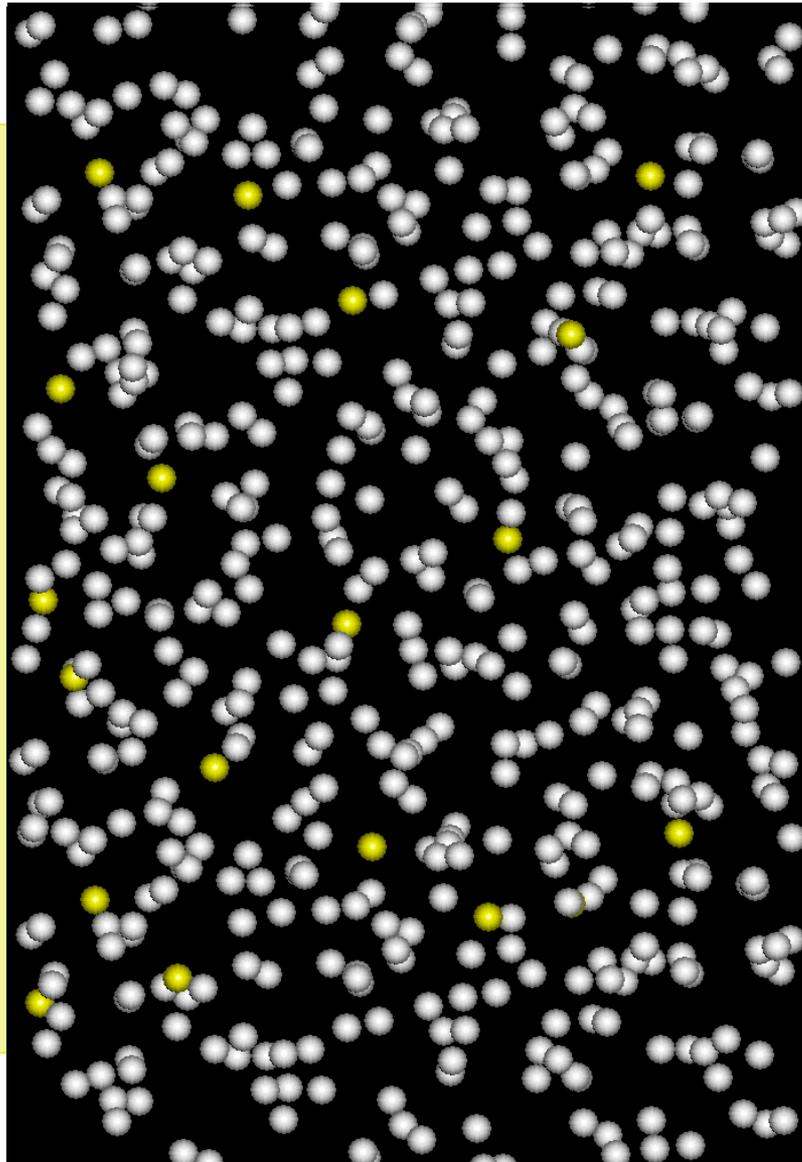
C , concentration (M);

N , total number of molecules illuminated by the laser.

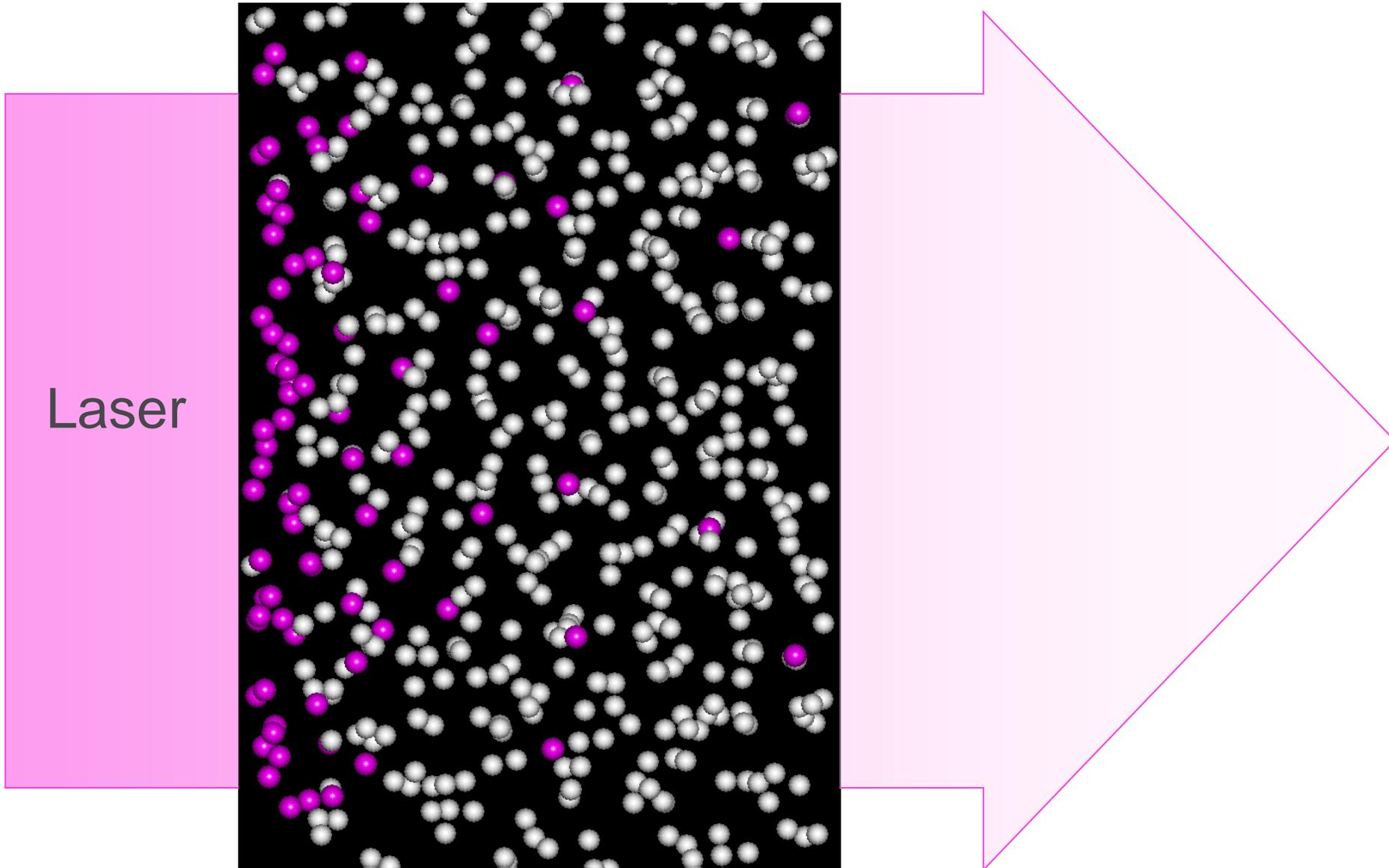


Sample requirements: X-ray and laser photon absorption cross section

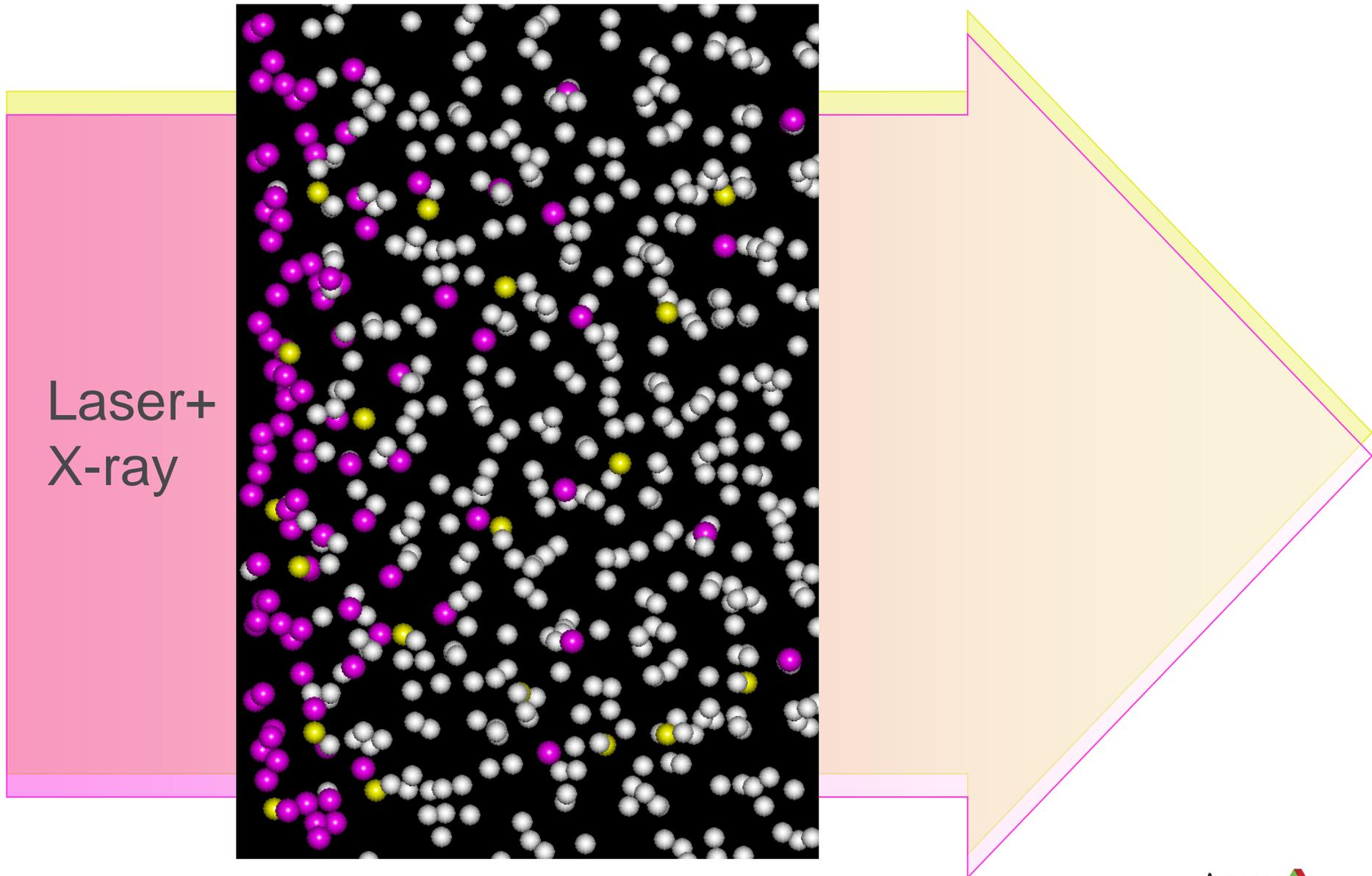
X-ray



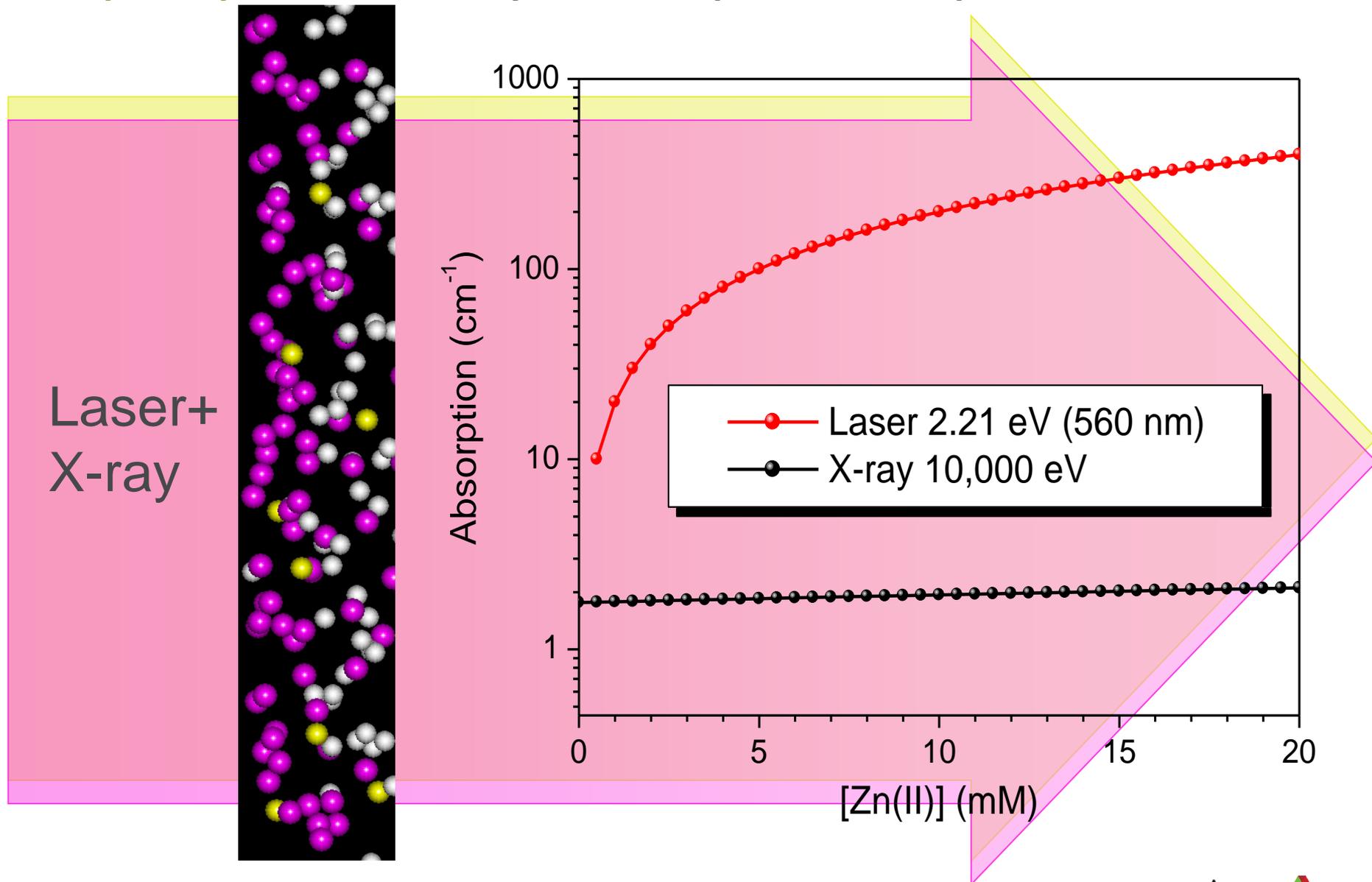
Sample requirements: X-ray and laser photon absorption cross section



Sample requirements: X-ray and laser photon absorption cross section



Sample requirements: X-ray and laser photon absorption cross section



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 λ ($M^{-1}cm^{-1}$);

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 λ , $\varepsilon_{ES}(\lambda) = 0$,

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

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

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:

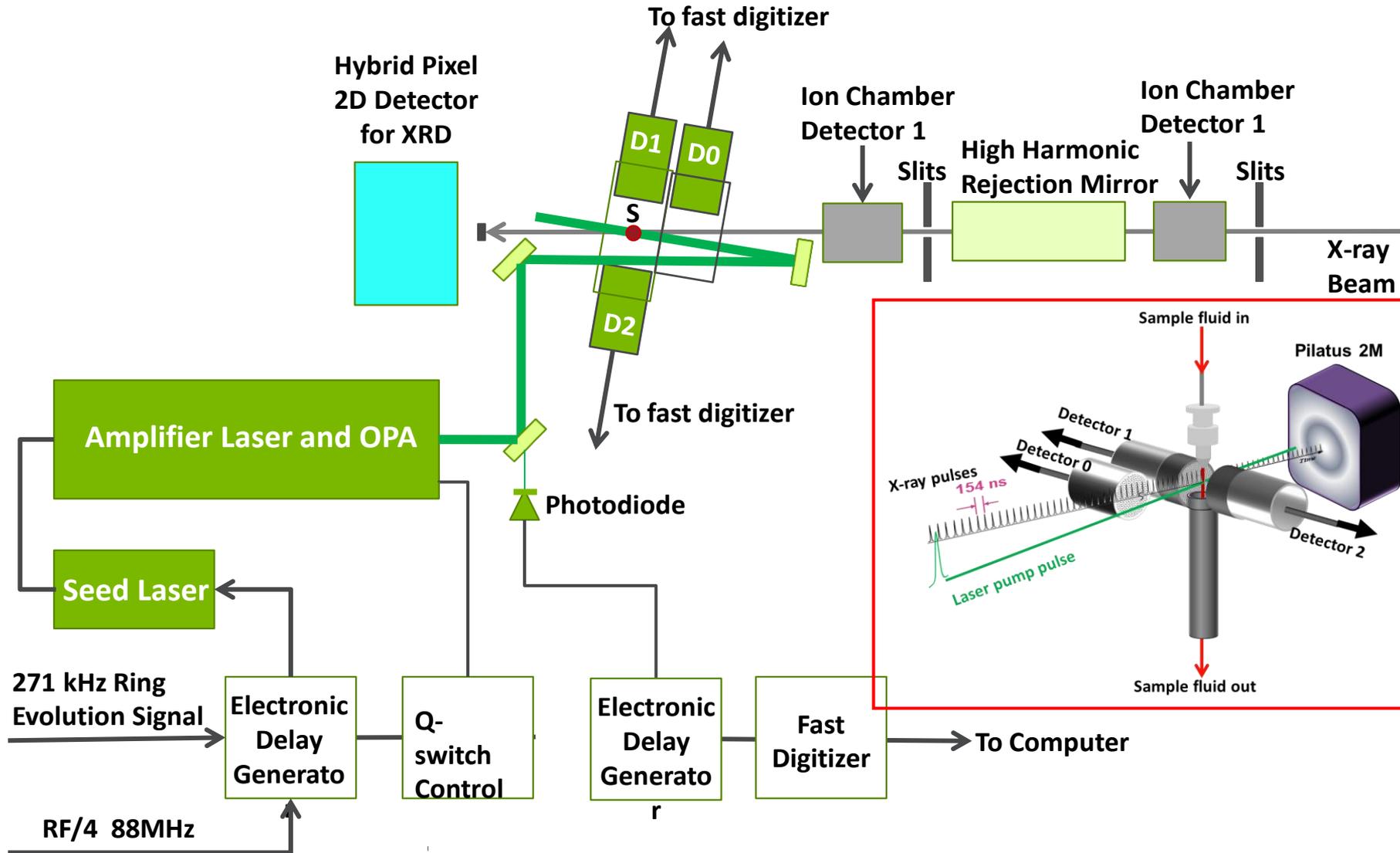
$$\min \left(\frac{1}{E_2 - E_1} \int_{E_1}^{E_2} \left[\left(\mu_{\text{exp}}^{\text{laser-on}} - \mu_{\text{exp}}^{\text{laser-off}} \right) - Y \left(\mu_{\text{theor}}^{\text{es}}(\delta p_1, \delta p_2) - \mu_{\text{theor}}^{\text{gs}} \right) \right]^2 dE \right)$$

Principal component analysis

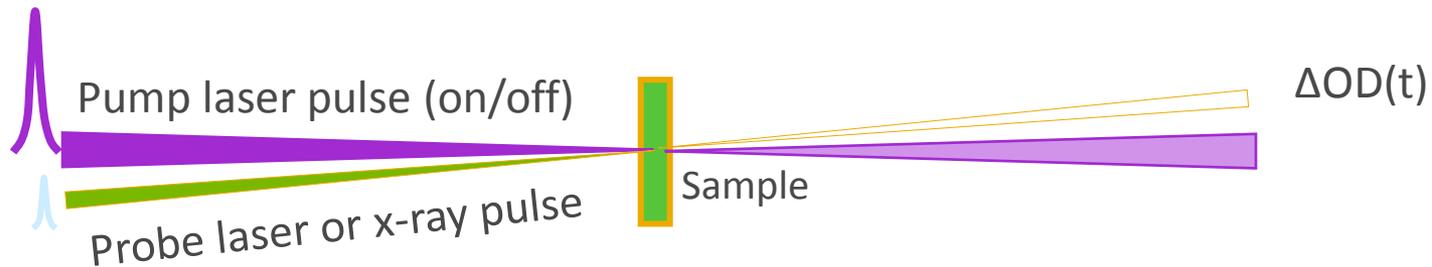
Smolentsev, G.; Soldatov, A. *Journal of Synchrotron Radiation* **2006**, 13, 19-29.

Smolentsev, G.; Soldatov, A. V. *Computational Materials Science* **2007**, 39, 569-574.

Detection and sample delivery



3. Transient Structural Information Investigated by XTA



Pump: creates changes or triggers reactions
Probe: interrogates changes

OTA:

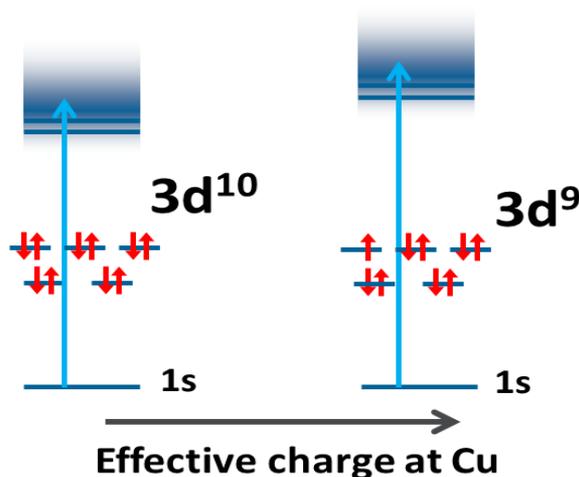
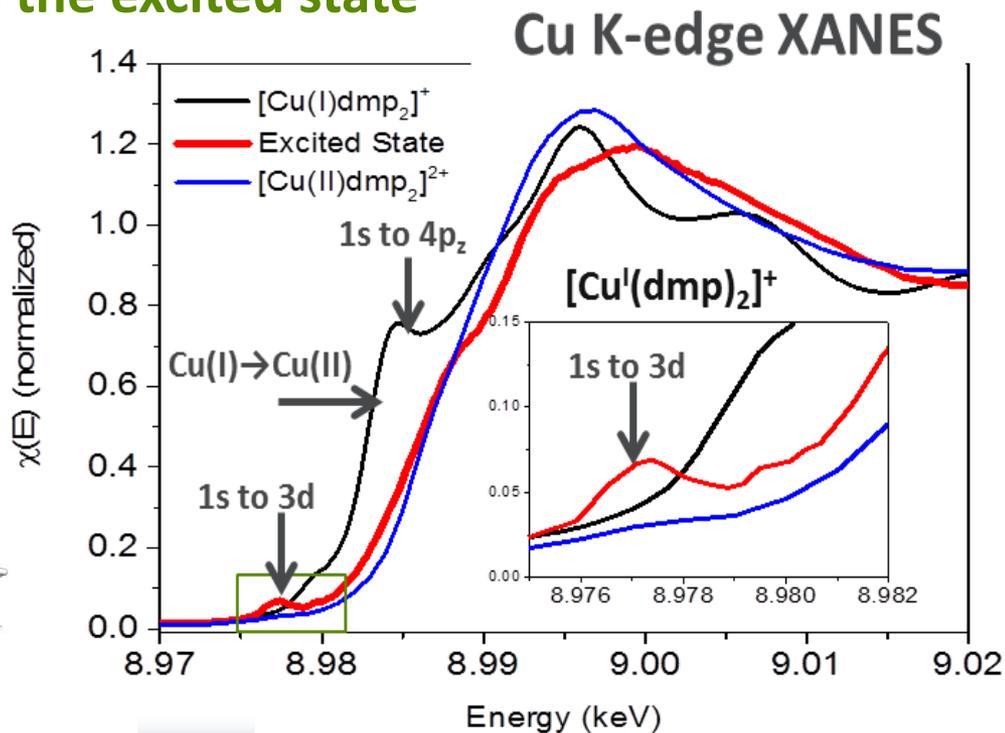
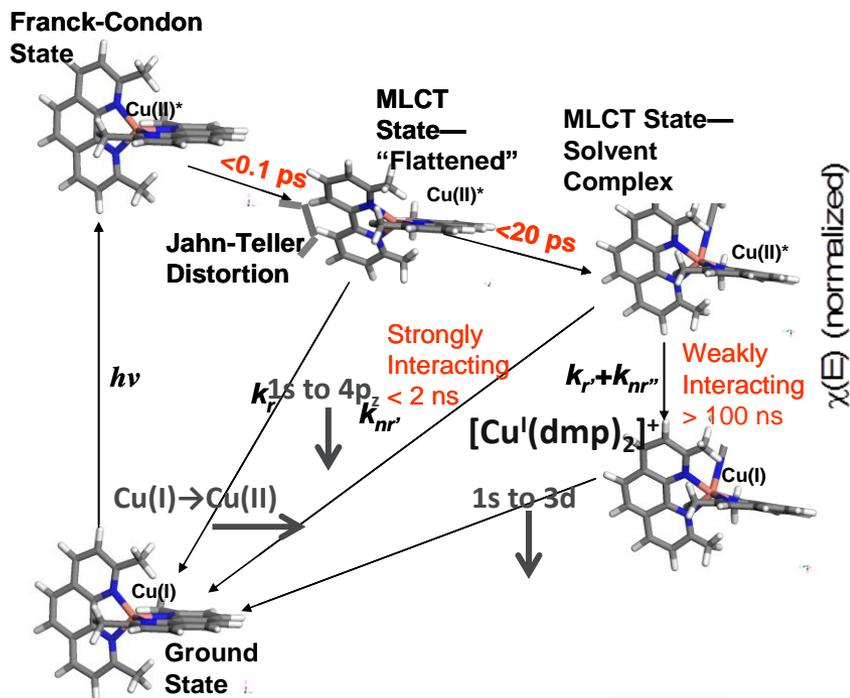
- How fast molecule moves;
- How to get from R \rightarrow P;
- How energy flows;
- Transient species population;
- Correlation of electronic transitions;
- How molecular movements affect functions.

XTA (New):

- Electronic configuration;
- Geometry;
- Oxidation states
- Molecular orbital energies;
- Transient species lifetime;
- Correlations of electronic transition with nuclear movements.

3. Transient Structural Information Investigated by XTA

Metal center oxidation state in the excited state

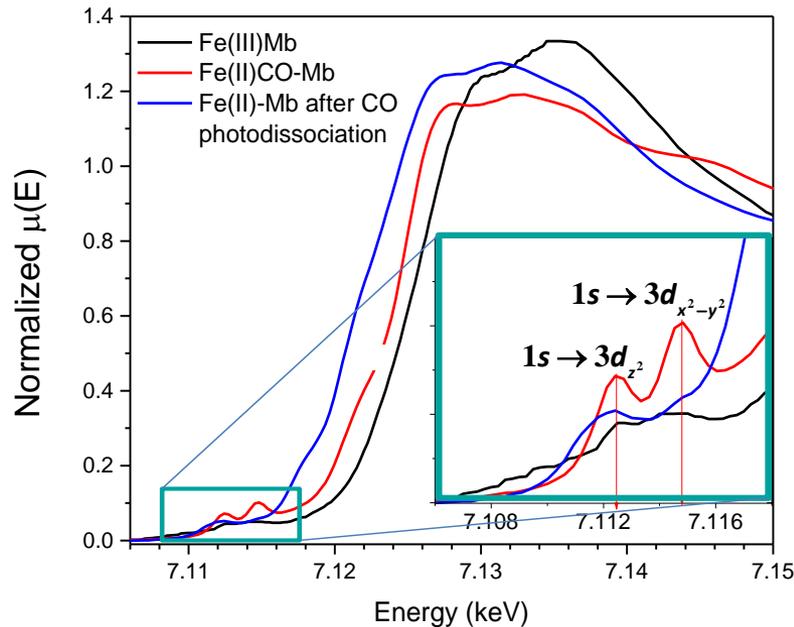
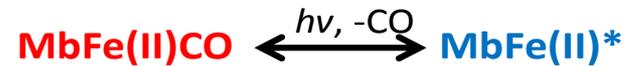
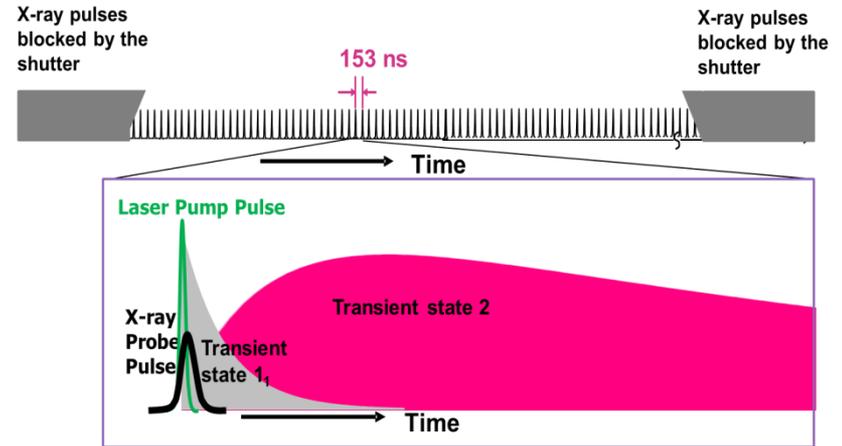
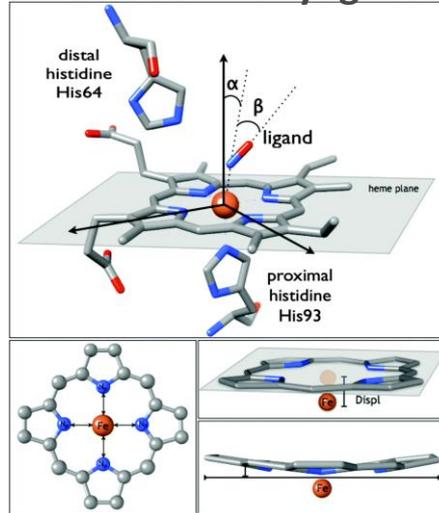
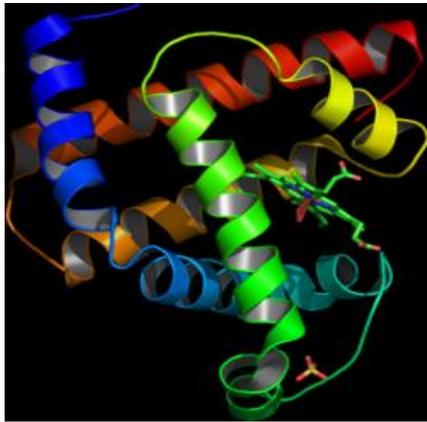


JACS 129, 2147 (2007),
125, 7022 (2003), 124,
10861 (2002).

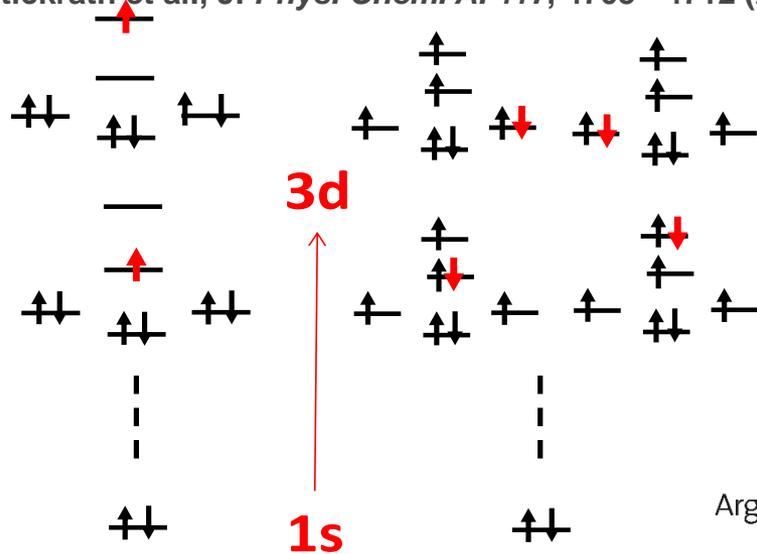
3. Transient Structural Information Investigated by XTA

Electron configuration and orbital energies of X-ray absorbing atoms

Photodissociation of CO from heme in myoglobin



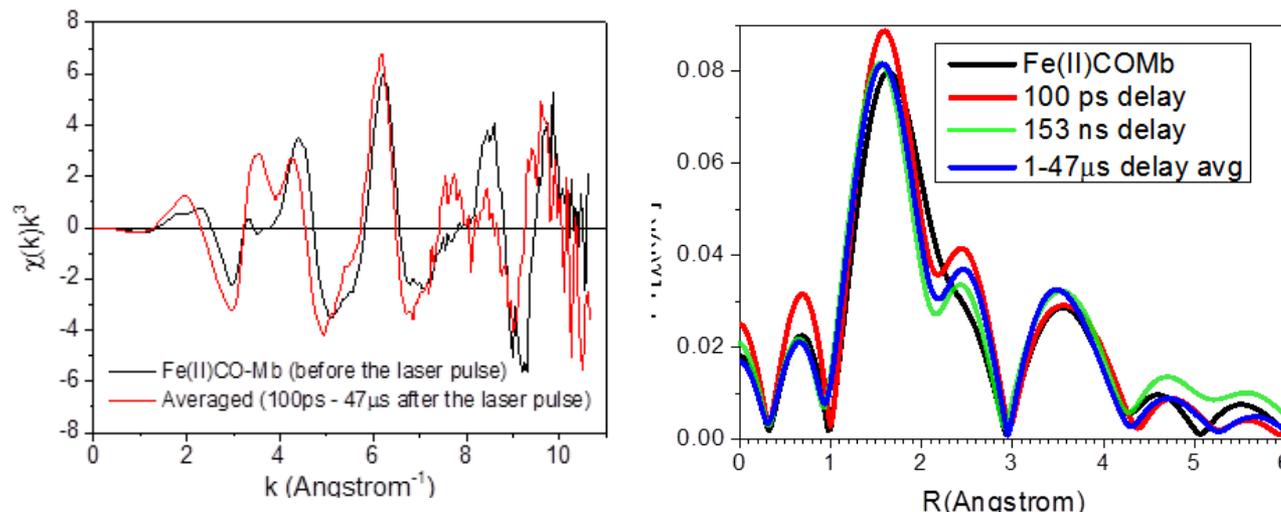
Stickrath et al., *J. Phys. Chem. A.* 117, 4705 - 4712 (2013)



3. Transient Structural Information Investigated by XTA

Transient coordination geometry of the metal center

Photodissociation of CO from heme in myoglobin



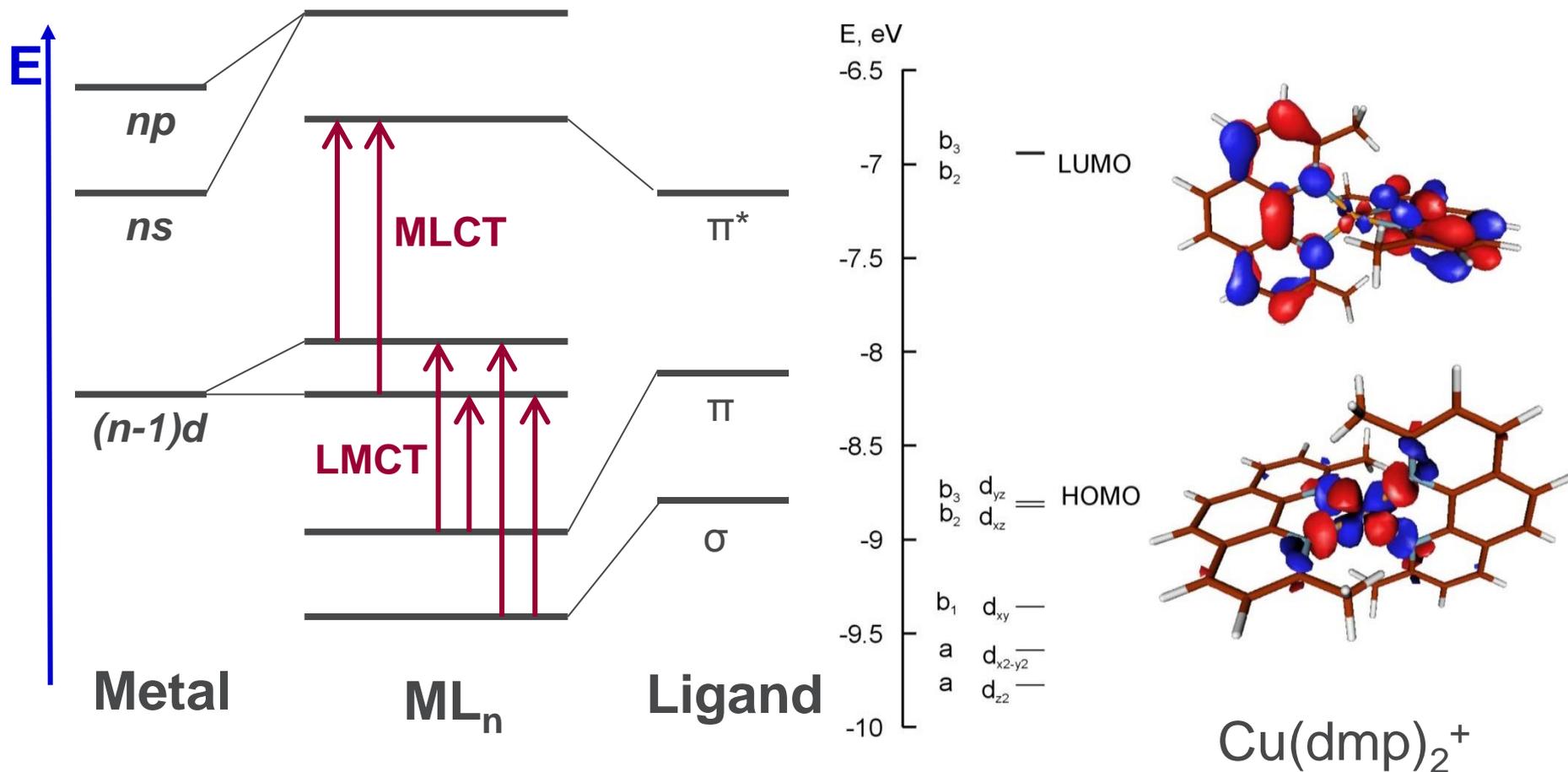
Stickrath et al.,
J. Phys. Chem. A. 117, 4705 -
 4712 (2013)

Table 1. Iron heme structural parameters (Residual = 8.11, $S^2 = 0.9$)

Fe(II)CO-Mb	CN	R(Å)	$\sigma^2(\text{Å}^2)$	$\Delta E(\text{eV})$	Fe(II)Mb	CN	R(Å)	$\sigma^2(\text{Å}^2)$	$\Delta E(\text{eV})$
Fe-C(O)	1	1.76	0.0001	18.10					16.47
Fe-N(His,Heme)	5	1.99	0.0013			5	2.05	0.0042	
Fe-O(CO)	1	2.84	0.0002						
Fe-C(CNC)	10	3.08	0.0080			10	3.05	0.0034	
Fe-C $_{\alpha}$	4	3.38	0.0001			4	3.47	0.0010	
Fe-C $_{\beta}$	10	4.41	0.0001			9	4.21	0.0023	

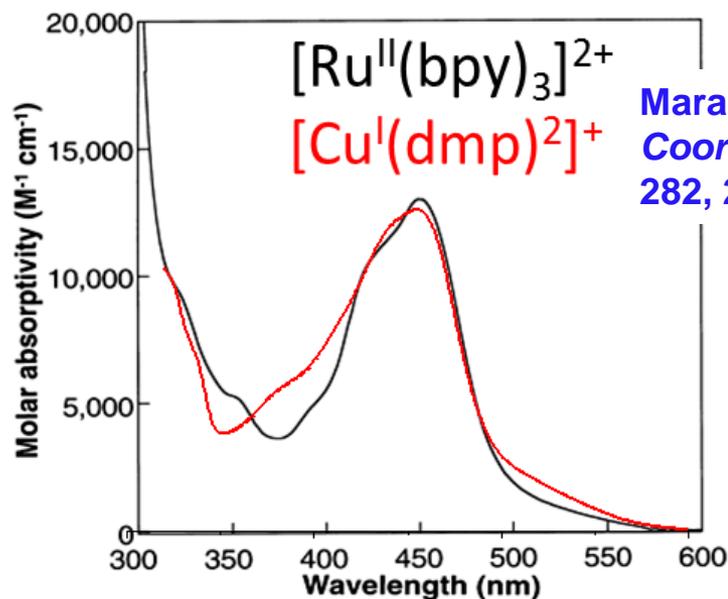
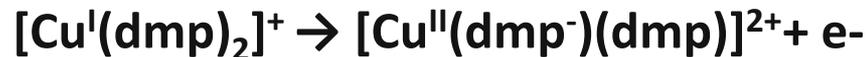
4. XTA spectroscopy, Examples

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.

Excited state structural dynamics of Cu(I) diimine complexes



Mara, Fransted, Chen,
Coord. Chem. Rev.,
 282, 2-18 (2015).

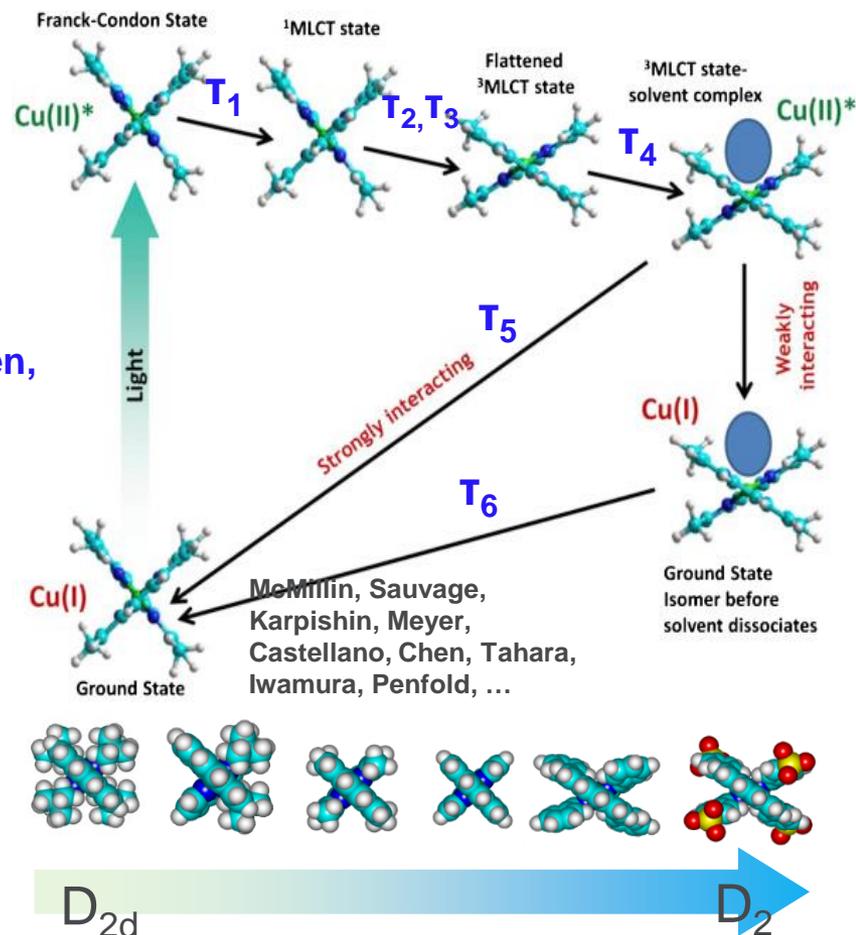
τ_1 - ¹MLCT formation;

τ_2 - J-T distortion, 0.3-0.6 ps;

τ_3 - ISC, 1-20 ps;

τ_4 , ³MLCT "ligation" > 100 ps?;

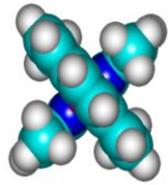
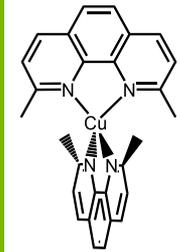
$\tau_{5,6}$ ³MLCT decay, 1ns to 3 μ s.



Two key structural factors:

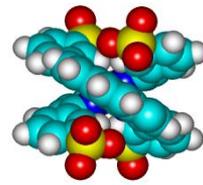
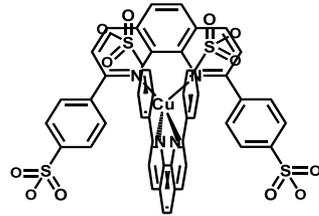
- Orientation of two ligand planes: ISC
- Solvent accessibility to the Cu* center – electron density transfer from "ligating" solvent to 3d, ³MLCT lifetime.

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$\tau_1 = 0.6 \text{ ps}$
 $\tau_2 = 13 \text{ ps}$
 $\tau_3 = 1.6/100 \text{ ns}$

$[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$

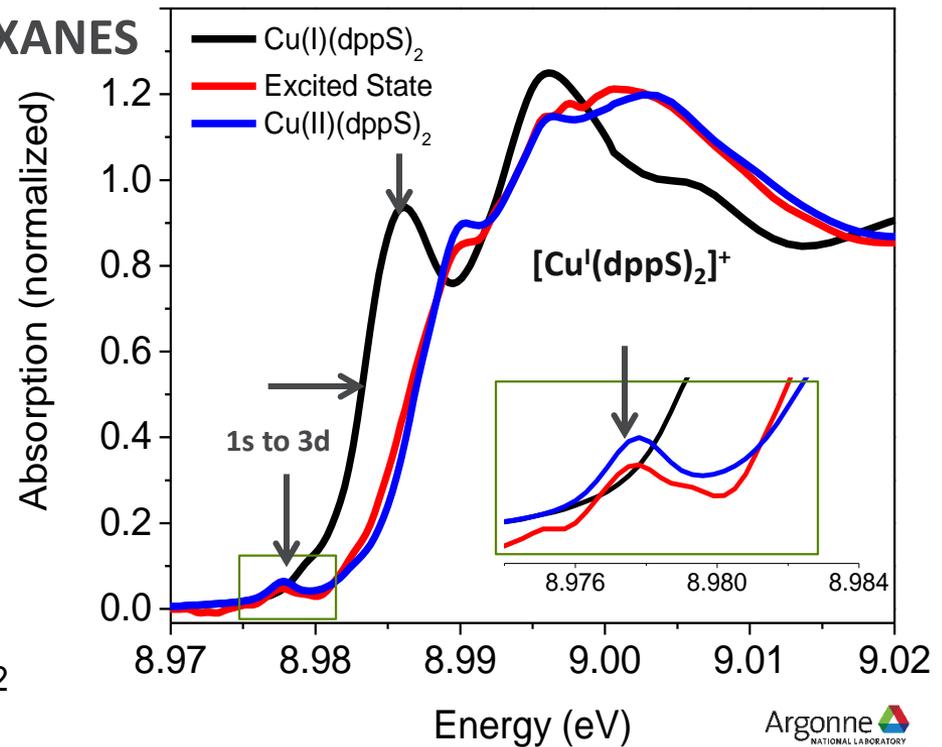
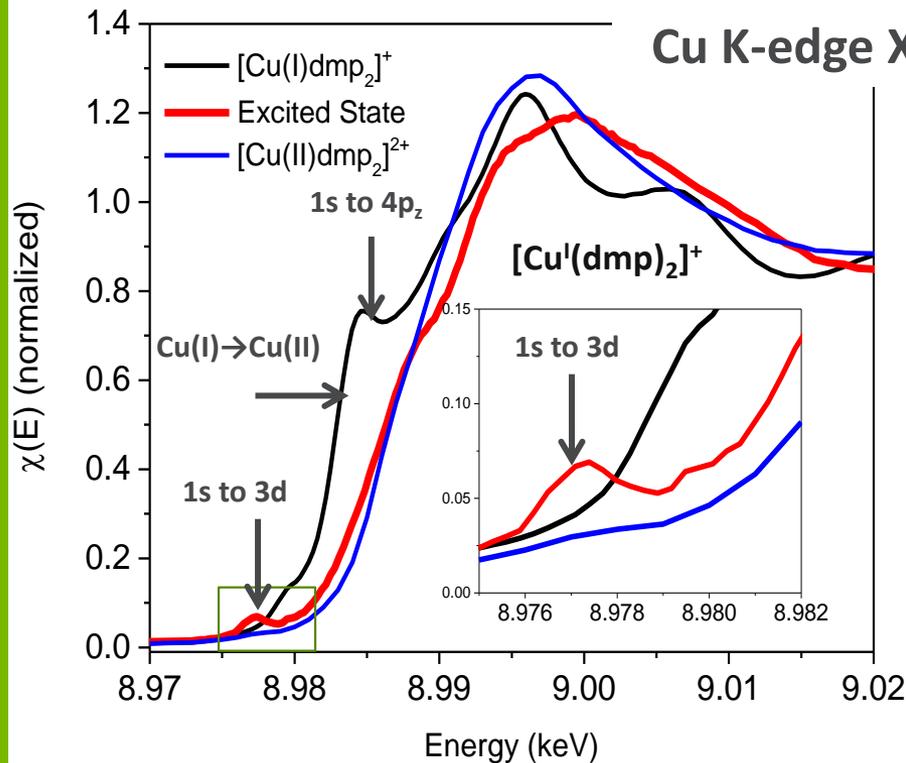


$\tau_1 = \text{N/A}$
 $\tau_2 = 13 \text{ ps}$
 $\tau_3 = 100/\text{N/A} \text{ ns}$

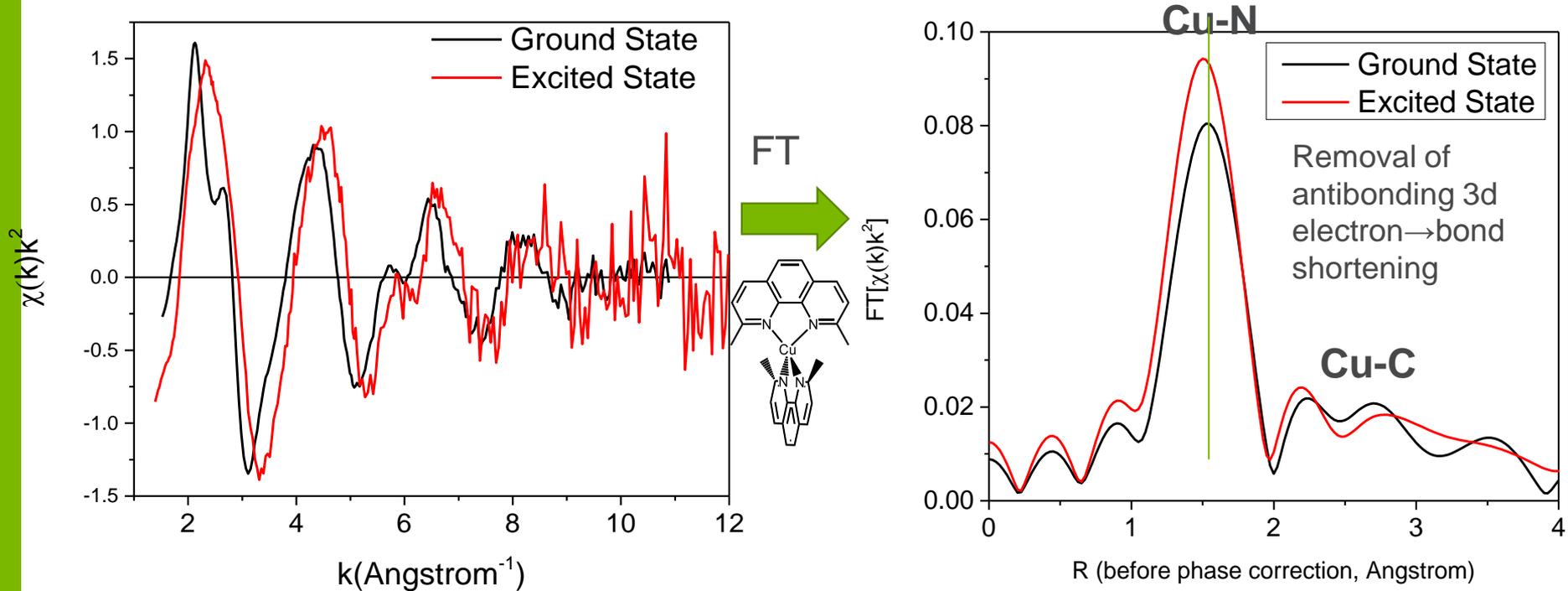
$[\text{Cu}^{\text{I}}(\text{dppS})_2]^+$

Transient Cu(II) in $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ MLCT state:
 3d hole remains – transient “ligation” and no formal bond forms with the solvent, but only direct access of the solvent to the Cu(II)* center could shorten the MLCT lifetime in coordinating solvent;
Cu(II) in $[\text{Cu}^{\text{II}}(\text{dmp})_2]^{2+}$:
 3d hole filled due to the ligation.¹⁶

(J.-P. Sauvage and coworkers)



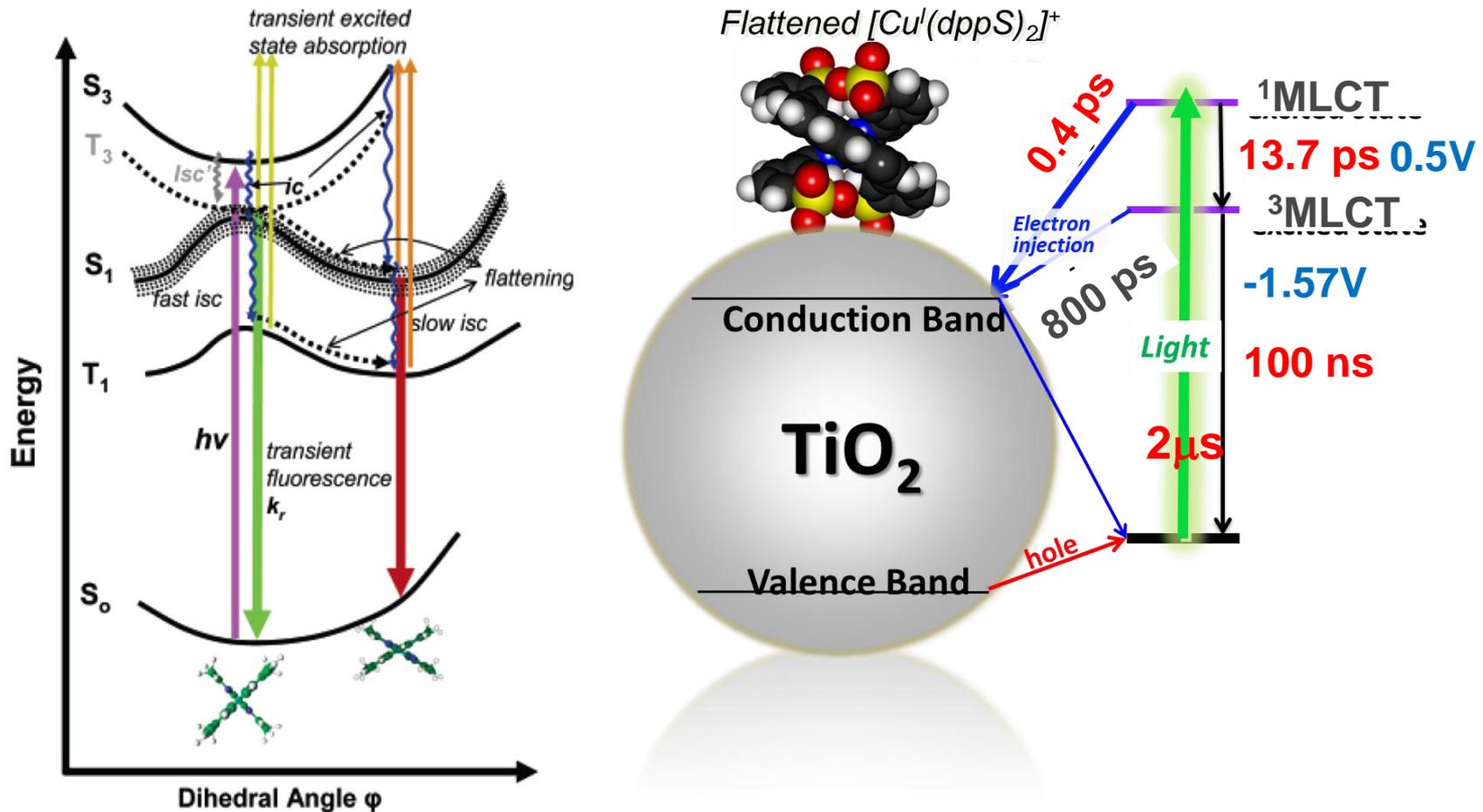
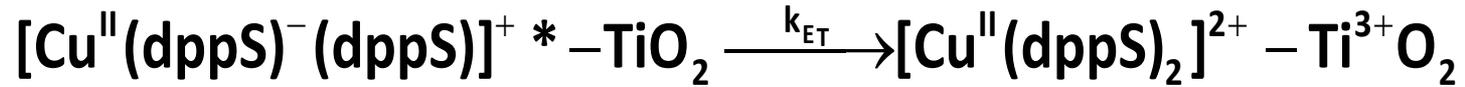
Excited state structural dynamics of Cu(I) diimine complexes

EXAFS of the MLCT State of $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ 

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

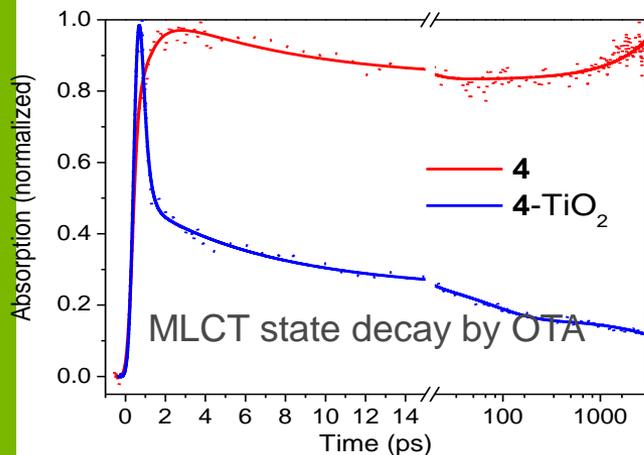
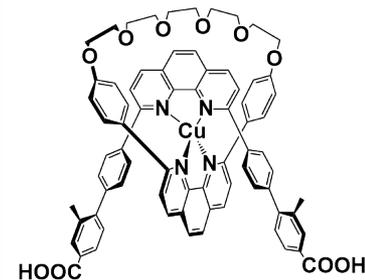
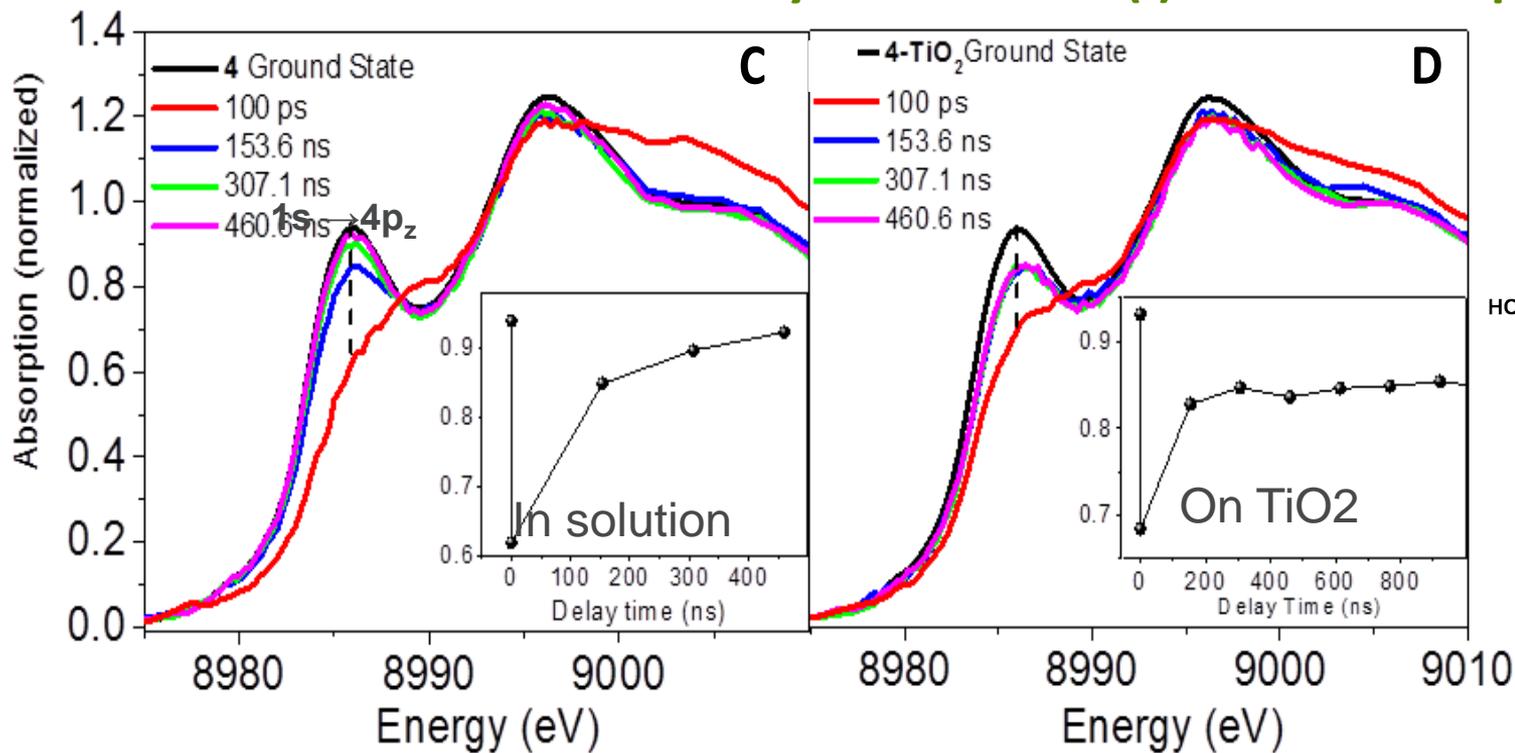
Transient exciplex forms when the space and the MLCT state lifetime allow, but not necessarily forms a normal bond between Cu(II) and solvent.

Excited state structural dynamics of Cu(I) diimine complexes



Mara, Coskun, Dimitrijevic, Barin, Kokhan, Stickrath, Ruppert, Tiede, Stoddart, Sauvage, Chen, *Angew. Chem. Intl. Ed.* 51, 12711–12715 (2012).

Excited state structural dynamics of Cu(I) diimine complexes

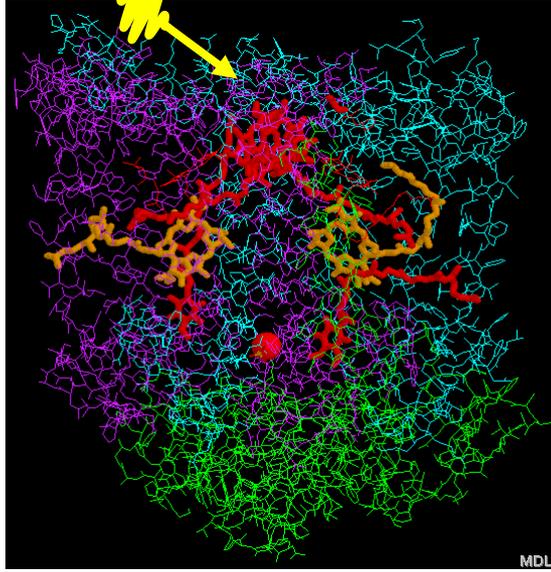


- ~40% injection yield, due to charge recombination;
- Linker length independent;
- Electron transfer mechanism and pathway: through bond;
- Future design aims at minimize charge recombination.

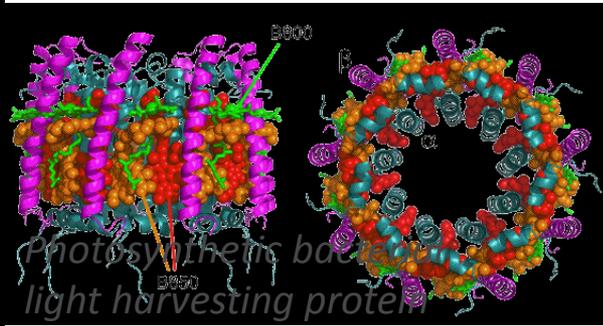
Mara, Coskun, Dimitrijevic, Barin, Kokhan, Stickrath, Ruppert, Tiede, Stoddart, Sauvage, Chen, *Angew. Chem. Intl. Ed.* **51**, 12711–12715 (2012).

4. XTA spectroscopy, Examples

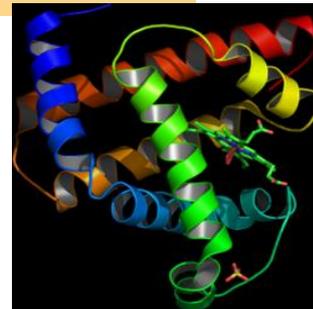
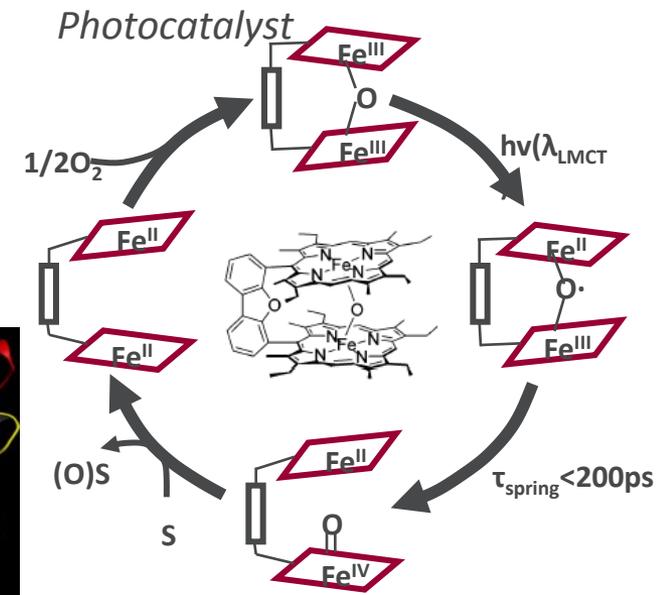
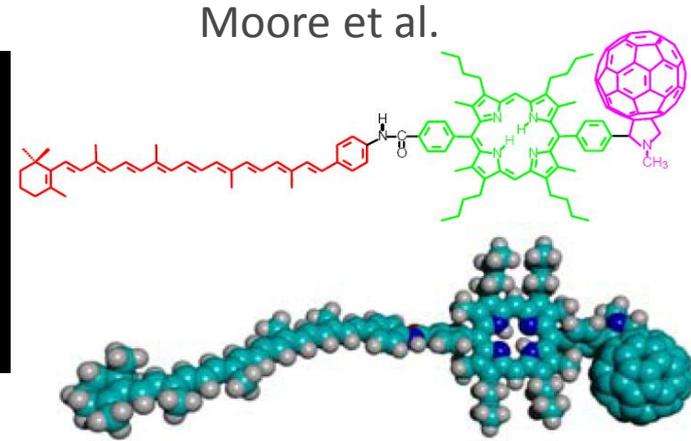
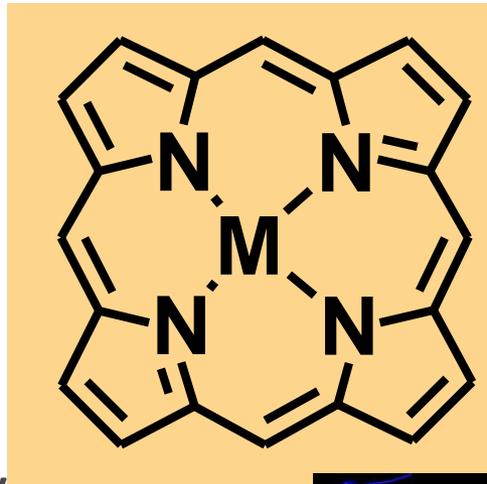
Metalloporphyrins



Photosynthetic bacterial reaction center protein



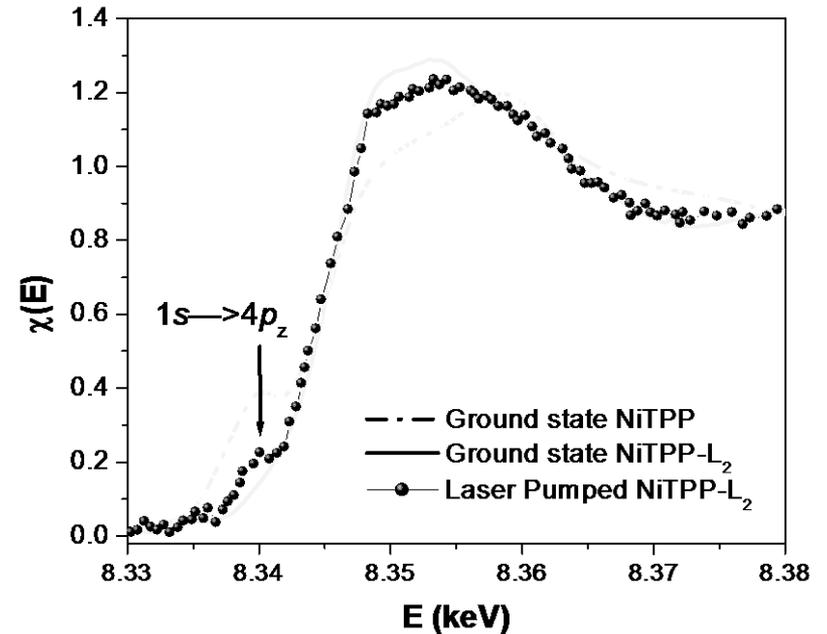
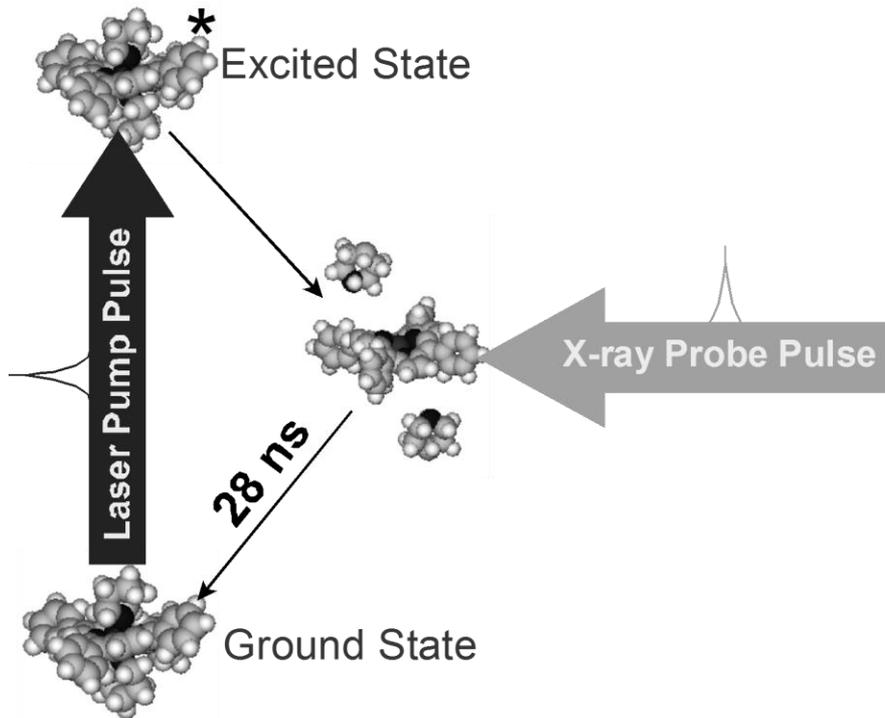
Photosynthetic bacterial light harvesting protein



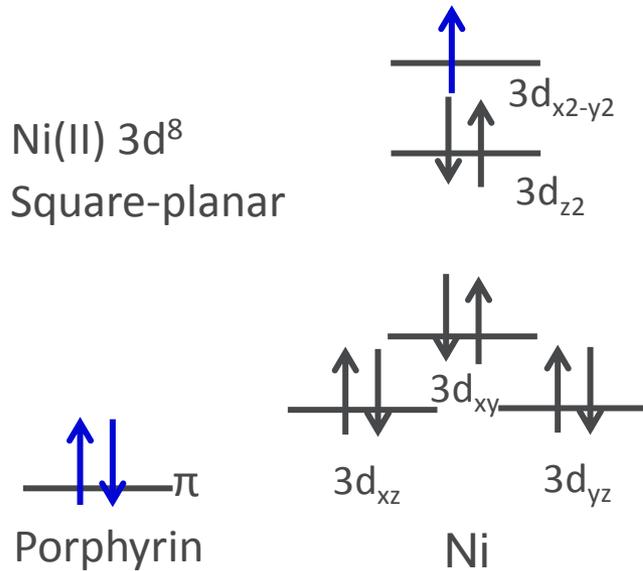
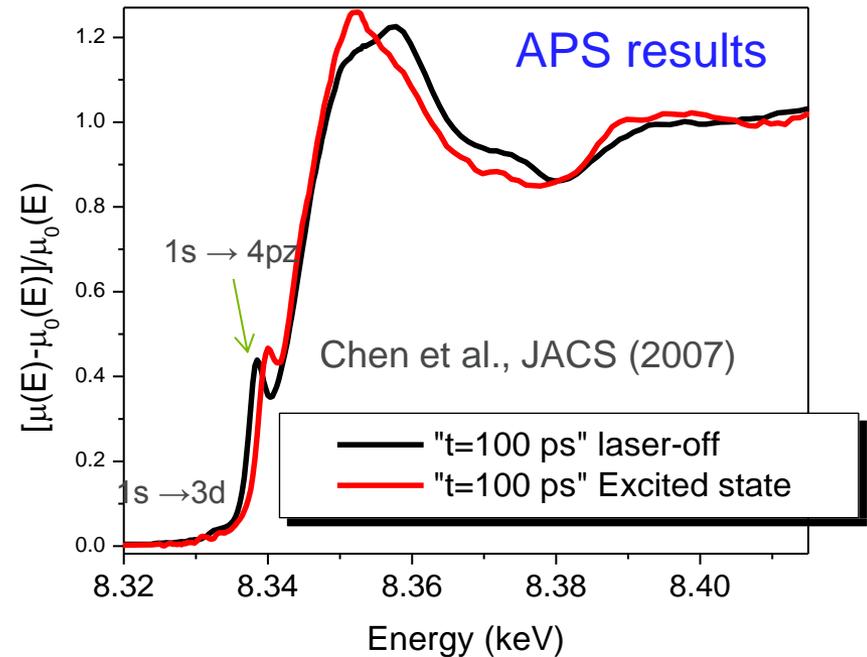
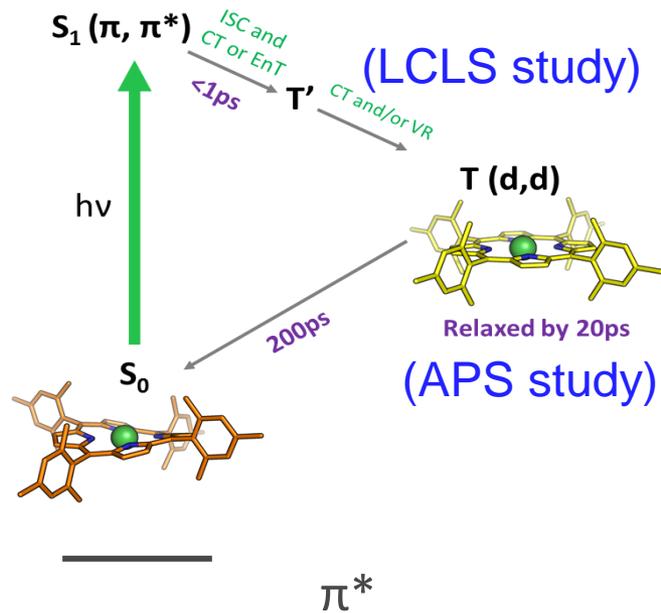
Myoglobin

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

Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure, L. X. Chen, W. J. H. Jäger, G. Jennings, D. J. Gosztola, A. Munkholm, J. P. Hessler, *Science*, **292**, 262-264(2001).

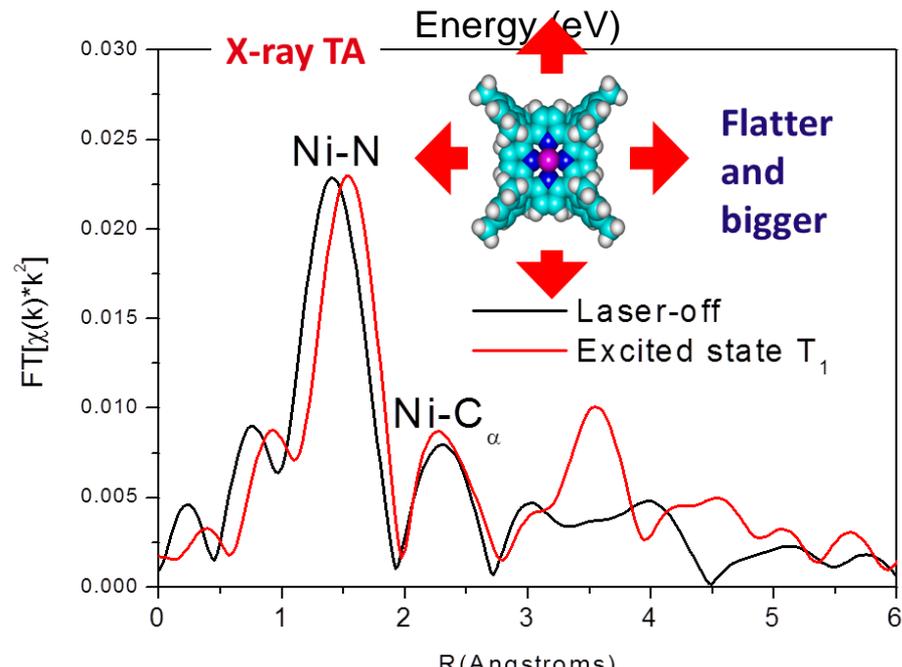
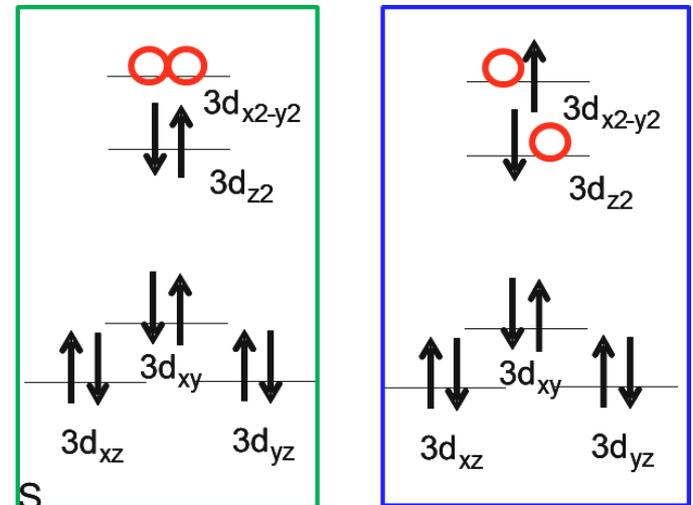
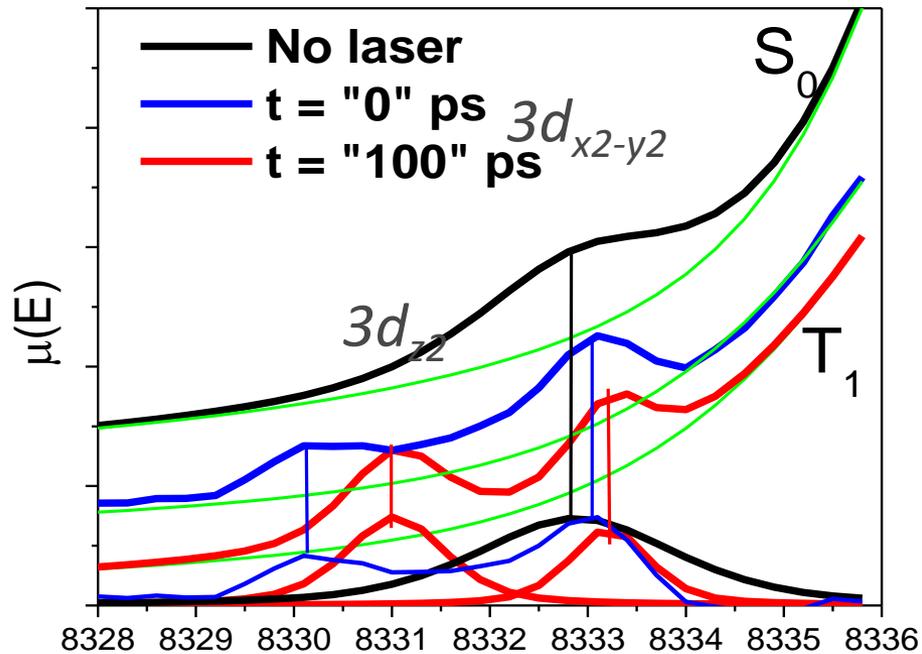


4. XTA spectroscopy, Examples



- $(\pi, \pi^*) \rightarrow (d, d)$ conversion mechanism;
- Multiple electron shift steps but sequence is unclear;
- Influence of excited state structures on MO energy levels;
- Role of the solvent and ligation;
- Transient oxidation state of Ni.

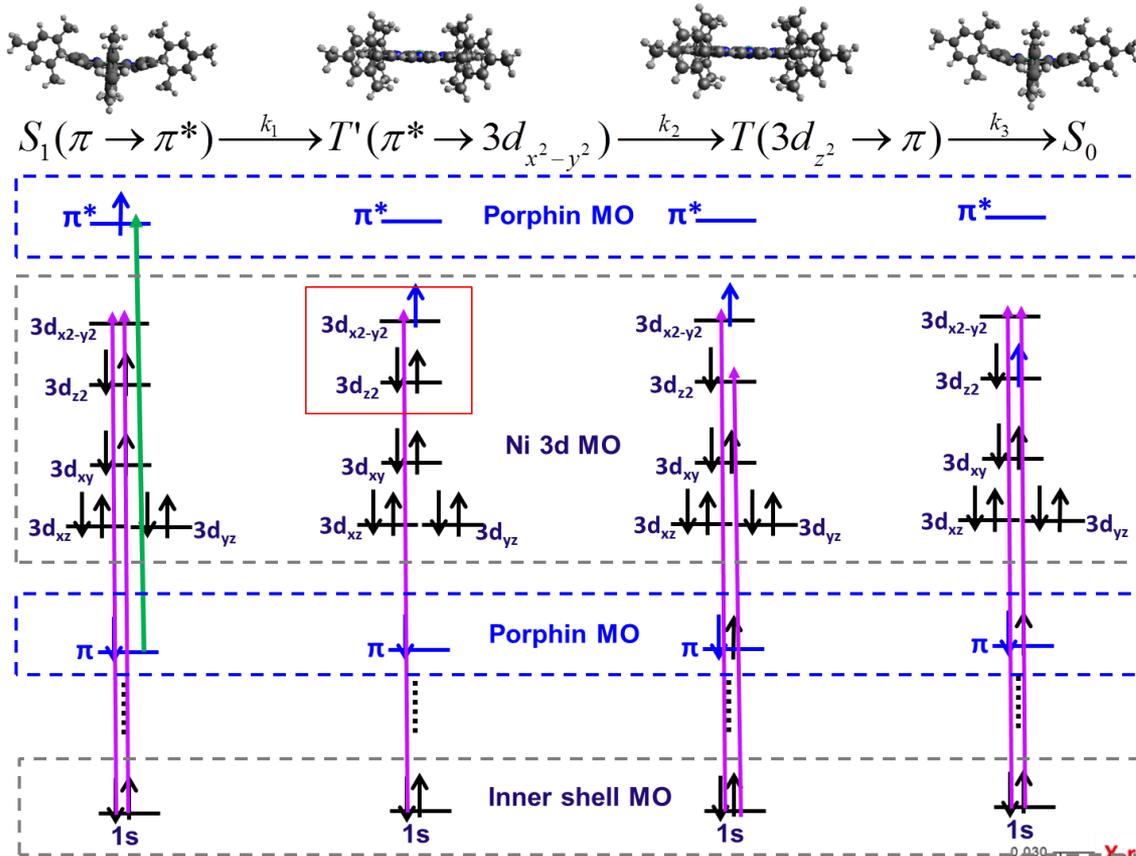
4. XTA spectroscopy, Examples



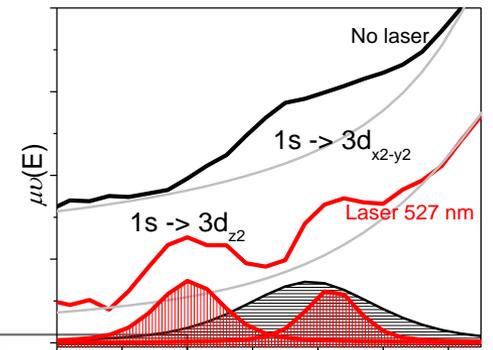
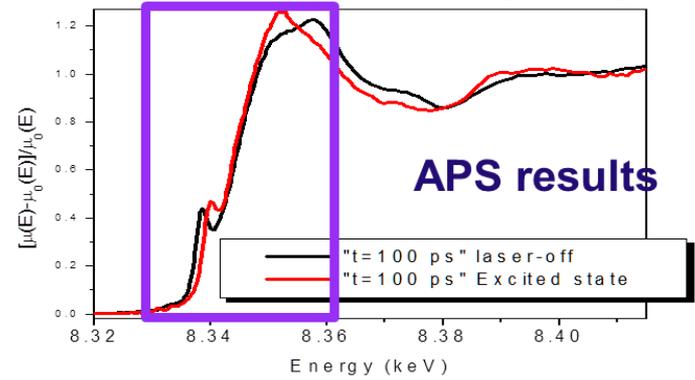
- Ni-N and Ni-C $_{\alpha}$ distances increase in the T_1 state due to the reduction of the bond order when the excitation adds electron to antibonding MO.
- The effective radius of Ni(II) is larger and fits porphyrin cavity better, and hence the macrocycle is flatter than in the ground state.

4. XTA spectroscopy, Examples

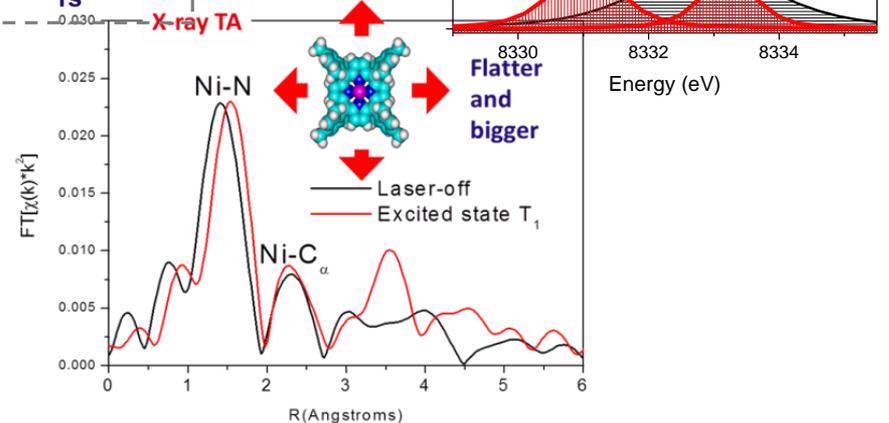
XTA at X-ray free electron laser source



APS: *JACS* (2007),
Chem. Sci. (2010).



LCLS exp. *Shelby et al., J. Am. Chem. Soc.* 138, 8752–8764 (2016)



4. XTA spectroscopy, Examples

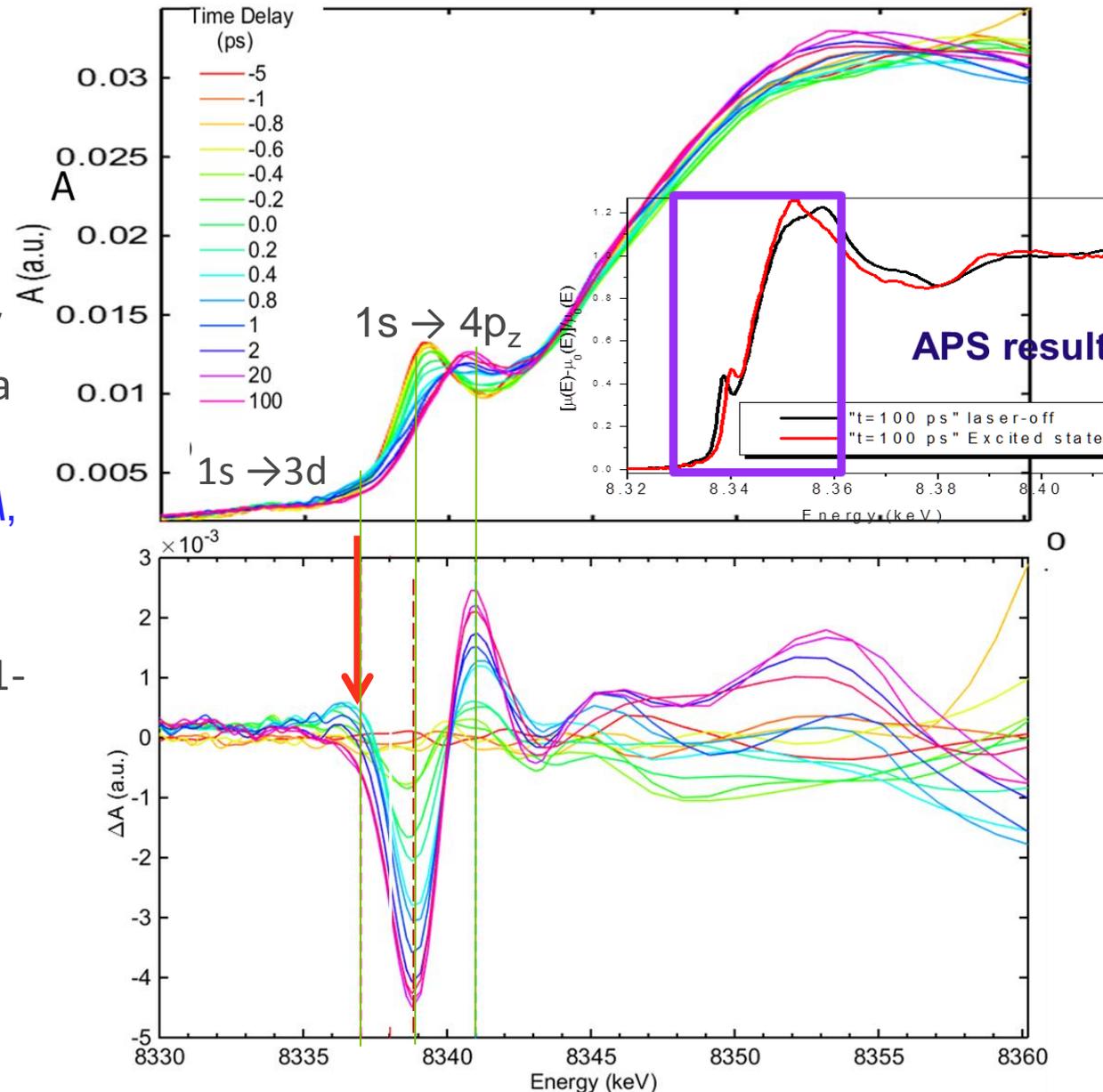
XTA at X-ray free electron laser source

- LCLS X-ray pulse: ~ 50 fs (fwhm), 10^{12} photons/pulse, 10^{3-4} x higher than pump-probe exp. at synchrotrons;
- Self-amplified-spontaneous emission (SASE) with ~ 50 eV energy range, XANES spectra only.

Lemke et al., *J. Phys. Chem. A*, 117, 735 (2013)

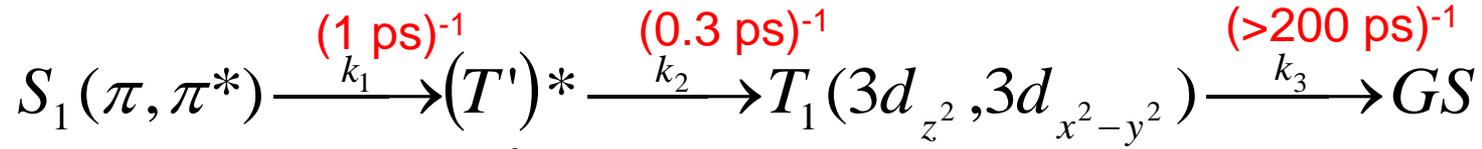
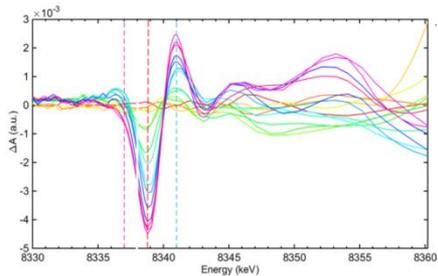
- A new transient feature in 1-2 ps detected: Ni(I)?;
- To be confirmed by calculations about the existence of Ni(I) T' state.

Shelby et al., *J. Am. Chem. Soc.* 138, 8752–8764 (2016)



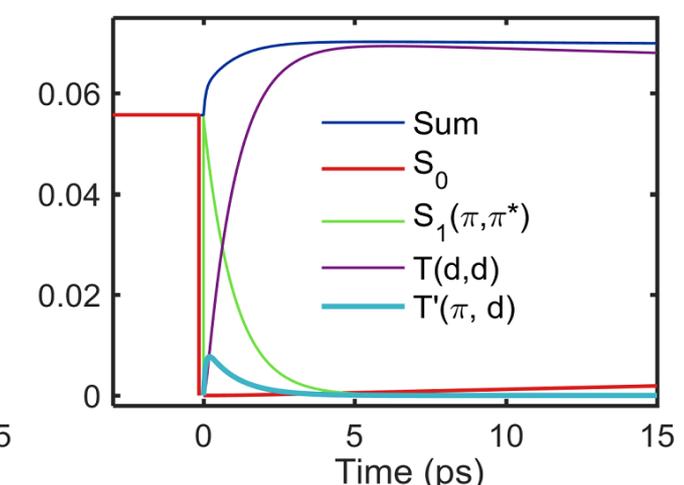
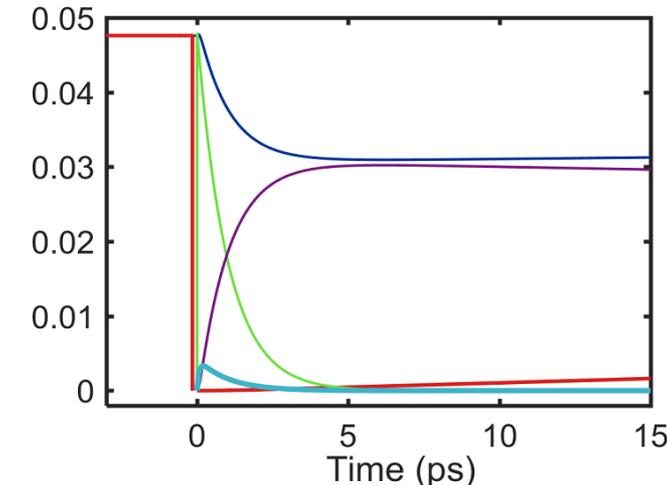
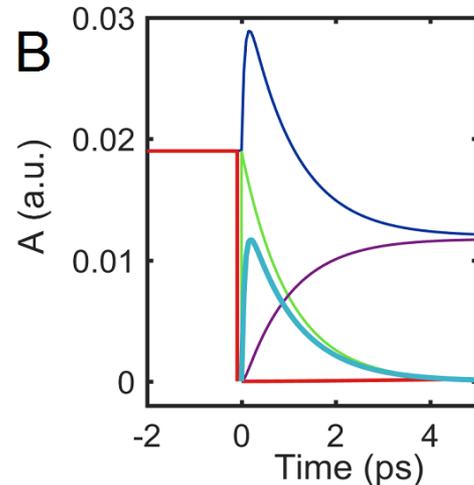
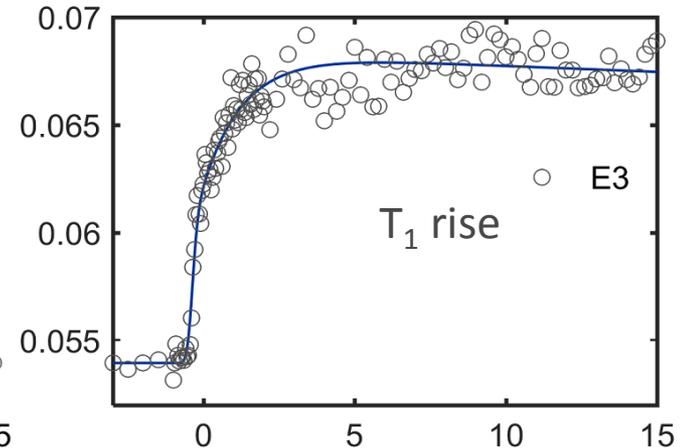
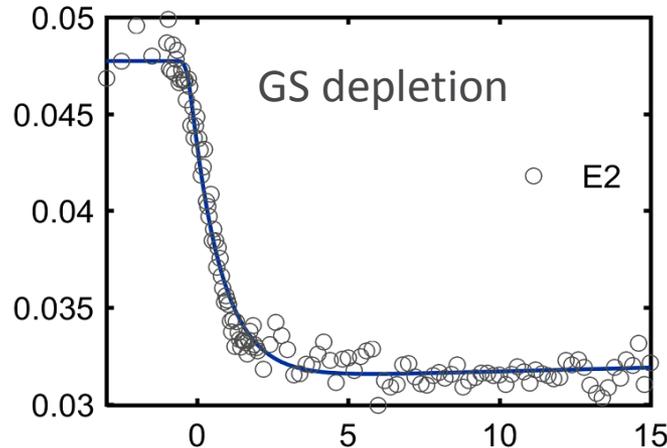
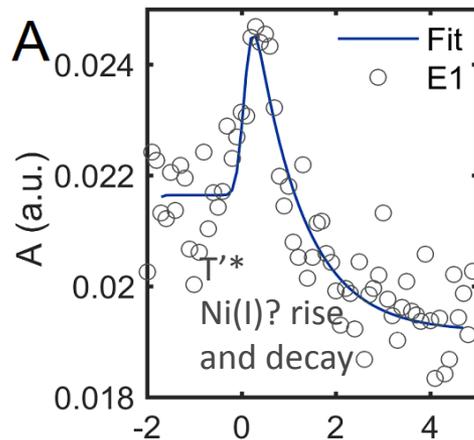
4. XTA spectroscopy, Examples

XTA at X-ray free electron laser source



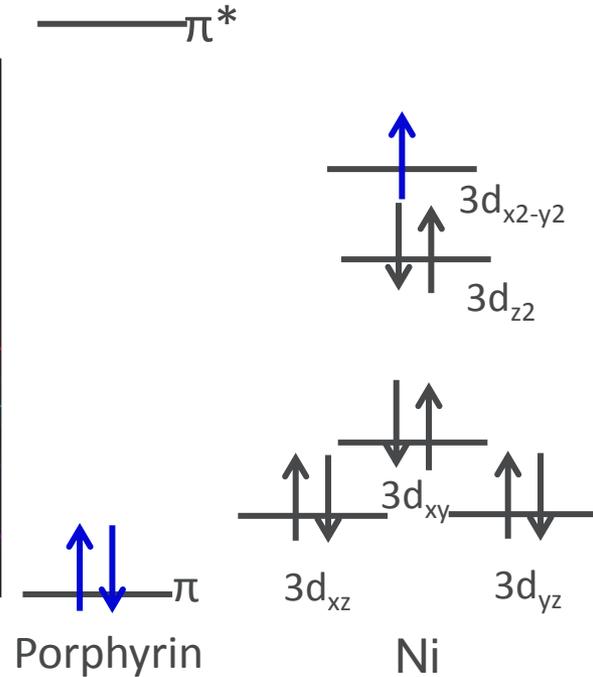
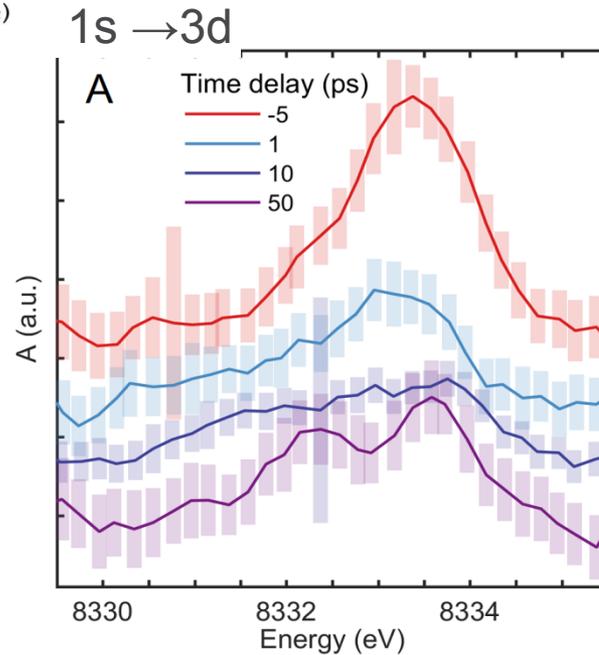
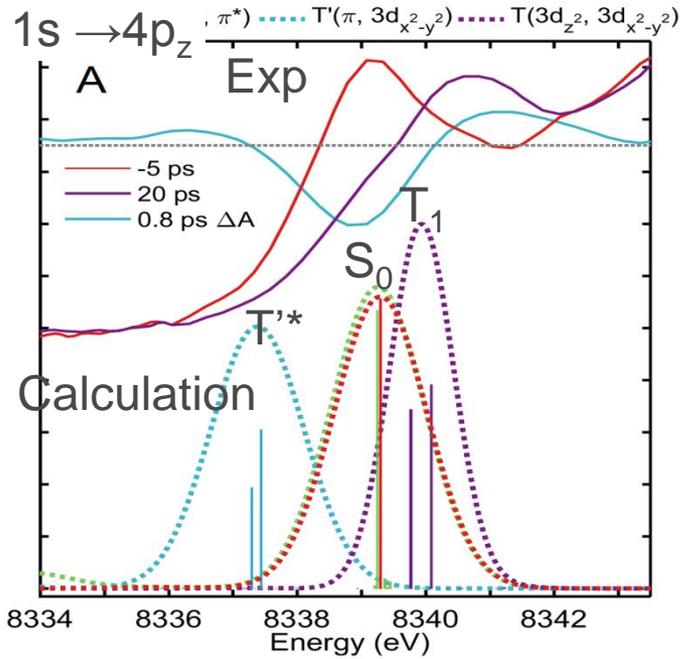
$$A_{total}(E, t) = \sum_{i=0}^3 A_i(E) P_i(t)$$

Inverted kinetics



4. XTA spectroscopy, Examples

XTA at X-ray free electron laser source



Orbital energies and changes in various excited states (Xiaosong Li)

	Inputs for excited-state XAS modeling							
Wavefunc.	S_0	$S_1(\pi, \pi^*)$	T'	$T(d,d)$	S_0	S_0	$T(d,d)$	$T(d,d)$
Geometry	S_0	$S_1(\pi, \pi^*)$	T'	$T(d,d)$	T'	$T(d,d)$	S_0	S_1
	Calculated Ni orbital energies (eV)							
1s α	-8167.47	-0.05	2.02	-1.17	0.37	-0.34	-0.67	-0.61
1s β	-8167.47	-0.05	2.03	-1.17	0.37	-0.34	-0.67	-0.61
4p _z α	1.39	-0.07	0.18	-0.23	0.06	-0.03	-0.15	-0.16
4p _z β	1.39	-0.06	0.05	-0.44	0.06	-0.03	-0.34	-0.34

Energy-specific TDDFT (ES-TDDFT) using the PBE1PBE and Ahlrichs' def2-TZVP basis set with diffuse functions on the nickel atom

5. Perspective of X-ray Transient Absorption Spectroscopy

- A wide range of transient structures during photochemical reactions have been captured by high quality XTA studies which become routine and sample property dependent;
- Capturing transition state in chemical reactions by fs x-ray pulses is still a significant challenge and will bring new insight into matter interactions with which requires X-ray free electron lasers with stable timing and spectral tunability;
- Computational and theoretical works are urgently needed to model photochemical pathways through unrelaxed excited states, excited state coherence, initial reaction conditions and core/valence excitations.
- Simultaneously obtaining the structural dynamics on the initial and stepwise catalytic reactions remain to be challenging.