ULTRAFAST TIME-RESOLVED X-RAY ABSORPTION SPECTROSCOPY

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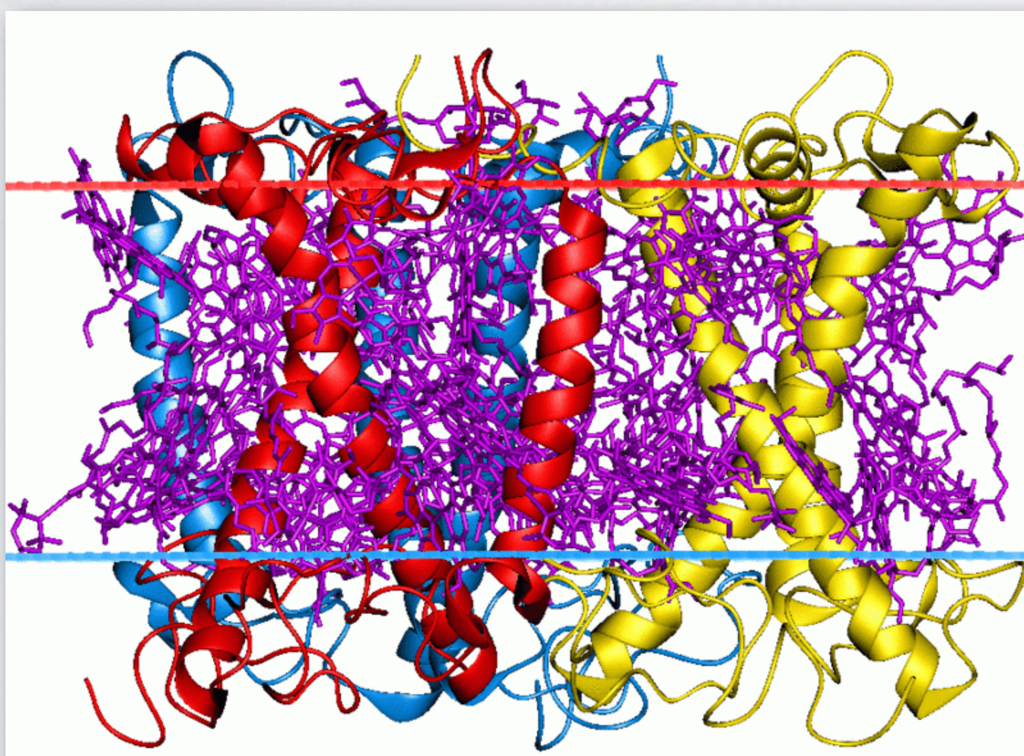
Outline

- ☑ Introduction
  - ☑ Structure vs. function
  - ☑ Ultrafast phenomena
- ☑ How to obtain structural information
  - ☑ XAS and time-resolved XAS
- ☑ Interesting results
  - ☑ Spin-crossover model - $[Fe^{II}(bpy)_3]^{2+}$
  - ☑ Photo-detachment of Myoglobin
- ☑ Summary

Is function structure or dynamics?

Structure

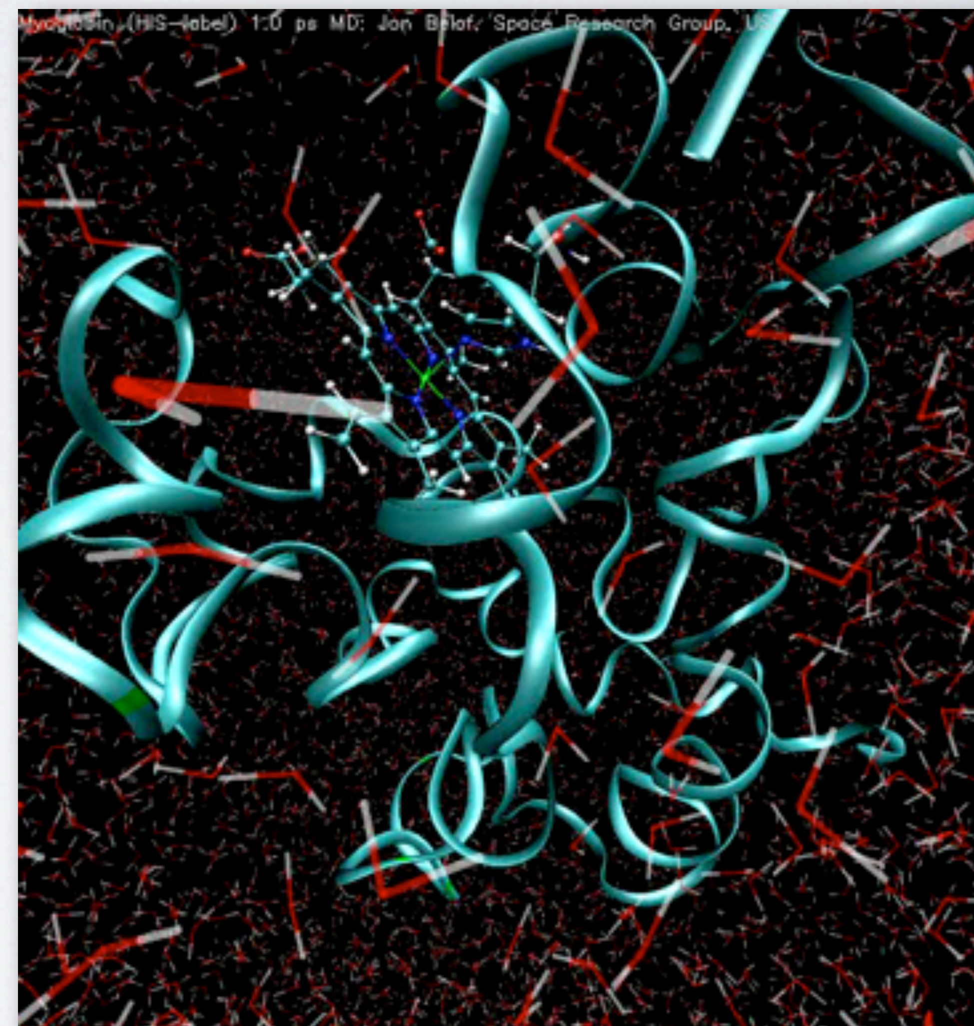
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR



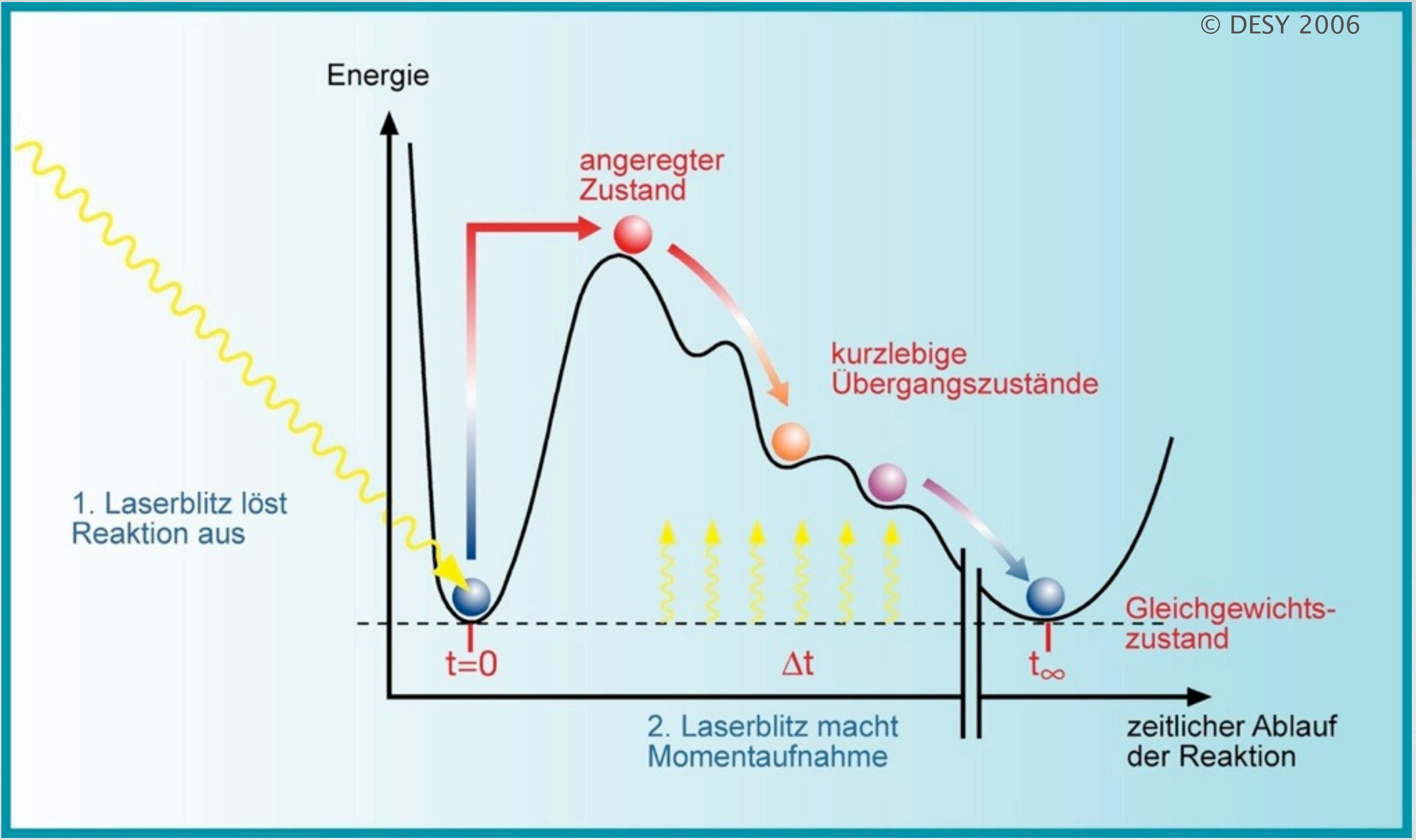
Side view of the light-harvesting complex II in chlorophyll (PDB)

Dynamics

- Laser spectroscopy
- NMR
- time-resolved diffraction
- X-ray absorption spectroscopy



Rotating hydrated myoglobin molecule
http://uweb.cas.usf.edu/chemistry/faculty/space/
B. Space & J. Belof (University of South Florida)



http:/bilder.desy.de

What are the length scales involved ?

http://www.newgrounds.com/portal/view/525347

What are the timescales involved ?

X-rays: laser plasma; X-FELs; laser-slicing; synchrotrons

high-harmonic generation

electronics

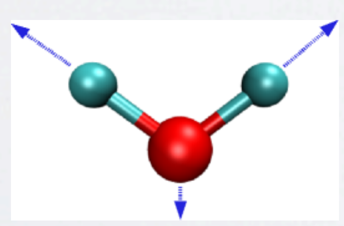
lasers

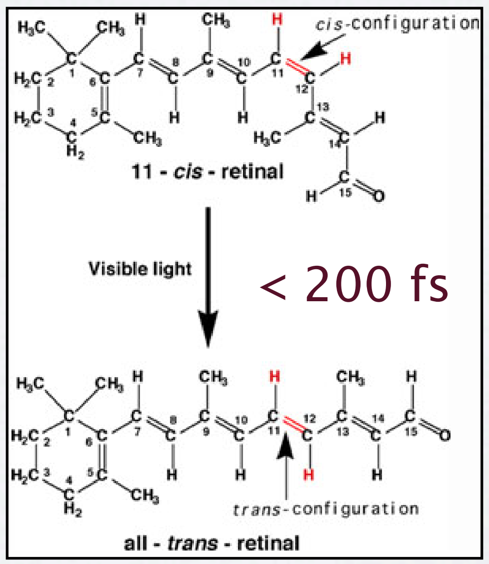
attoseconds 10^{-18} s	femtoseconds 10^{-15} s	picoseconds 10^{-12} s	nanoseconds 10^{-9} s	microseconds 10^{-6} s	milliseconds 10^{-3} s
electron motion core-hole lifetimes	motion of nuclei molecular vibrations optical phonons molecular bond formation	rotation of molecules molecular librations vibrational dephasing	electronic relaxation fluorescence thermal effects	large-scale protein motion phosphorescence	protein folding chemical kinetics

110 as delay between electron emission from conduction band and lower-lying states in Tungsten upon irradiation

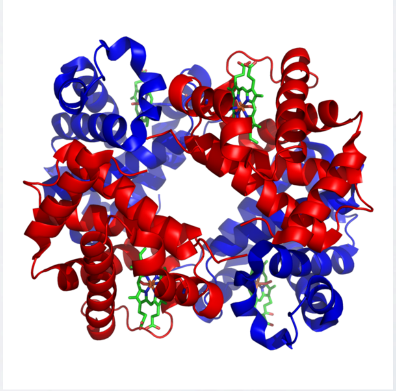
The Fe K-edge core-hole lifetime is 4 fs

period of the symmetric stretch in H_2O is 10 fs



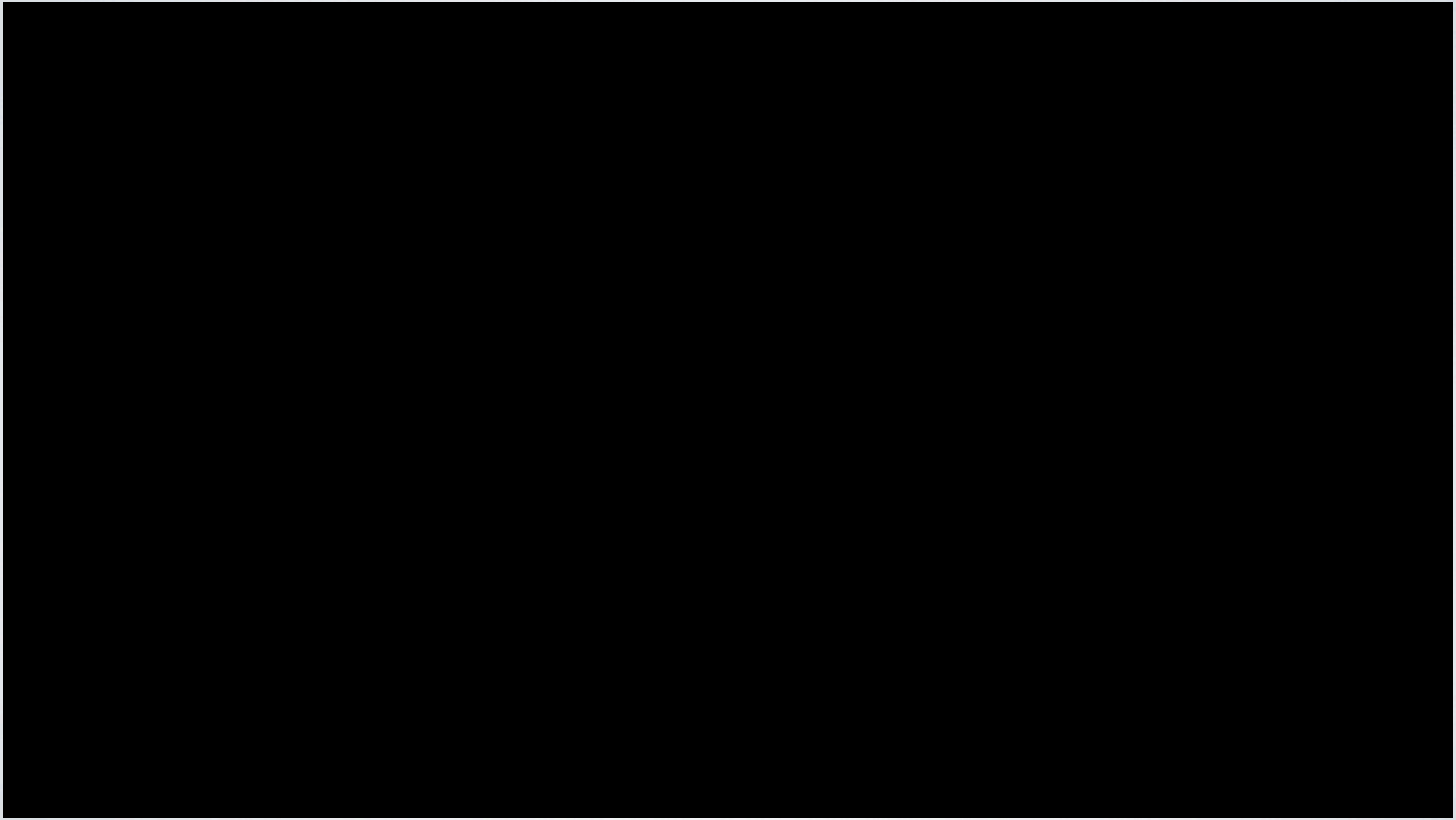


Hemoglobin R->T transition takes microseconds



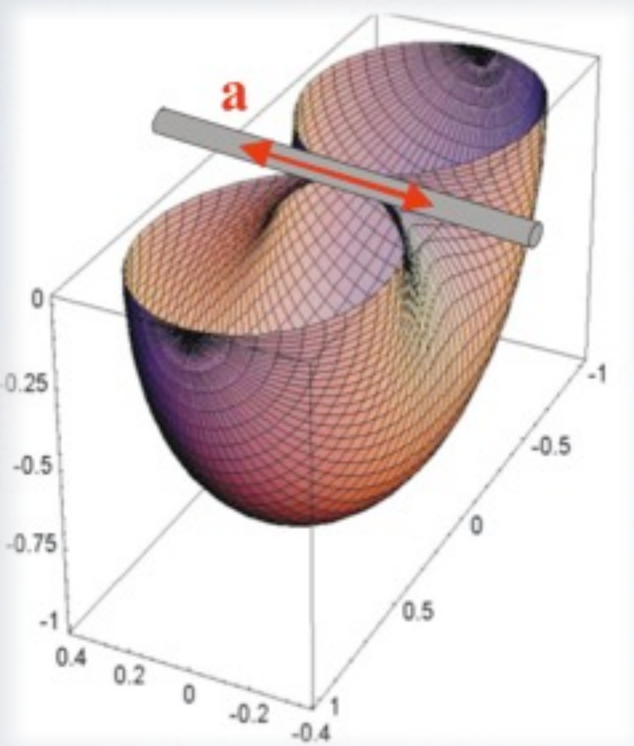
Camera shutter speeds range from ms through to seconds

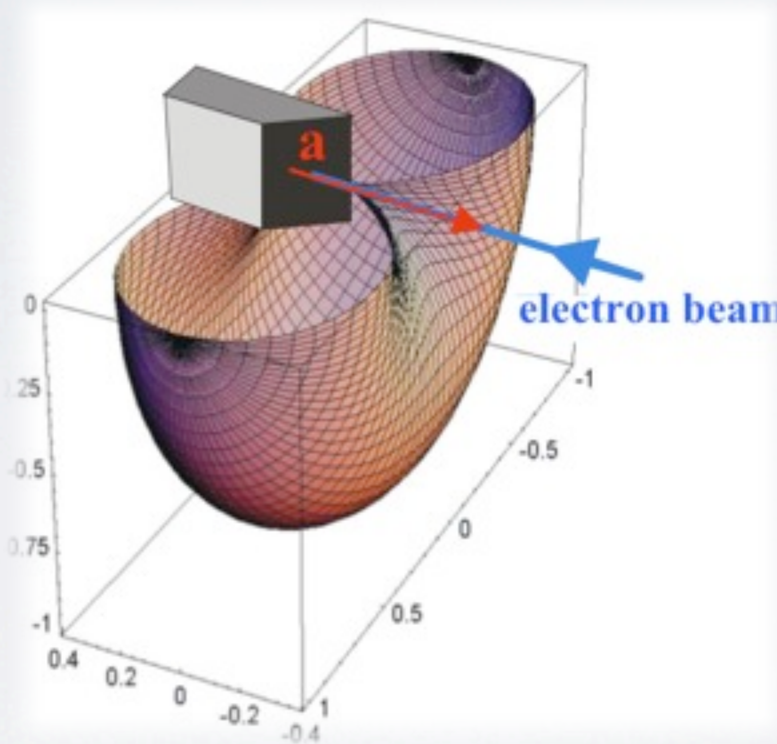
Where can we do that?

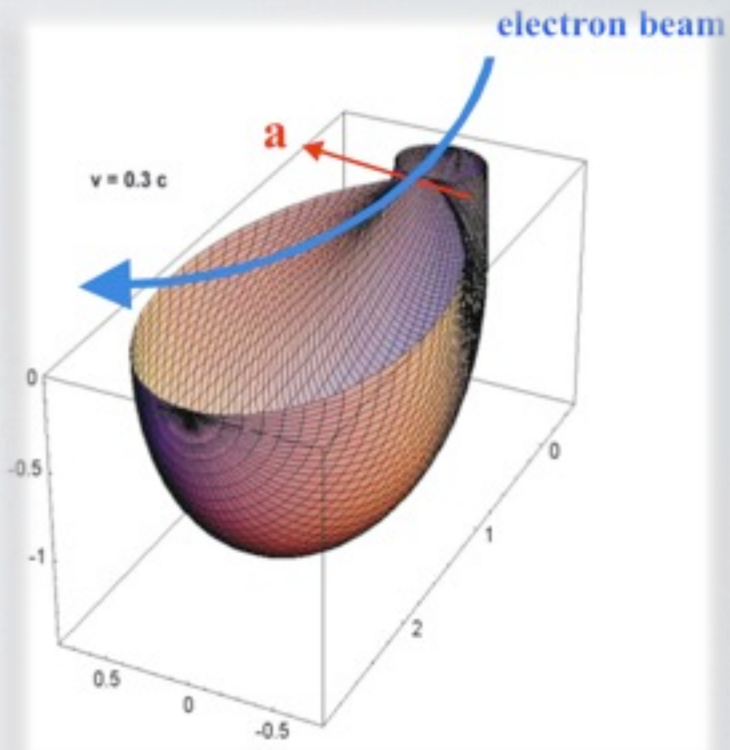


Synchrotron radiation

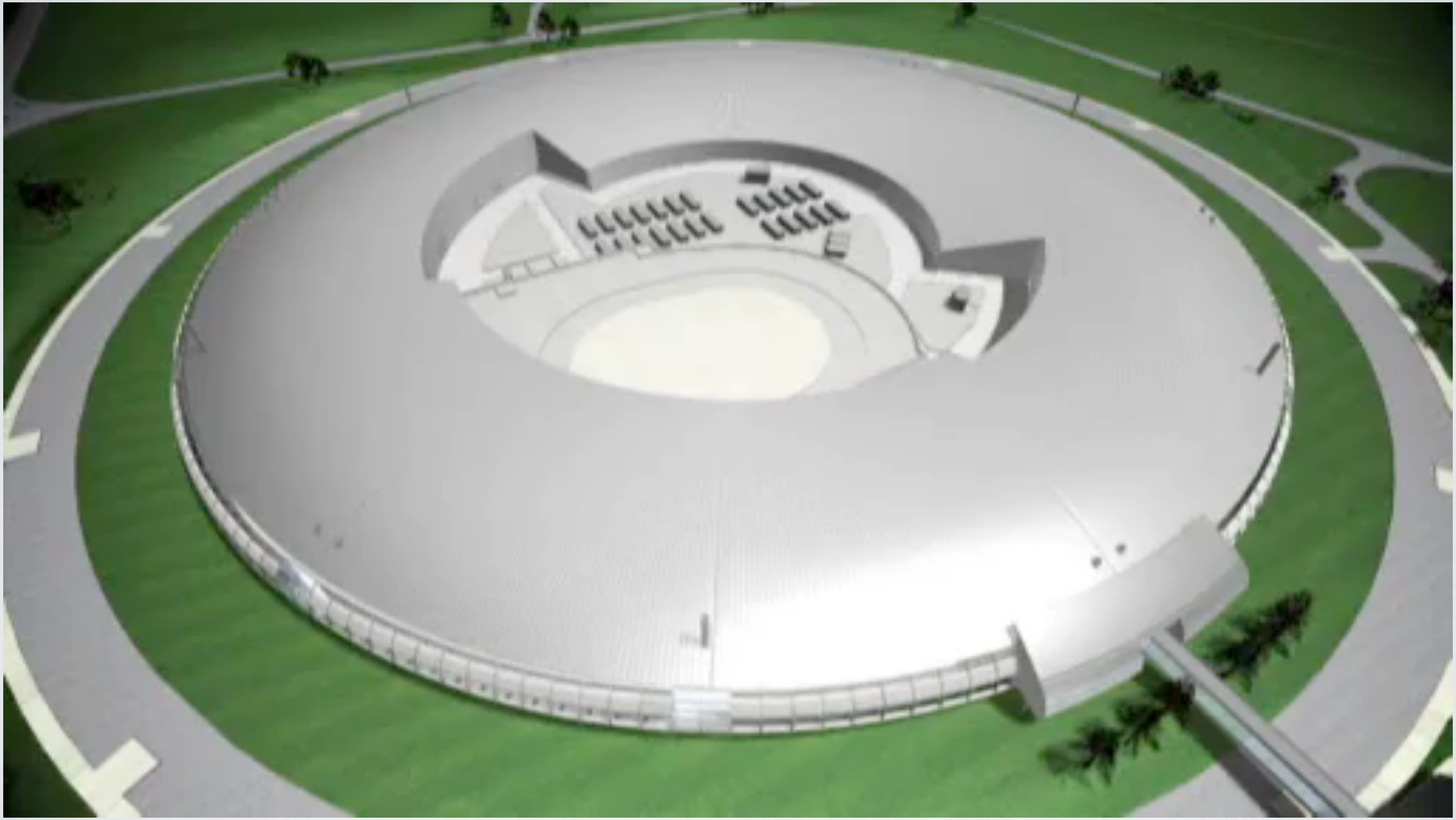
- ☑ Synchrotron radiation ➔ relativistic accelerated charges





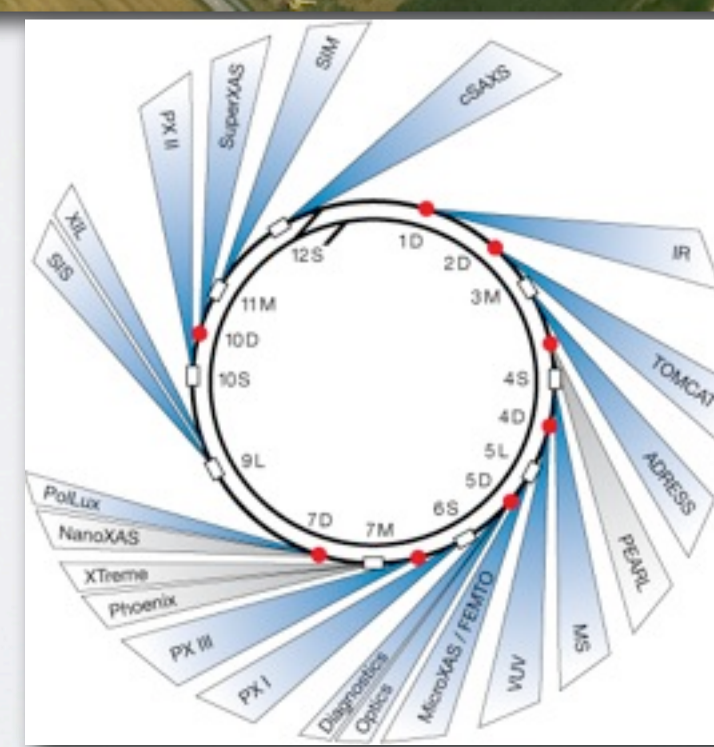


Synchrotron radiation



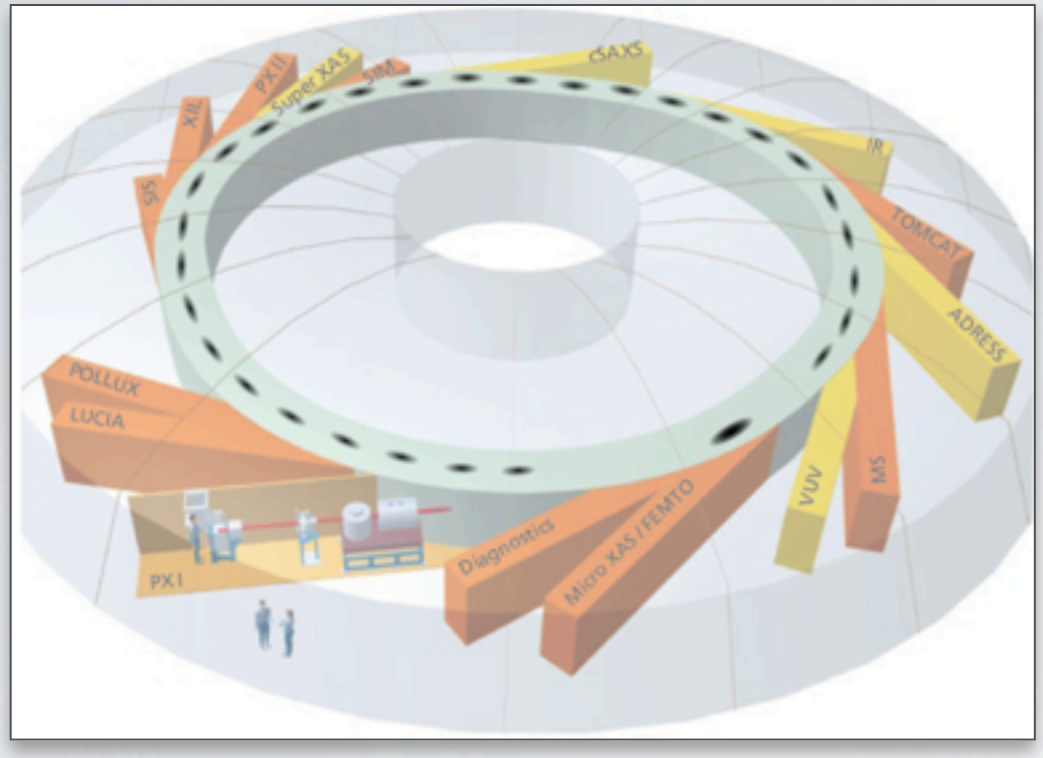
http://www.diamond.ac.uk/Home/About/Films/technology.html

The Swiss Light Source



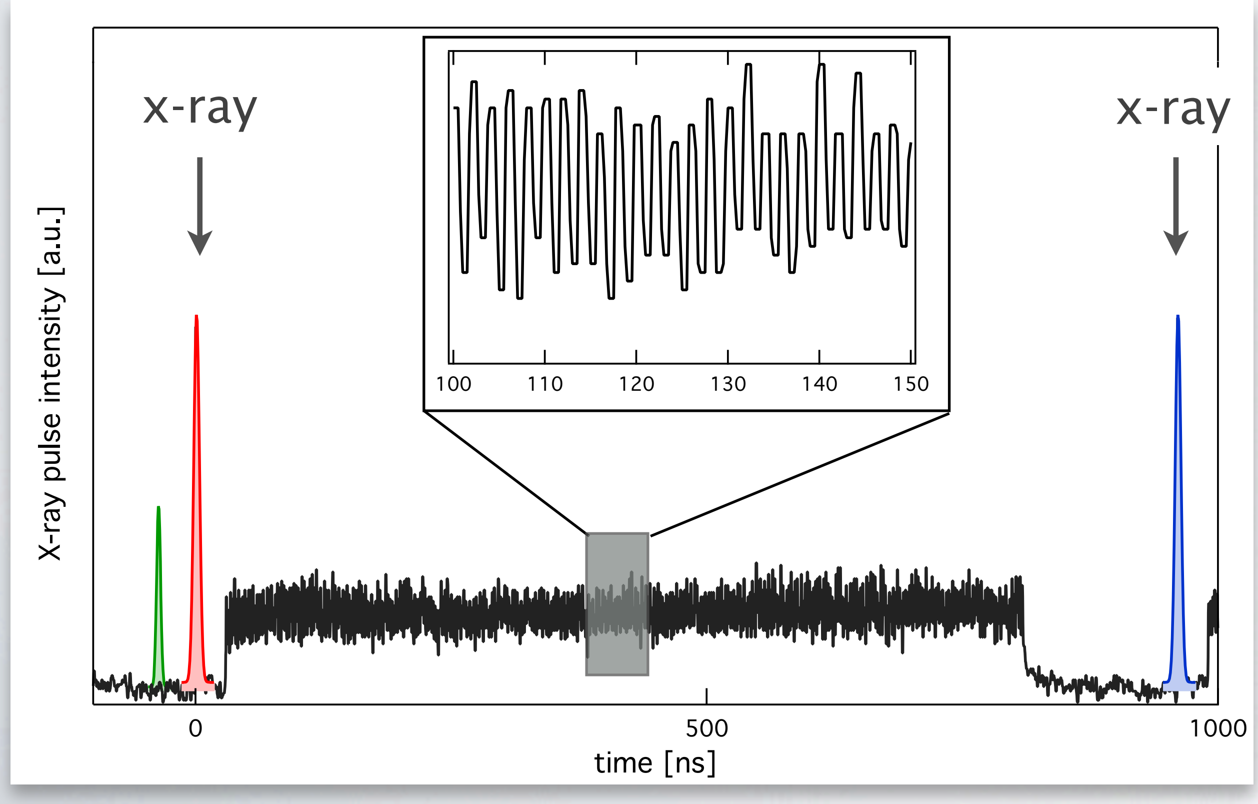
- ☑ 3rd generation synchrotron light source located one hour from Zürich
- ☑ 2.4 GeV energy, operating on top-up mode
- ☑ Up to Sept. 2009 only femtosecond hard x-ray source in the world

Ultrafast X-ray Sources: picosecond



MicroXAS beamline
- tunable hard x-ray in-vacuum undulator (4-20 keV)
- Si (111), Ge(111) & Si(311) monochromator crystals
- micro-focus capability (< 1mm^2)
- 10^{12} photons/second

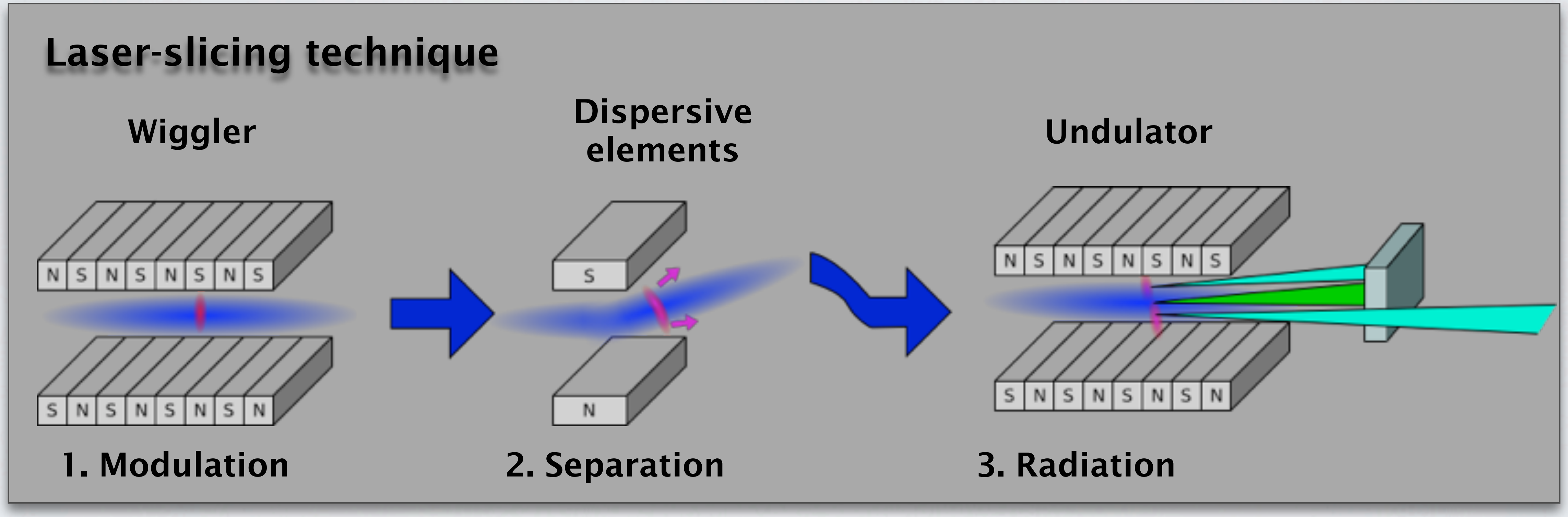
PHOENIX beamline
- tunable ‘tender’ x-ray in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb monochromator crystals
- micro-focus capability (< 1mm^2)
- 10^{11}-10^{12} photons/second



Using fast avalanche photodiodes and either boxcar integrators or track-and-hold circuits we can selectively measure using only the camshaft pulse giving us 70 ps time resolution

Ultrafast X-ray Sources: femtosecond

- An ultrashort (fs) laser pulse co-propagate with an electron bunch causing a modulation on its energy
- Electrons with different energy are further separate in space via dispersive elements on the synchrotron ring

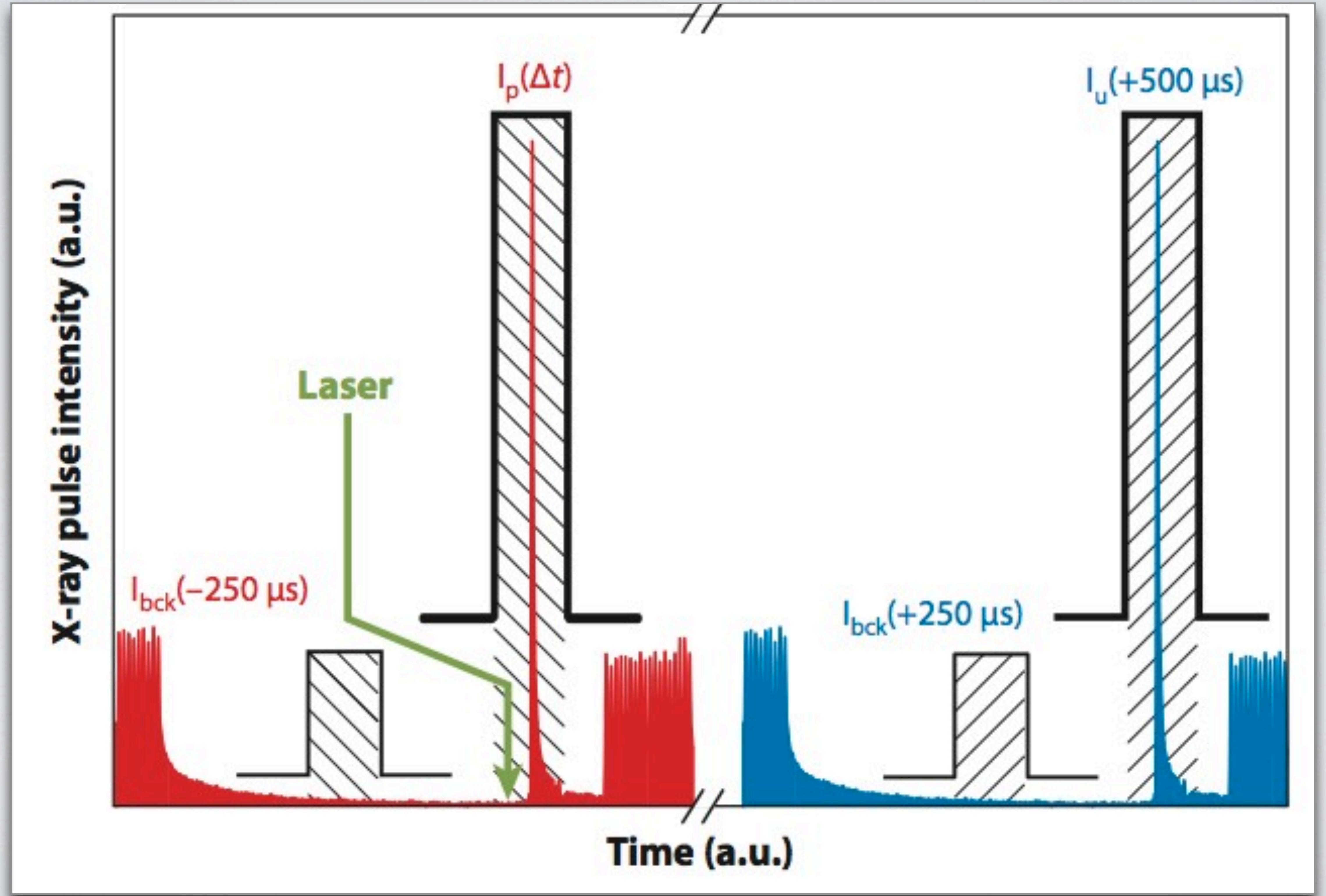


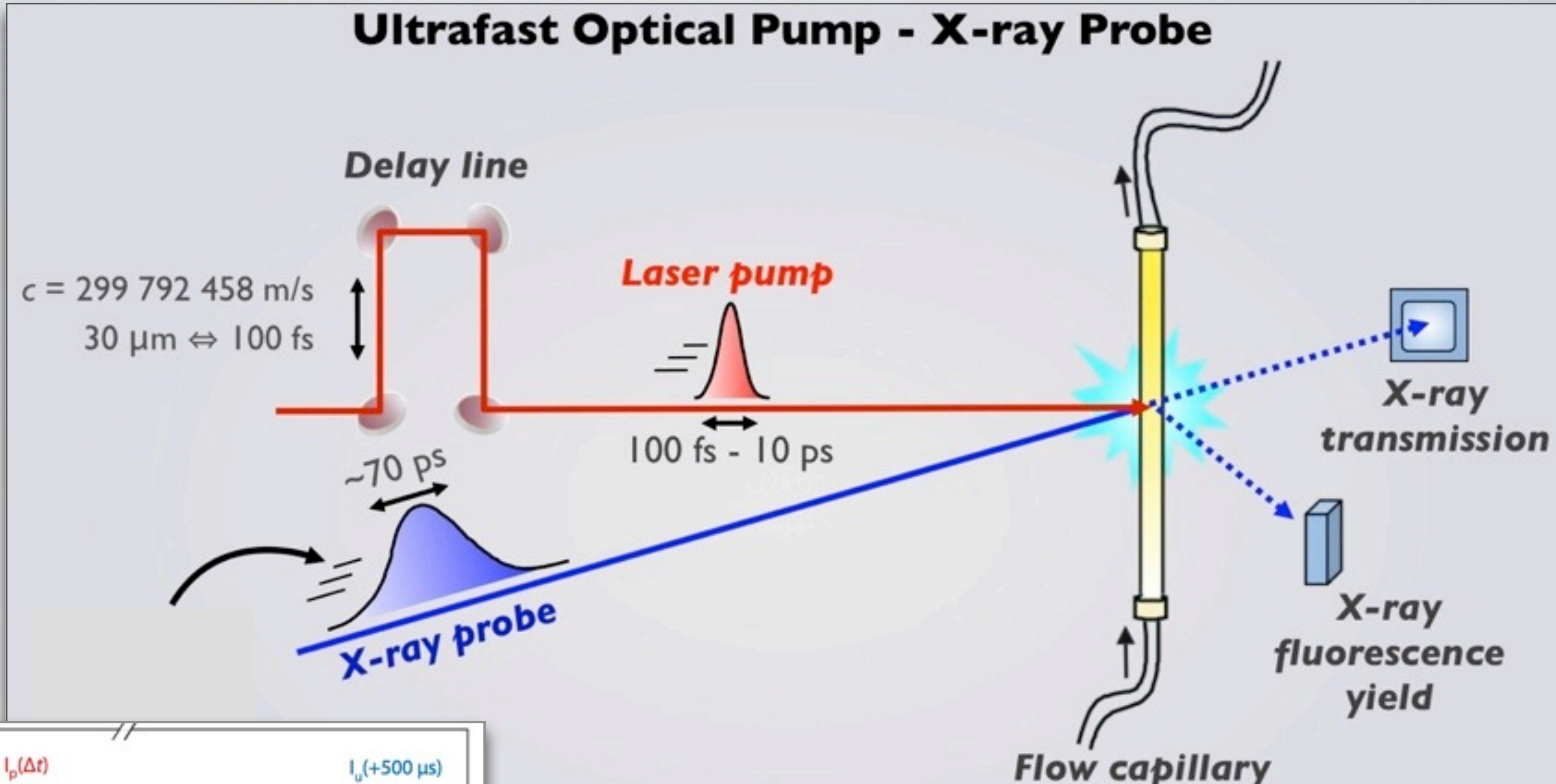
The FEMTO slicing source at the SLS

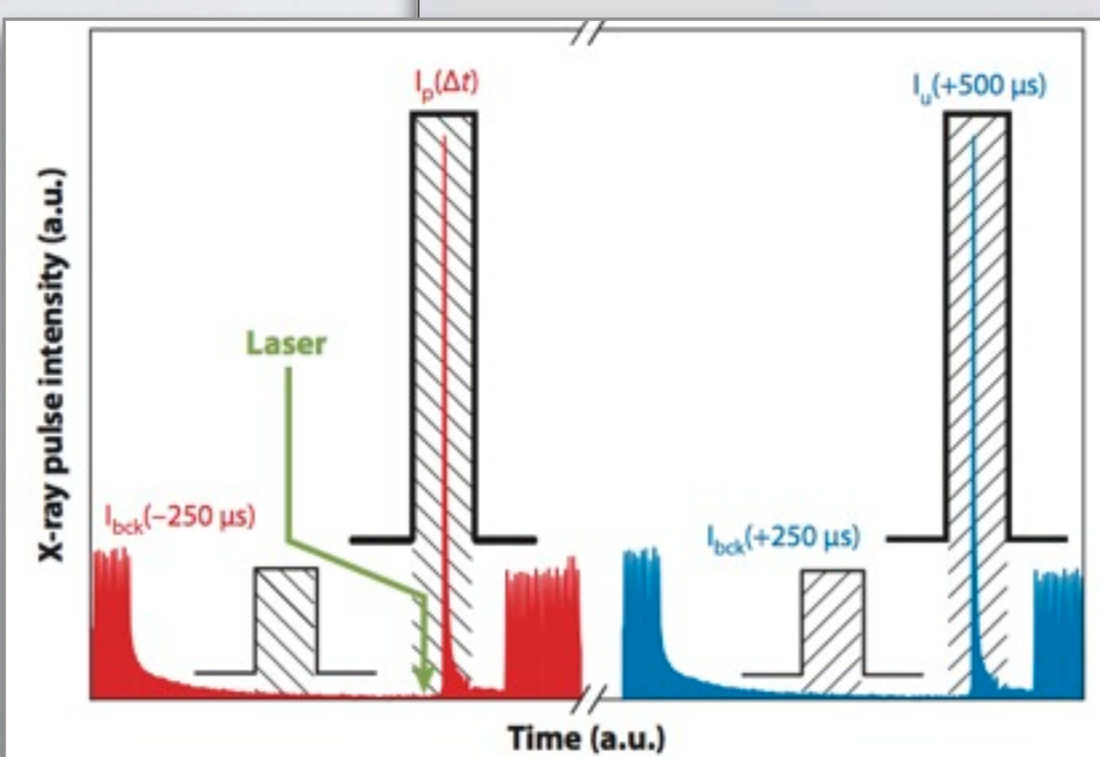
- tunable from 4 to 14 keV
- 140 ± 30 fs x-ray pulse duration
- timing stability of < 30 fs RMS over days
- 10^5 photons/second

R. Schoenlein, et al., *Science*, **287**:2237–2240 (2000)
R. Schoenlein, et al., *Appl. Phys.* **B**, 71:1–10 (2000)
P. Beaud, et al., *Phys. Rev. Lett.* **99**, 174801 (2007)

How the (time-resolved) experiments are done







$$\Delta A(E,t) = f(t) \cdot [A_{Pumped}(E,t) - A_{Unpumped}(E)]$$

signal

fraction of excited species

Bressler, C. and Chergui, M., *Annu. Rev. Phys. Chem.* 61 pp.263 (2010)
Lima, F. A., *in preparation* (2011)

X-ray Absorption Spectroscopy

☑ An x-ray photon is absorbed by an atom when its energy is transferred to a core-level electron which is ejected from the atom.

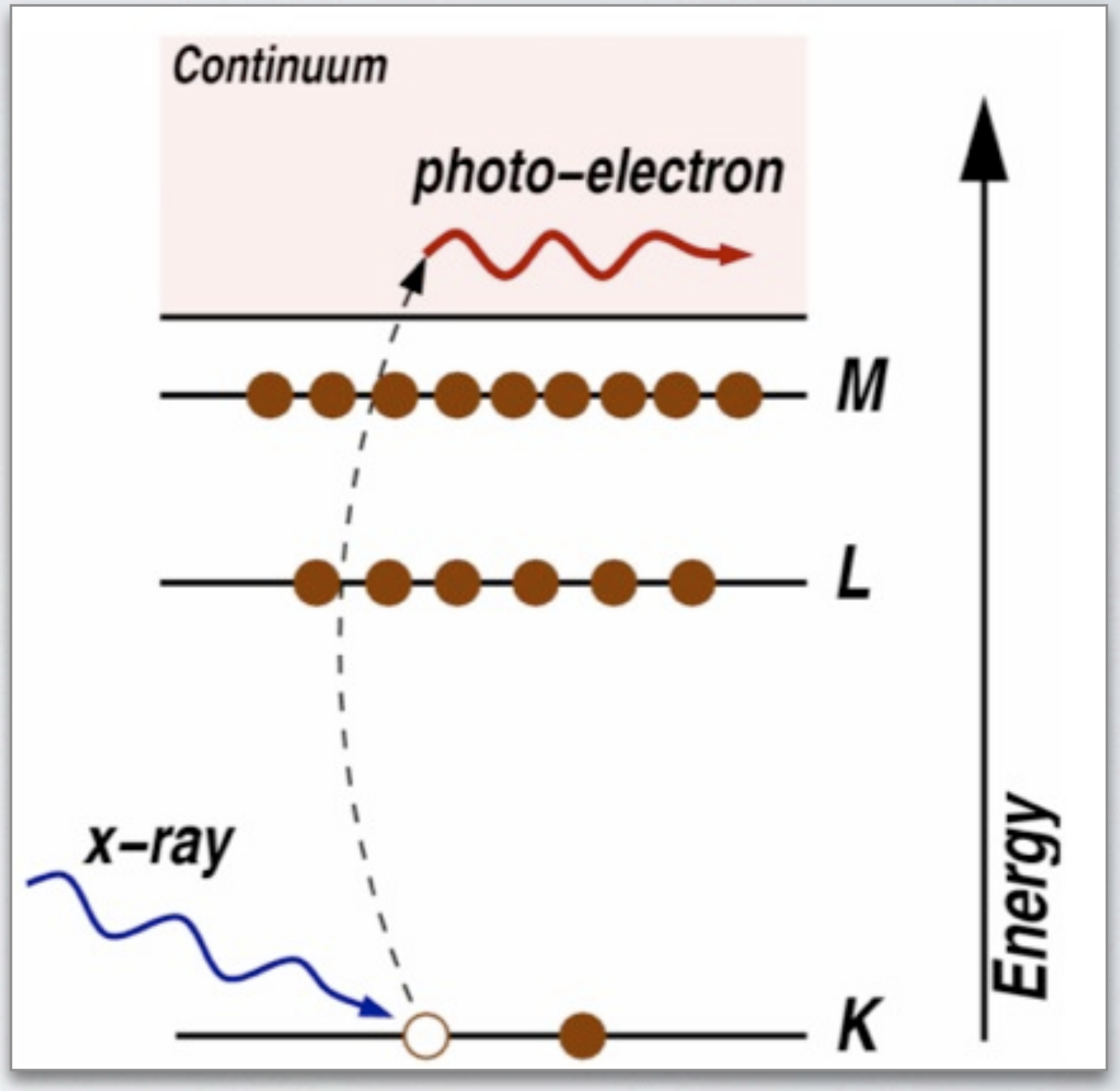
↓

Photo-electron effect

☑ The photo-electrons are emitted as spherical waves which are damped out rapidly due to inelastic effects caused by the extended valence orbitals of the nearby-lying atoms.

↓

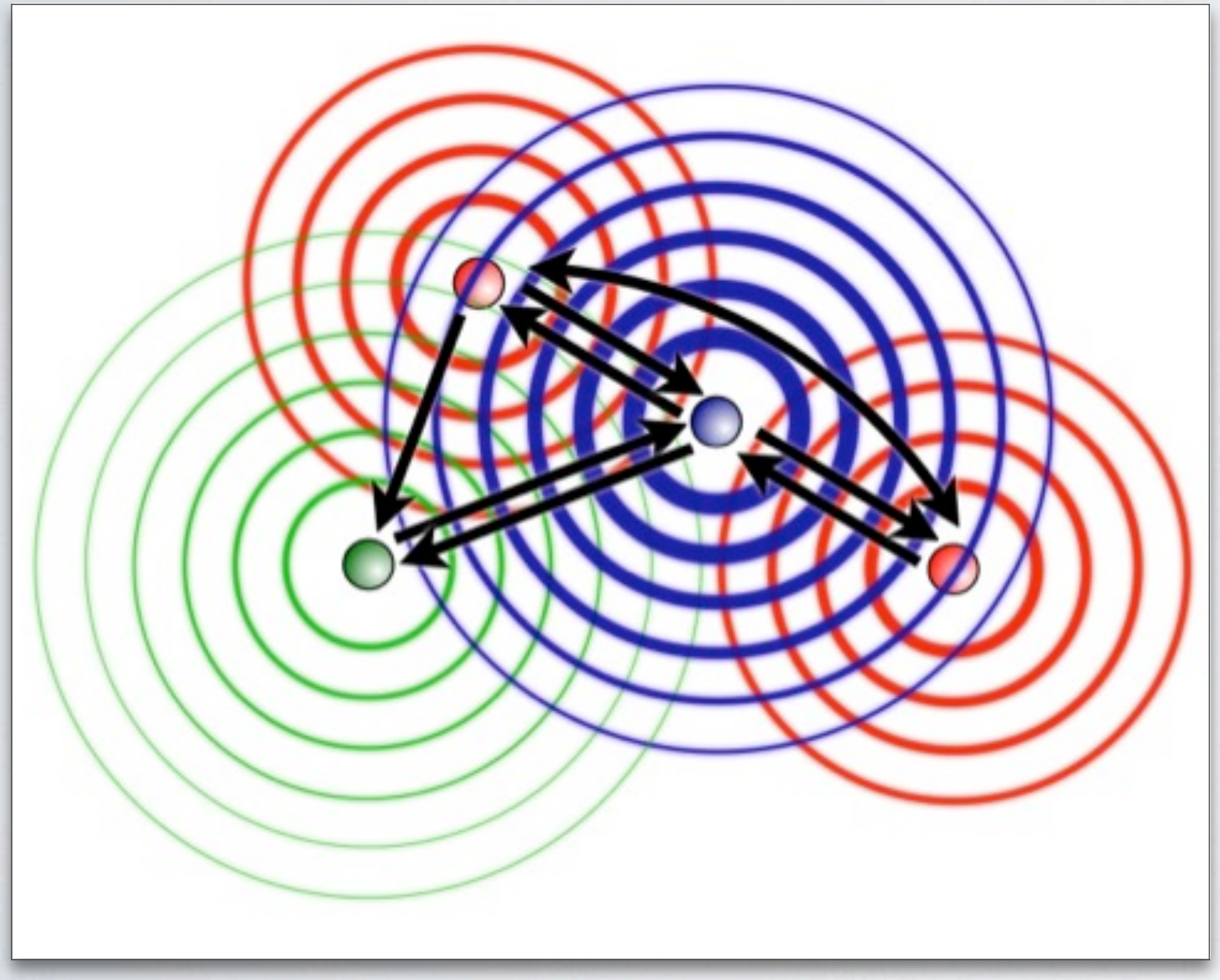
XAS is a local probe!

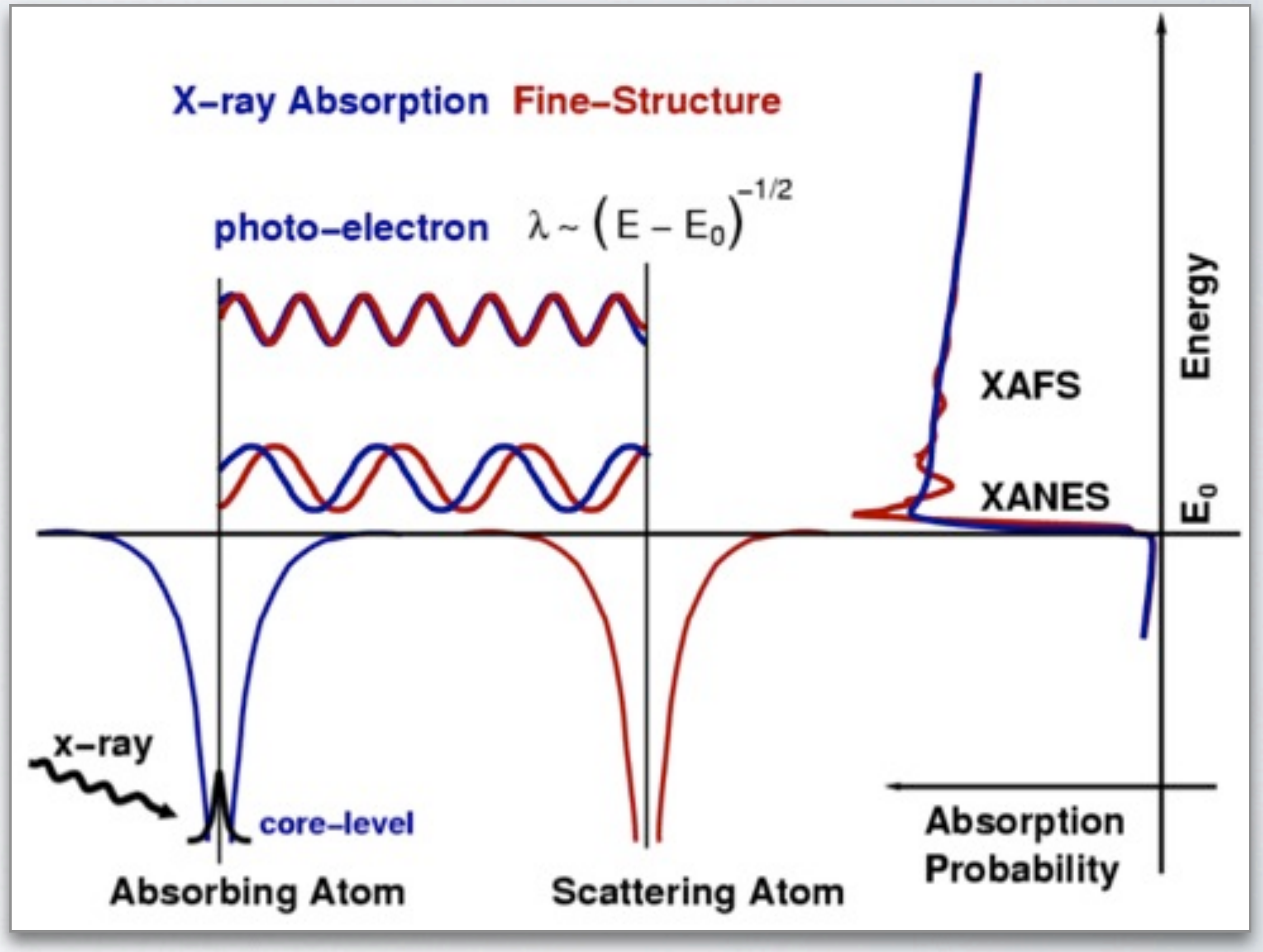


http://xafs.org/

- The (x-ray) absorption process depends whether or not there's an *available state* for the photo-electron.

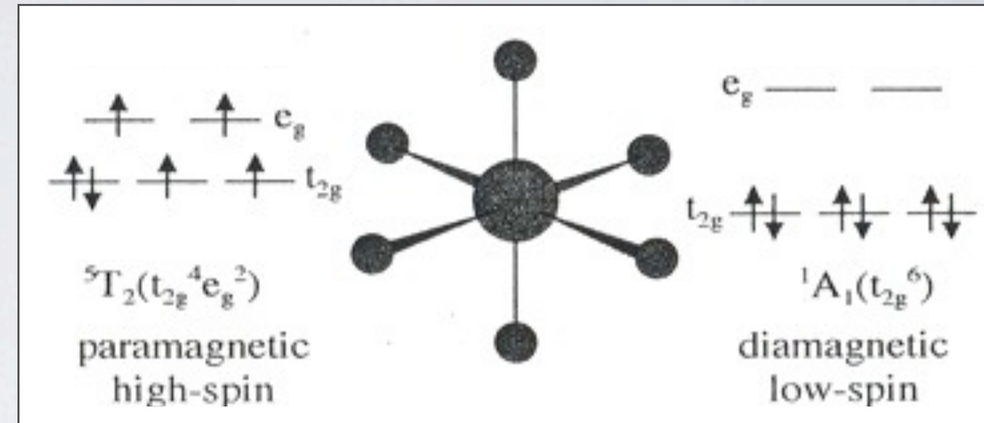
- Neighboring atoms scatter the emitted photo-electron → modification of the absorption coefficient **μ**.

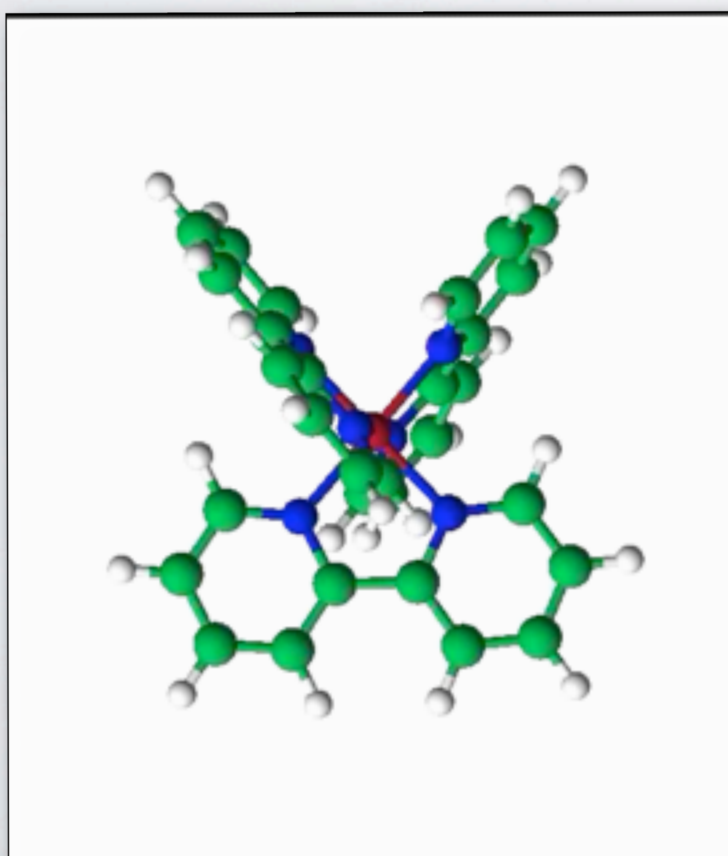


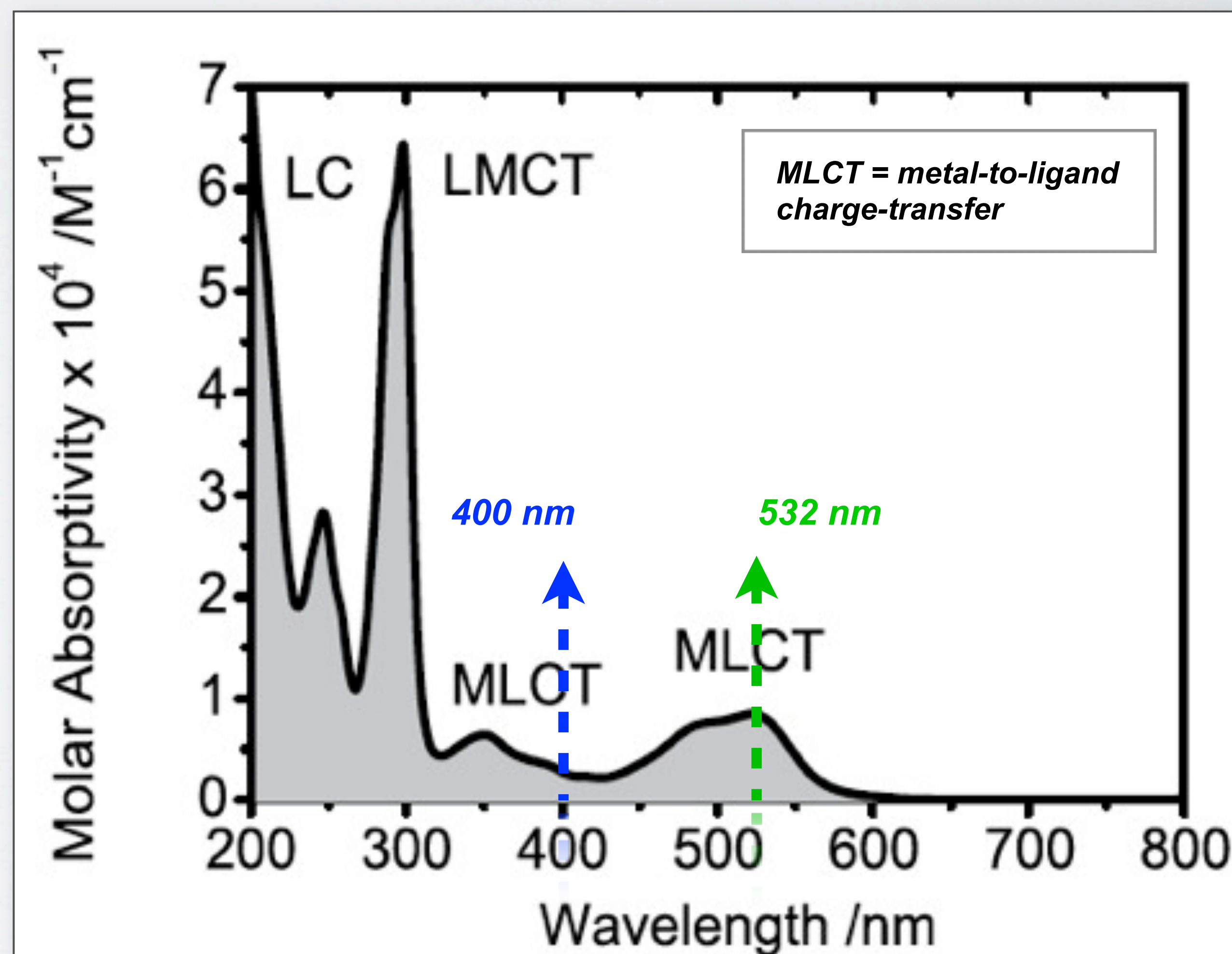


Aqueous $[Fe^{II}(bpy)_3]^{2+}$

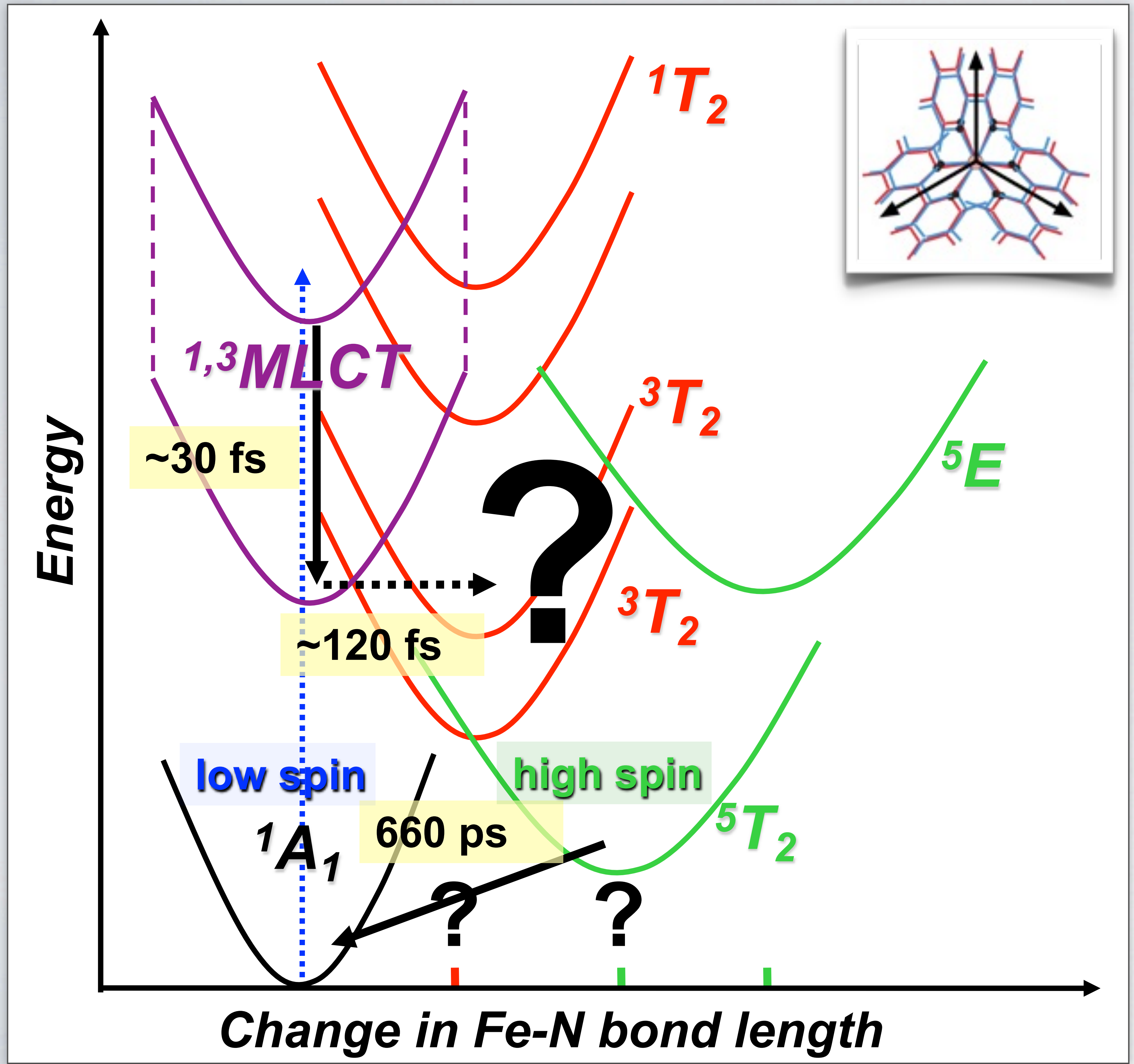
- ☑ Light-induced spin crossover effect
- ☑ Porphyrin-like model system (Myoglobin)
- ☑ Magnetic switching and data storage
- ☑ Model system in the group of *polypyridine photosensitizers*

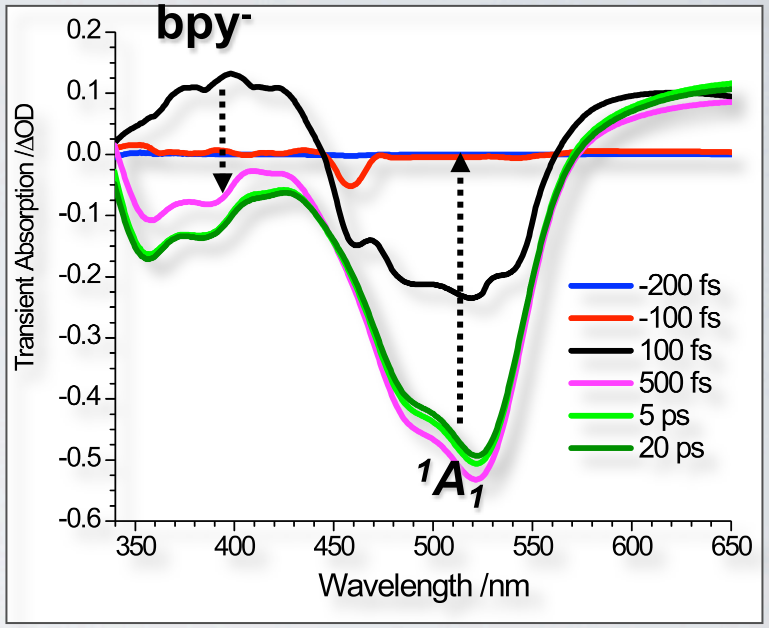


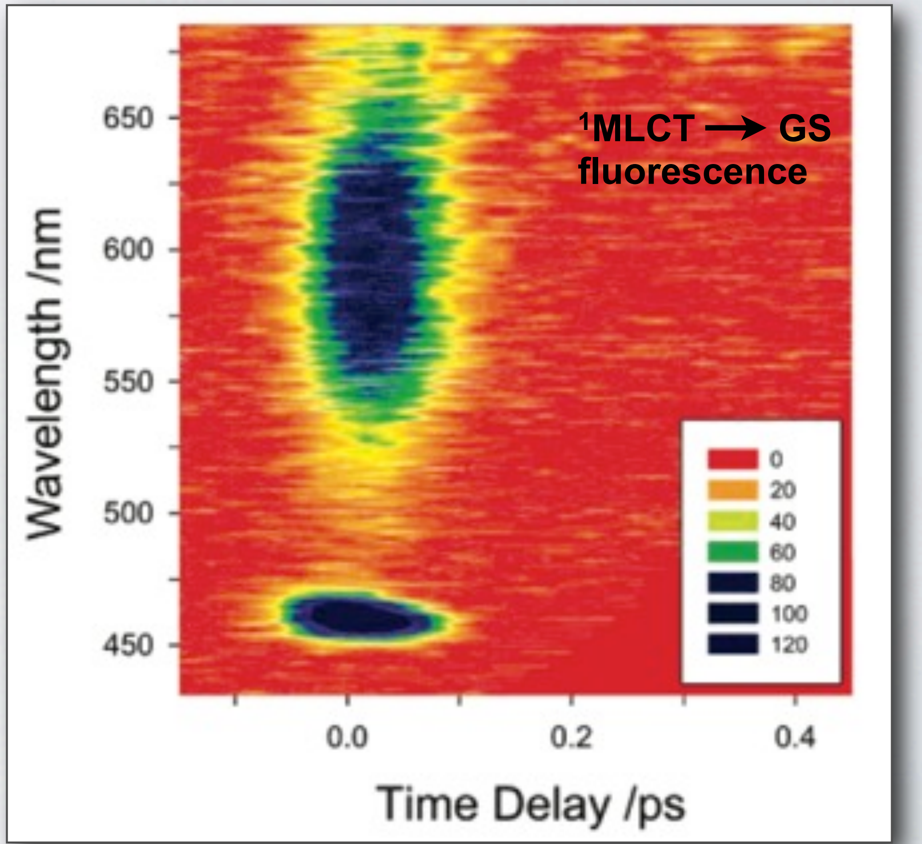




Aqueous $[Fe^{II}(bpy)_3]^{2+}$

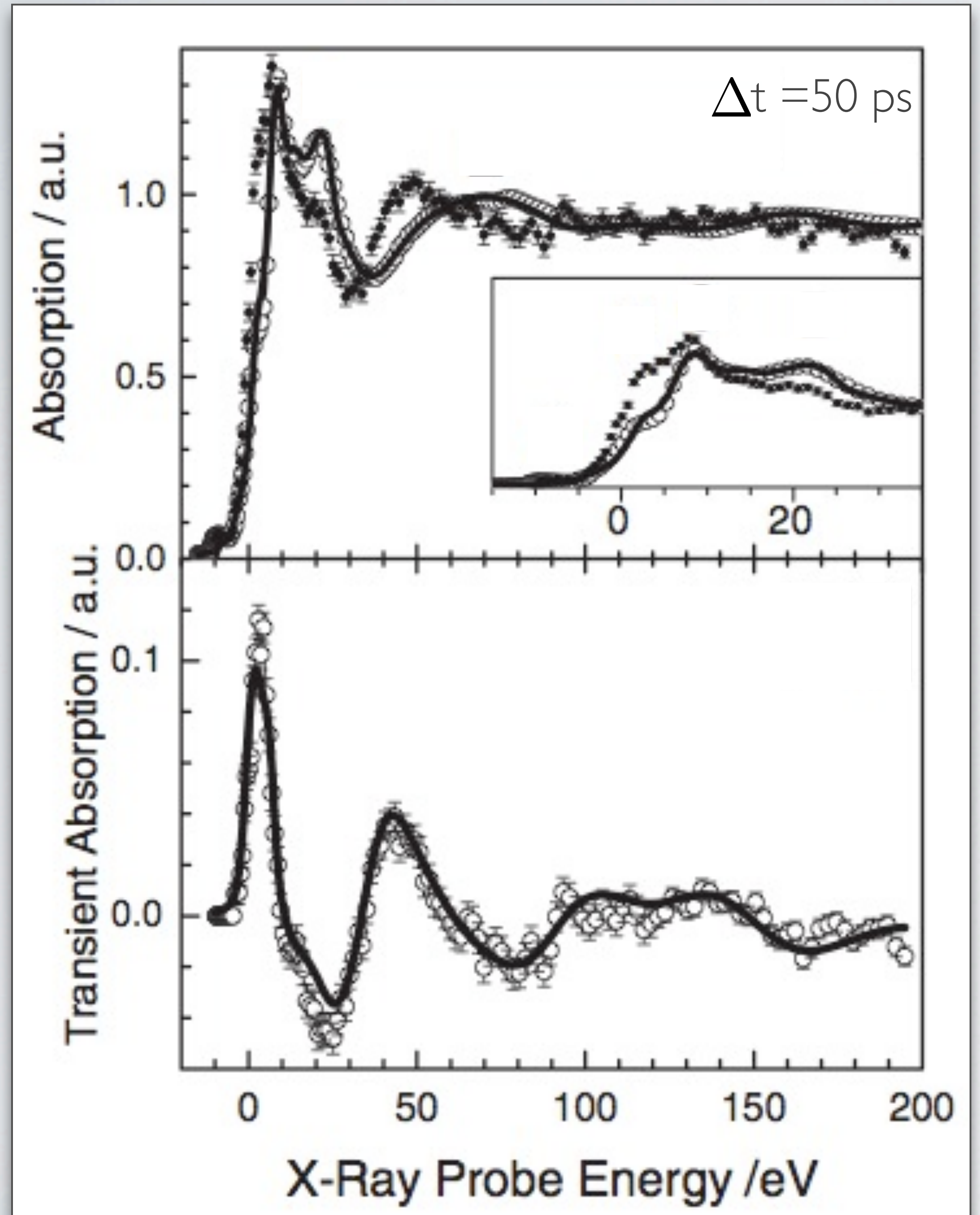


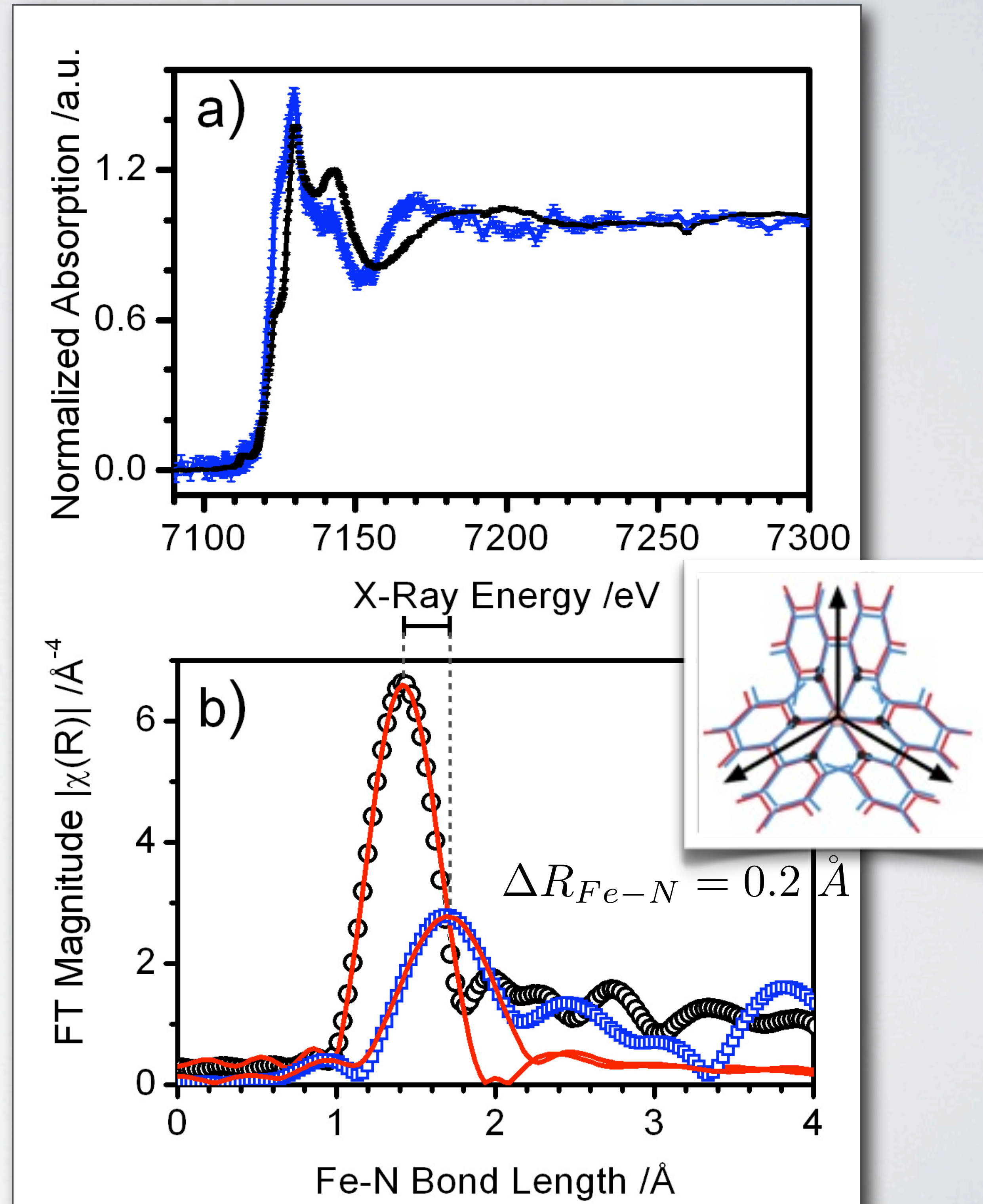




Gawelda, W., et al., *J. Am. Chem. Soc.*, **129**, 8199 (2007).

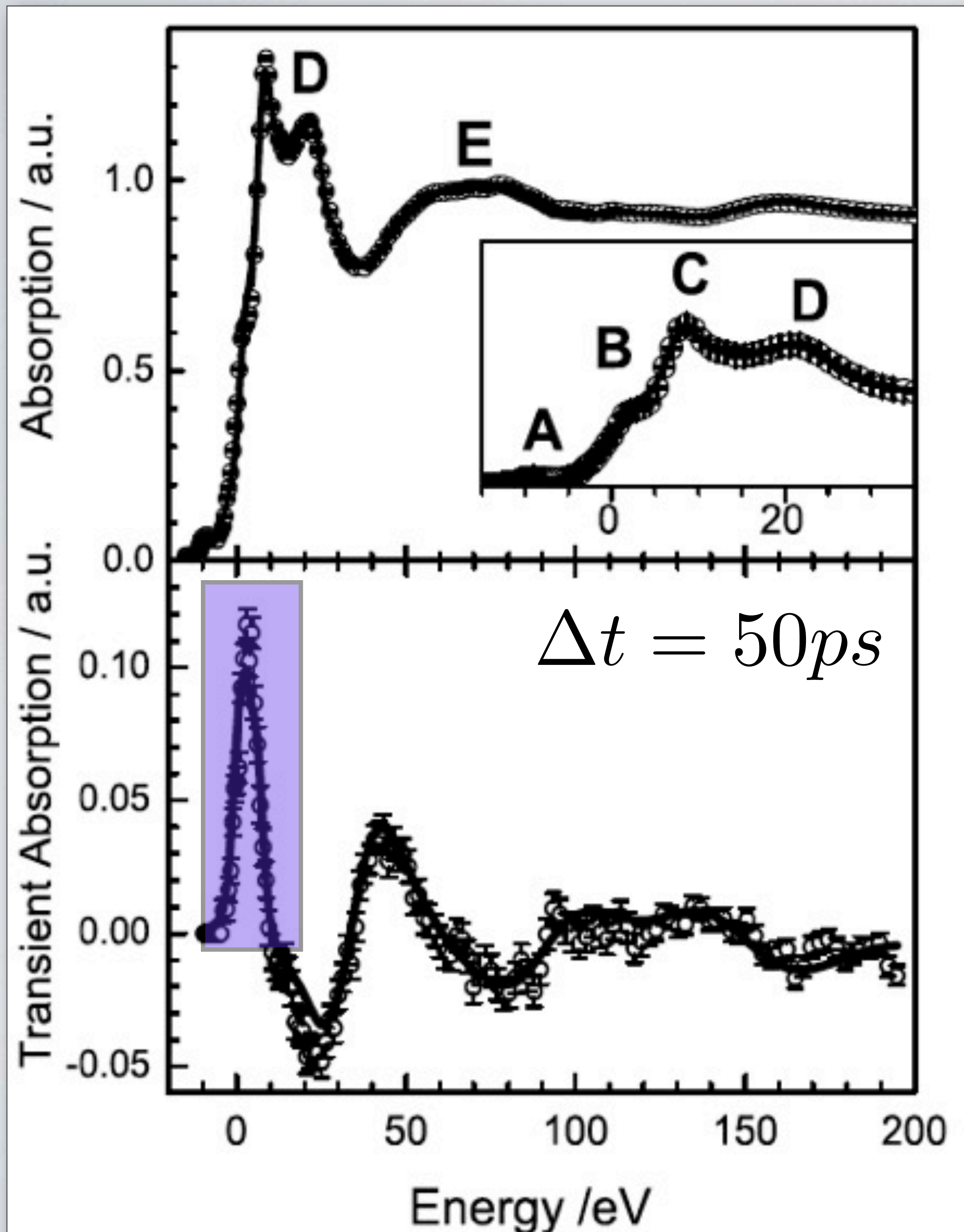
Aqueous $[Fe^{II}(bpy)_3]^{2+}$





Gawelda, W., et al., *Physical Review Letters*, **98**, 057401 (2007).
Gawelda, W. (2006), EPFL PhD thesis

Aqueous $[Fe^{II}(bpy)_3]^{2+}$: Femtosecond XAS planning



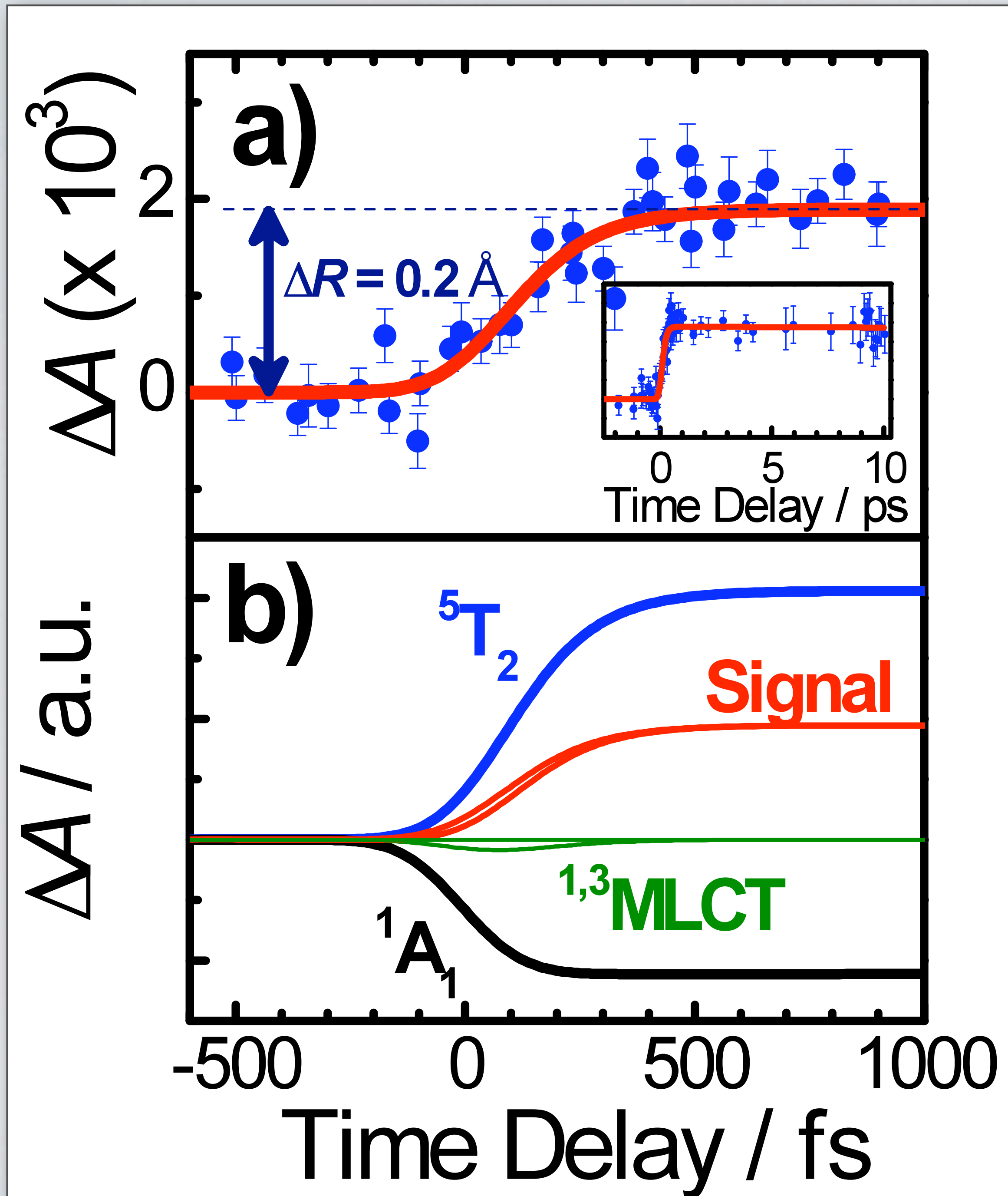
With a loss of 4 orders of magnitude of x-ray photons we need to be smart about the experiment

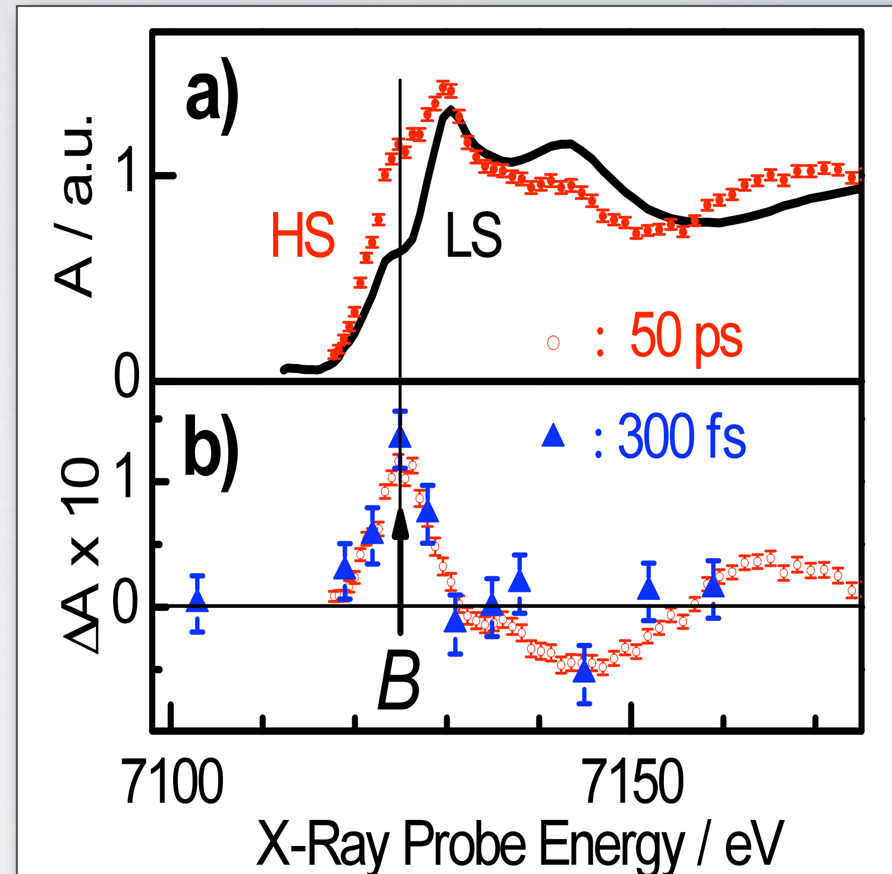
The largest transient signal is at the B feature which is a multiple-scattering feature sensitive to the Fe-N bond distance

The picosecond experiments suggest it will take 30-60 minutes per data point to acquire S/N of ~ 4:1

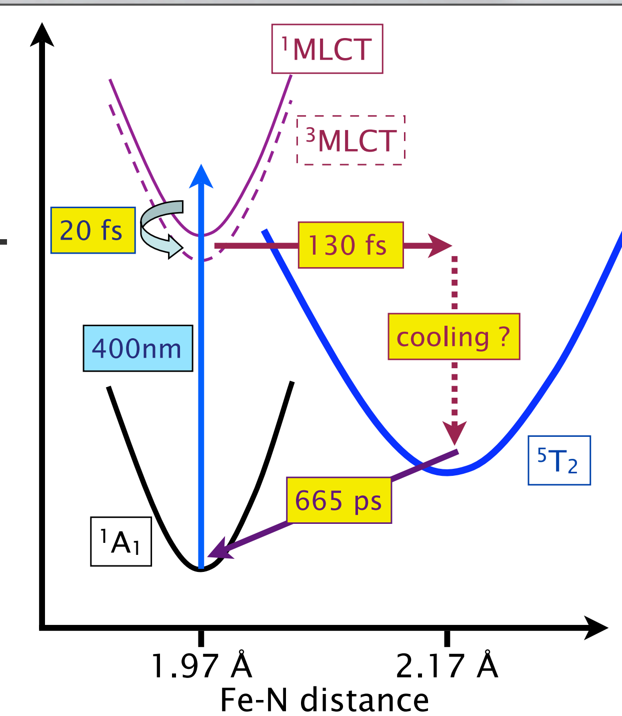
Proposal
Tune the energy to the maximum transient signal (7126 eV) and perform a time scan

Aqueous $[Fe^{II}(bpy)_3]^{2+}$: Femtosecond XAS results



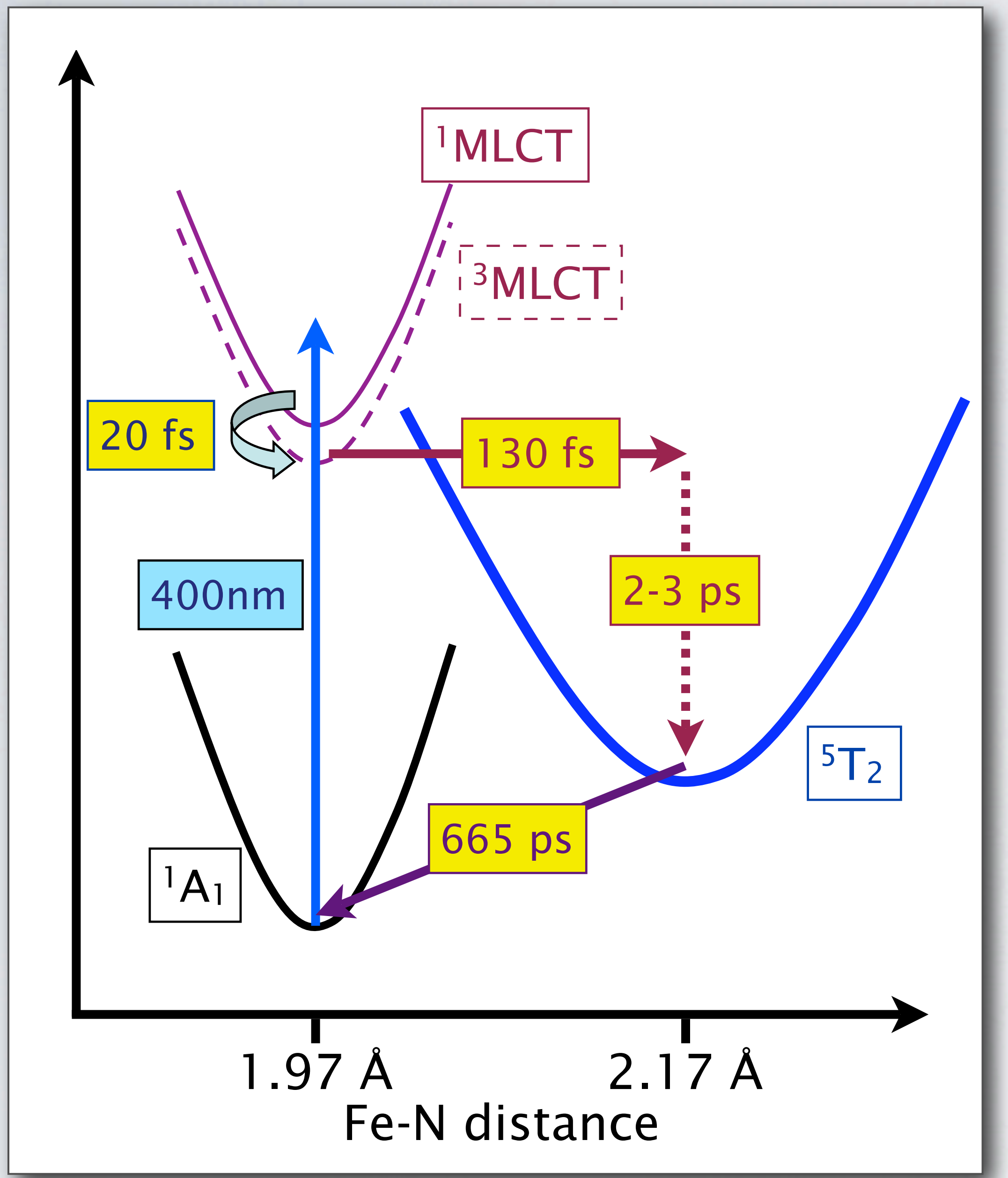


The molecule arrives in the high-spin state directly from the ^{3}MLCT in ~150 fs



Ch. Bressler et al. Science 323, 498 (2009)

Aqueous $[Fe^{II}(bpy)_3]^{2+}$: Conclusions



☑ Picosecond EXAFS has successfully resolved the transient high-spin state structure of a spin-crossover molecular system in solution to sub-Å resolution

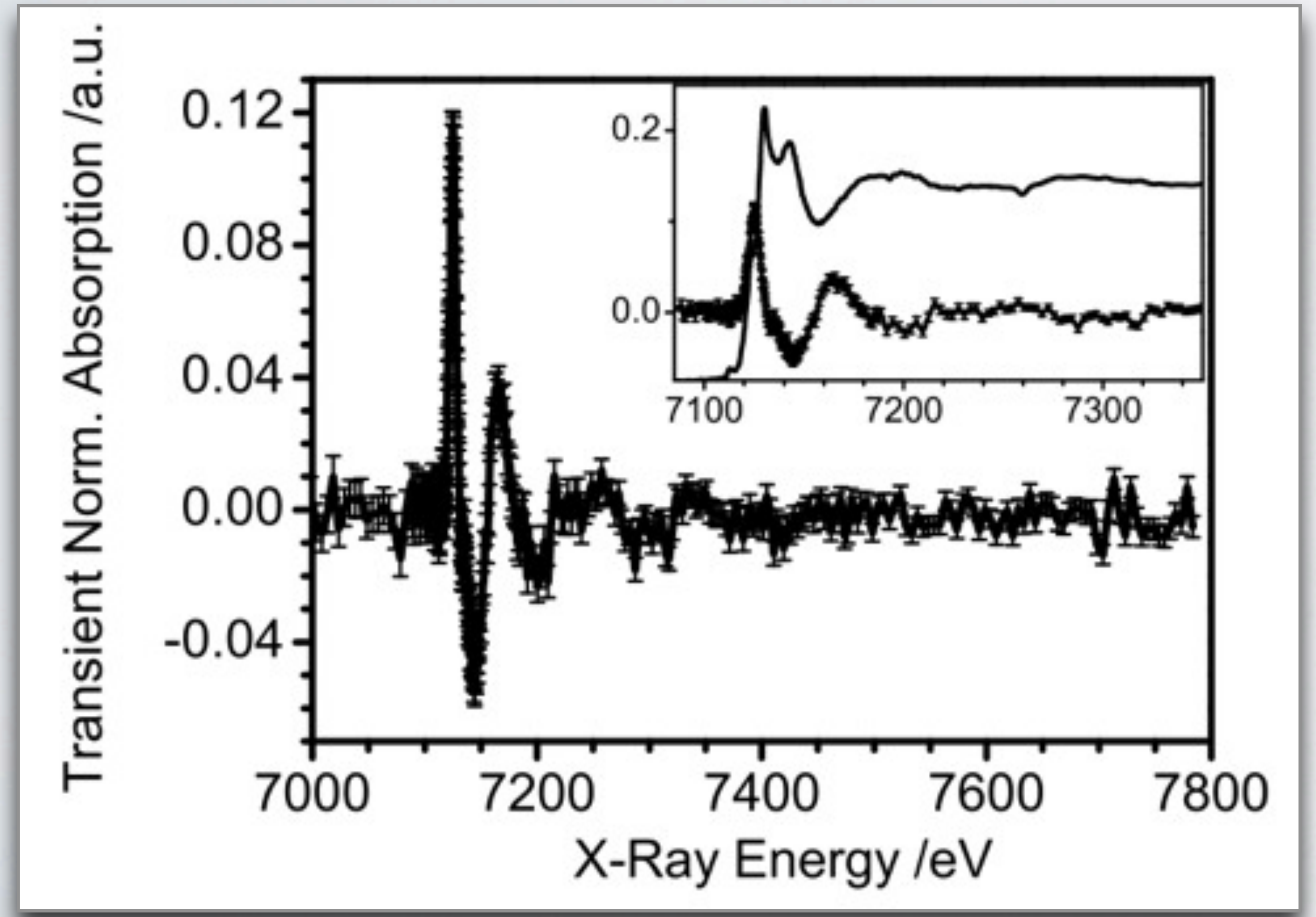
☑ Femtosecond XANES has allowed us to watch the arrival of an excited molecular system in its high-spin state

By combining ultrafast optical techniques and ultrafast x-ray techniques we have completely characterized the structure and dynamics of a molecular spin-crossover system

Aqueous $[Fe^{II}(bpy)_3]^{2+}$ revised

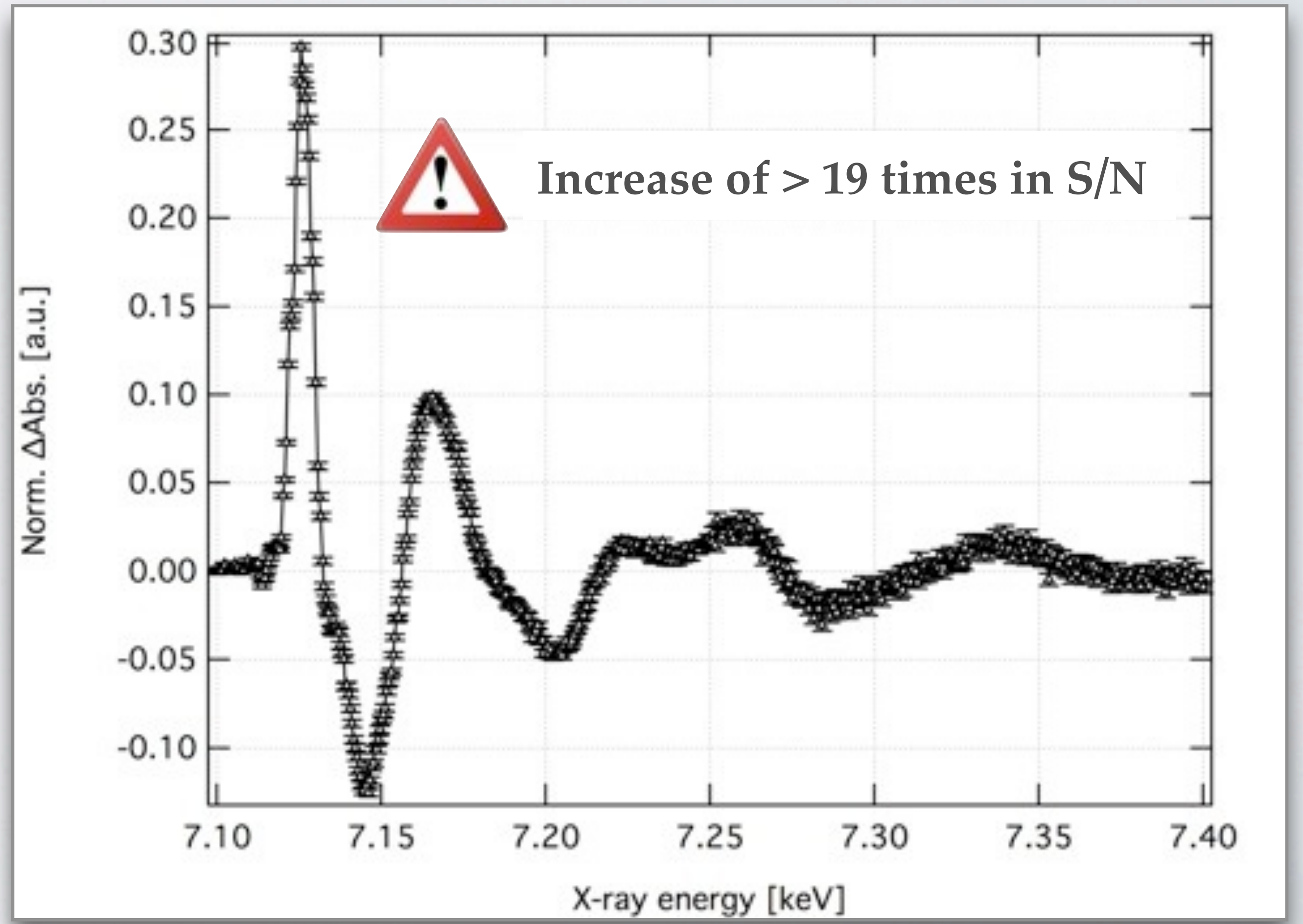
- ☑ The newly-implemented MHz data scheme allows the collection of high-quality data
- ☑ More details of the transient excited-state structures can be studied

kHz

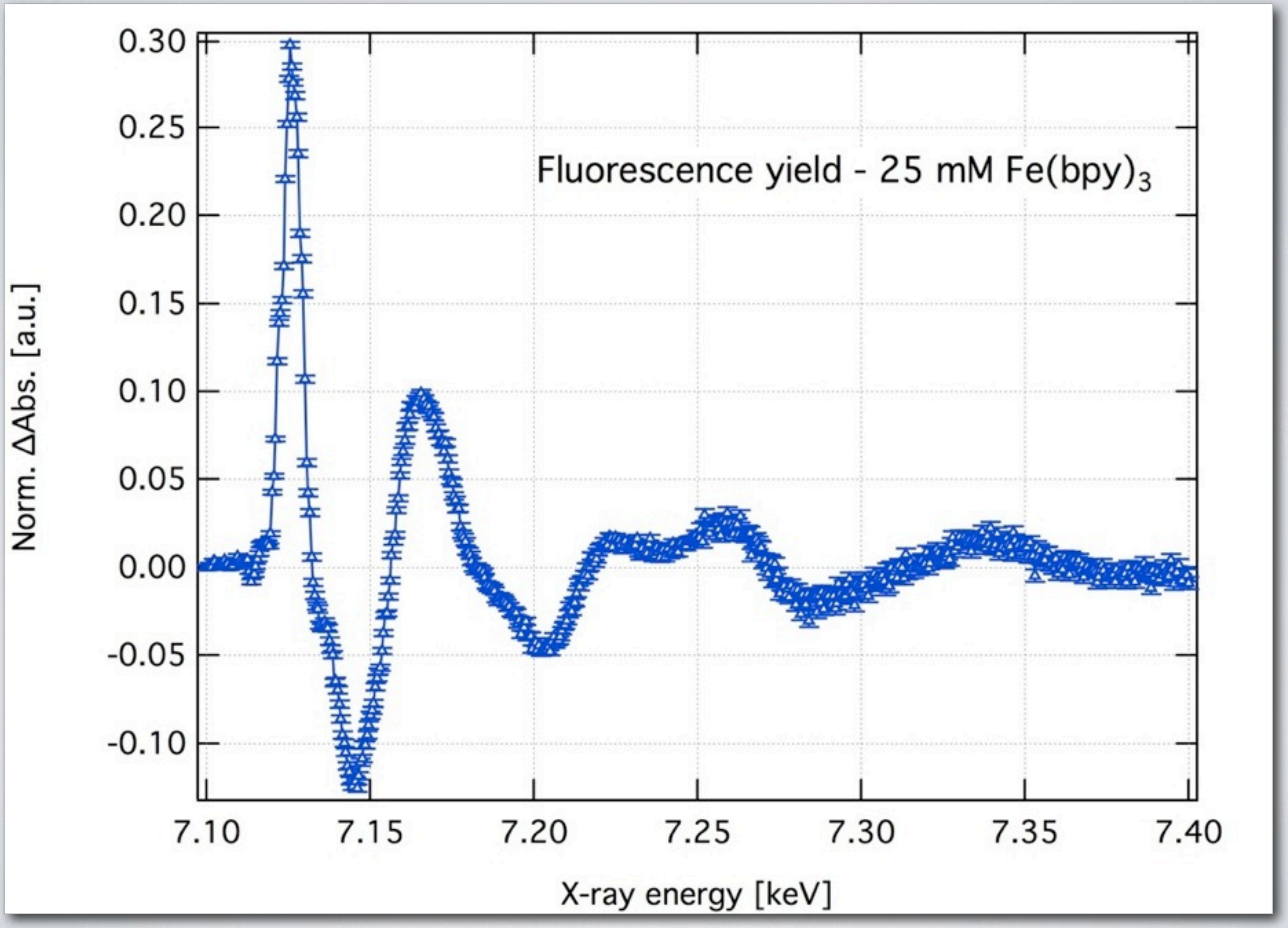


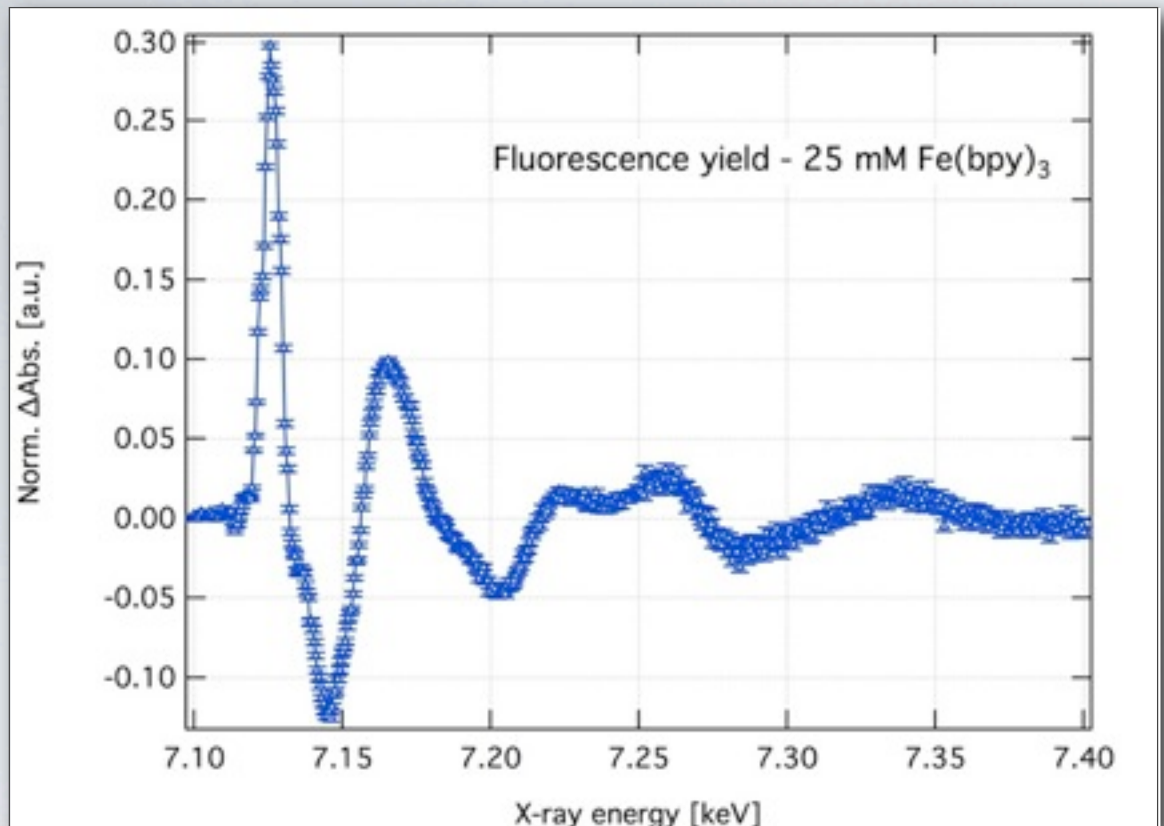
Gawelda, W., *et al.*, *PRL* **98** 057401 (2007).

MHz

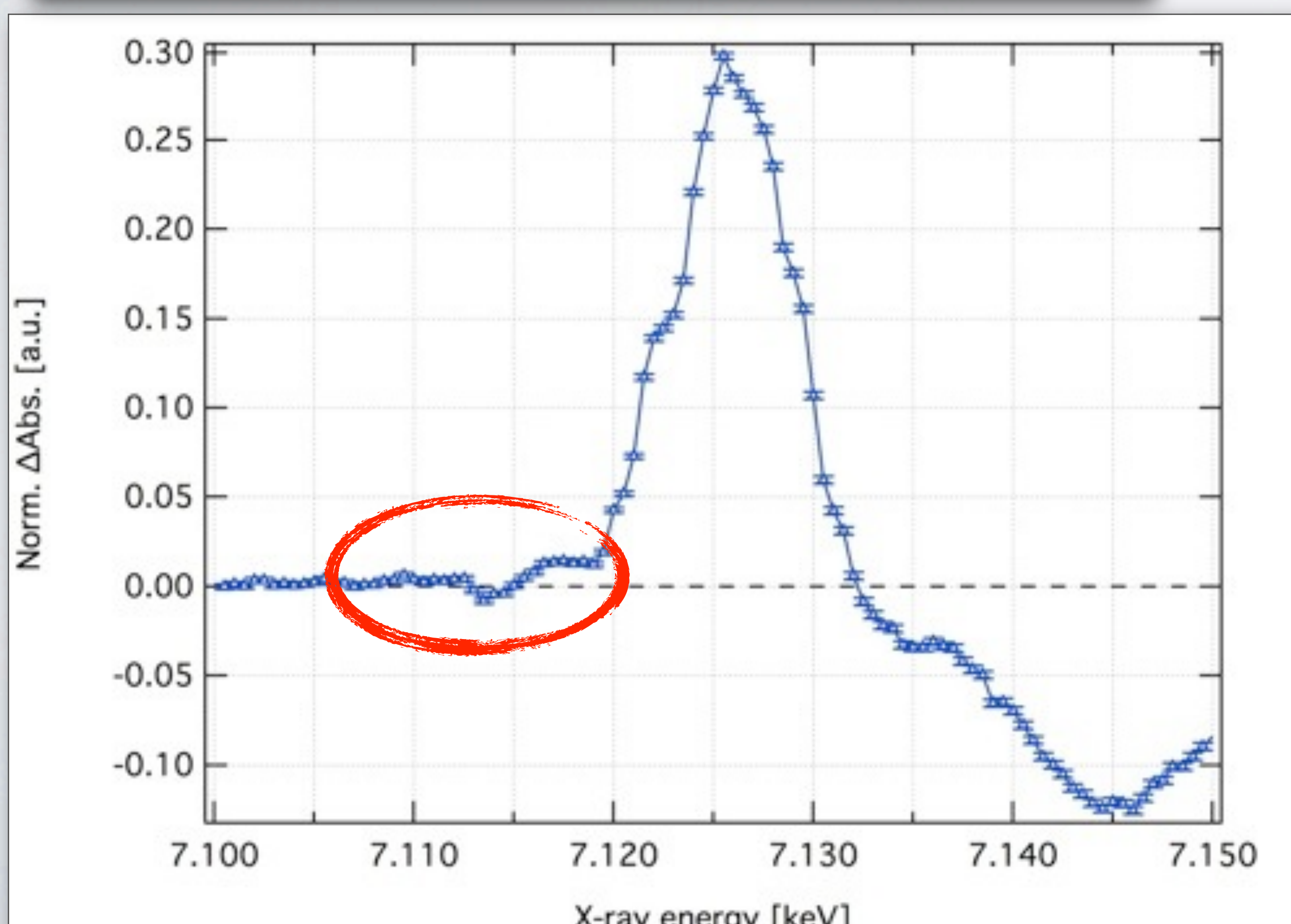


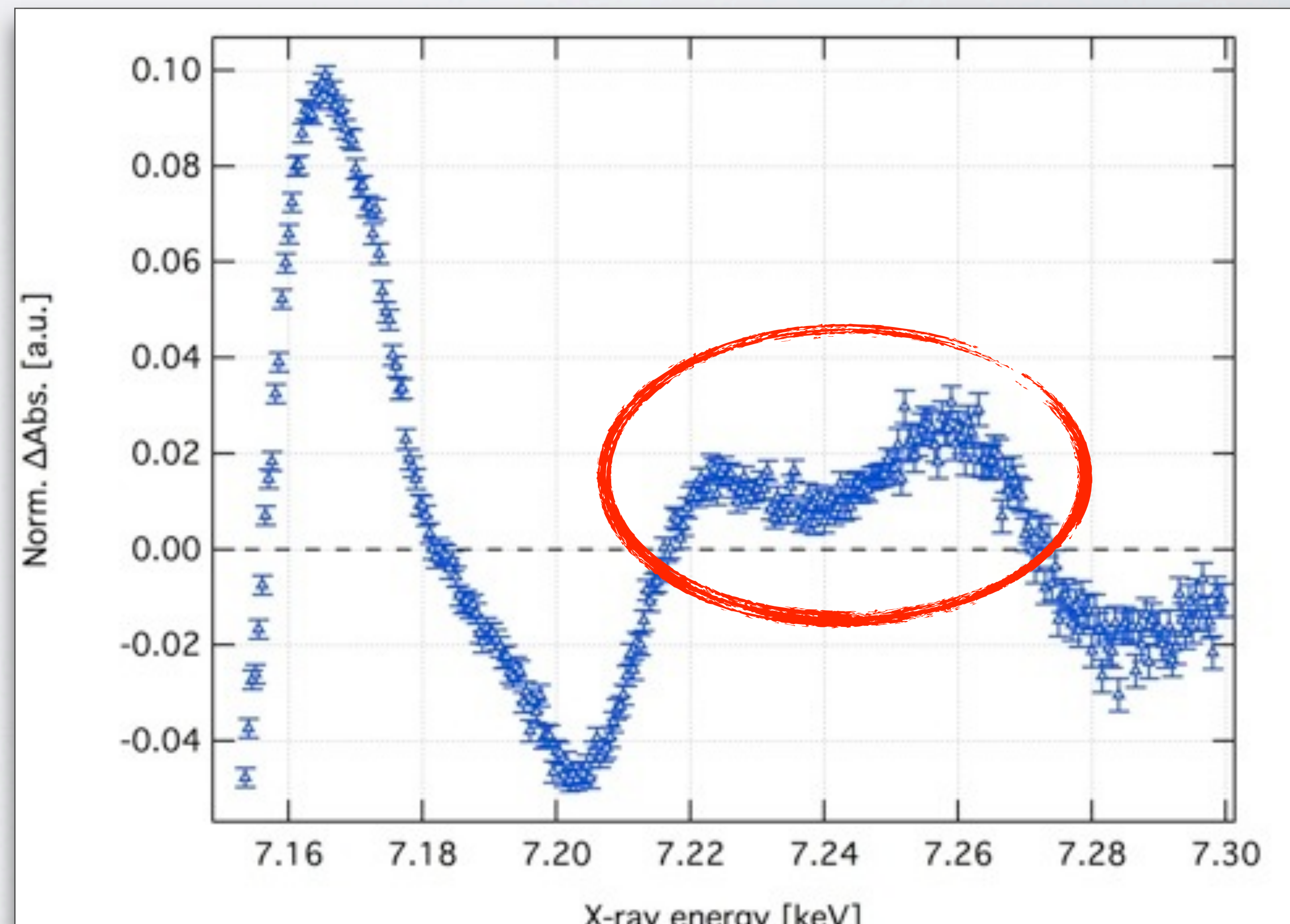
Lima, F. A.., *et al.*, *in preparation* (2011).

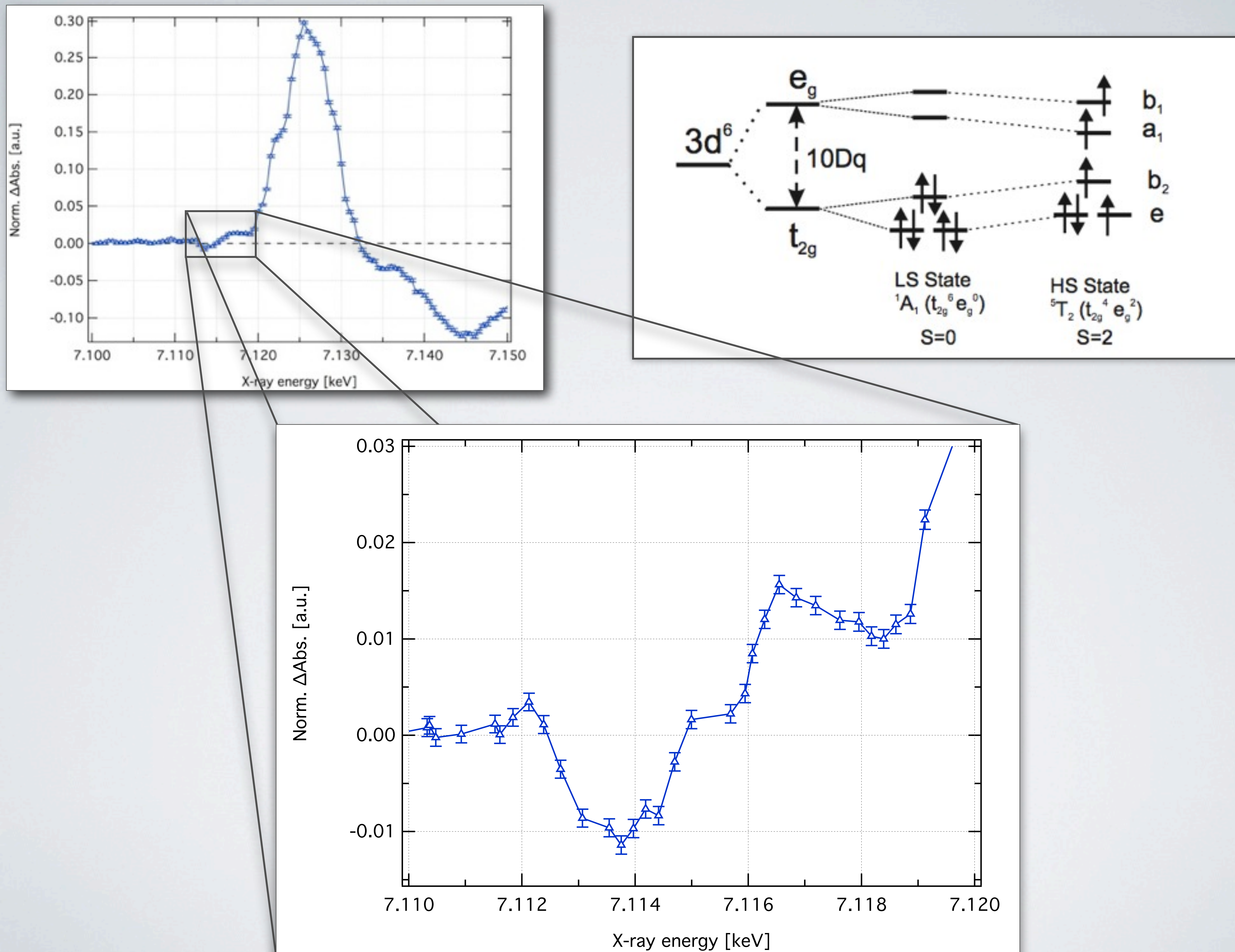

Fluorescence yield - 25 mM Fe(bpy)3
Norm. ΔAbs. [a.u.]
X-ray energy [keV]
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
7.10
7.15
7.20
7.25
7.30
7.35
7.40



- ☑ The increased S/N allows the collection of high-quality data in less time
- ☑ Possibility to investigate subtle details of the transient structure.
- ☑ Allows the measurement of highly-diluted systems, e.g., proteins in solution

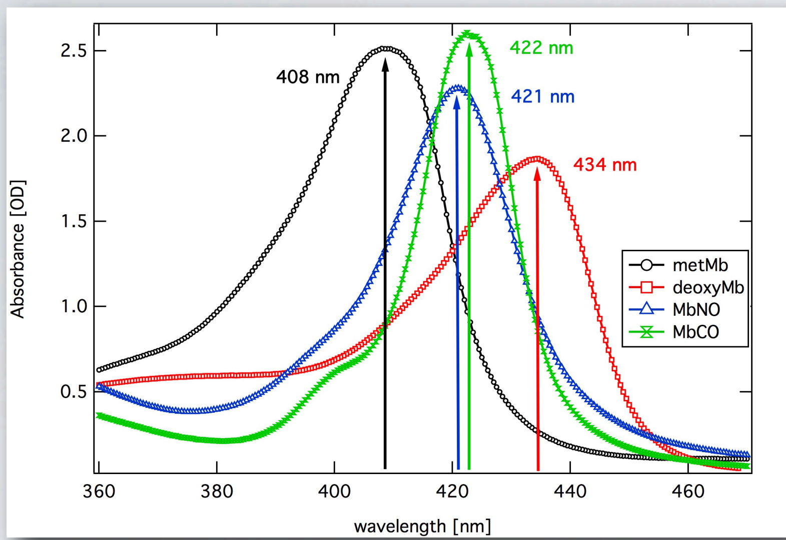




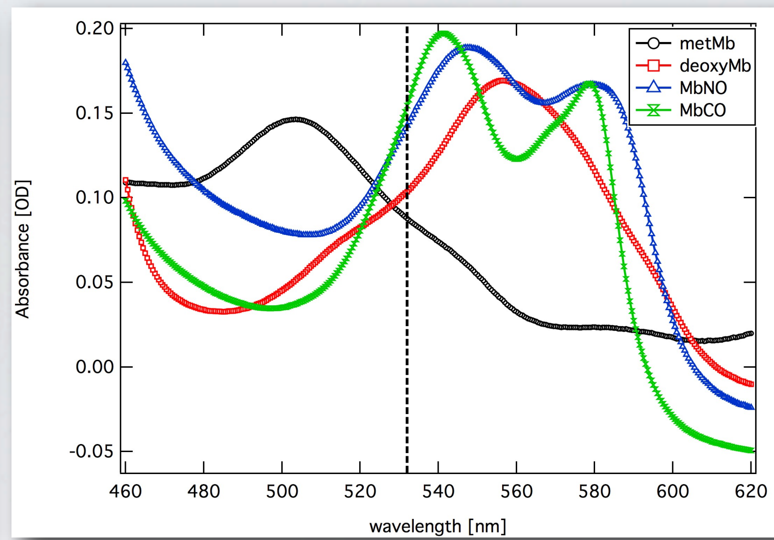

0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
Norm. ΔAbs. [a.u.]
7.100
7.110
7.120
7.130
7.140
7.150
X-ray energy [keV]
3d6
eg
t2g
10Dq
b1
a1
b2
e
LS State
1A1 (t2g6 eg0)
S=0
HS State
5T2 (t2g4 eg2)
S=2
0.03
0.02
0.01
0.00
-0.01
Norm. ΔAbs. [a.u.]
7.110
7.112
7.114
7.116
7.118
7.120
X-ray energy [keV]

Biological systems: Myoglobin

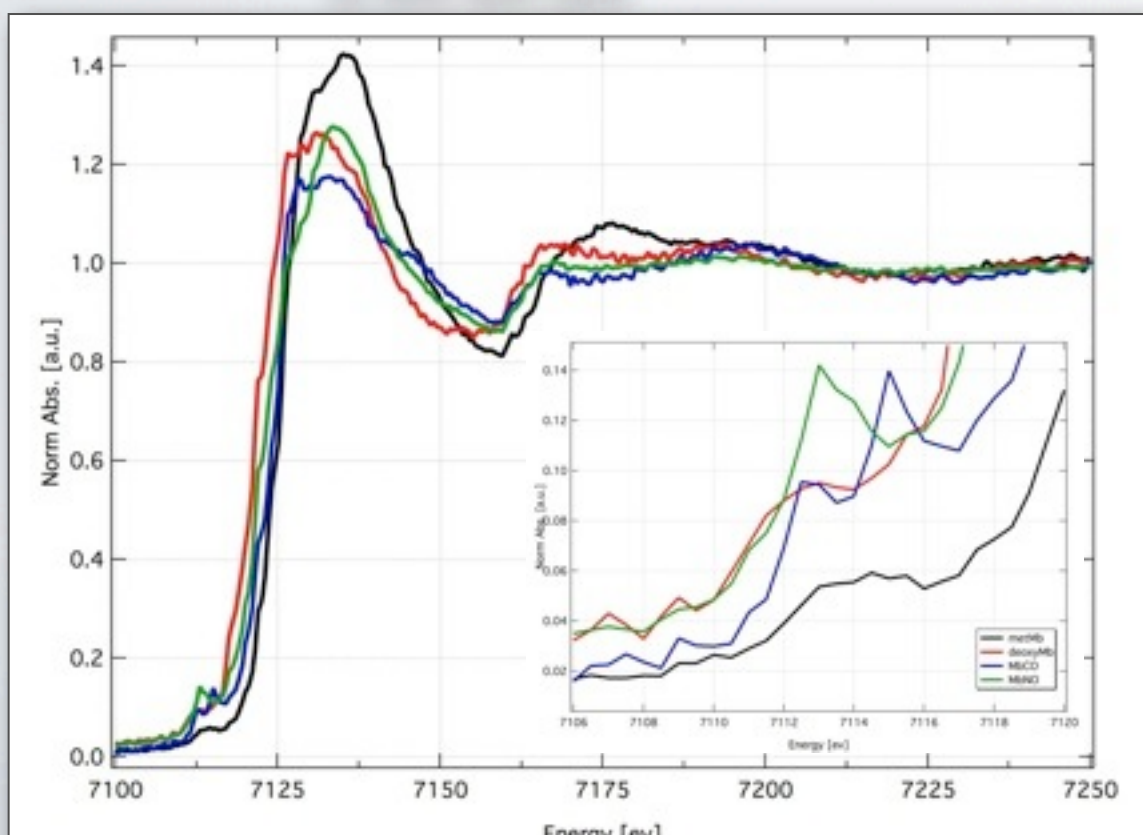
Myoglobin is an oxygen transport/storage protein that has the ability to bind small molecules such as O_2, CO, NO and CN



(a) Soret band region

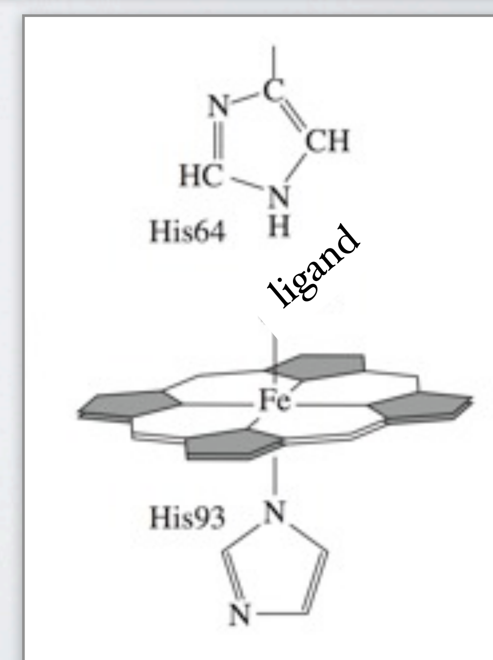


(b) Q-bands region



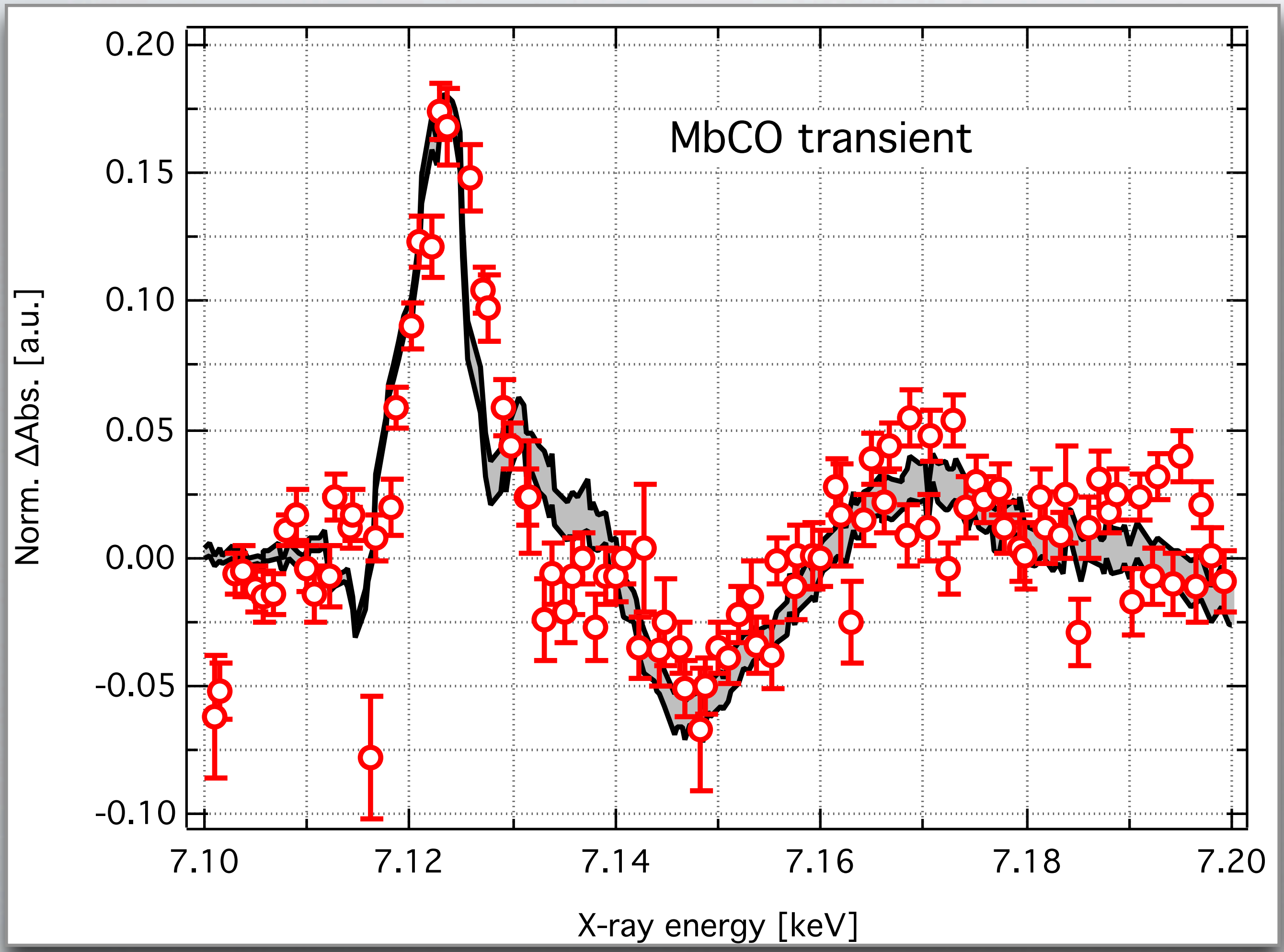
Small changes in the ligand character have profound spectroscopic effects

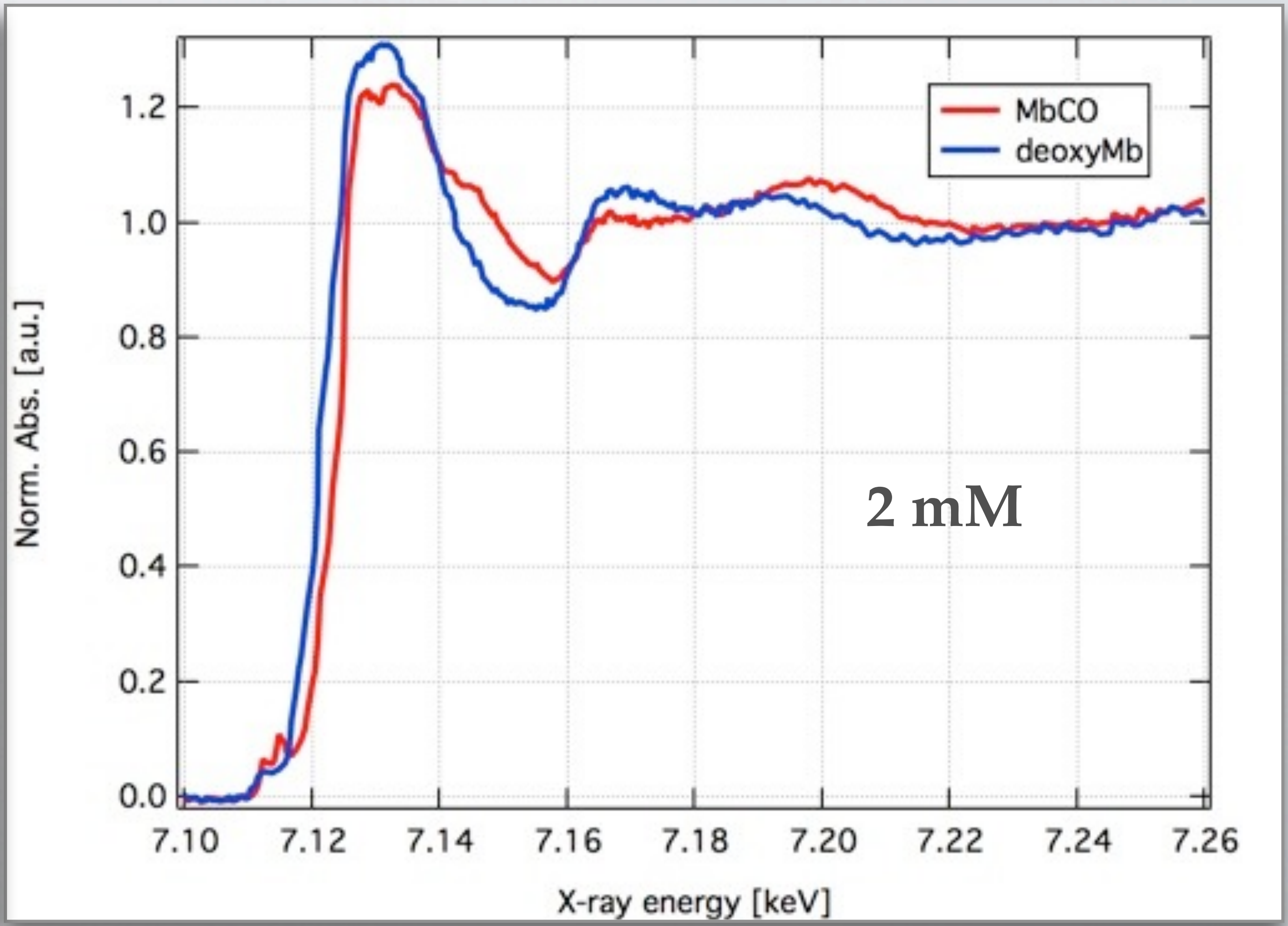
We can knock this ligand off with a photon of green or blue light



Proof-of-principle: MbCO

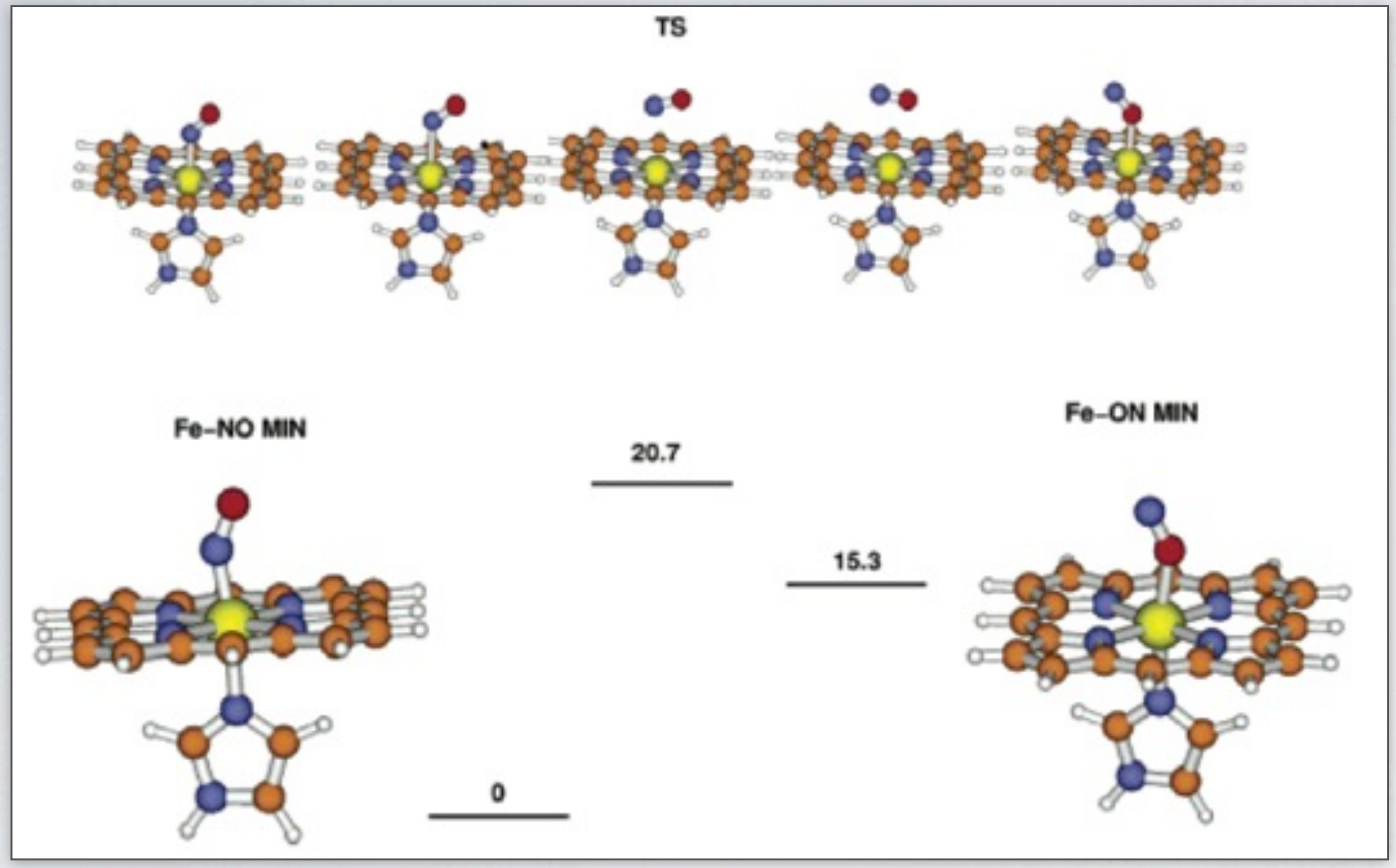
- ☑ First ever time-resolved x-ray experiment [1]
- ☑ Alternative data-collection strategy due to the high repetition rate and long photo-excited lifetime
- ☑ Liquid sample under physiological conditions





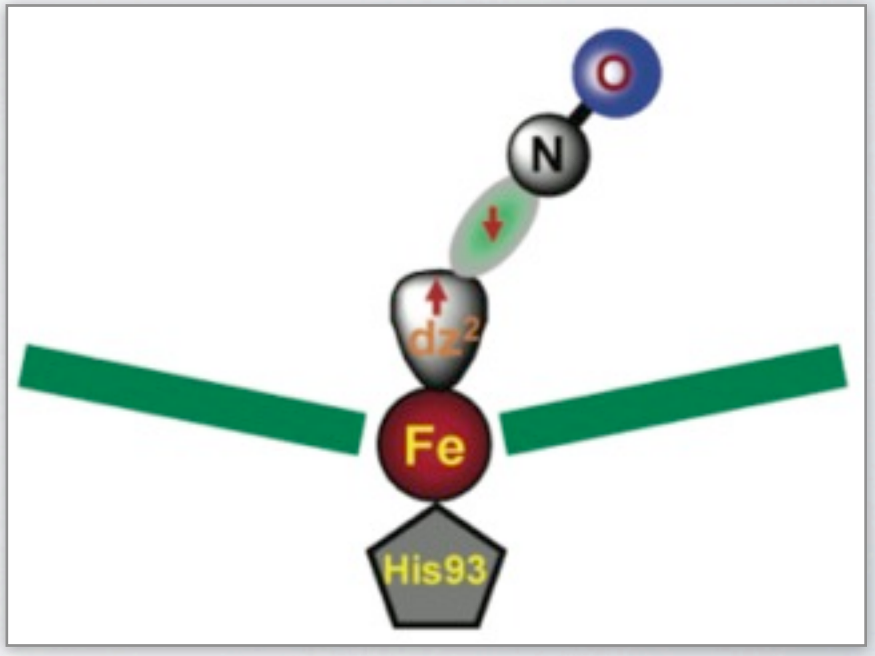
[1] Mills, D.M.., *et al.*, *Science* **223** pp. 811 (1984).

MbNO - dynamics of ligand detachment

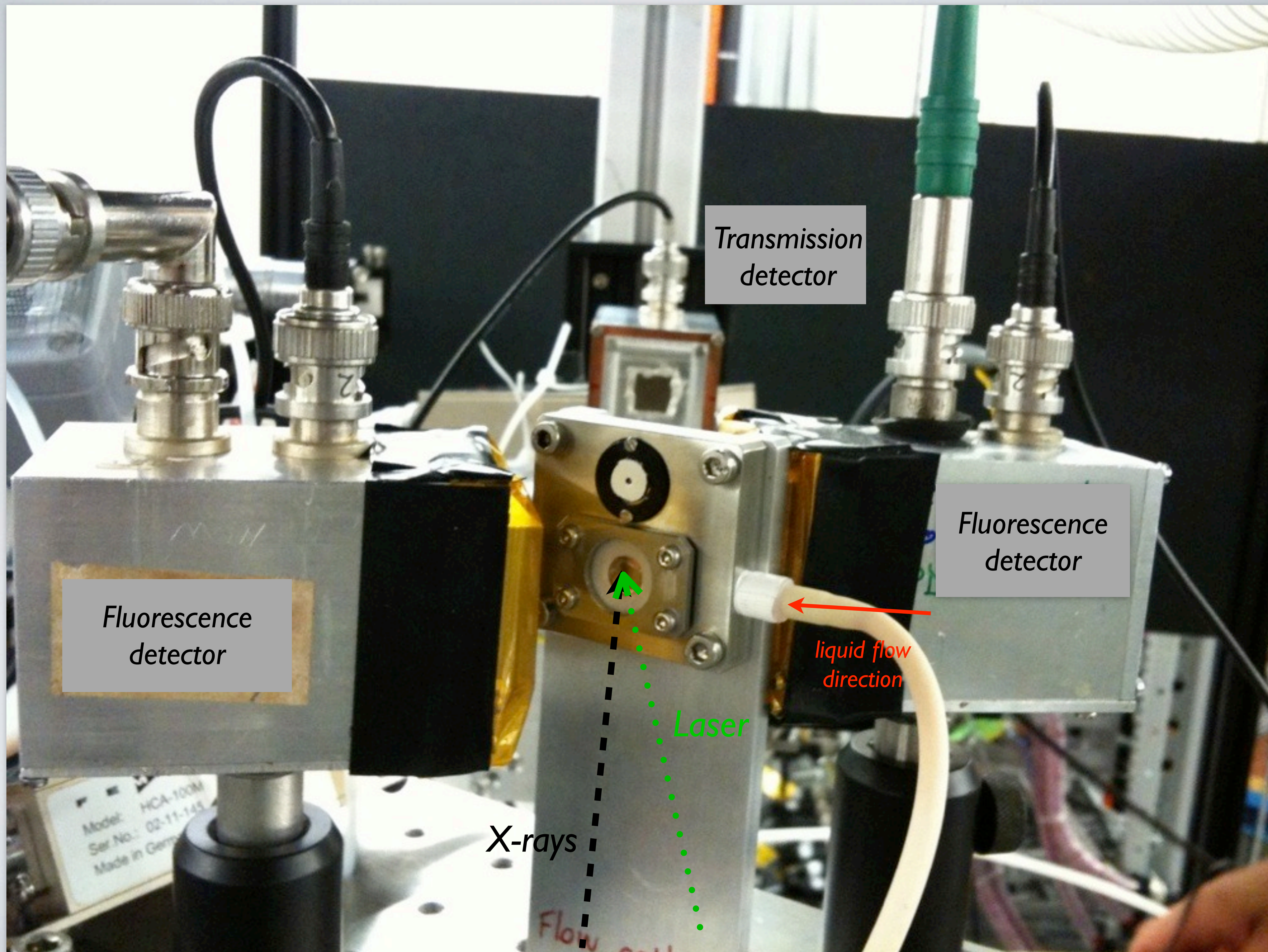


- ☑ What's the spin-state & electronic structure of the Fe atom on the transient structure?
- ☑ What's the geometry of the transient structure?
- ☑ Is there more than one excited state structure?
- ☑ Can we see a bound MbON structure? [1]

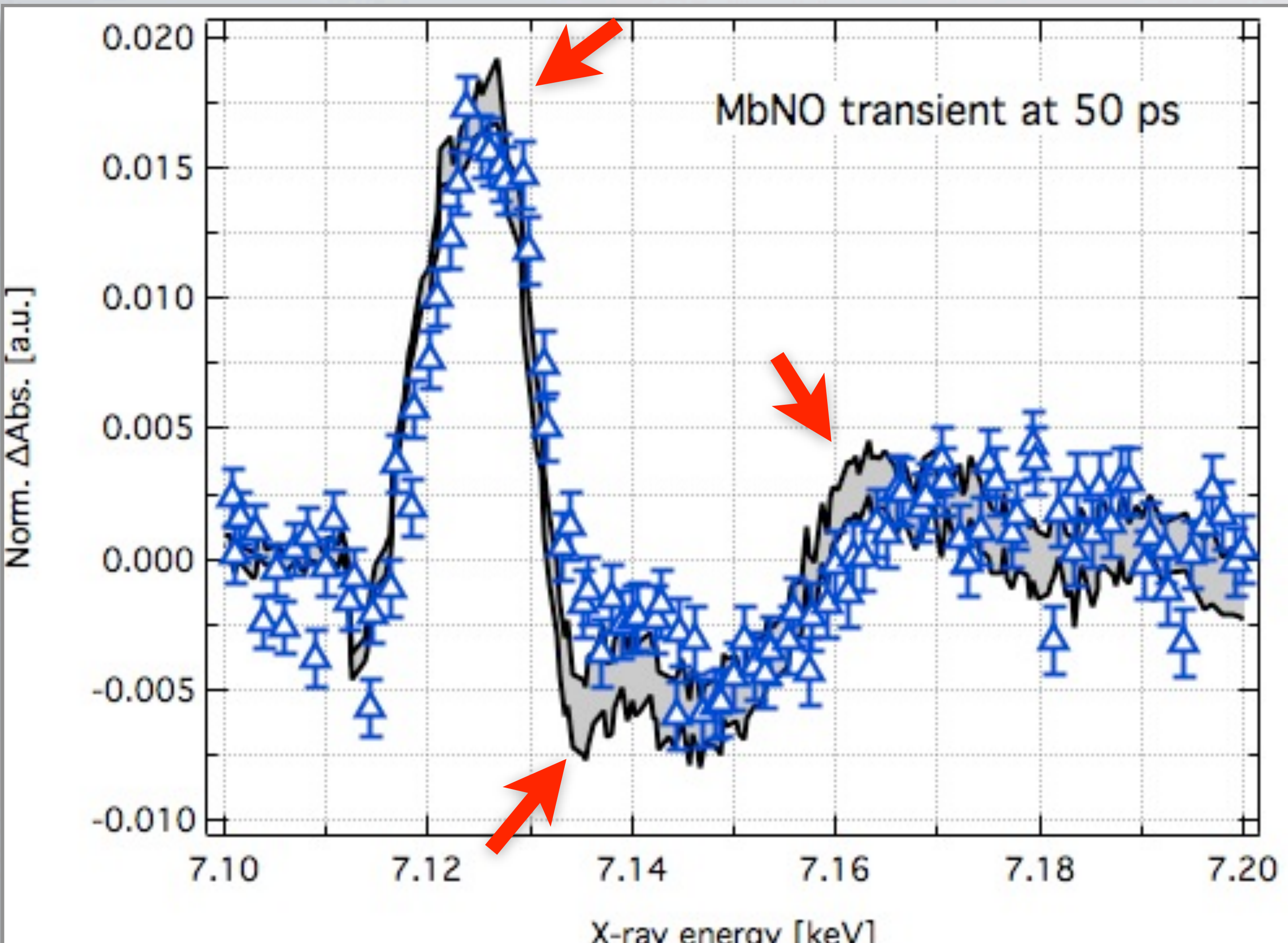
- ☑ How fast is the geminate recombination?
- ☑ Existence of a 6-coordinate domed structure on MbNO? [2]

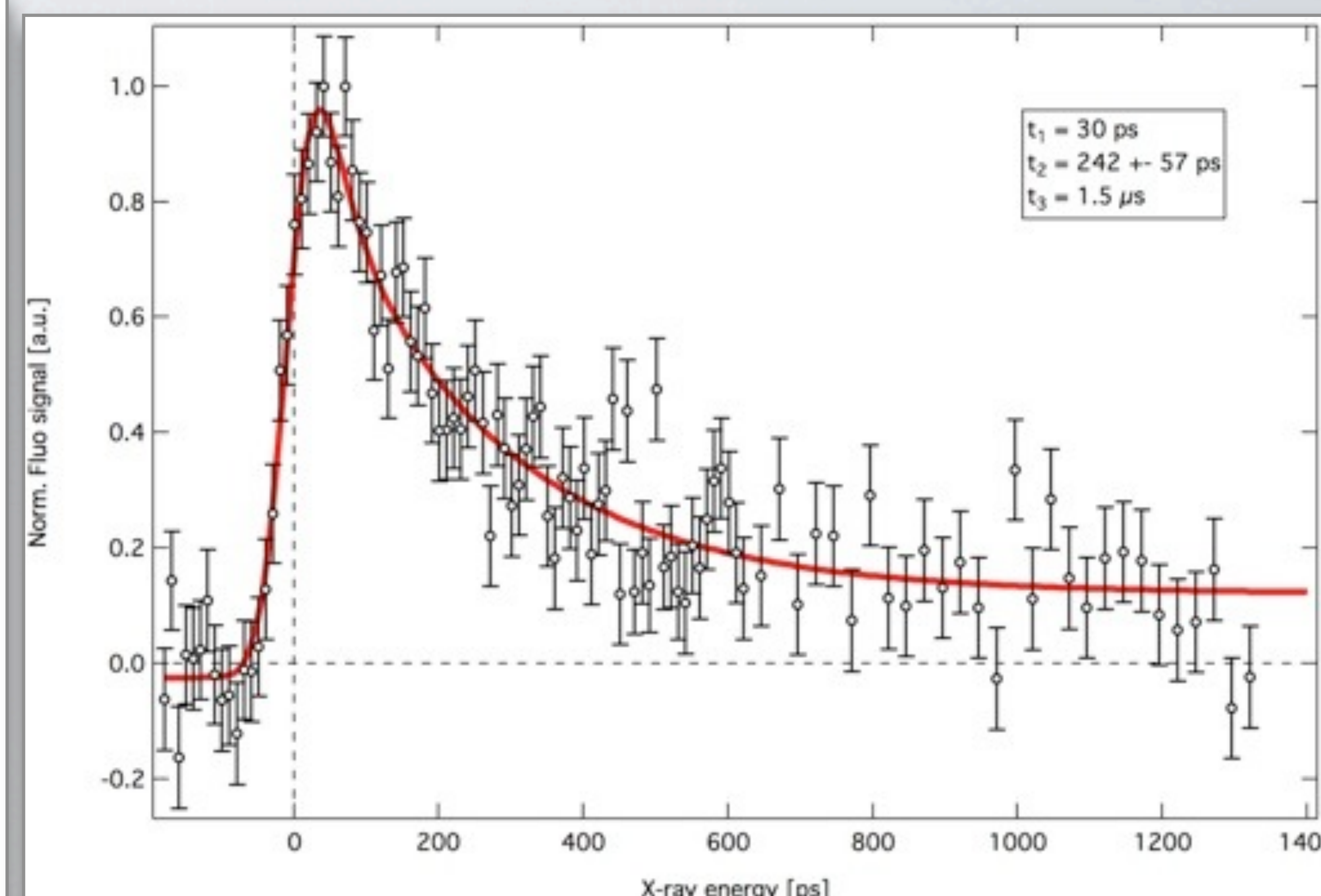


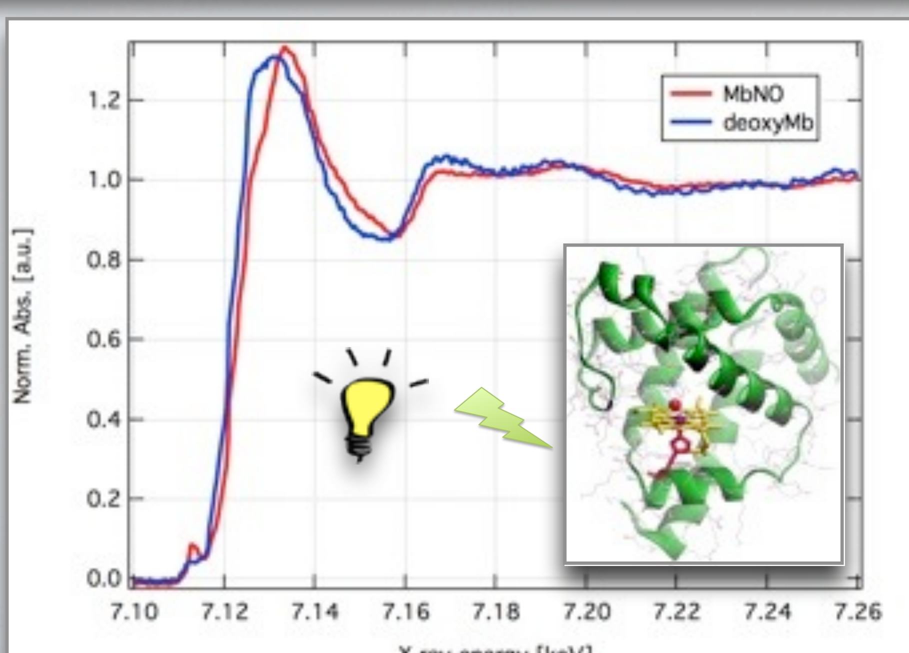
[1] D. Nutt et al. J. Phys. Chem. **B 109**, 21118 (2005)
[2] S. Kruglik et al. PNAS **107**, 13678 (2010)


Transmission detector
Fluorescence detector
Fluorescence detector
liquid flow direction
Laser
X-rays

MbNO







- ☑ Fast dynamics (ca. 200 ps) captured on the fly
- ☑ Small discrepancy from the predicted signal might be an indication of a 30 ps domed ligated (6-coordinated) configuration. [1]

[1] Kruglik, S.G., *et al.*, *PNAS* **107** (31) pp. 13678 (2010).

Summary

☑ The potential inherent to time-resolved XAS is enormous, we can measure structural changes in excited systems on the timescale of atomic motion

☑ Using higher data acquisition repetition rate we can study subtle details of the transient (excited) structures and/or more complex systems

☑ The ultrafast structural dynamics of excited-state biological systems under physiological conditions can be followed

☑ Extending the technique to the soft x-ray regime will allow the study of L-edges of transition metals and K-edges of C, N, O, etc

☑ More to come with new sources of ultrafast x-rays: XFEL

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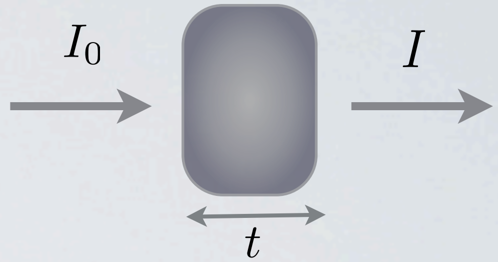
For more information on ultrafast structural dynamics visit
http://lsu1.epfl.ch/dyna/



- The intensity of an x-ray beam passing through a material of thickness **t** is given by the absorption coefficient **μ**.

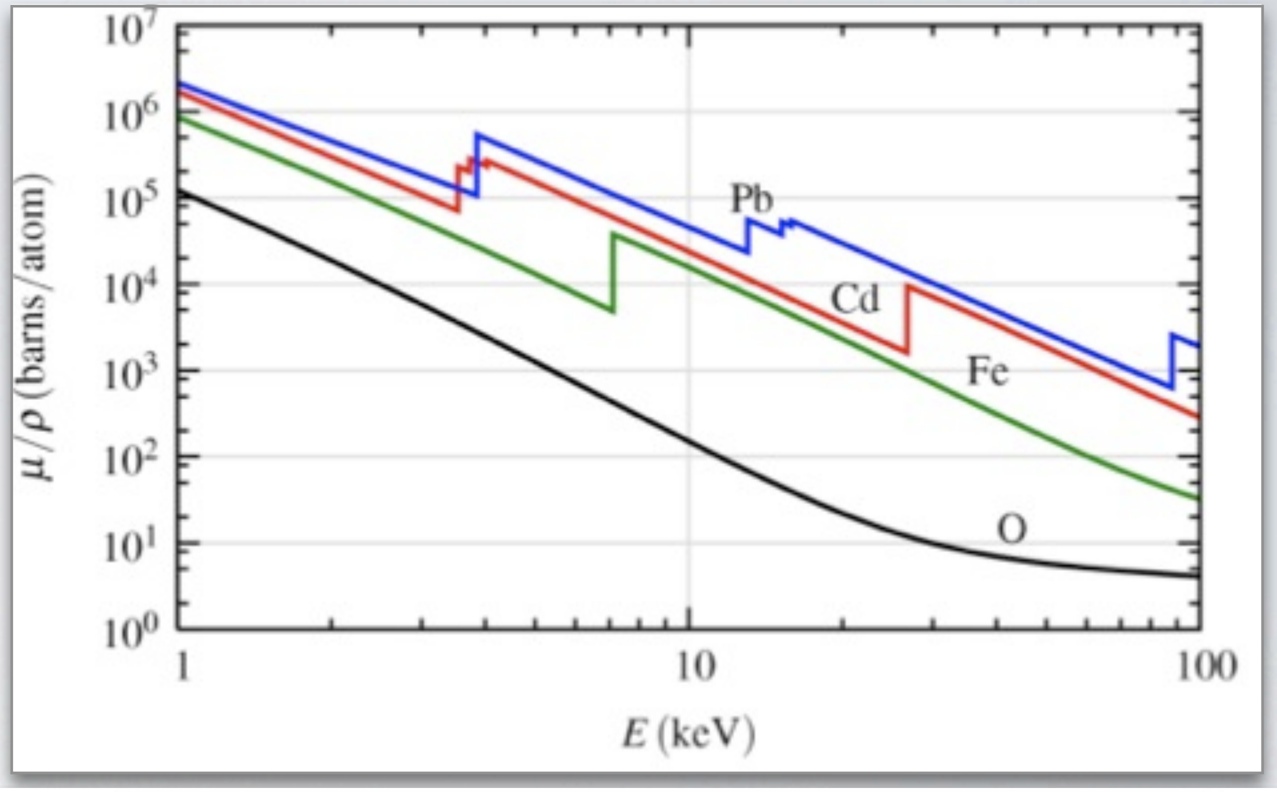
- Beer-Lambert law → $I = I_0 e^{-\mu t}$

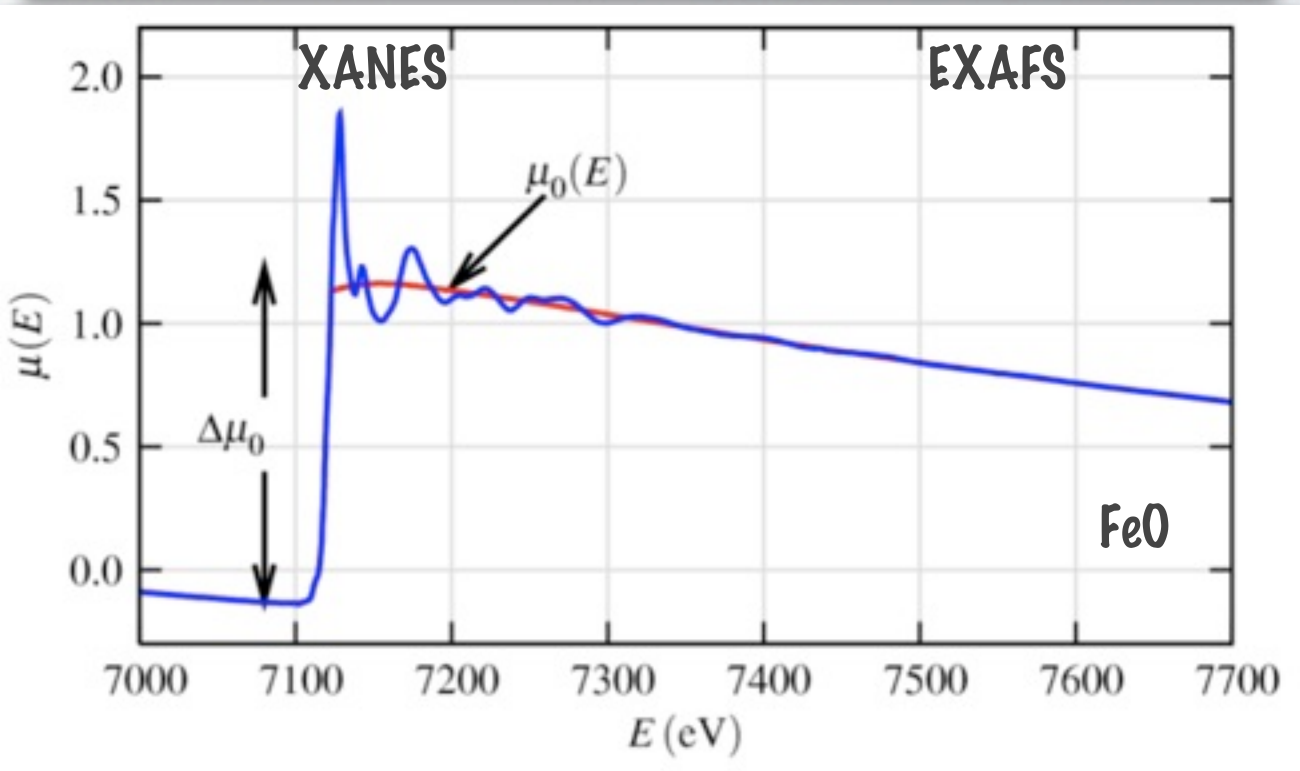
- **μ** depends strongly on x-ray energy **E**, atomic number **Z**, on the density **ρ** and on the atomic mass **A**

$$\mu \approx \frac{\rho Z^4}{A E^3}$$

- X-ray absorption fine structure function:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)}$$





X-ray Absorption Spectroscopy

- Fermi's Golden Rule

$$\mu(E) \propto | \langle i \mid H \mid f \rangle |^2$$

$$| f \rangle = | f_0 \rangle + | \Delta f \rangle$$

$$\mu(E) \propto | \langle i \mid H \mid f \rangle |^2 \left[1 + | \langle i \mid H \mid \Delta f \rangle \frac{\langle f_0 \mid H \mid i \rangle}{| \langle i \mid H \mid f_0 |^2} + C.C.\right]$$

$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

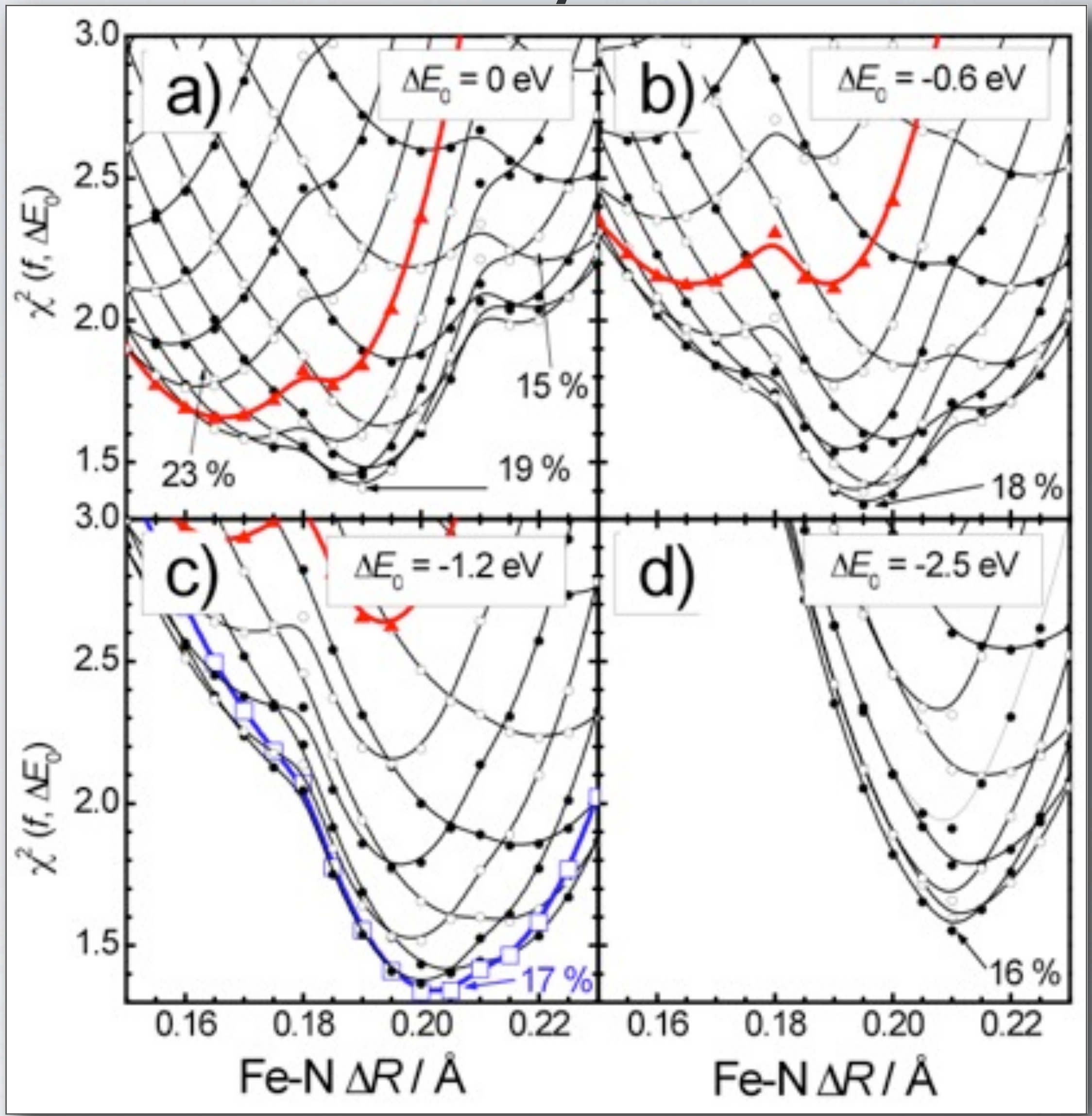
Aqueous $[Fe^{II}(bpy)_3]^{2+}$: (picosecond) Data analysis

- ☑ optimize ground-state structures and parameters
- ☑ generate a set of EXAFS spectra for a given model by moving specific coordinates
- ☑ Calculate the transient spectrum

$$\Delta\chi_i^{TH}(\Delta R_i, E') = \chi_i^{ES}(\Delta R_i, E') - \chi^{GS}(E)$$

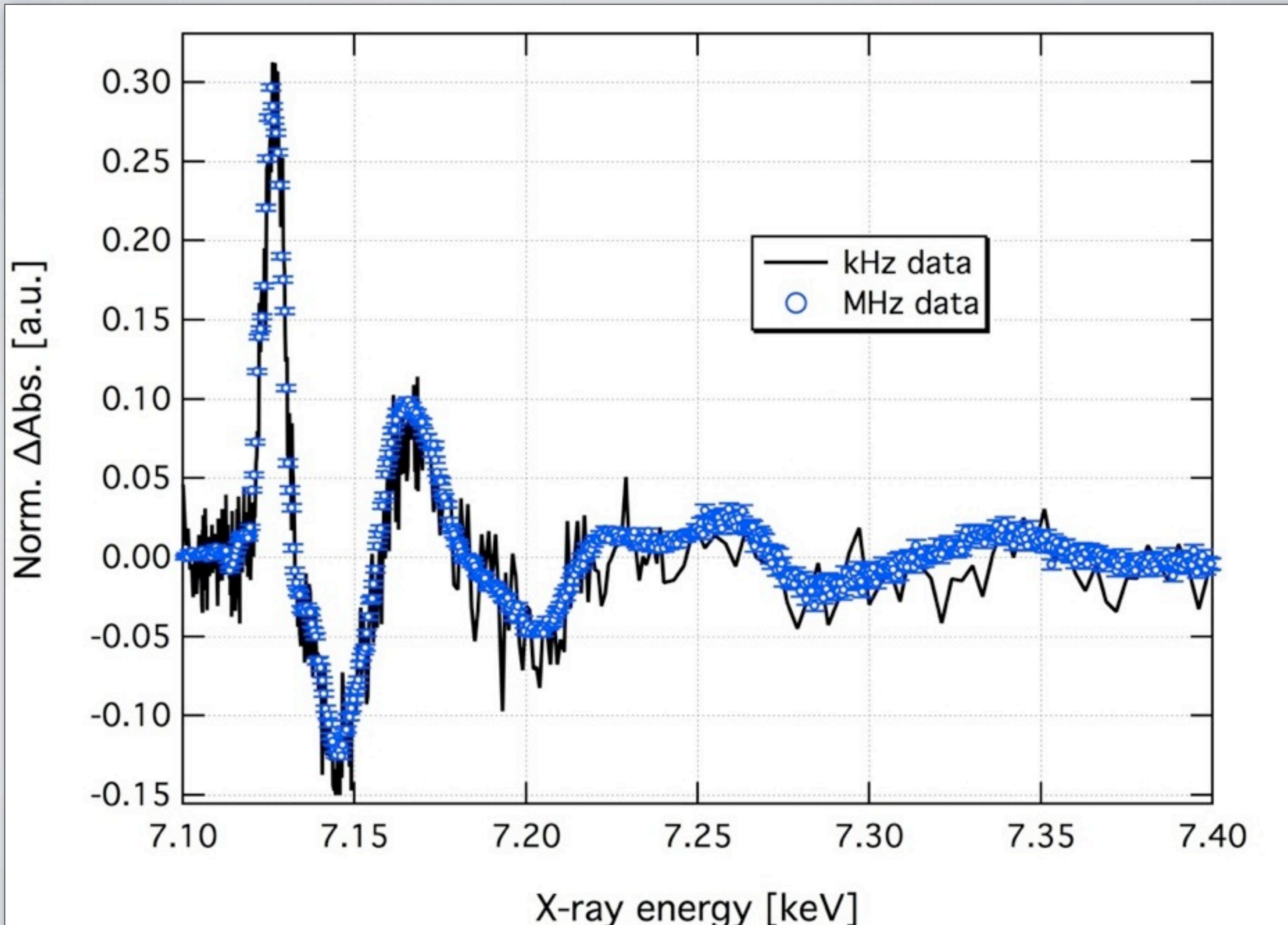
- ☑ Minimize the reduced chi squared function

$$\chi_r^2(i, f, \Delta E_0) = \frac{1}{N-1}\sum_{j=1}^{N}\left(\frac{x_j/f - \Delta\chi_{i,j}^{TH}(\Delta R_i, E')}{\sigma_j^x/f}\right)^2$$

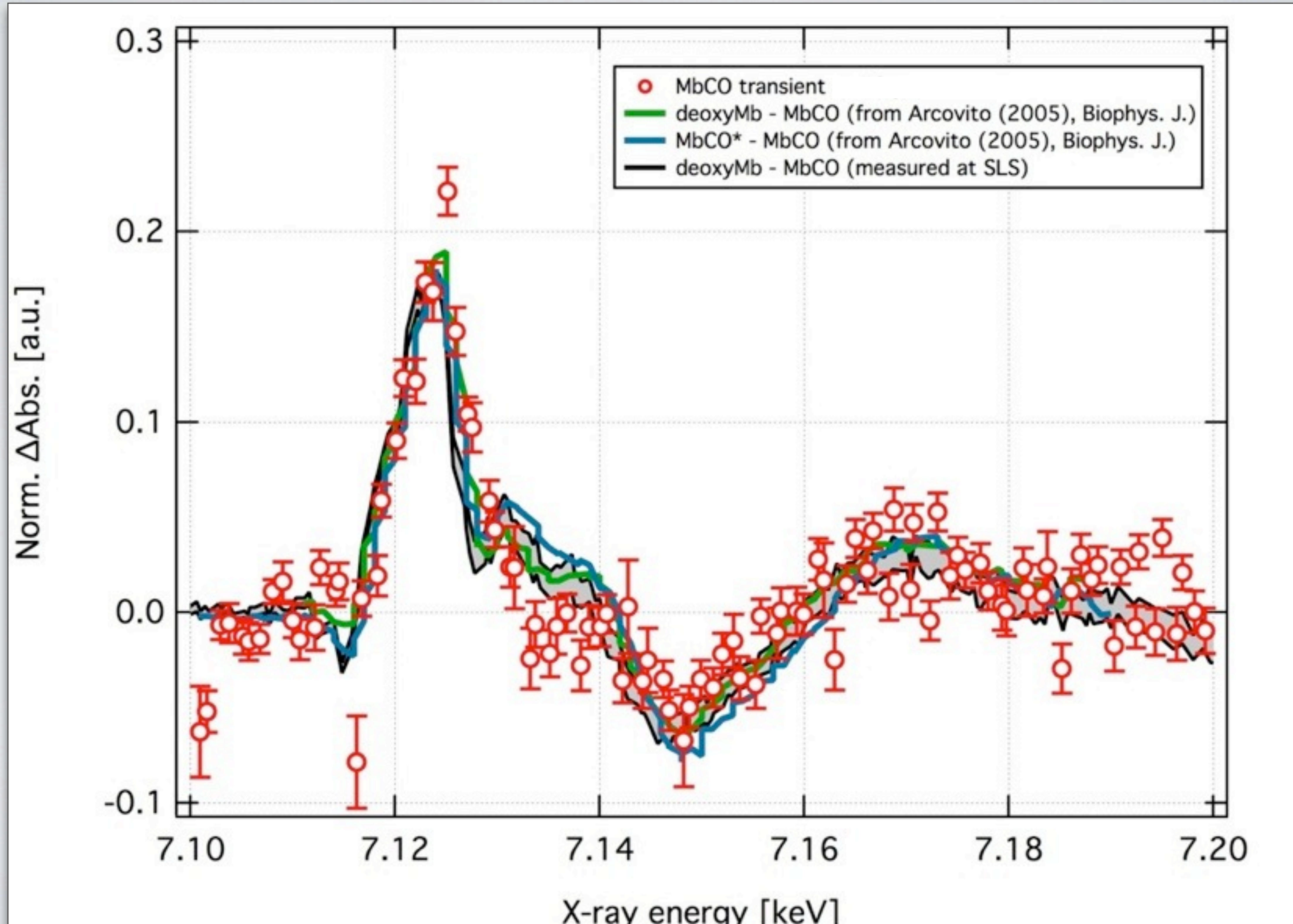


Fe-N(Å)	Error(Å)	f(%)	ΔE_0(eV)	Source
0.2	±0.02	22	-2.8±0.5	EXAFS analysis
0.19	±0.03	21.5±1.5	-2.5	MXAN analysis with fixed ΔE_0
0.2	±0.04	22	-2.5±0.5	MXAN analysis with fixed f
0.203	-0.035, +0.012	22±1	-2.5±0.5	this analysis with f=22% and ΔE_0=-2.5 eV
0.2005	-0.0165,+0.0135	17±1	-1.2±0.6	this analysis 90% confidence levels
0.203	±0.008	17±1	-1.2±0.6	this analysis 95% confidence levels

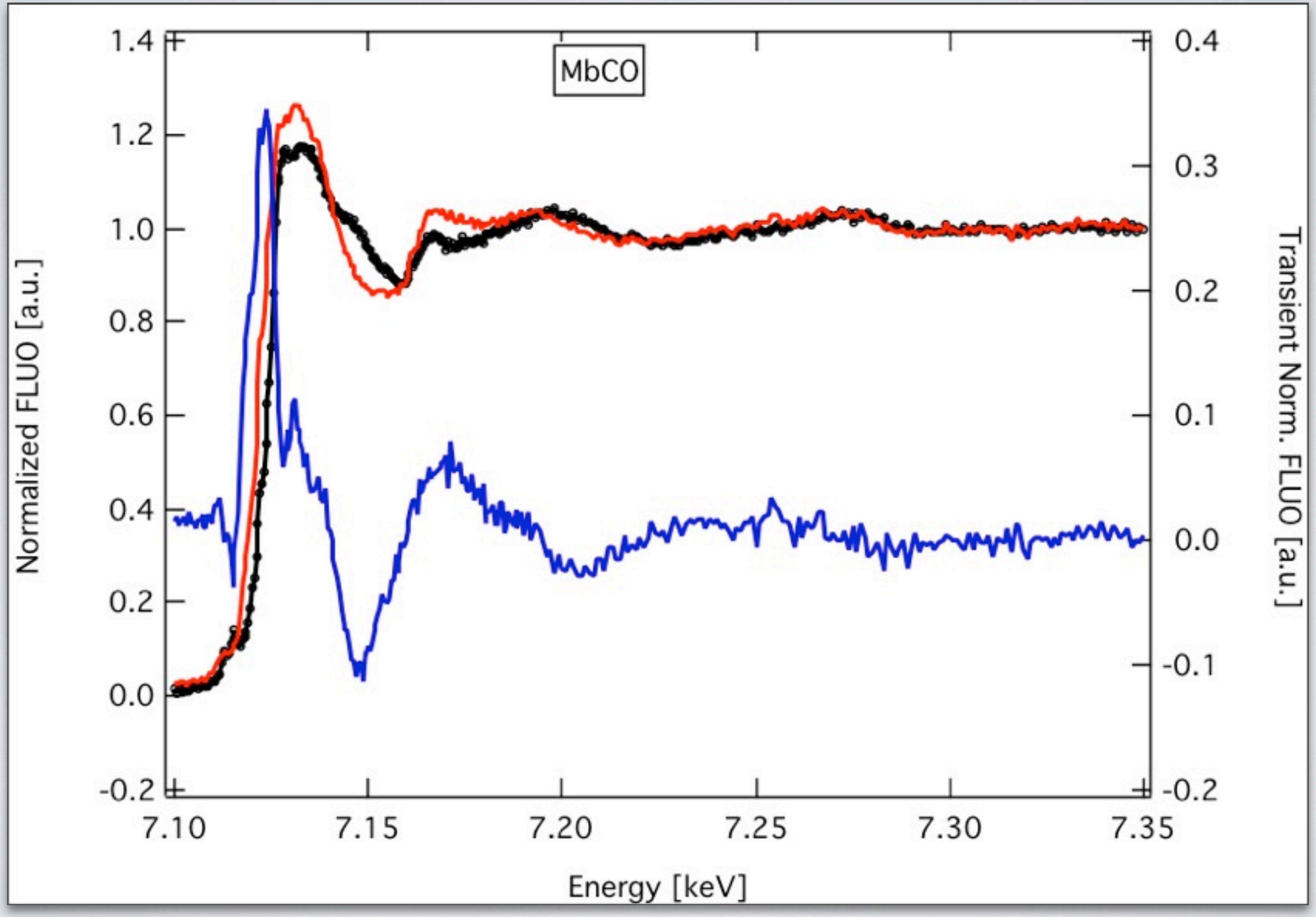
[1] W. Gawelda, et al., JCP 124520, 130 (2009)


Norm. ΔAbs. [a.u.]
X-ray energy [keV]
kHz data
MHz data
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
7.10
7.15
7.20
7.25
7.30
7.35
7.40

Myoglobin - expected signal on TR-XAS

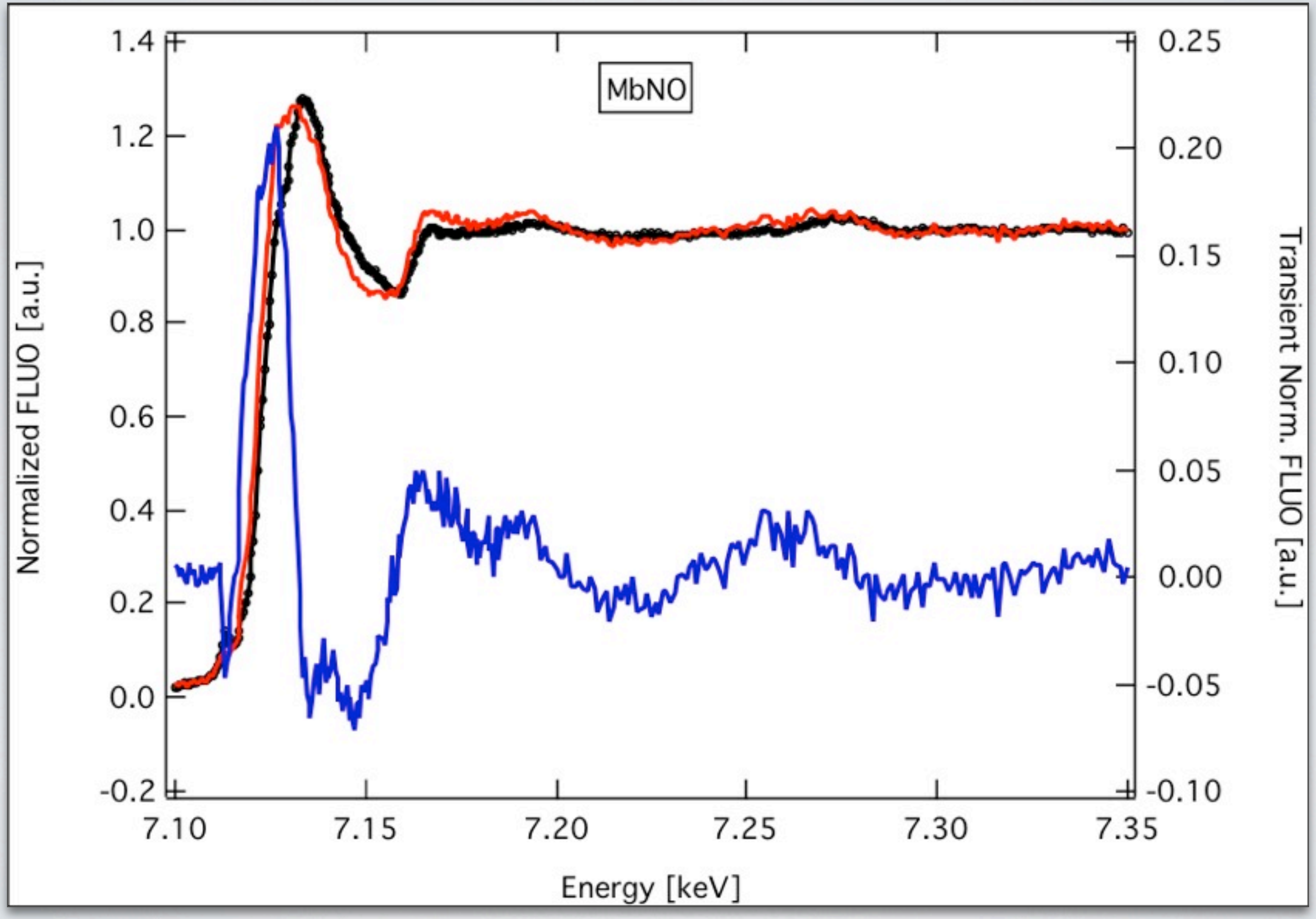


MbCO - expected signal on TR-XAS



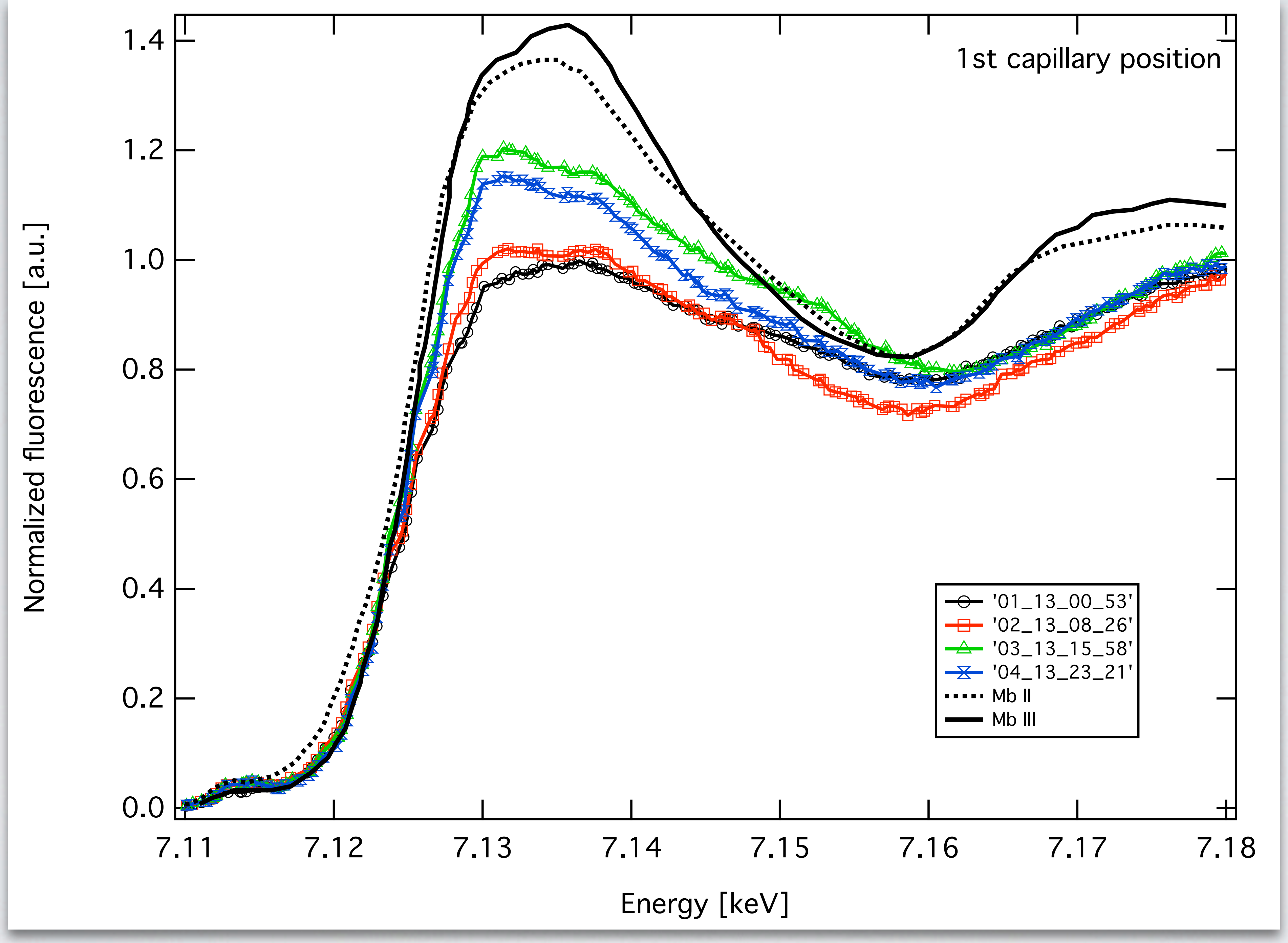
F. Lima. D. Amarasinghe, C. Milne, private data

MbNO - expected signal on TR-XAS



F. Lima. D. Amarasinghe, C. Milne, private data

Myoglobin - static XAS and radiation damage



F. Lima. D. Amarasinghe, C. Milne, private data 2009

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