Ultrafast time-resolved x-ray absorption spectroscopy: Watching atoms dance

Chris J. Milne[1,2], F.A. Lima[1,2], H. Rittmann-Frank[1,2], M. Reinhard[1], J. Rittmann[1,2], T.J. Penfold[1,3,4], R. Abela[3], F. van Mourik[1], and M. Chergui[1]

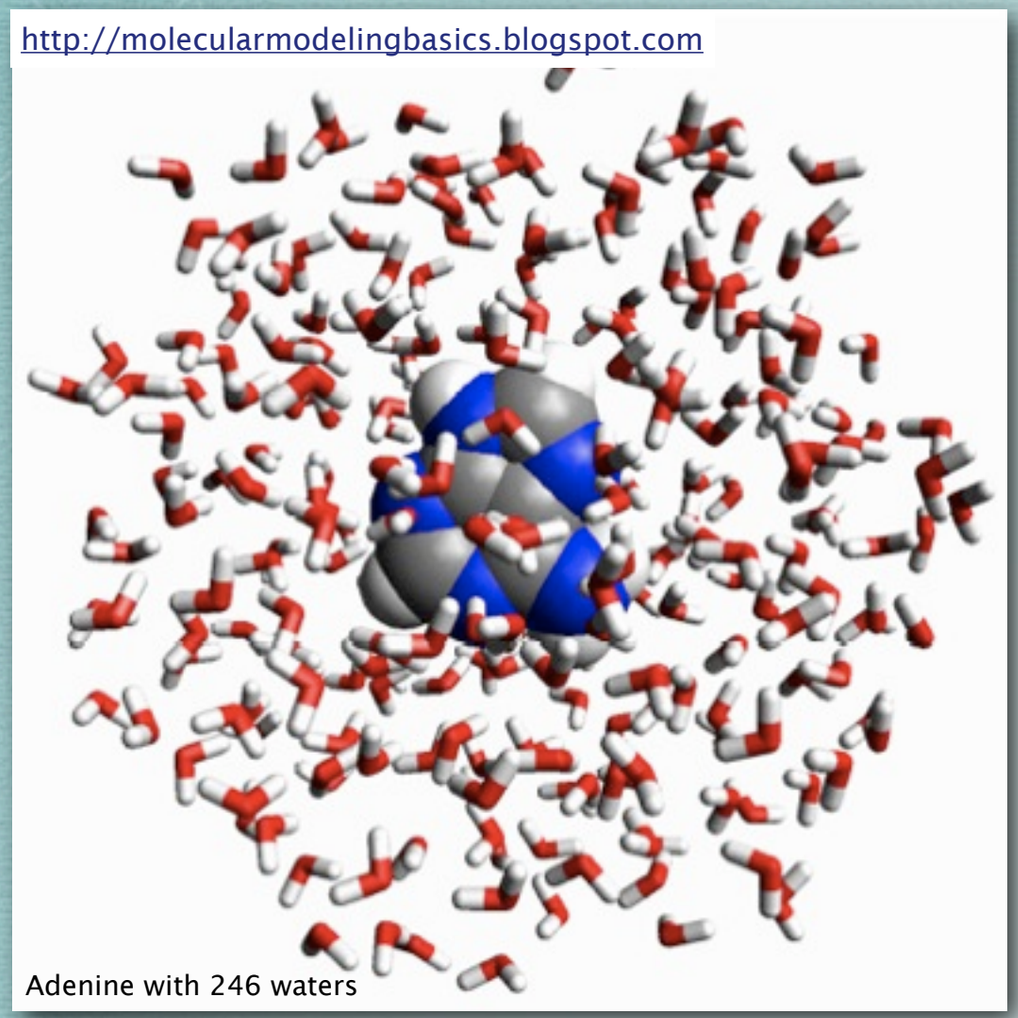
[1]Laboratoire de Spectroscopie Ultrarapide, EPFL, CH-1015 Lausanne
[2]Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen
[3]SwissFEL, Paul Scherrer Institut, CH-5232 Villigen
[4]Laboratoire de Chimie et Biochimie Computationelles, EPFL, CH-1015 Lausanne

LSU laboratoire de spectroscopie ultrarapide

EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

PAUL SCHERRER INSTITUT PSI

What are we interested in ?



➡ Investigating excited state dynamics of species in solution to try to understand how energy moves in these strongly interacting systems

➡ How does the solvent interaction play a role in the relaxation of these systems ?

➡ How does the excitation perturb the structure and how does this structural change affect the energy transfer and relaxation ?

➡ Can we relate this information to functionality ?

How do these things work ?

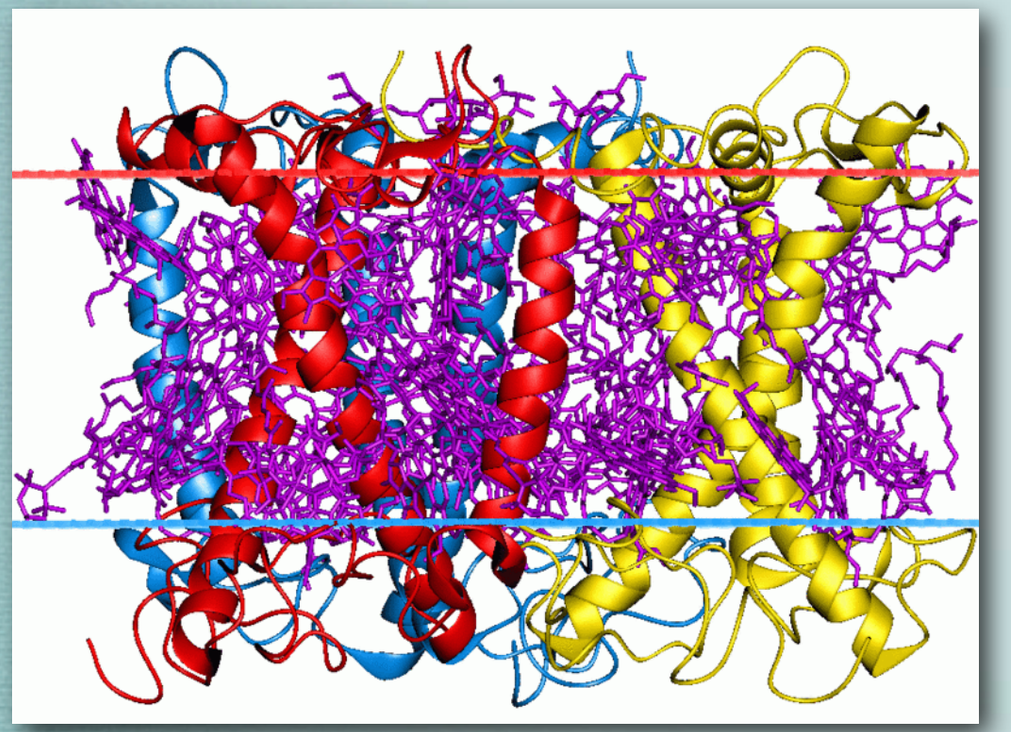
Can we extrapolate from model systems to understand more complicated systems ?

What will be our probe ?

Is function structure or dynamics ?

Structure

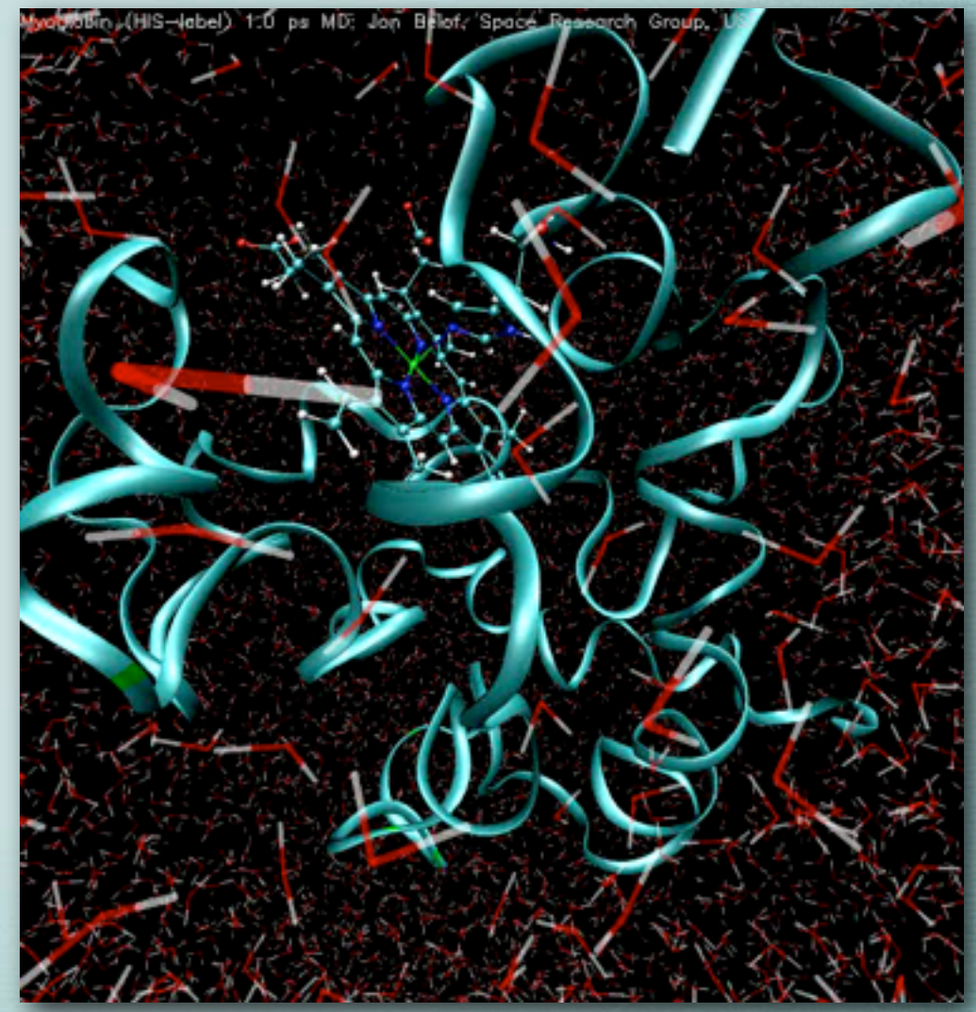
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR



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

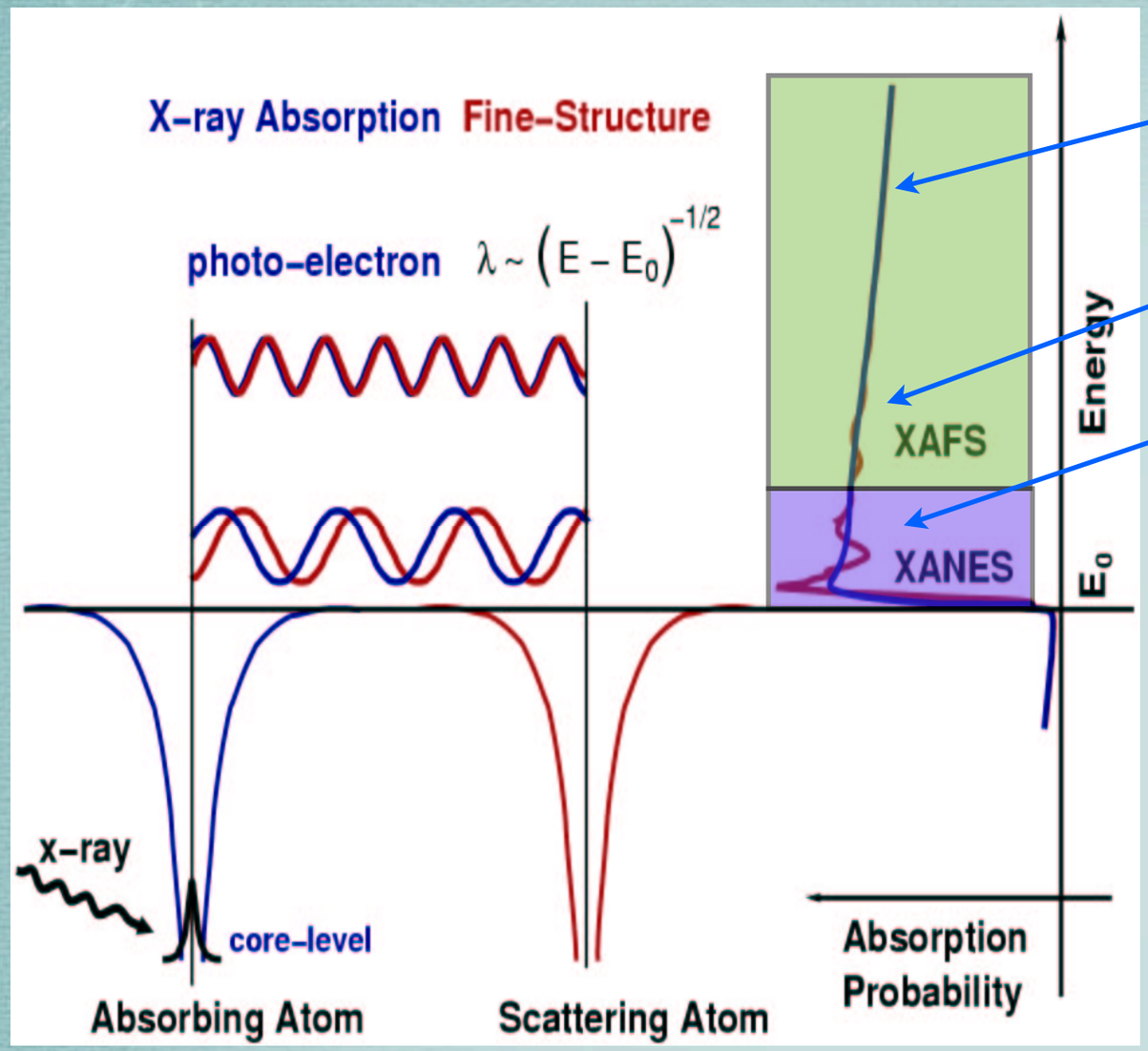
Dynamics

- 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)

X-ray absorption spectroscopy: Retrieving structure



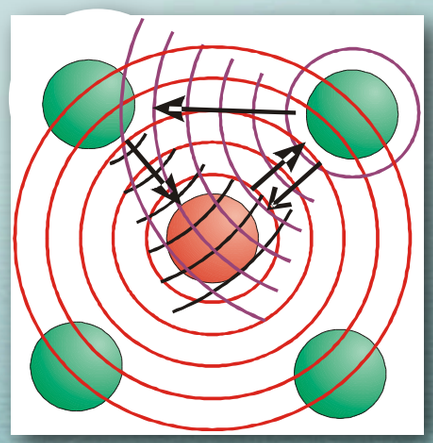
atomic background absorption contribution

Extended x-ray absorption fine structure (EXAFS)

X-ray absorption near-edge structure (XANES)

EXAFS: distances to neighbouring atoms

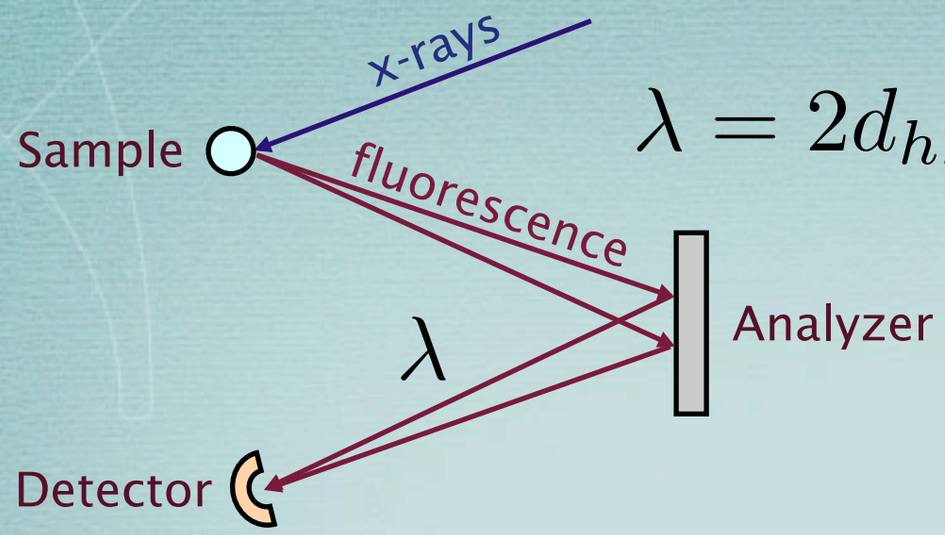
XANES: oxidation state, geometry, coordination environment



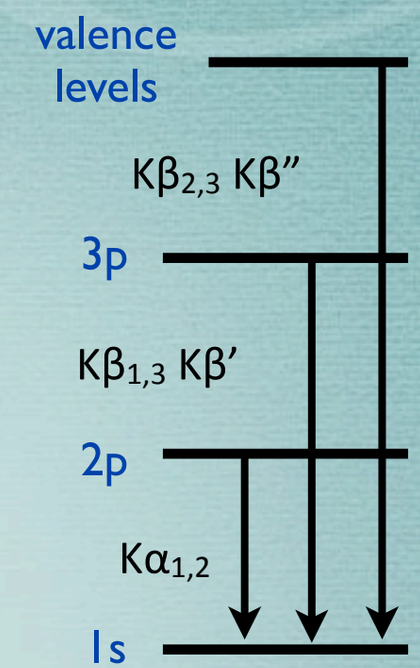
This works in any medium and is element-specific

C.J. Milne, Stockholm Workshop 2012

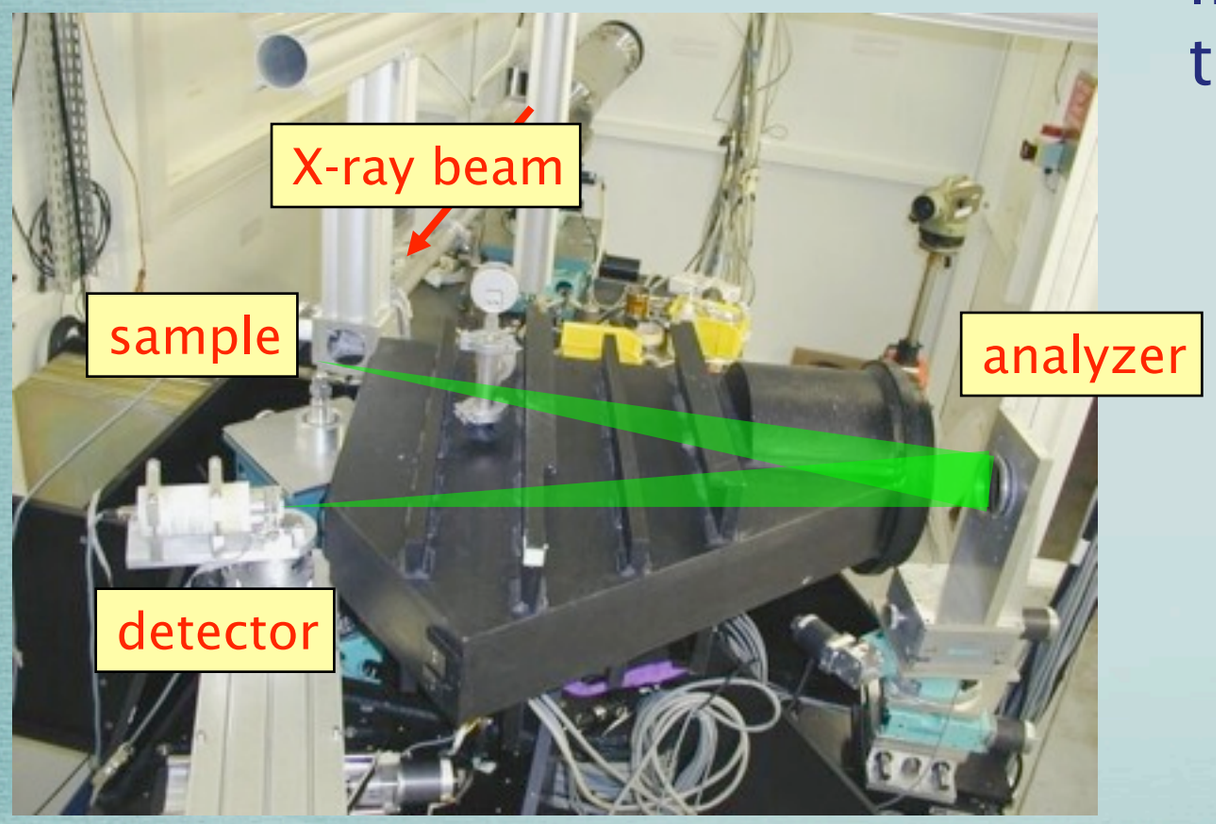
X-ray emission: Retrieving electronic information

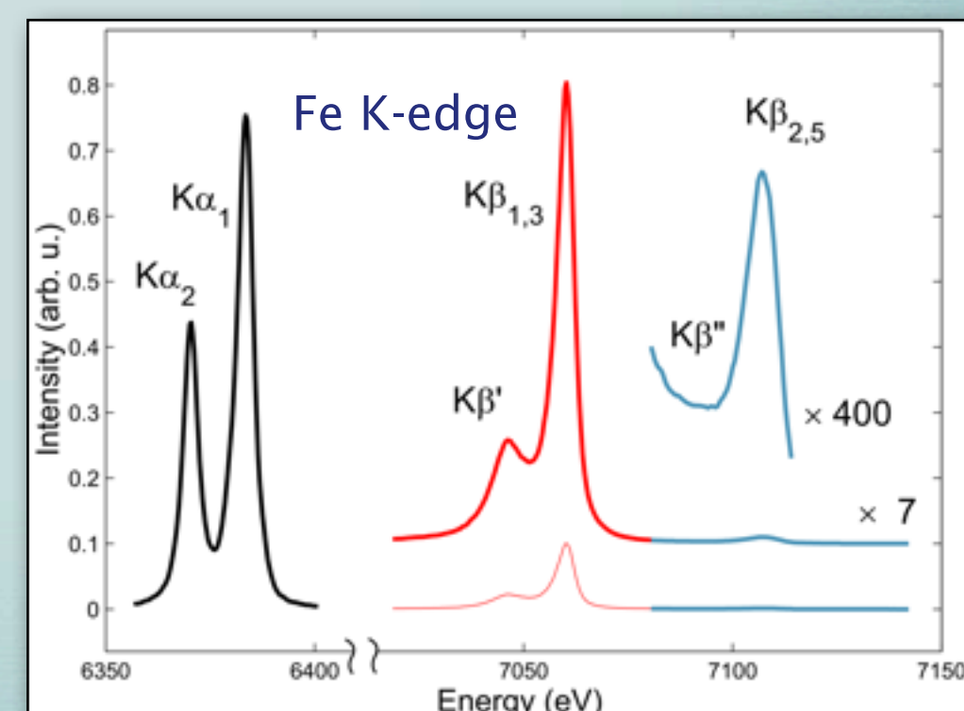


$$\lambda = 2d_{hkl} sin\theta_B$$



As with optical spectroscopy you will see all the emission lines if you're above the absorption edge



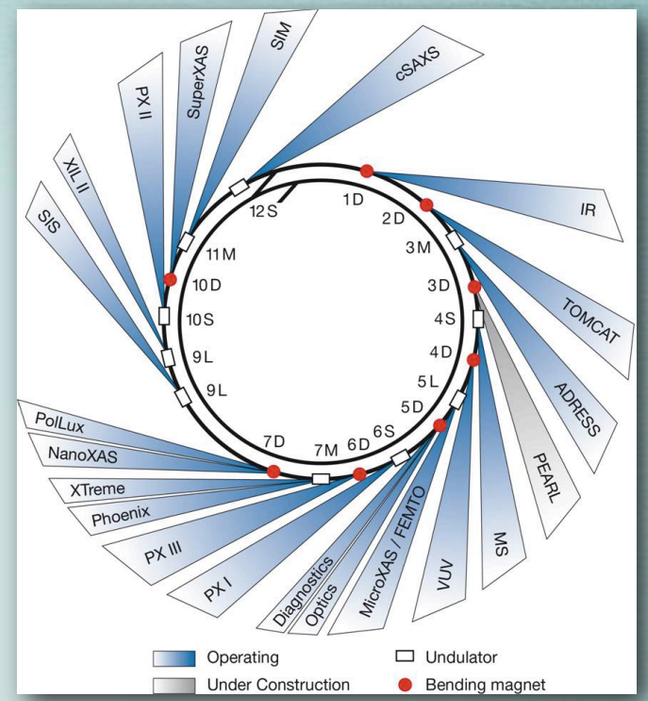


P. Glatzel et al. *Coord. Chem. Rev.* **249**, 65 (2005)
G. Vankó et al. *JPCB* **110**, 11647 (2006)

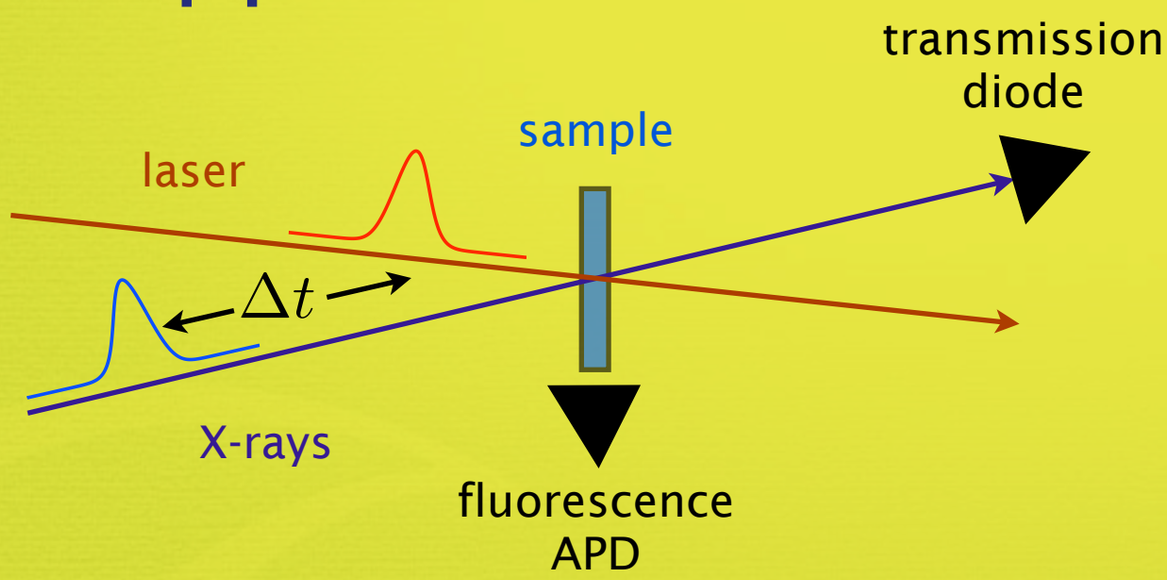
XES gives information on the occupied electronic states

X-ray source: The Swiss Light Source at PSI

3rd generation synchrotron light source located one hour from Zurich (2.4 GeV)



Pump-probe measurements



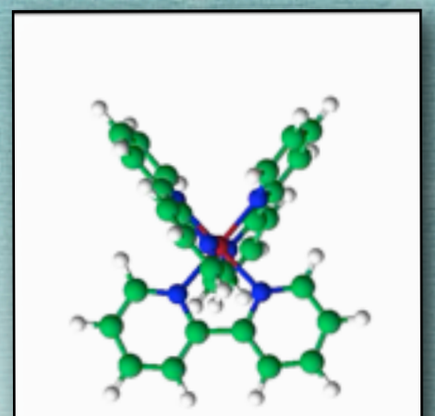
SuperXAS
- SuperBend from 4.5 to 35 keV
- Si(111) monochromator
- X-ray emission spectrometers
- 10^{11}-10^{12} photons/second

PHOENIX beamline
- in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb mono crystals
- micro-focus capability (< 1μm²)
- 10^{11}-10^{12} photons/second

microXAS beamline
- in-vacuum undulator (4-20 keV)
- Si (111), Ge(111) & Si(311) mono crystals
- micro-focus capability (< 1μm²)
- 10^{12} photons/second

The FEMTO slicing source at microXAS
- 4 to 20 keV
- bandwidth 1%, 0.03%, 0.015%
- 140 ± 30 fs x-ray pulse duration
- timing stability of <30 fs RMS over days
- 10^5 photons/second @ 1% BW

Investigating spin-crossover dynamics



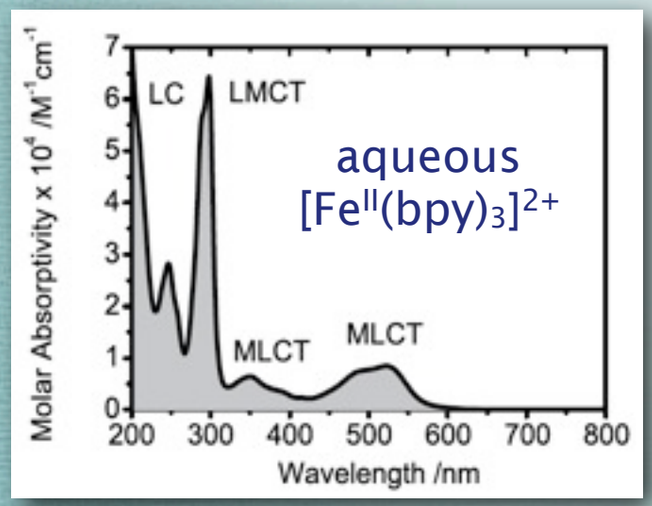
$[Fe^{II}(bpy)_3]^{2+}$

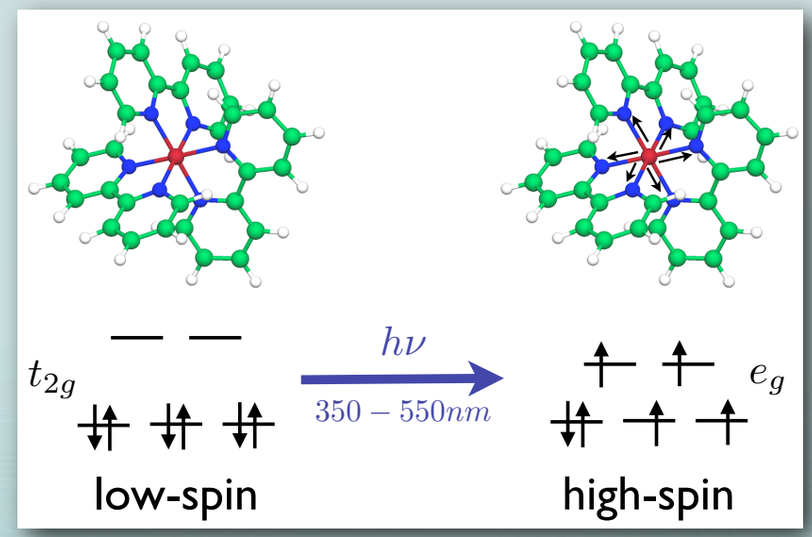
Spin-crossover phenomenon: a transition from a low-spin ground state to a high spin excited state

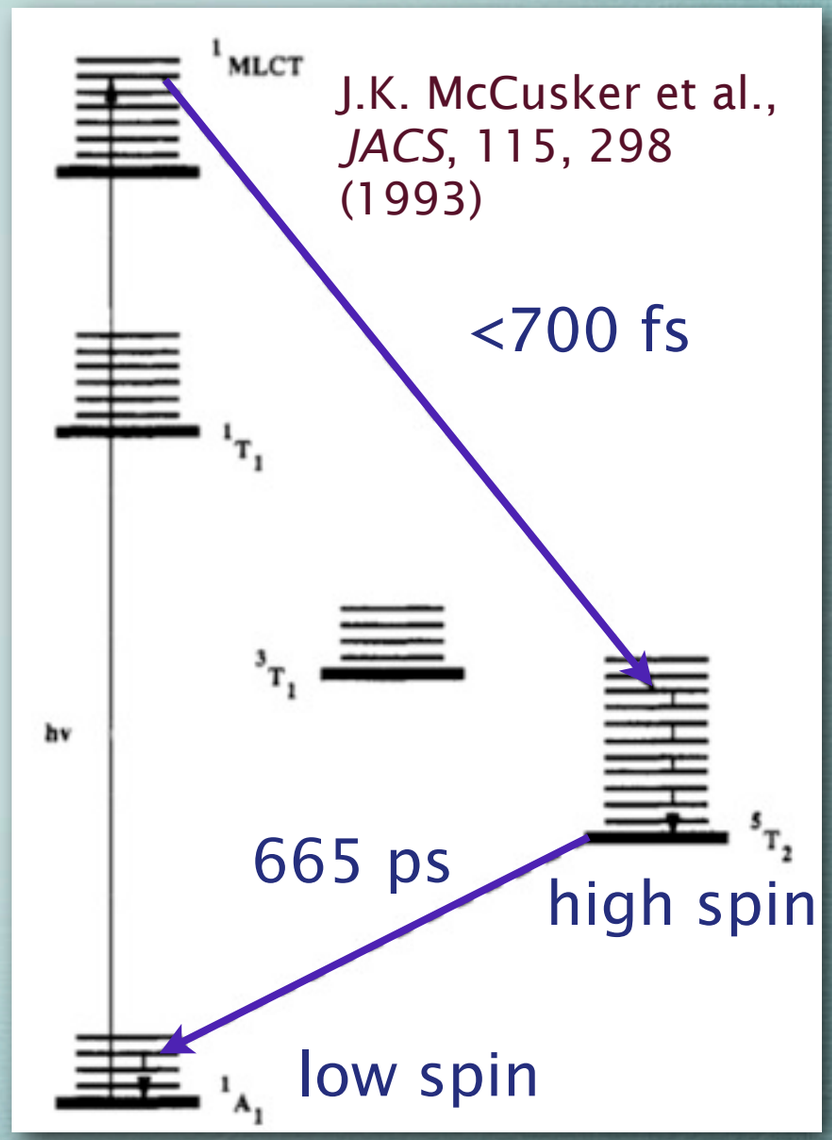
- can be induced by temperature or light
- Fe(II) compounds represent a general class of spin-crossover systems

Applications:

- ultrafast magnetism
- bistable devices
- model biological systems (heme proteins)

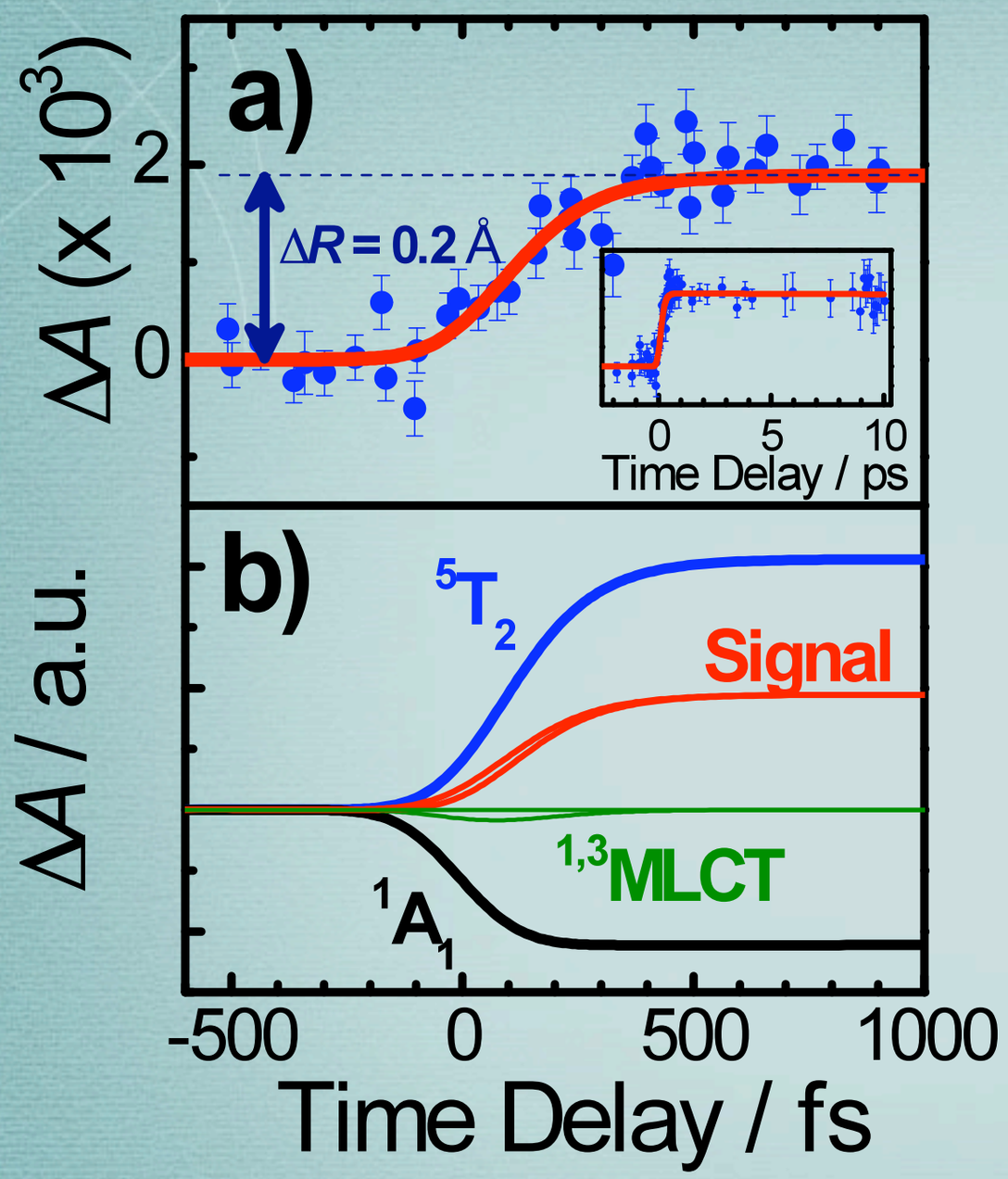


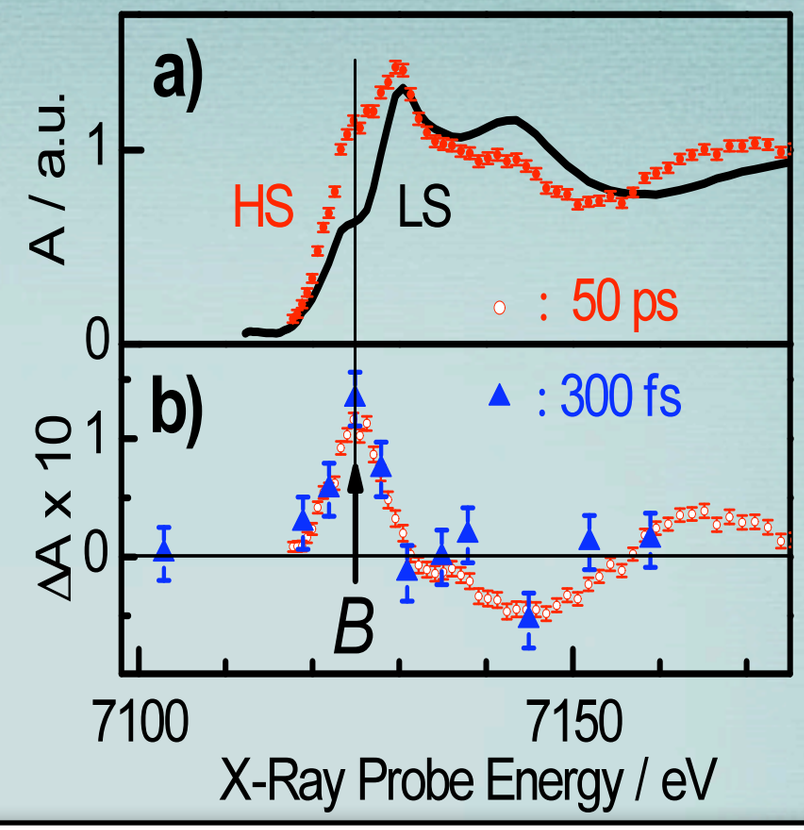




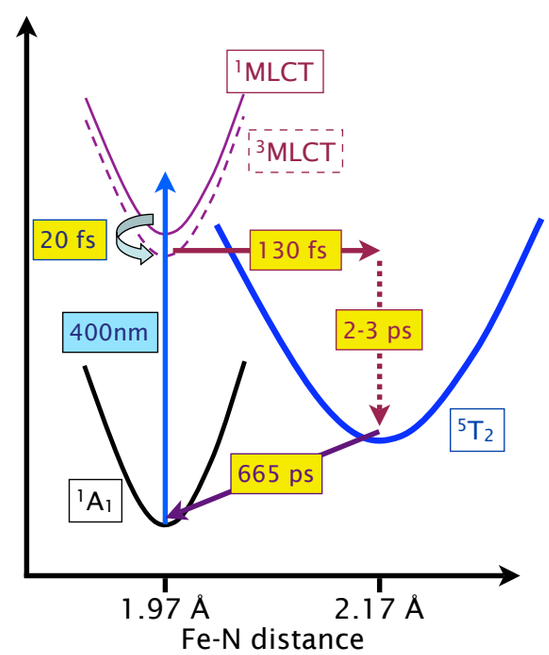
$[Fe^{II}(bpy)_3]^{2+}$ requires optical excitation and shows fs to ns relaxation dynamics

Spin crossover dynamics: Ultrafast XAS results



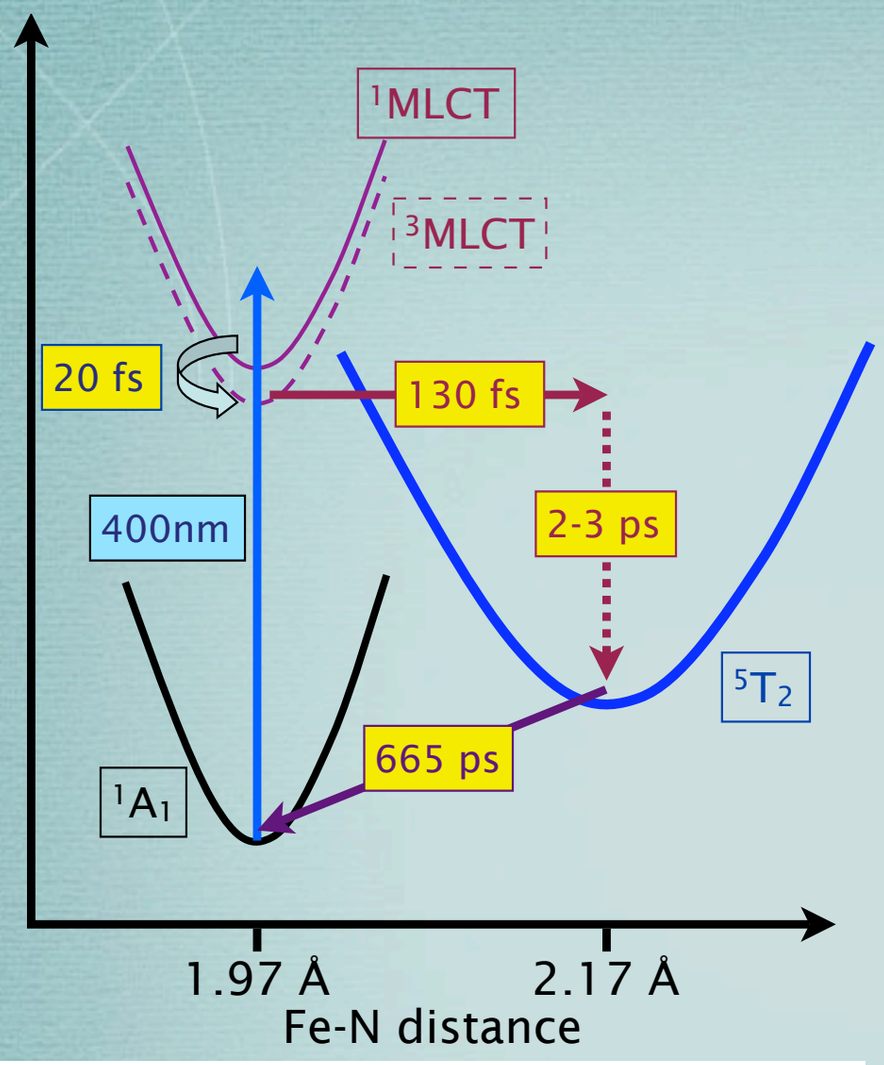


The molecule arrives in the high-spin state directly from the ^{3}MLCT in ~150 fs



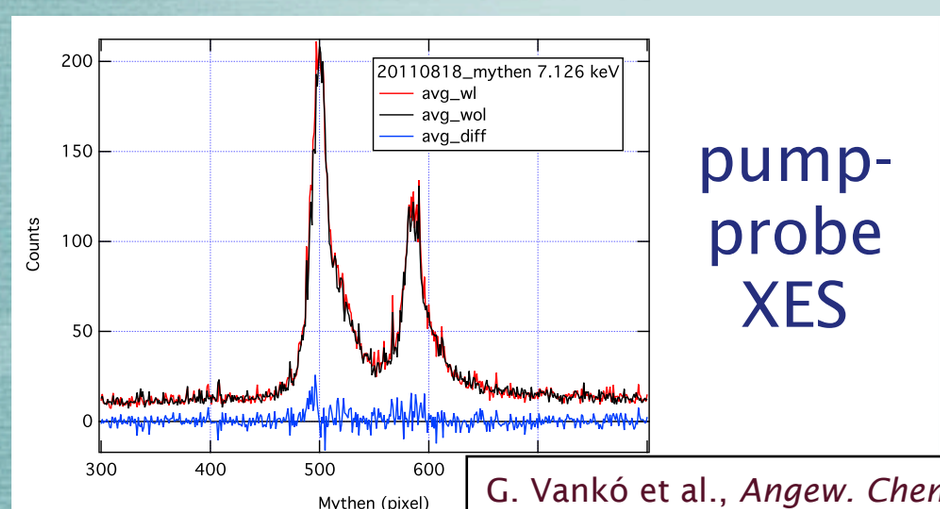
W. Gawelda et al. *JACS* **129**, 8199 (2007)
W. Gawelda et al., *Phys. Rev. Lett.*, **98** 057401 (2007)
Ch. Bressler et al. *Science* **323**, 498 (2009)
C. Consani et al. *Angew. Chem. Int. Ed.* **48**, 7184 (2009)

Spin crossover dynamics: SwissFEL possibilities



Picosecond EXAFS has resolved the 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



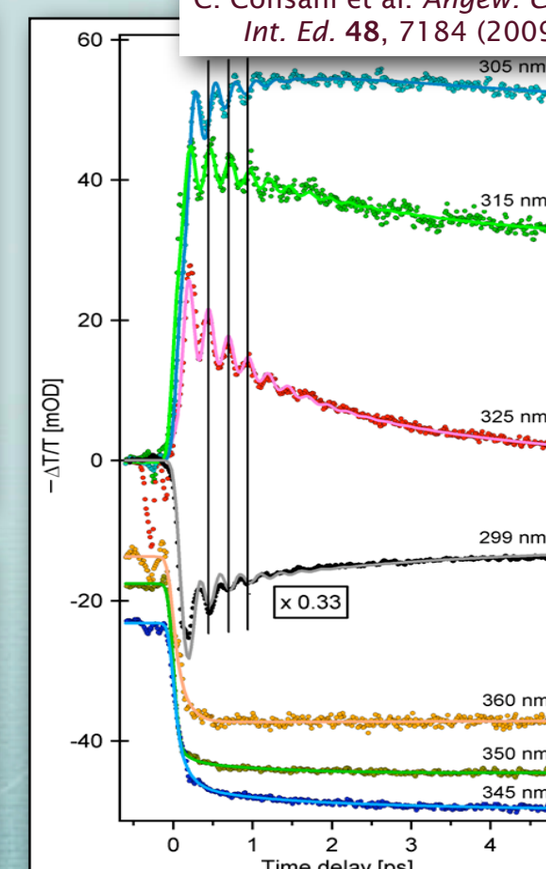
pump-probe XES

G. Vankó et al., *Angew. Chem. Int. Ed.*, **49**, 5910 (2010)

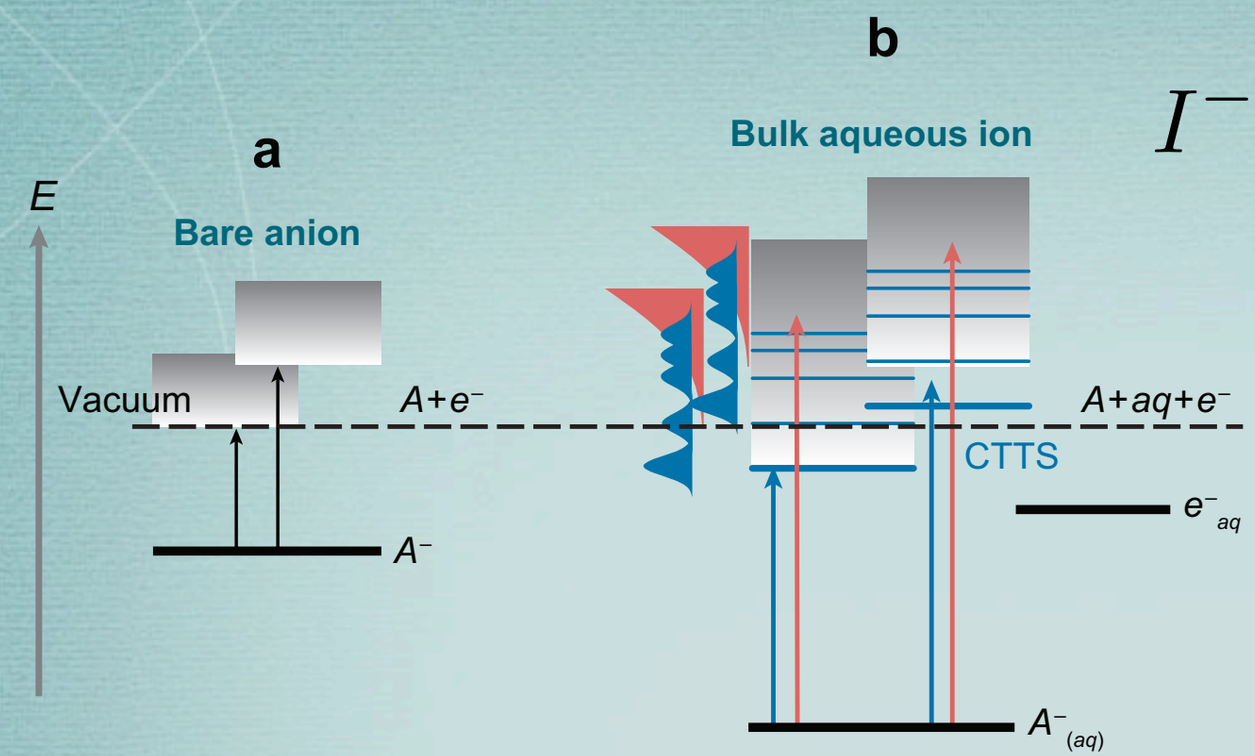
With SwissFEL we should be able to resolve the initial MLCT excitation and follow the relaxation into the high-spin state

<u>Requirements:</u>
<20 fs time resolution
lots of photons
7.126 keV

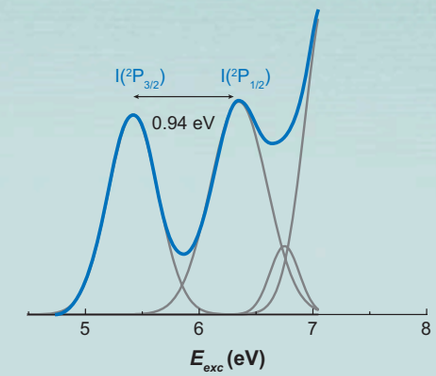
C. Consani et al. *Angew. Chem. Int. Ed.* **48**, 7184 (2009)



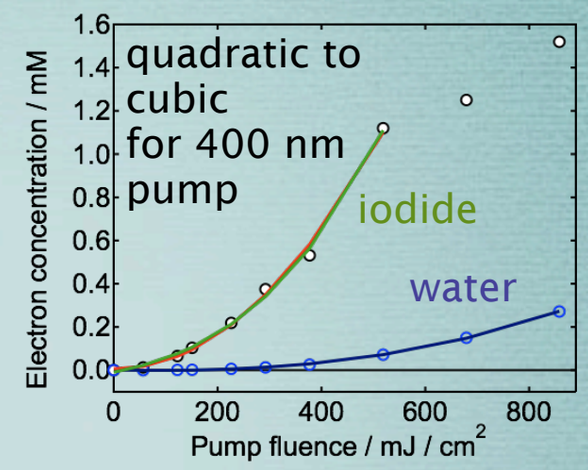
Solvation dynamics: aqueous iodide

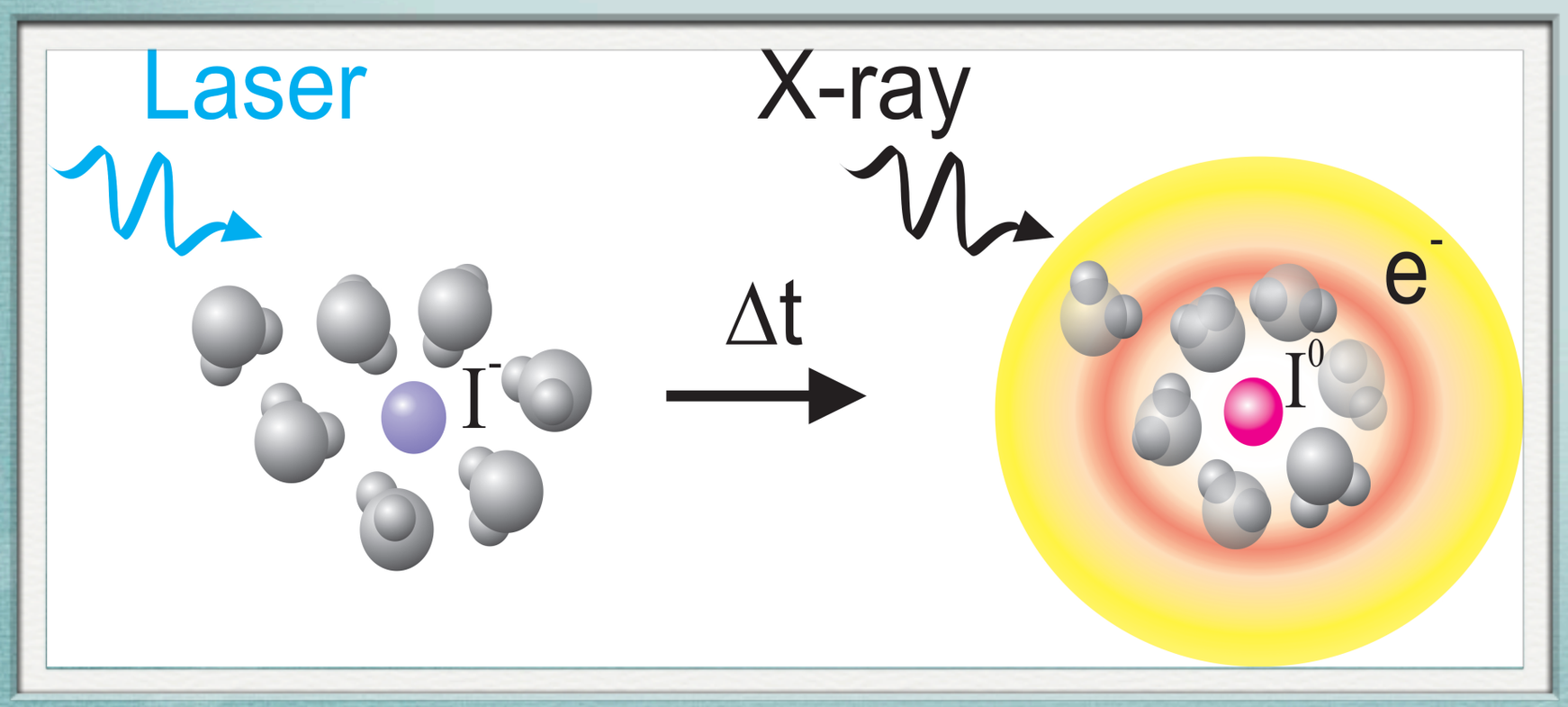


$$I^- + H_2O \xrightarrow[\text{UV}]{h\nu} I^0 + e^- + H_2O$$



Chen & Bradforth
ARPC **59**, 203 (2008)



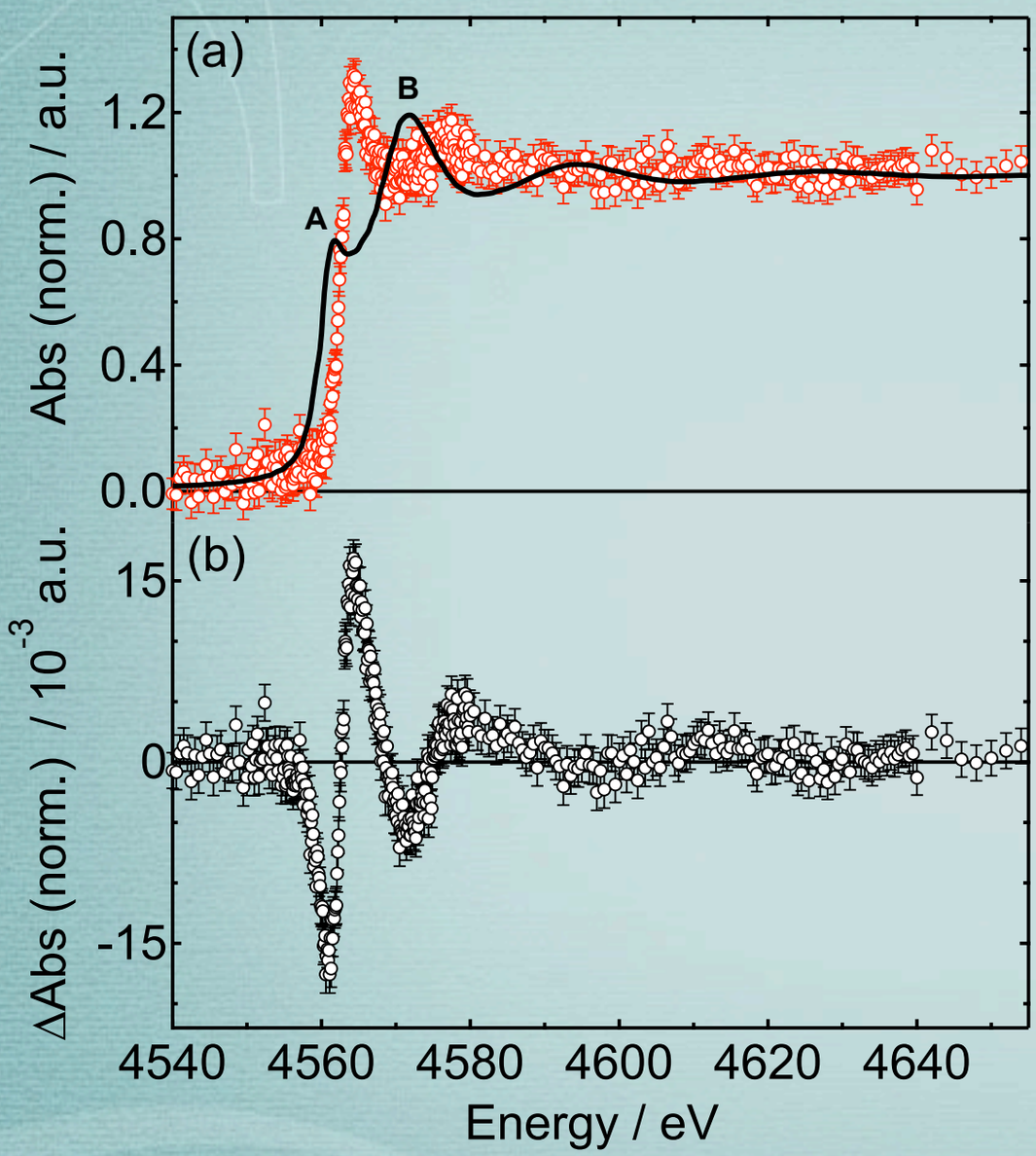


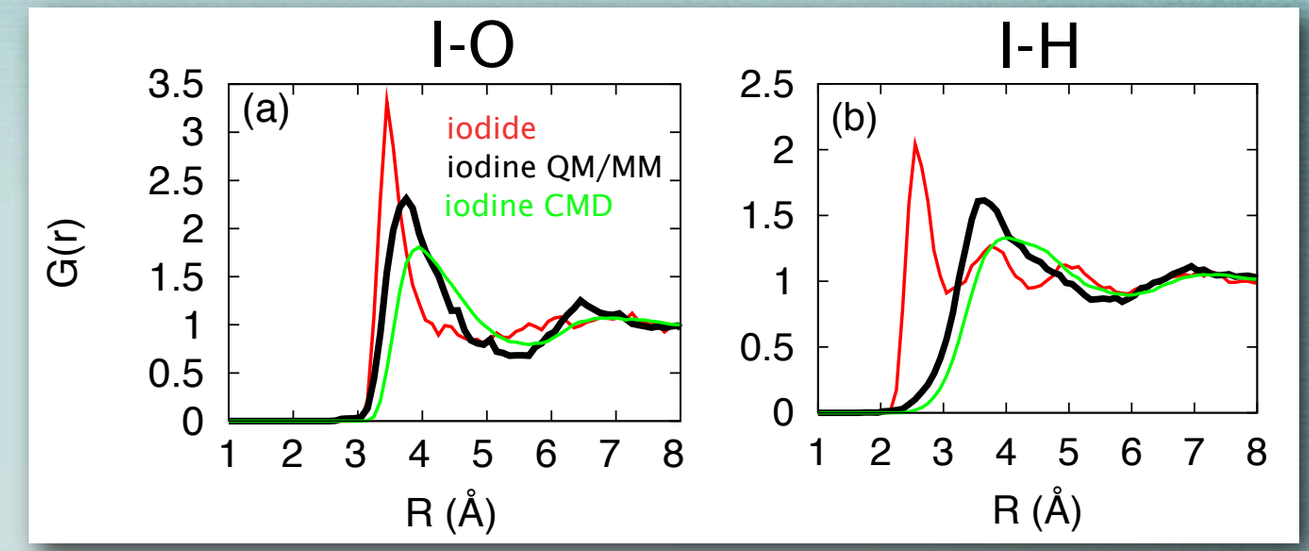
How does the water respond ?

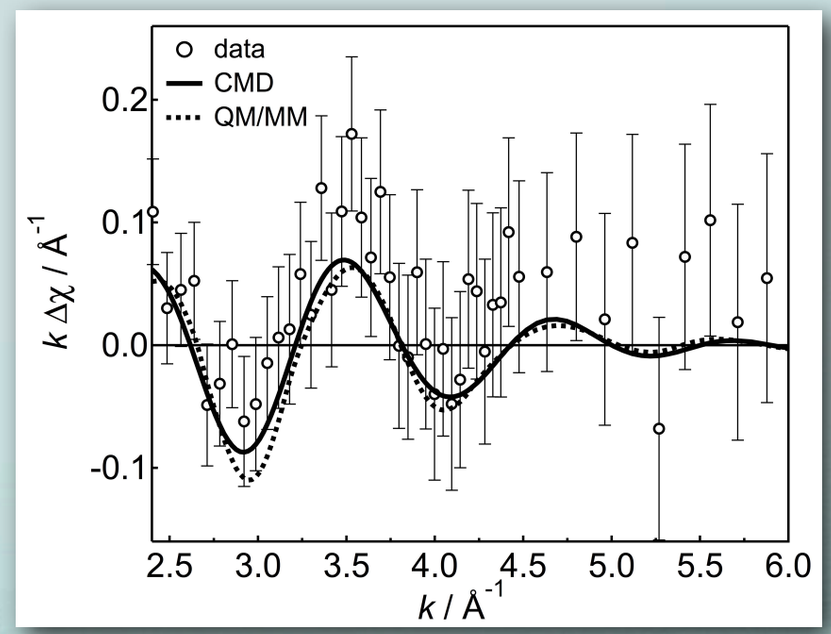
Can we extract electronic information as well as structural ?

Solvation dynamics: water structure around iodine

50 ps after multi-photon excitation at 400 nm







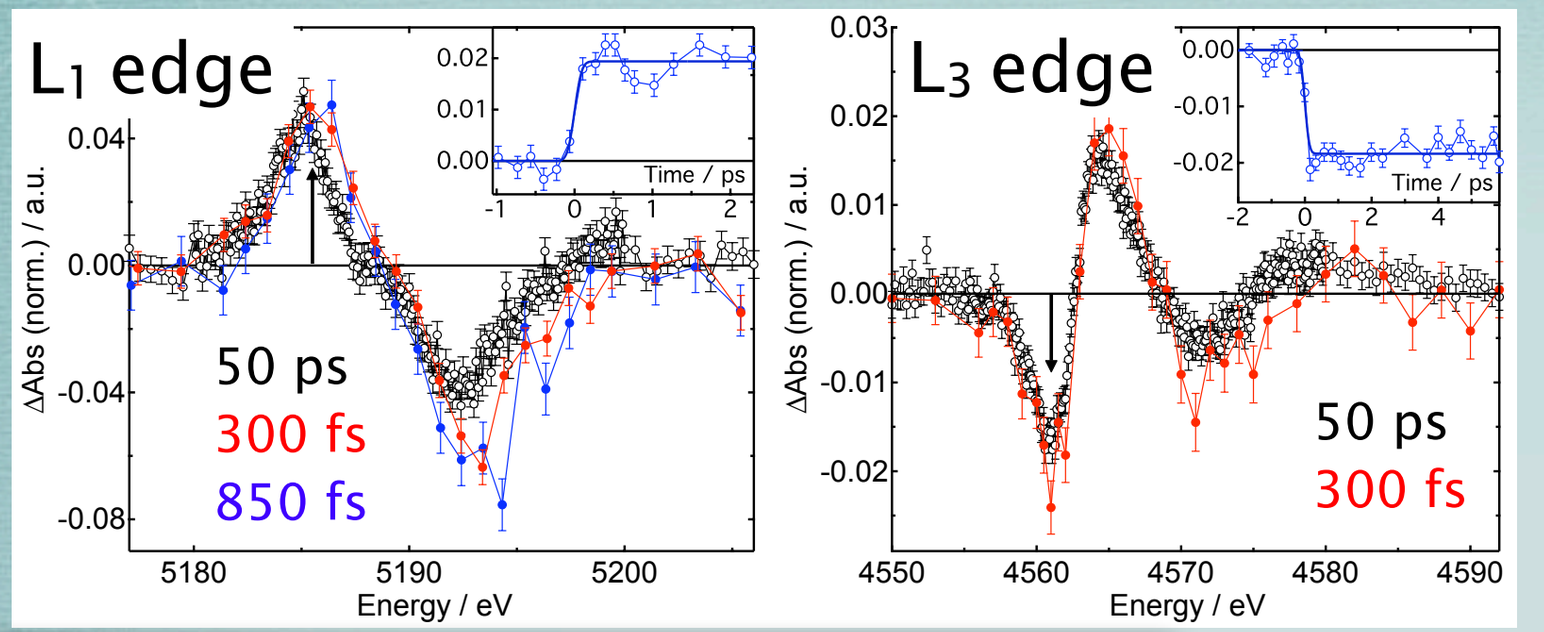
We see an increase in the solvent cage radius of 5-20%

We're seeing hydrophobic cavity formation around I^0

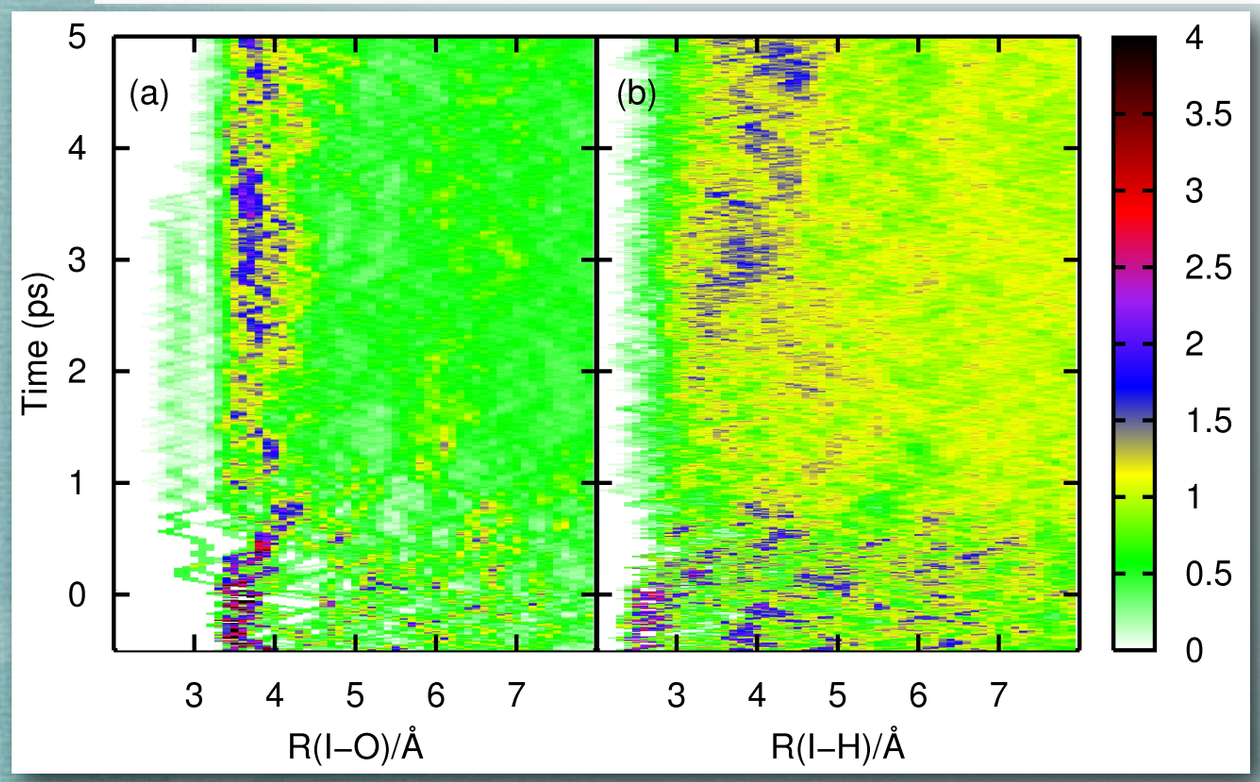
V-T. Pham, T.J. Penfold et al., *JACS*, **133**, 12740 (2011)

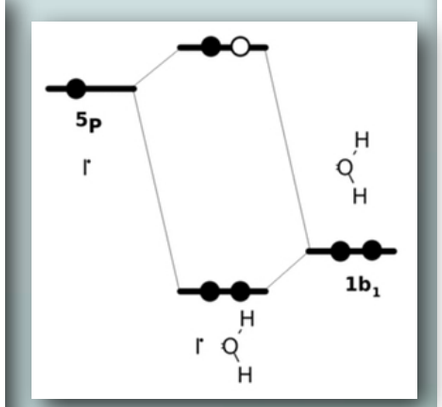
Solvation dynamics: femtosecond timescales

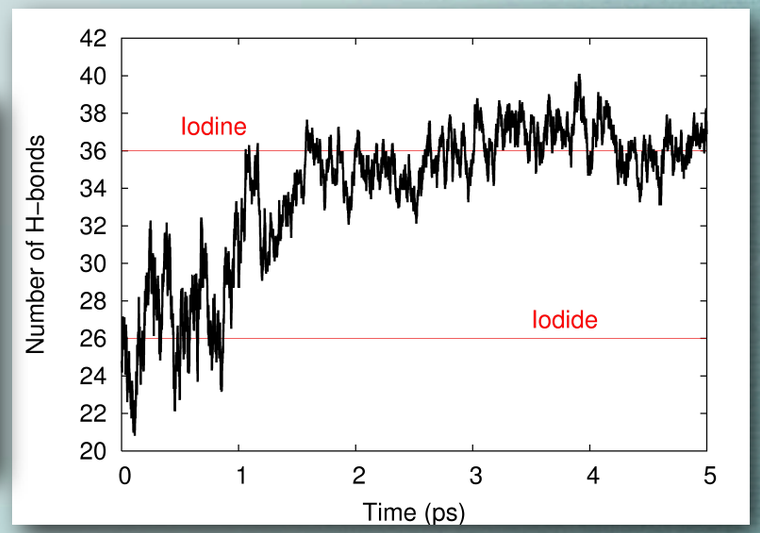
Moving into the femtosecond timescale with sliced x-rays



The fs L_1-edge transient XAS signal shows a broadening to higher energy compared to the signal at 50 ps





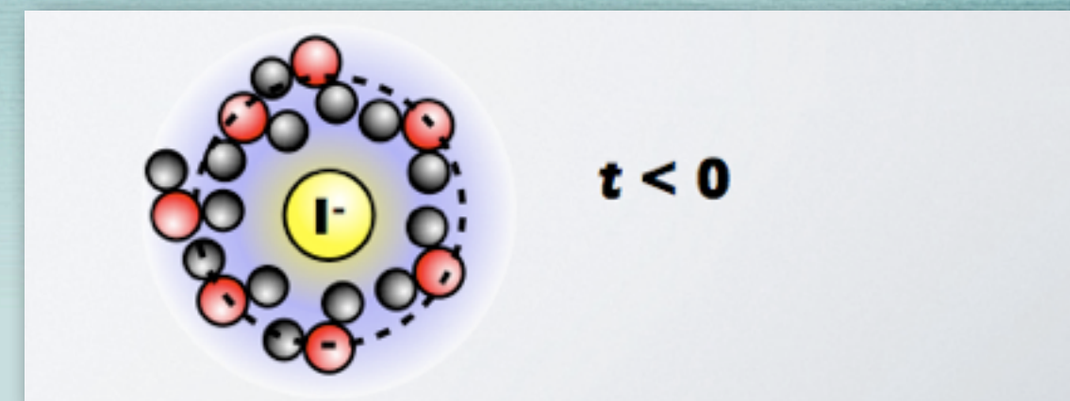


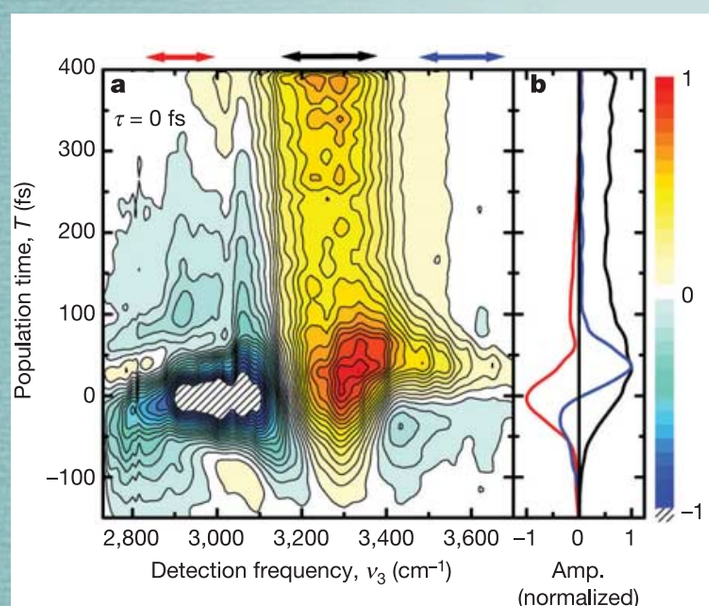
200-300 fs: breakup of first shell, most waters move away but one water moves closer (40% probability)
3-4 ps: the first shell reforms and the lone water recombines with the bulk

V-T. Pham, T.J. Penfold et al., *JACS*, **133**, 12740 (2011)

Solvation dynamics: SwissFEL possibilities

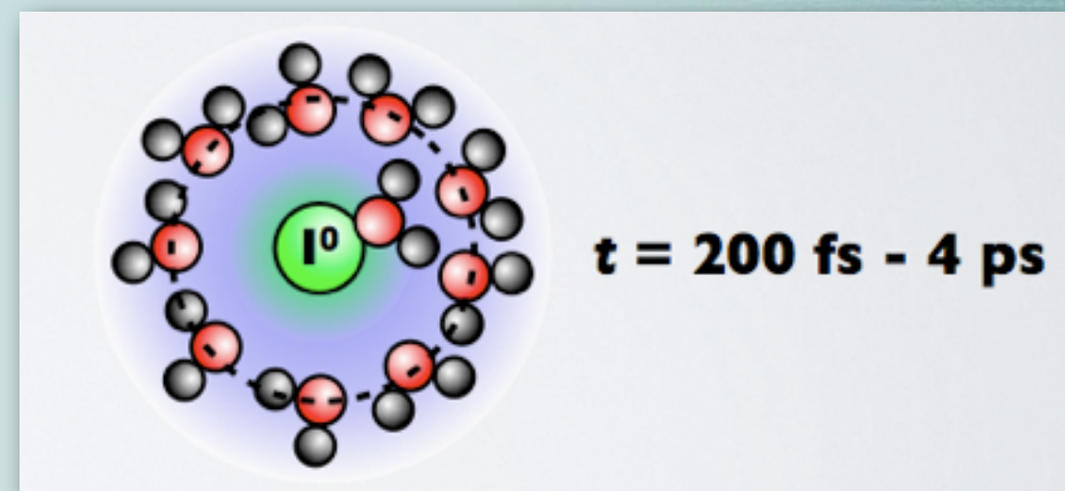
With SwissFEL we should be able to resolve the fast solvation dynamics, perhaps even the structural evolution of the water

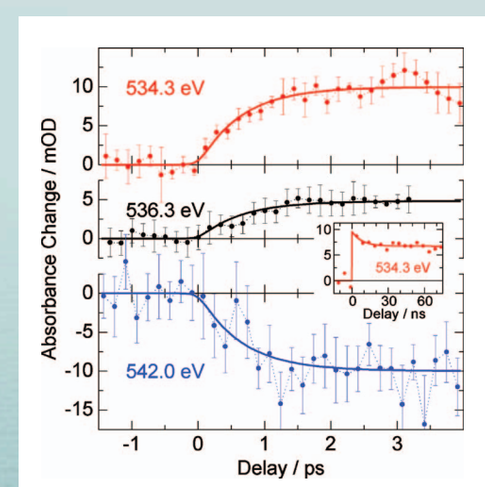




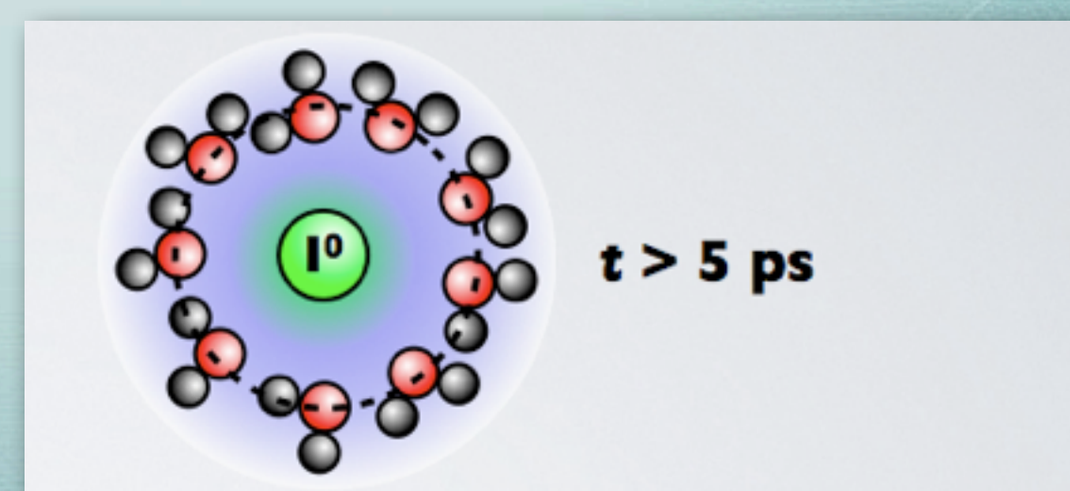
Water is fast
< 50 fs energy redistribution from O-H stretch

M. Cowan et al., *Nature*, **434**, 199 (2005)





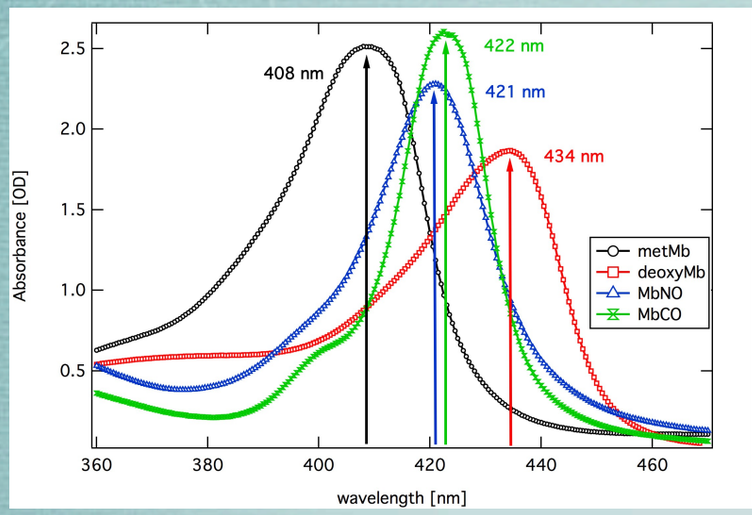
H. Wen et al., *JCP*, **131**, 234505 (2009)



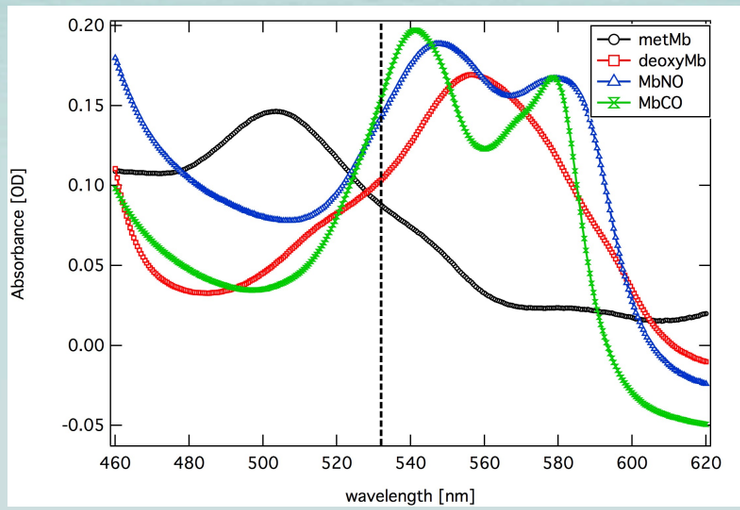
Requirements:
<10 fs time resolution
lots of photons
5.185 keV or 535 eV

Hemoproteins: Investigating biological function

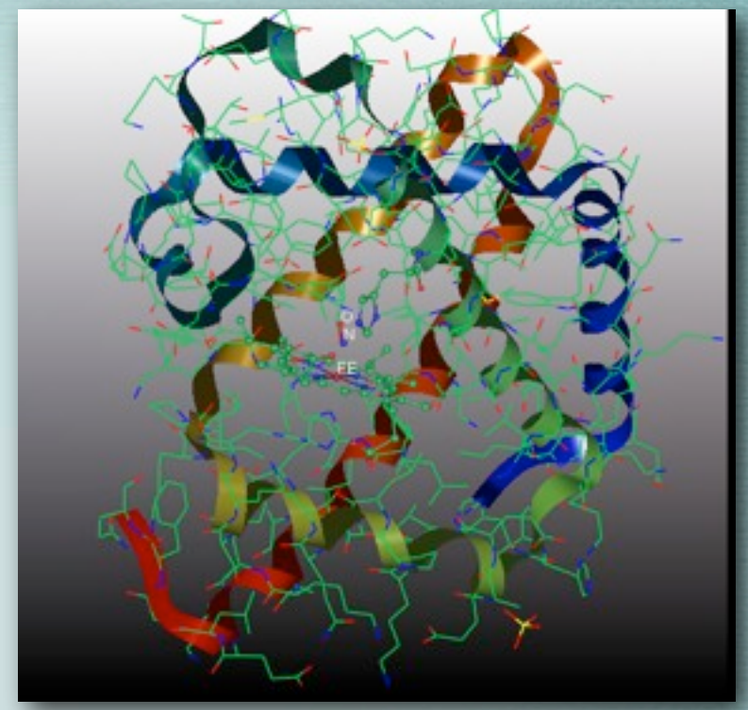
Myoglobin is an oxygen transport protein that has the ability to bind small molecules such as O_2, CO, NO and CN

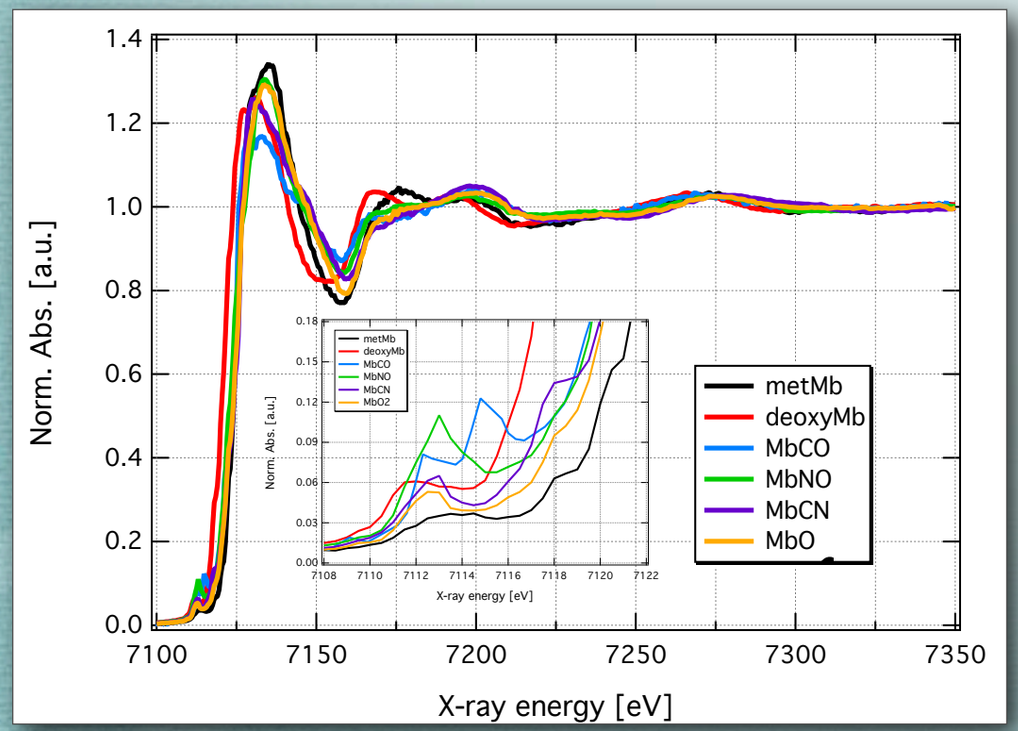


(a) Soret band region



(b) Q-bands region



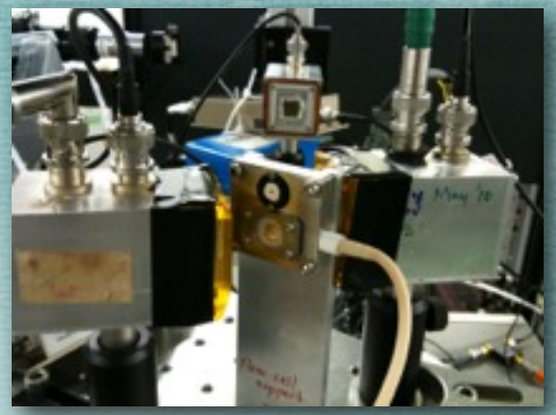


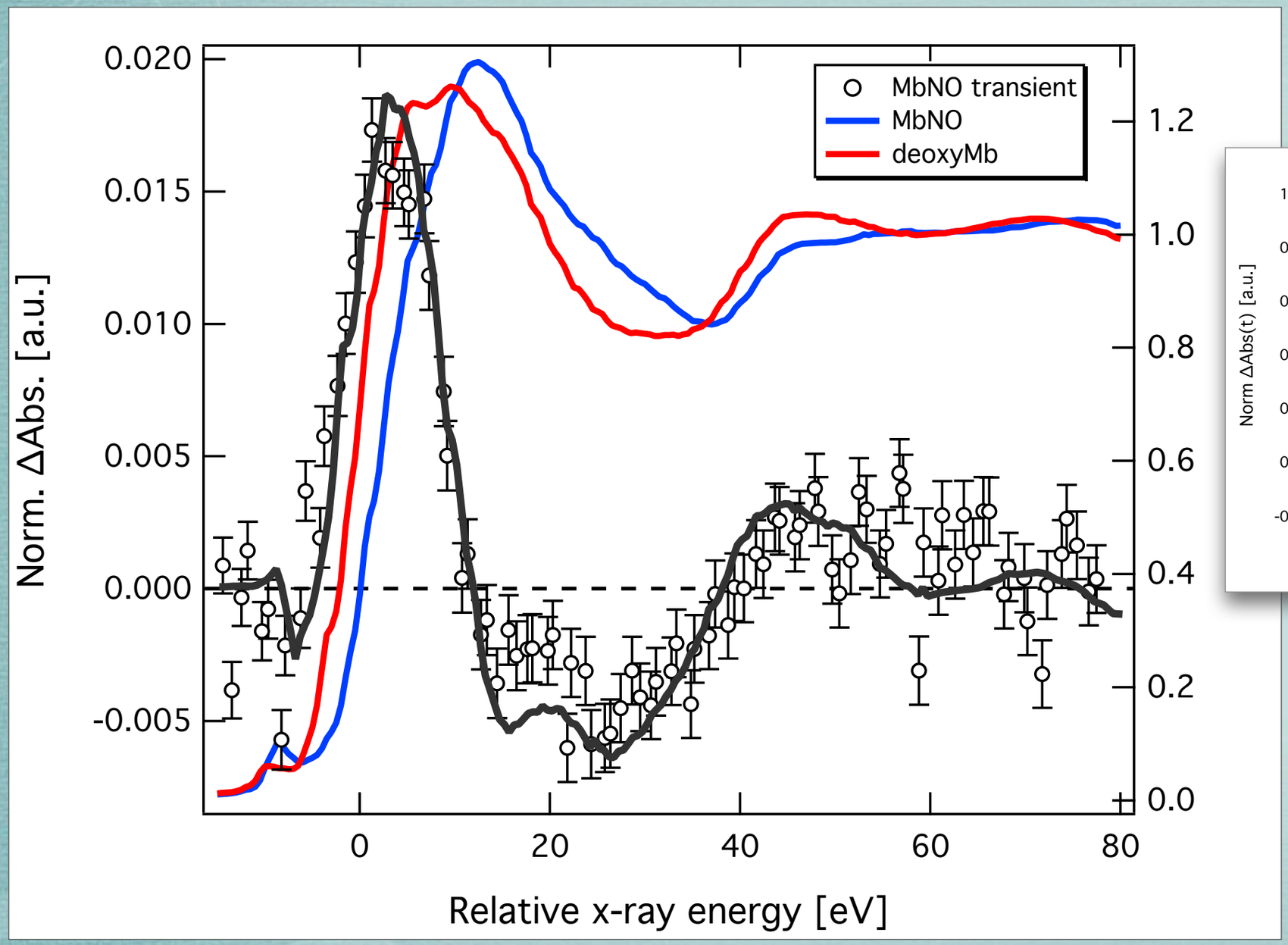
Small changes in the ligand character have profound spectroscopic effects

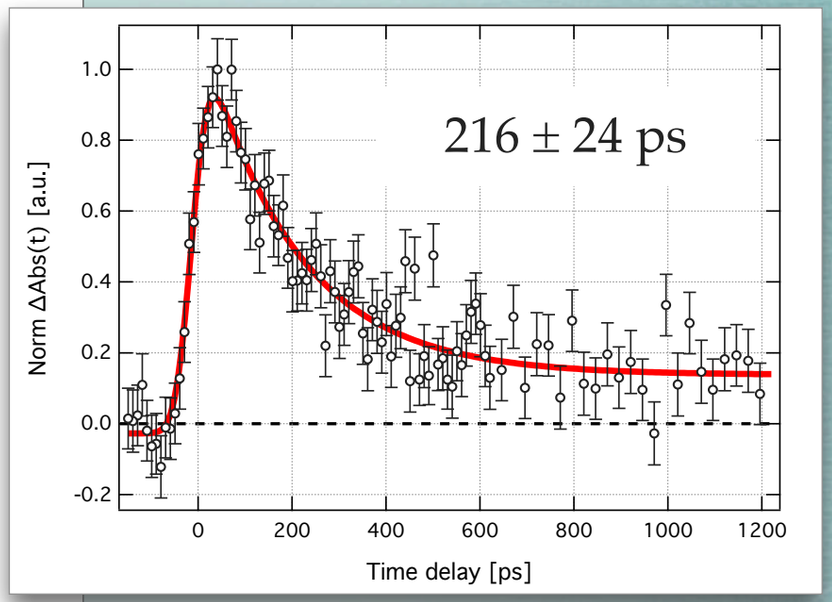
We can knock this ligand off with a photon of green or blue light

Hemoproteins: MbNO pump-probe XAS

4 mM MbNO excited at 532 nm and probed at the Fe K-edge

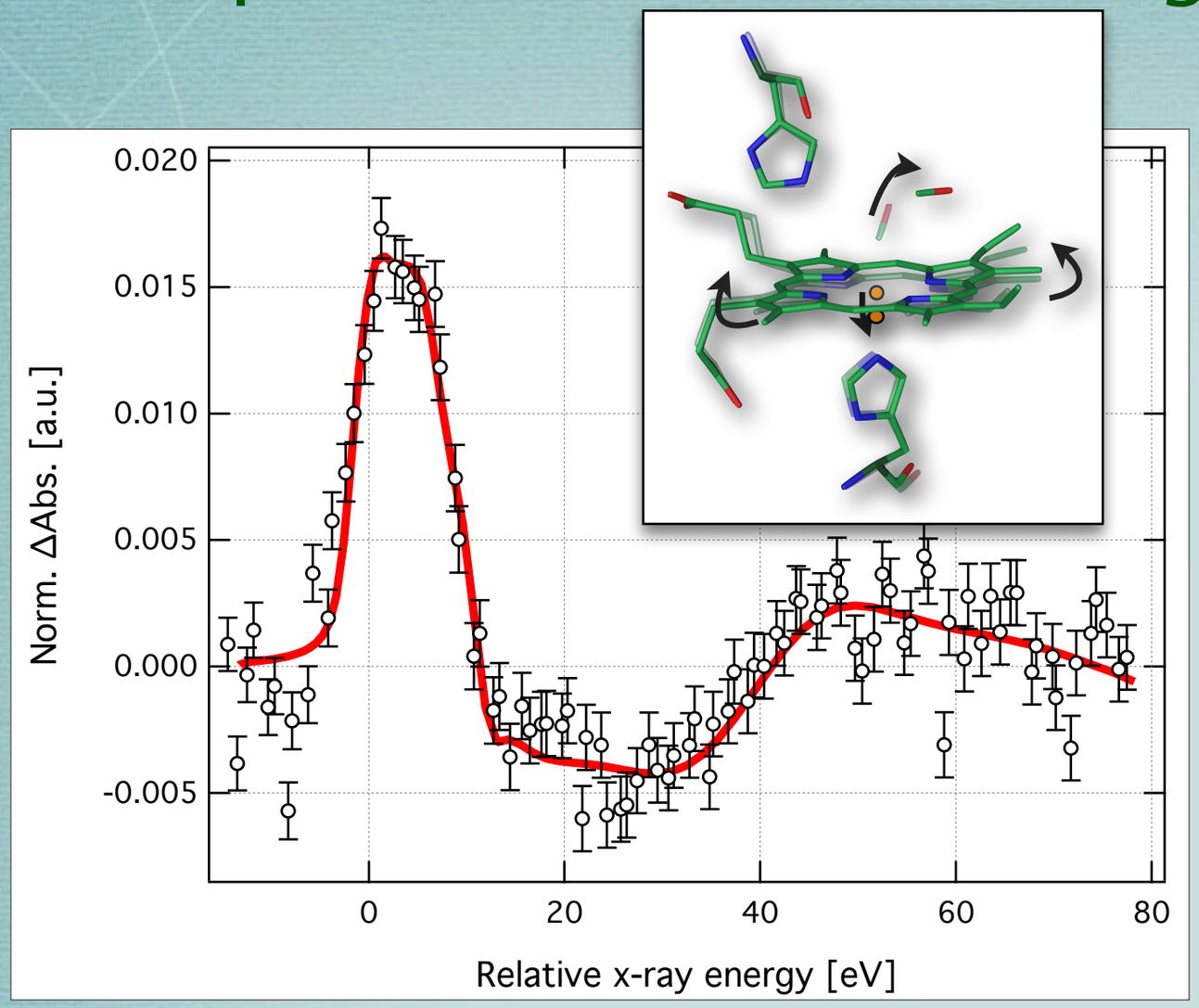






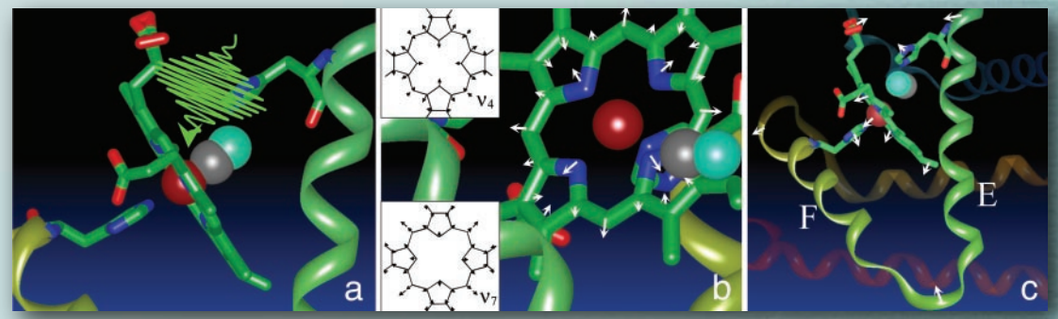
Can we extract further information ?

Hemoproteins: understanding MbNO

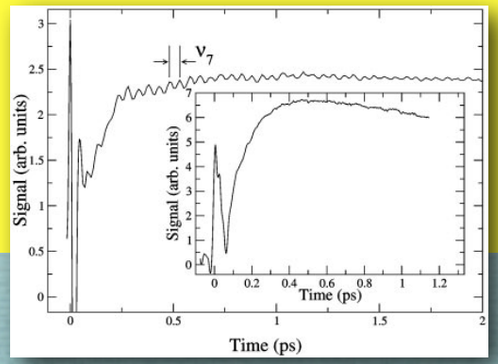


- A domed ligated (6-coordinated) configuration with 30 ps lifetime is unlikely Kruglik et al. *PNAS* **107**, 13678 (2010)
- We can't distinguish between MbNO and MbON

- ☑ Fe move down 0.16 ± 0.03 Å
- ☑ Heme domed ~ 0.03 Å
- ☑ Fe-NO 2.88 ± 0.09 Å
- ☑ Fe-His93 2.23 ± 0.07 Å



With SwissFEL we should be able to resolve the fast geminate recombination and with better S/N resulting in more accurate structures



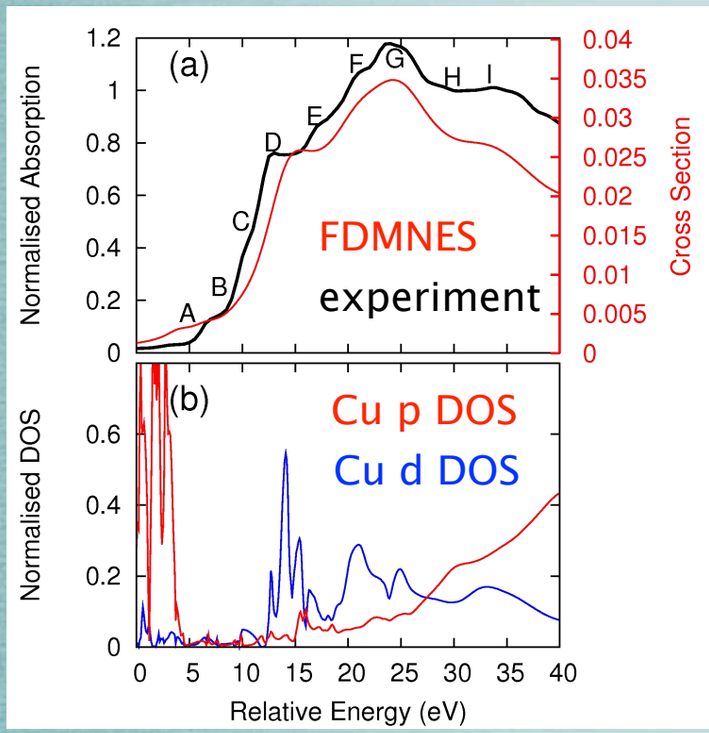
M.R. Armstrong et al., *PNAS*, **100**, 4990 (2003)

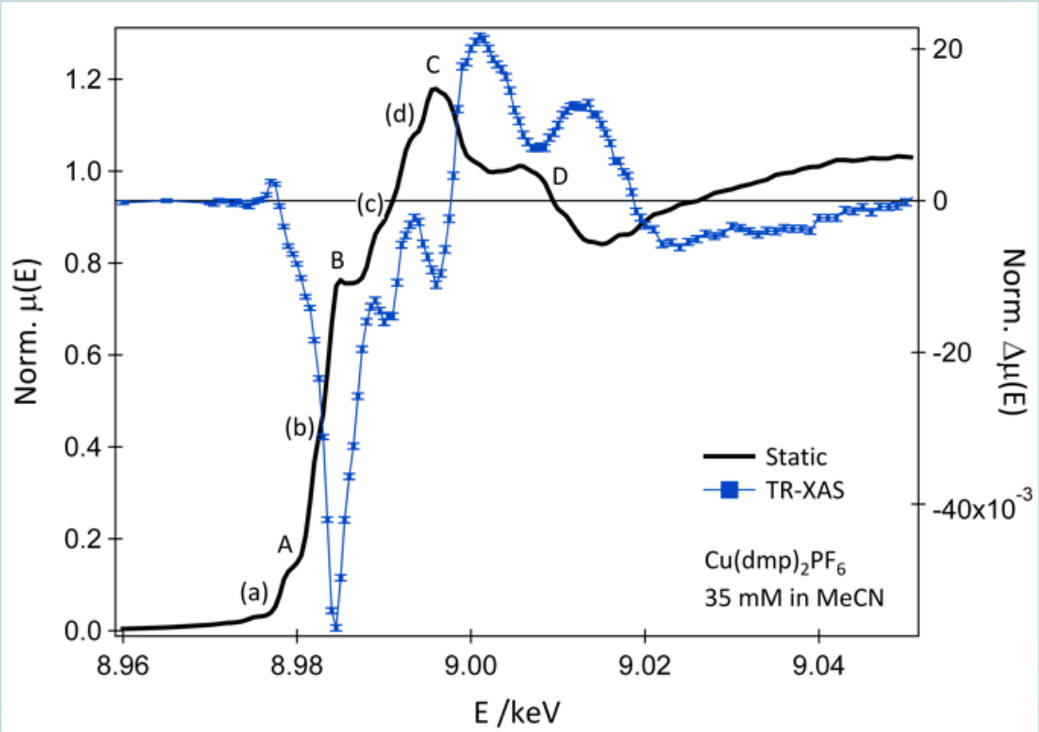
<u>Requirements:</u>
<10 fs time resolution
lots of photons
7.125 keV

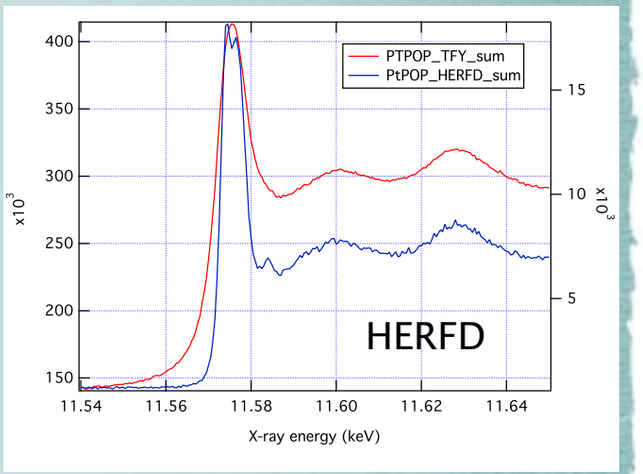
Ultrafast XAS at XFELs: Caveats

- XAS requires some tuneability which is difficult for XFELS
- Nonlinear XAS needs to be avoided (you need to do a probe intensity dependence)
- Synchrotrons are by no means obsolete for time-resolved measurements but significant effort is necessary to move beyond expert users

F.A. Lima, C.J. Milne et al. *Rev. Sci. Instr.* **82**, 063111 (2011)







Theory now badly lags experiment for both ground-state and excited-state spectra

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