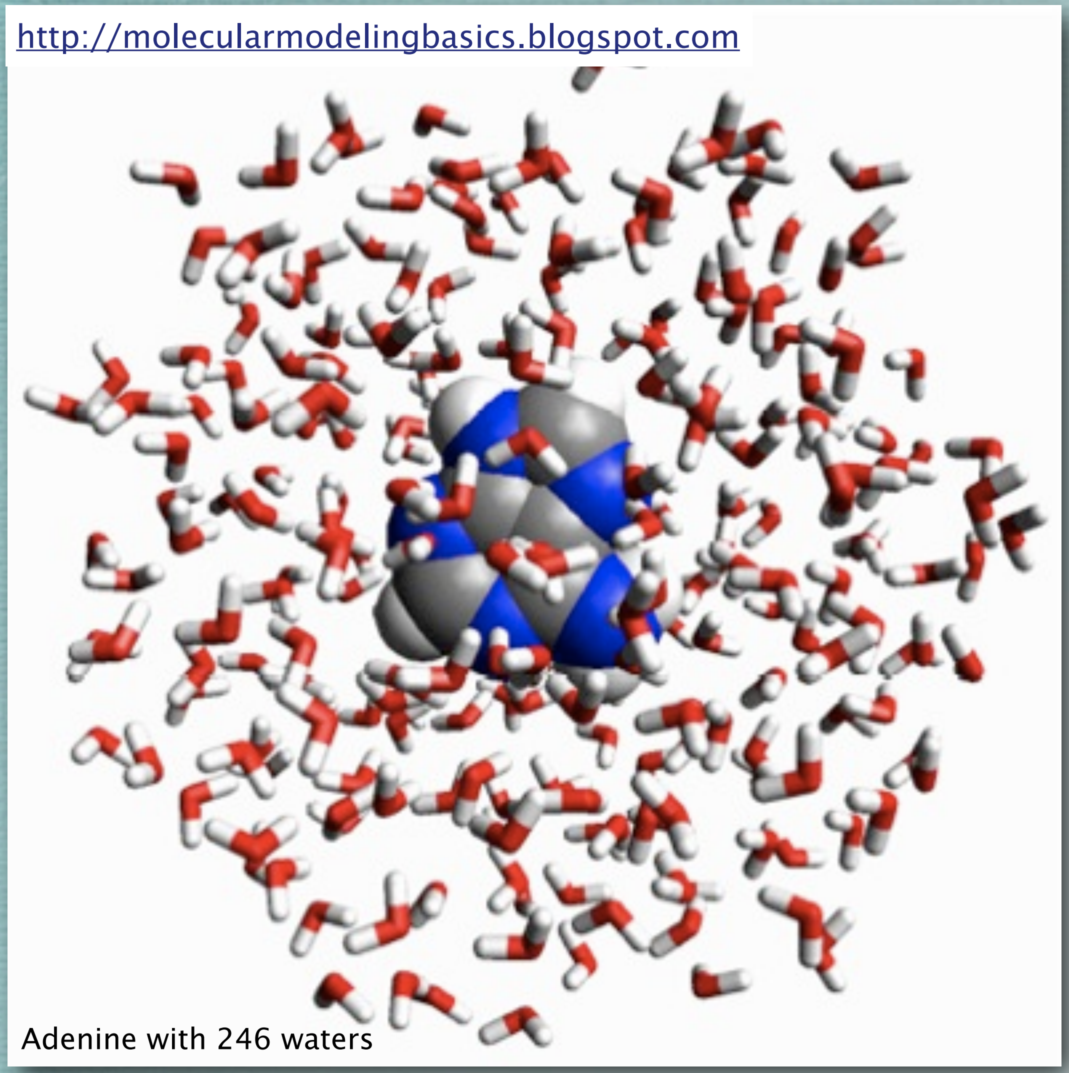
SwissFEL Aramis Instrumentation Workshop: ESA X-ray pump-probe station

Chris J. Milne

Laboratoire de Spectroscopie Ultrarapide,
EPFL, CH-1015 Lausanne

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 ?

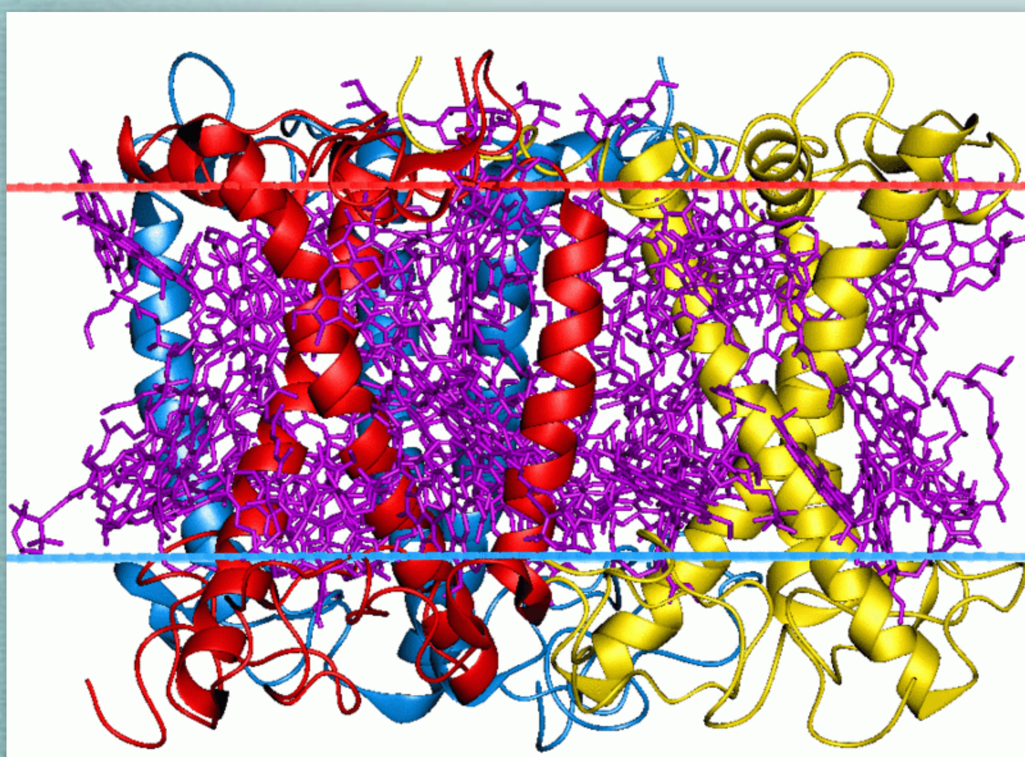
Can we extrapolate from model systems to understand more complicated systems ?

What will be our probe ?

Is function structure or dynamics ?

Structure

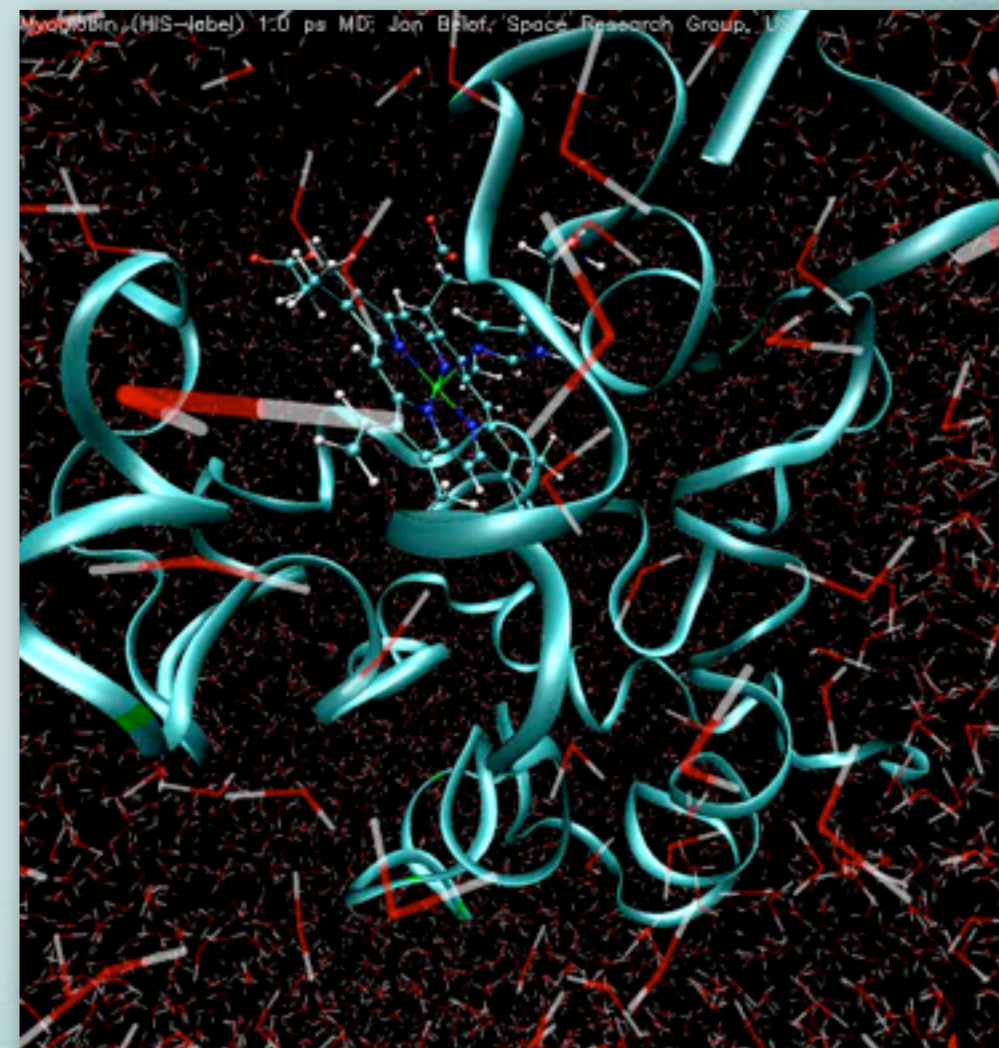
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR



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

Dynamics

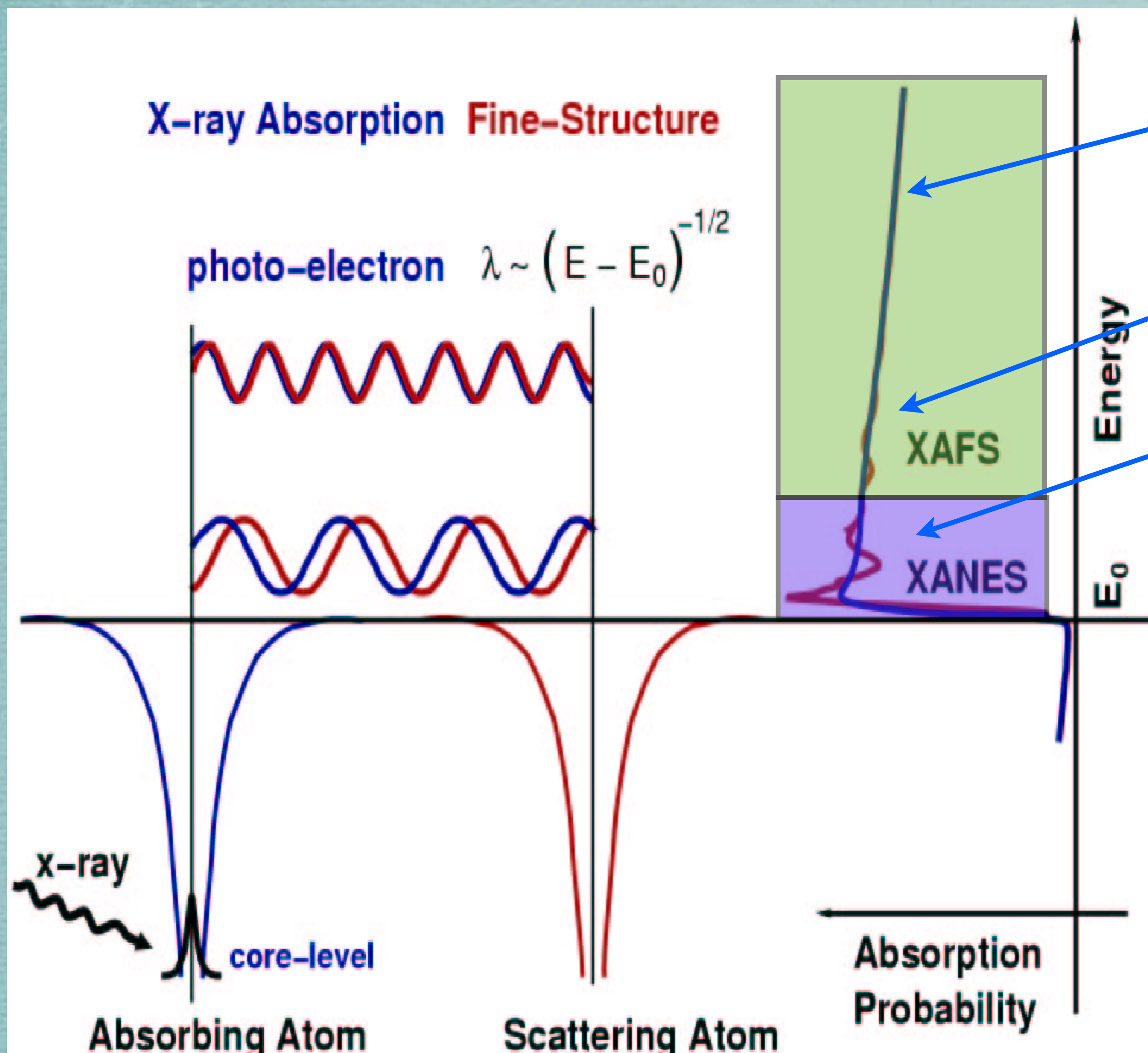
- Laser spectroscopy
- NMR
- time-resolved diffraction
- X-ray absorption spectroscopy



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

Timescales

X-ray absorption spectroscopy: Retrieving structure



atomic background absorption contribution

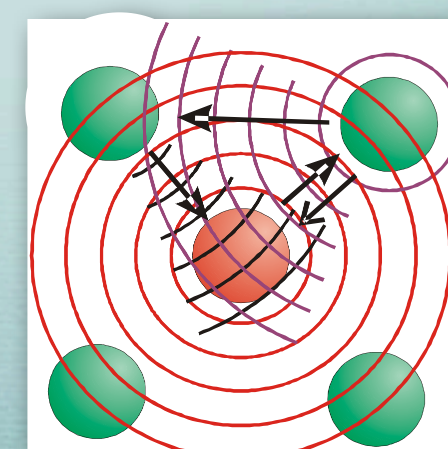
Extended x-ray absorption fine structure (EXAFS)

X-ray absorption near-edge structure (XANES)

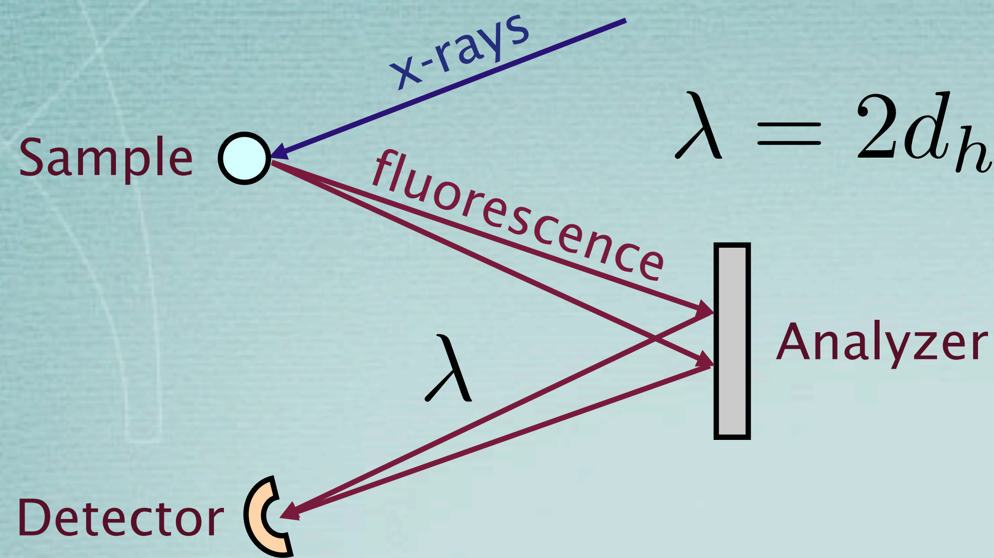
EXAFS: distances to neighbouring atoms

XANES: oxidation state, geometry, coordination environment

This works in any medium and is element-specific

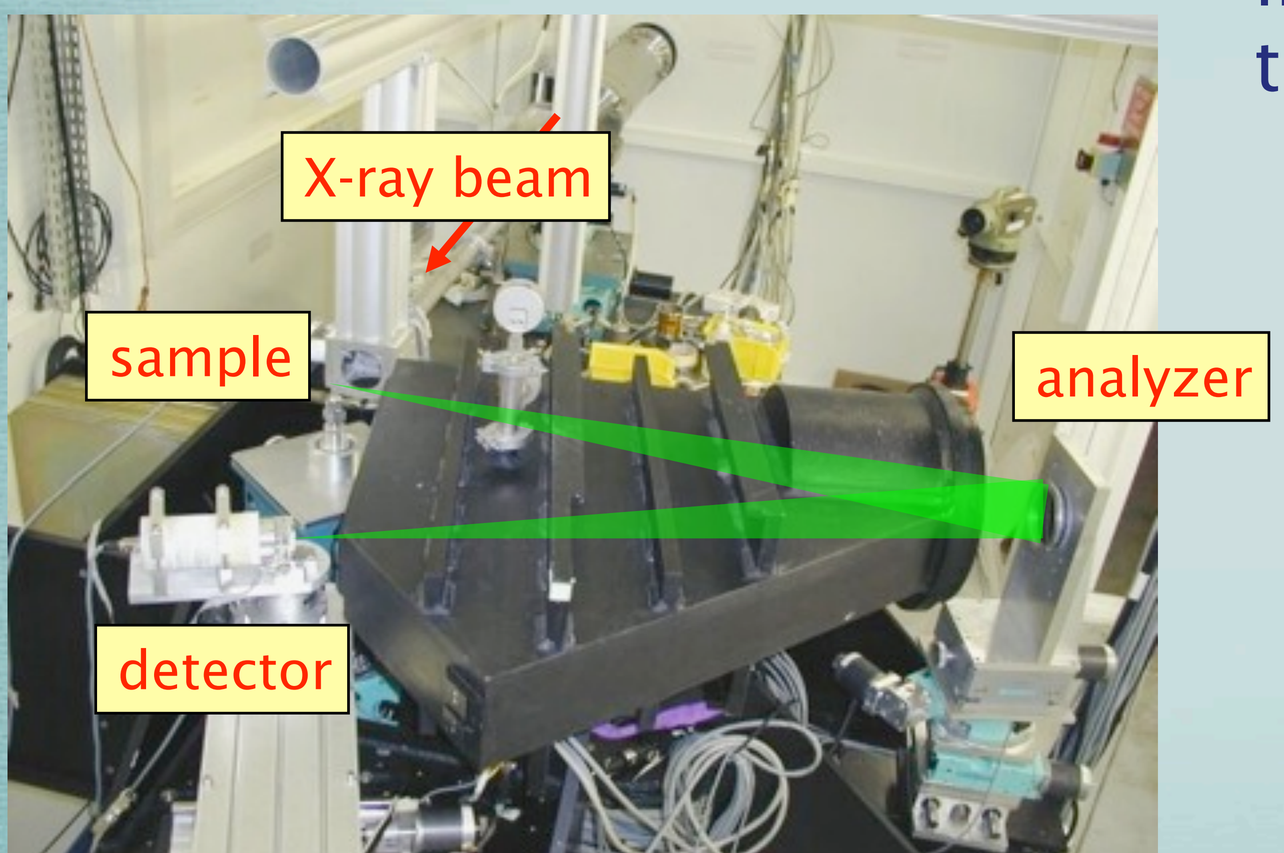


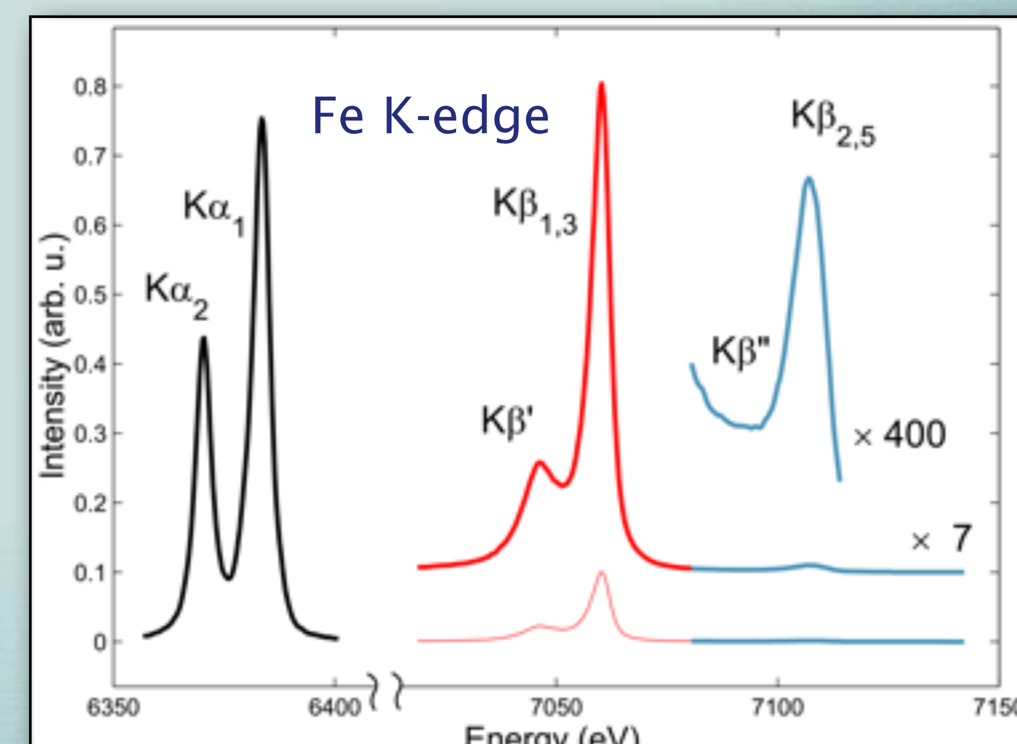
X-ray emission: Retrieving electronic information



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

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



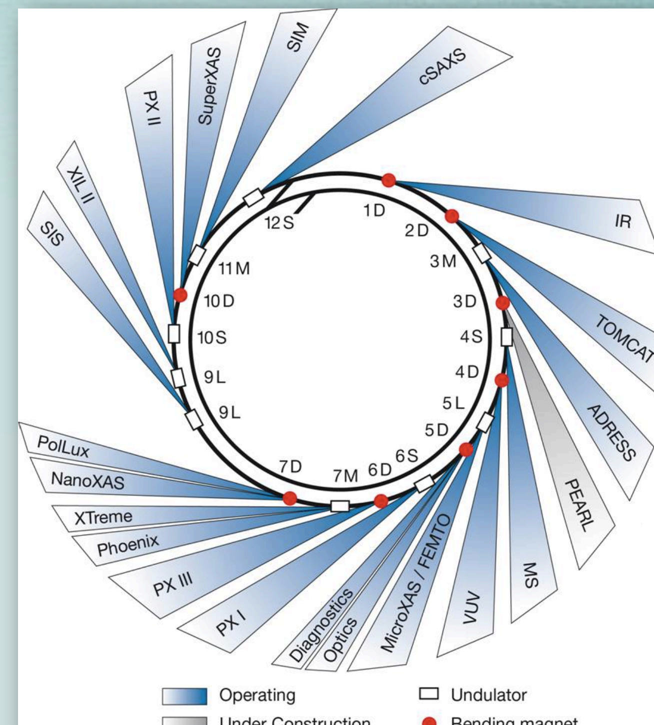


XES gives information on the occupied electronic states

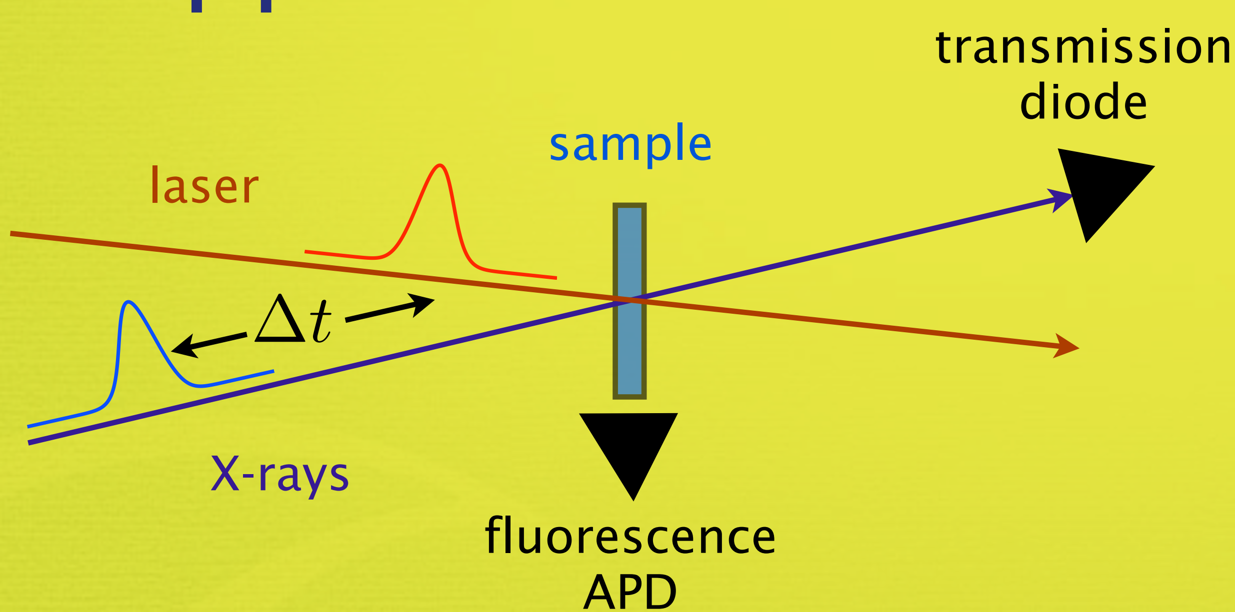
P. Glatzel et al. *Coord. Chem. Rev.* **249**, 65 (2005)
G. Vankó et al. *JPCB* **110**, 11647 (2006)

X-ray source: The Swiss Light Source at PSI

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



Pump-probe measurements



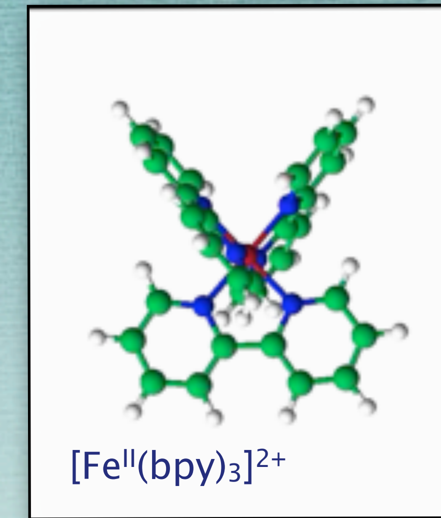
SuperXAS
- SuperBend from 4.5 to 35 keV
- Si(111), Si(311) mono crystals
- X-ray emission spectrometers
- 10^{11}-10^{12} photons/second

PHOENIX beamline
- in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb mono crystals
- micro-focus capability (< 1μm^2)
- 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 (< 1μm^2)
- 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

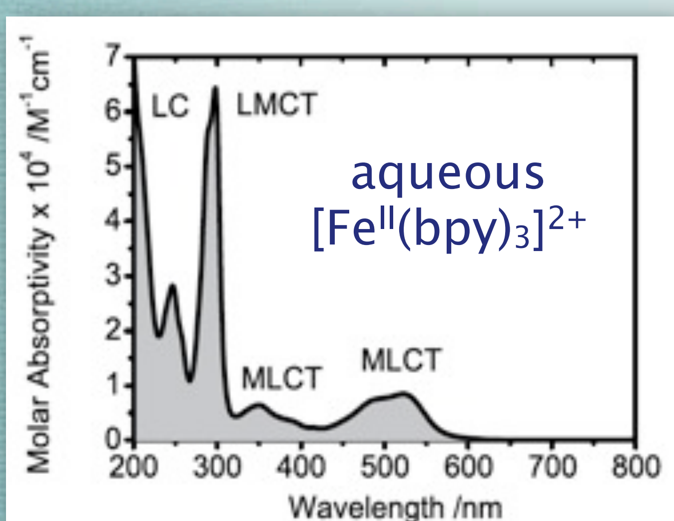


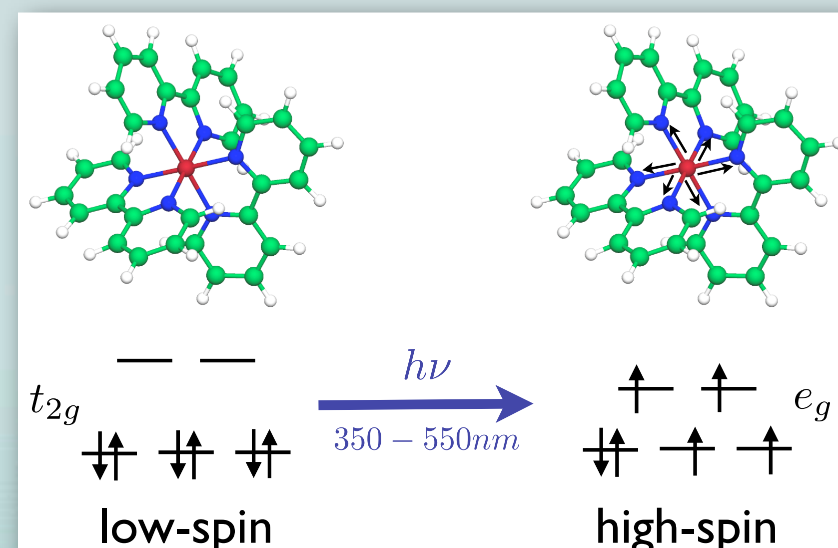
Spin-crossover phenomenon: a transition from a low-spin ground state to a high spin excited state

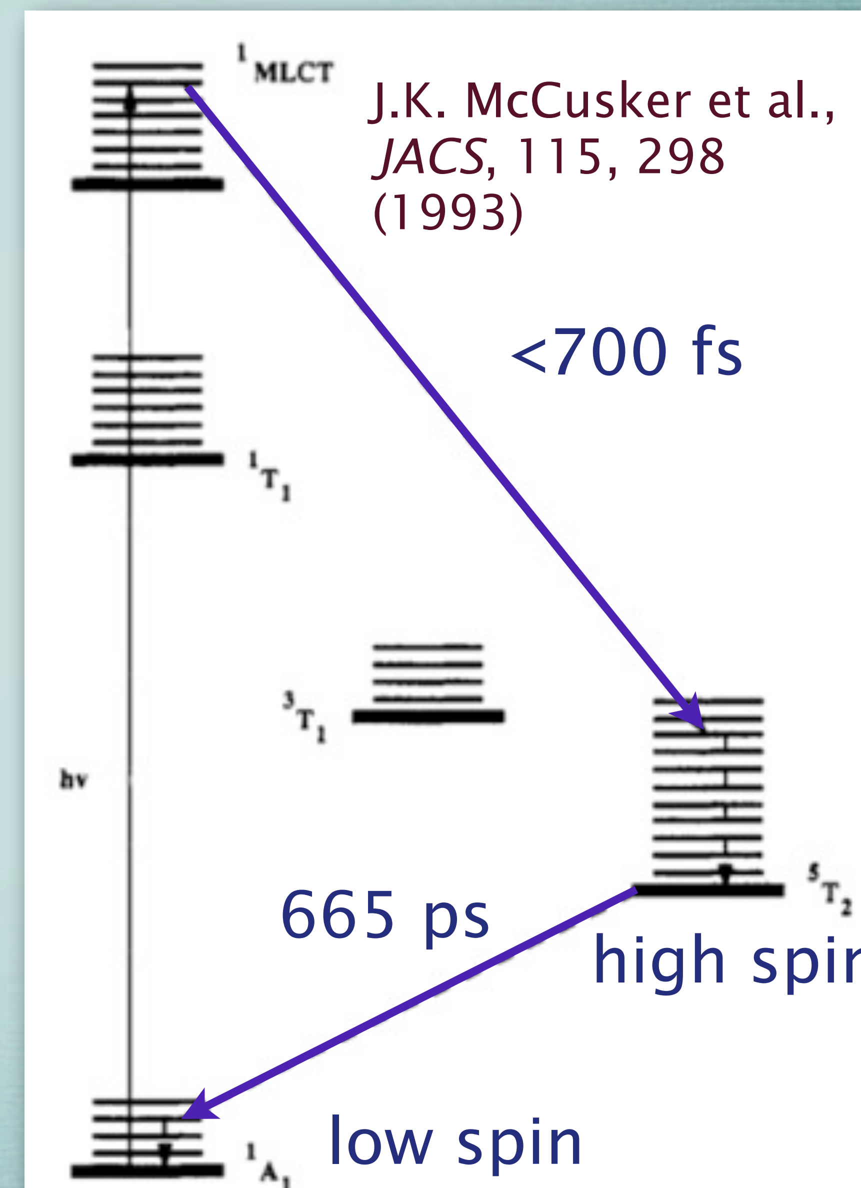
- can be induced by temperature or light
- Fe(II) compounds represent a general class of spin-crossover systems

Applications:

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

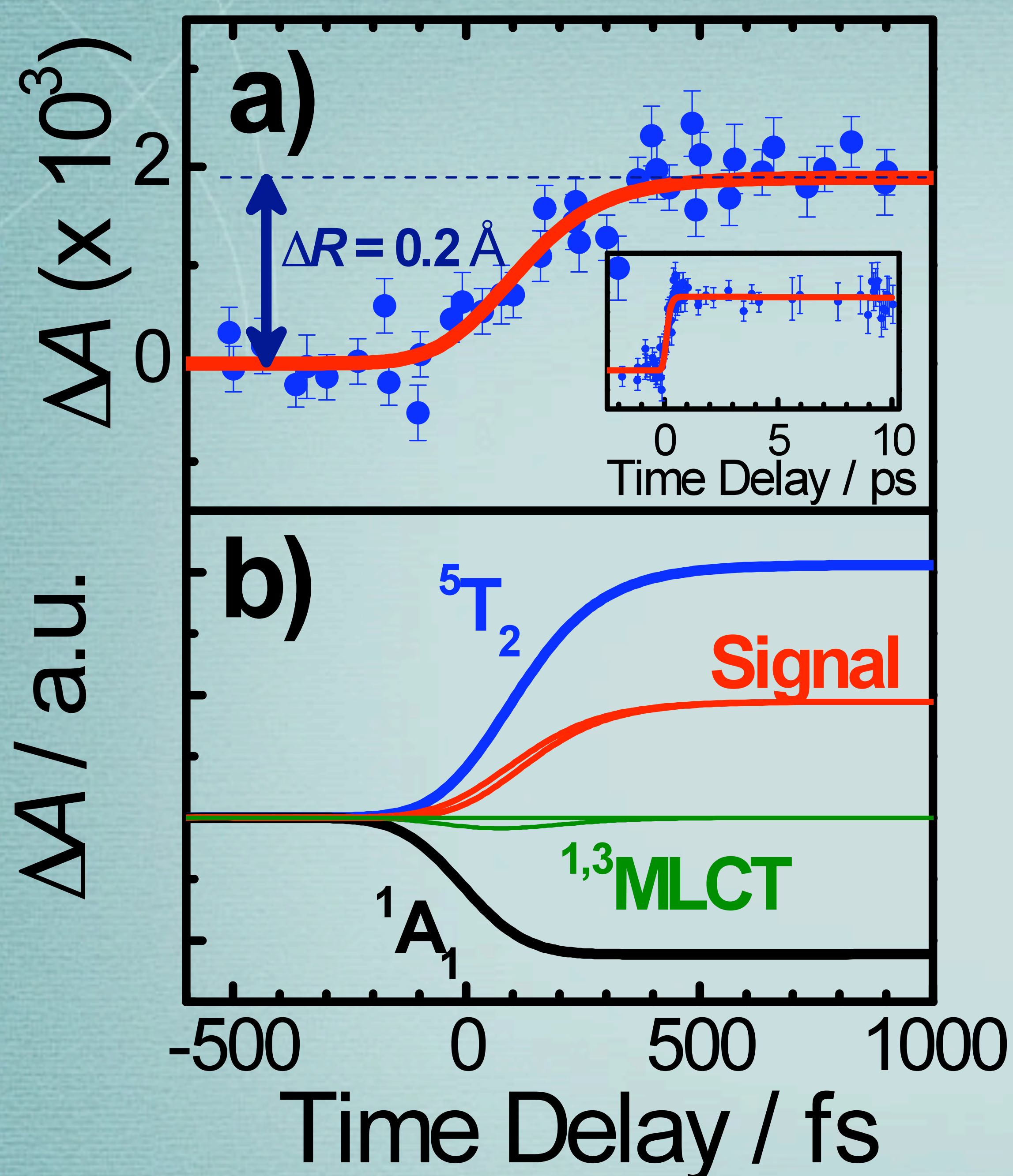


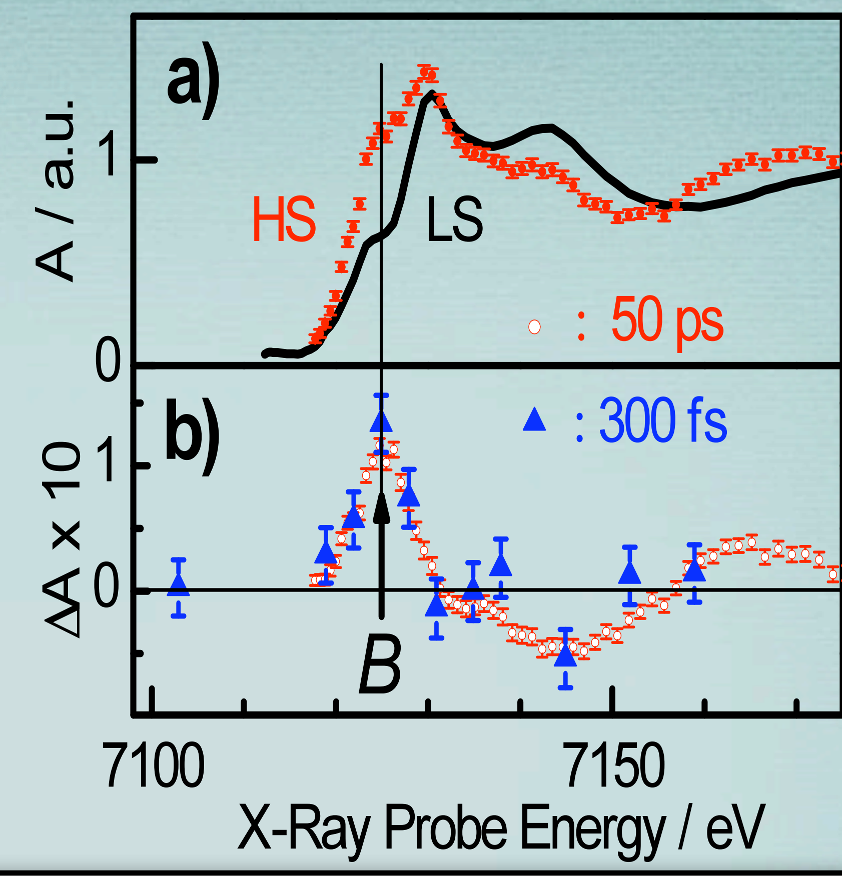




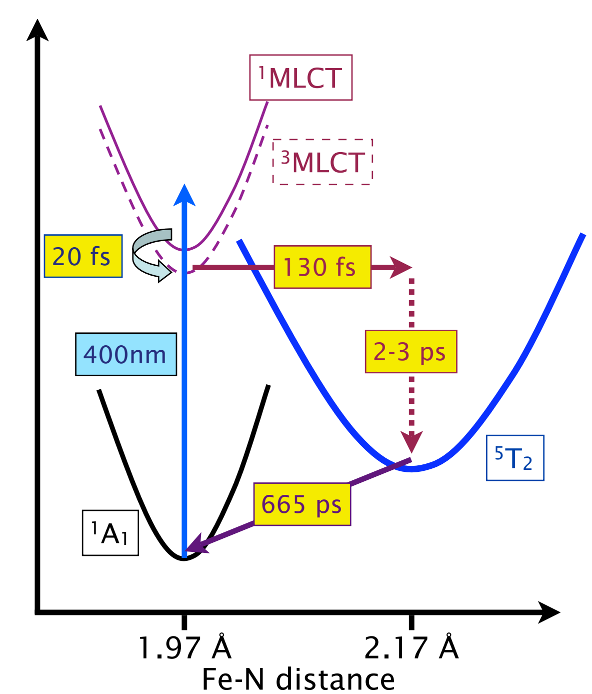
$[Fe^{II}(bpy)_3]^{2+}$ requires optical excitation and shows fs to ns relaxation dynamics

Spin crossover dynamics: Ultrafast XAS results



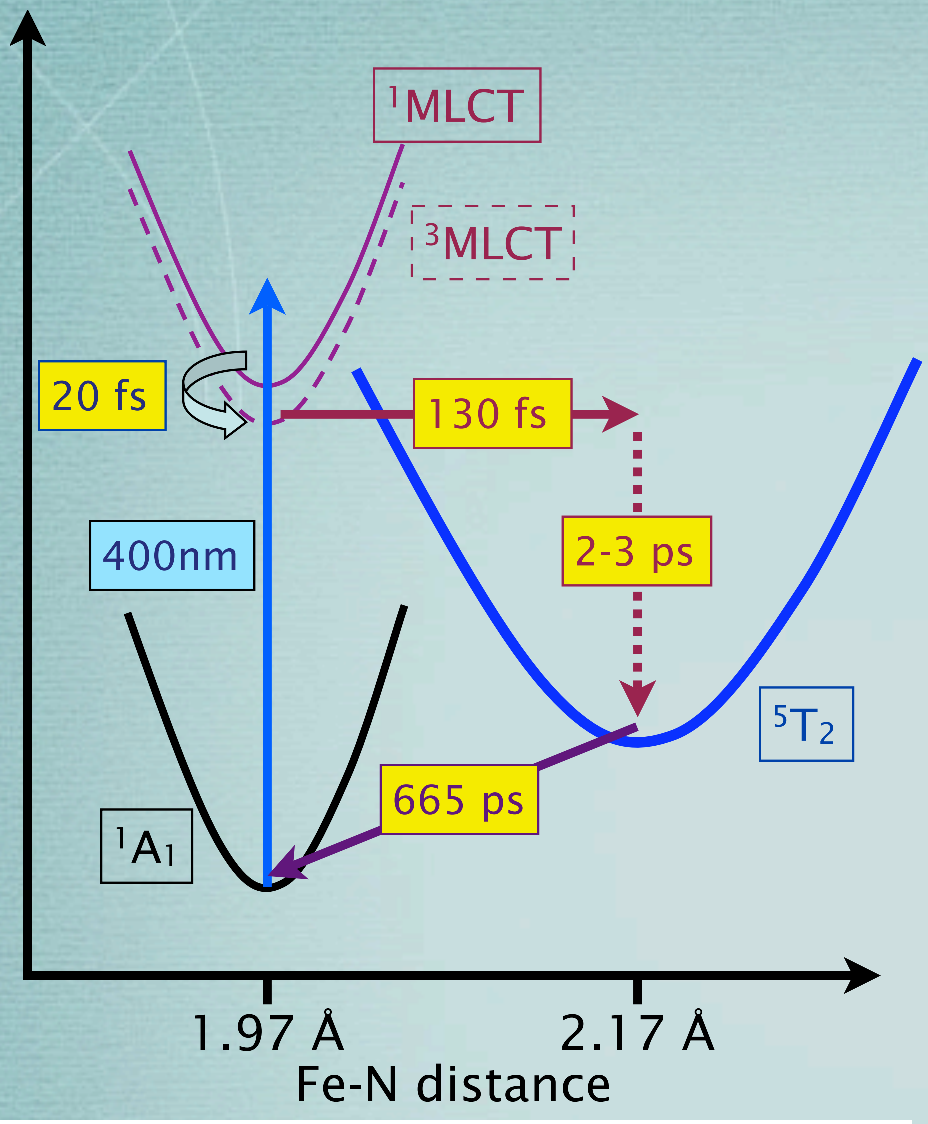


The molecule arrives in the high-spin state directly from the ^{3}MLCT in ~150 fs



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

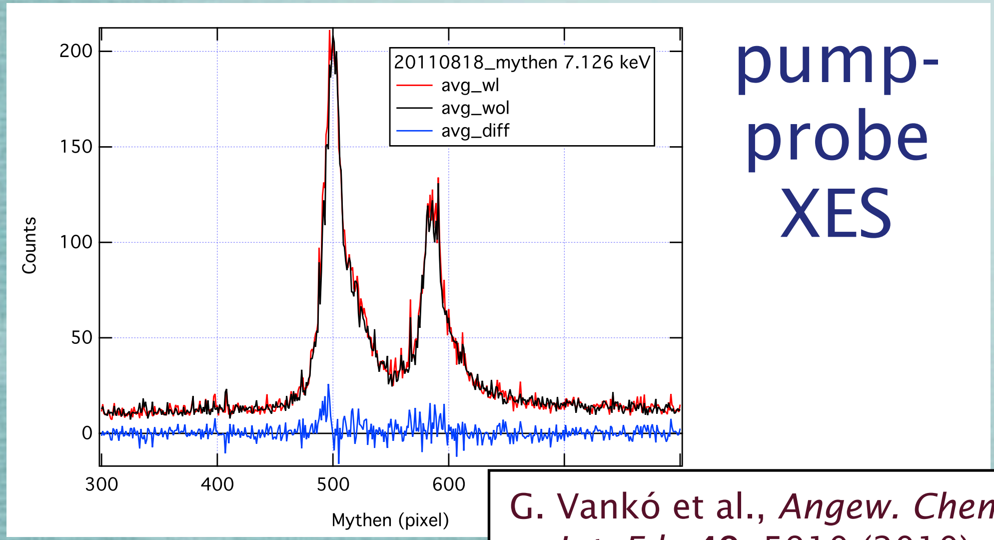


Picosecond EXAFS has resolved the high-spin state structure of a spin-crossover molecular system in solution to sub-Å resolution

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

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

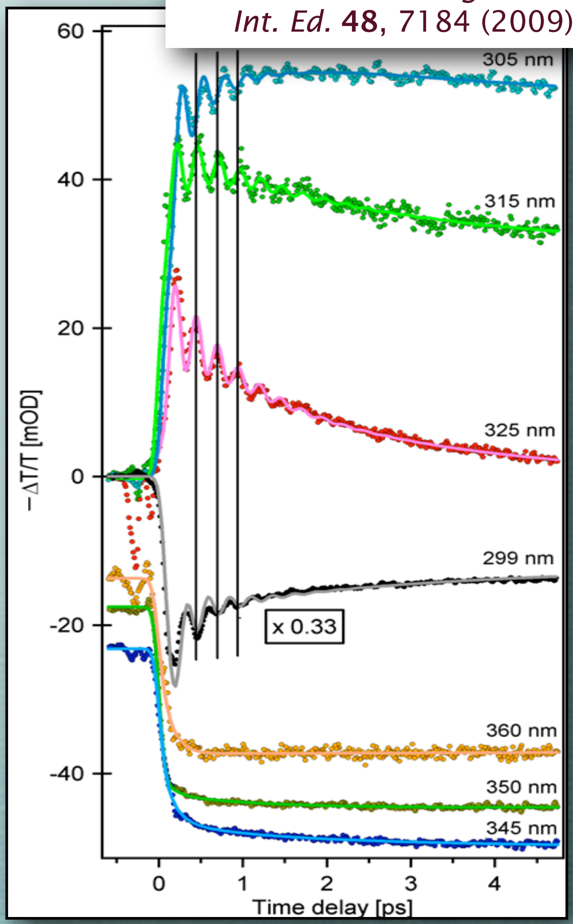
<u>Requirements:</u>
<20 fs time resolution
lots of photons
7.126 keV



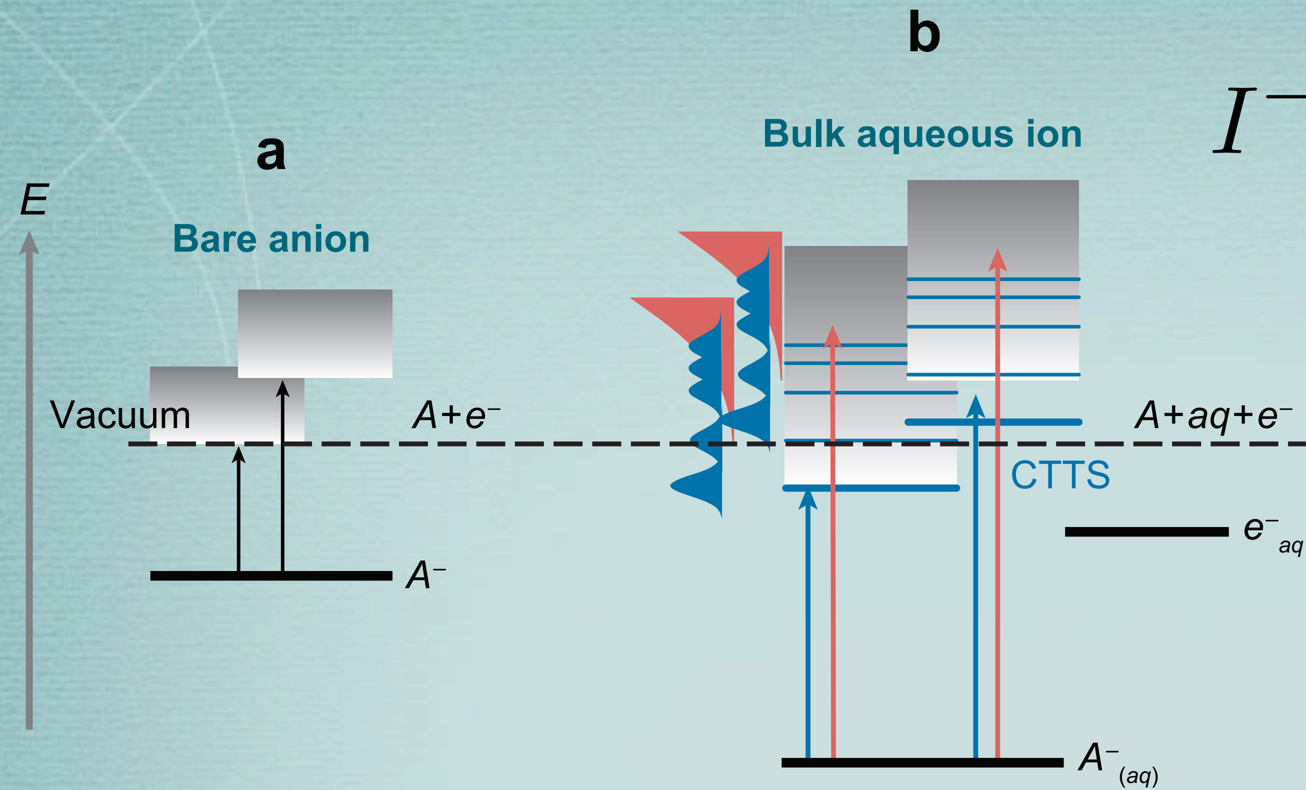
pump-probe XES

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

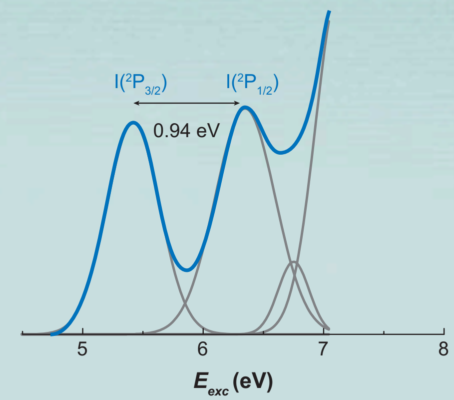
C. Consani et al. *Angew. Chem. Int. Ed.* **48**, 7184 (2009)



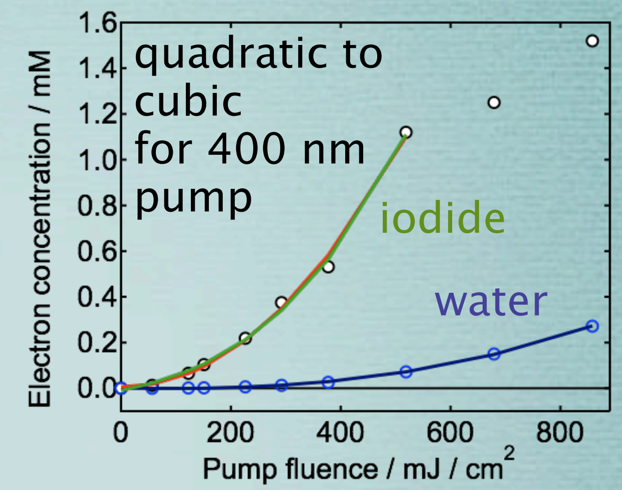
Solvation dynamics: aqueous iodide

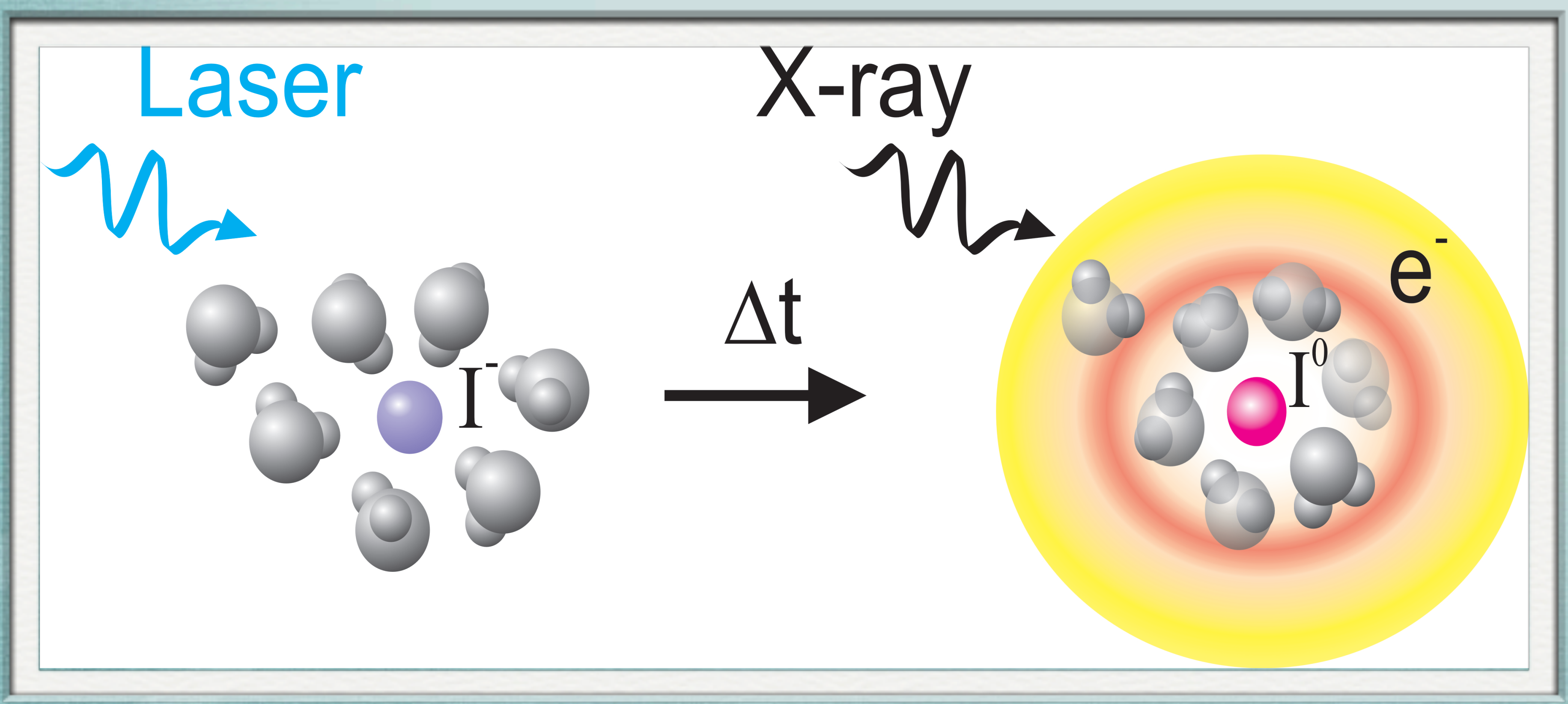


$$I^- + H_2O \xrightarrow[\text{UV}]{h\nu} I^0 + e^- + H_2O$$



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



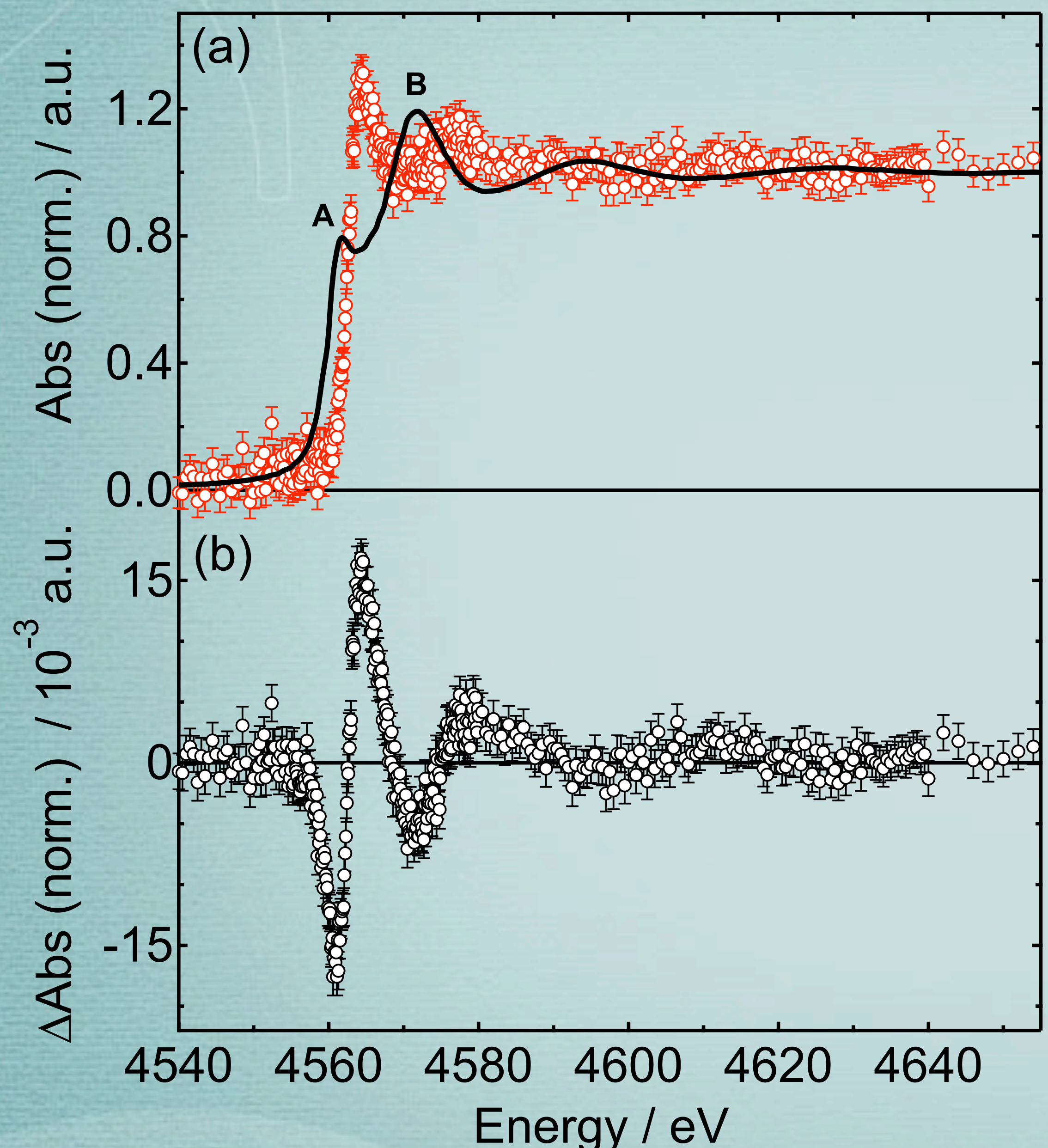


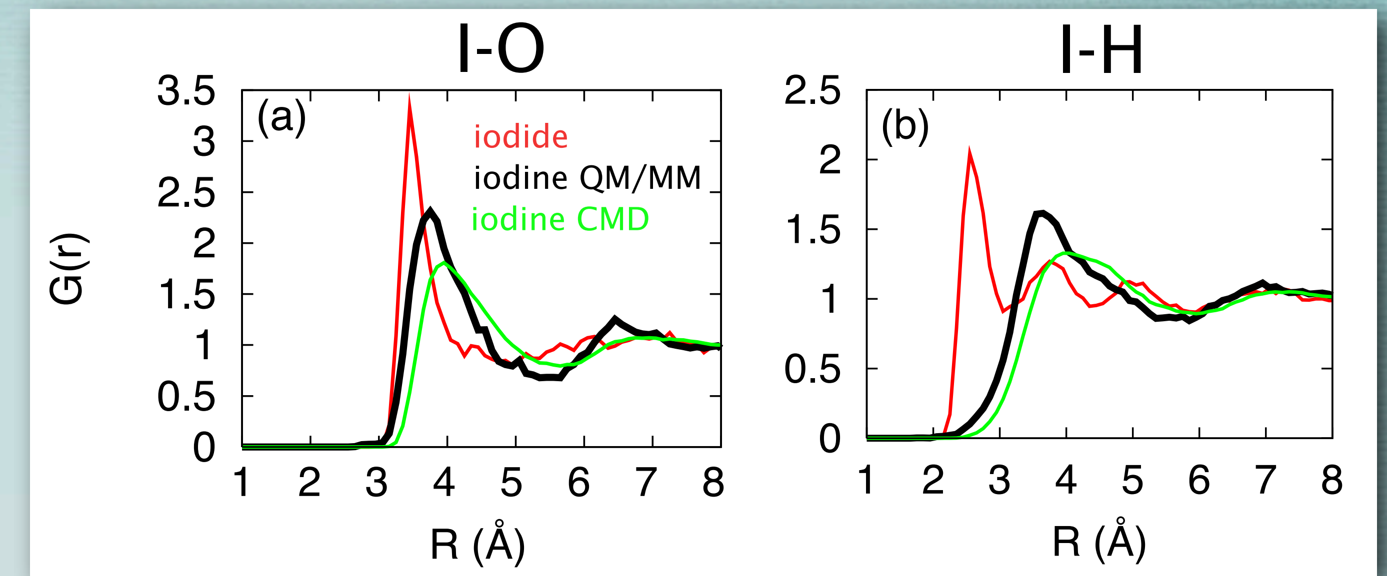
How does the water respond ?

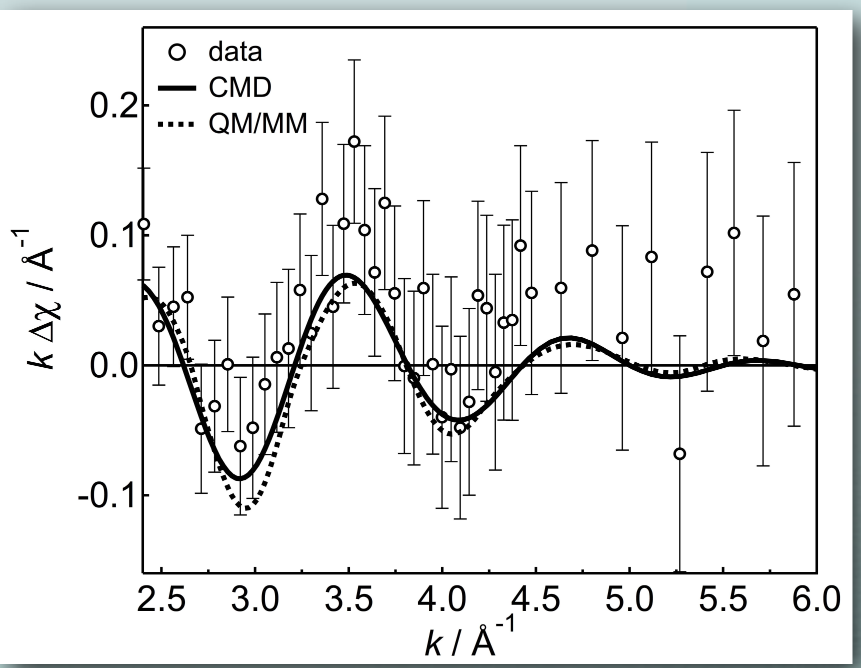
Can we extract electronic information as well as structural ?

Solvation dynamics: water structure around iodine

50 ps after multi-photon excitation at 400 nm







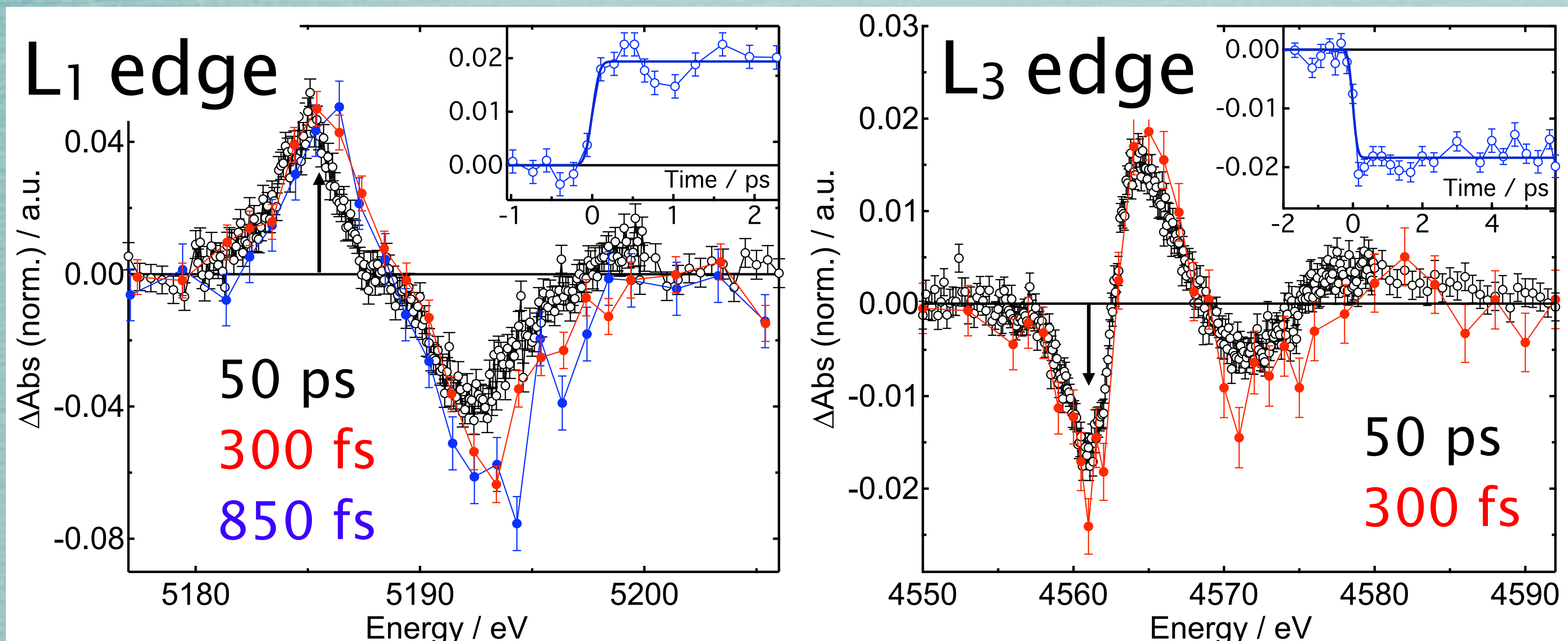
We see an increase in the solvent cage radius of 5-20%

We're seeing hydrophobic cavity formation around I^0

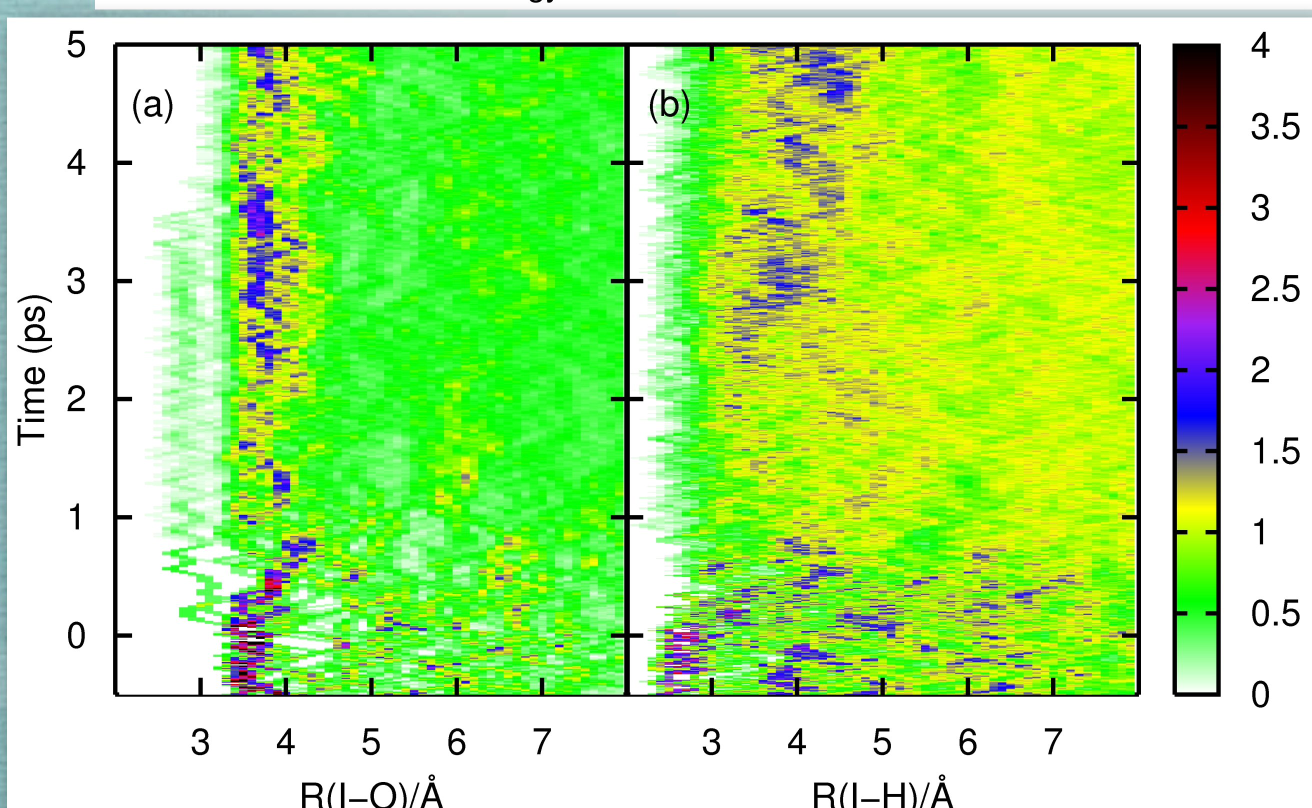
V-T. Pham, T.J. Penfold et al., *JACS*, **133**, 12740 (2011)

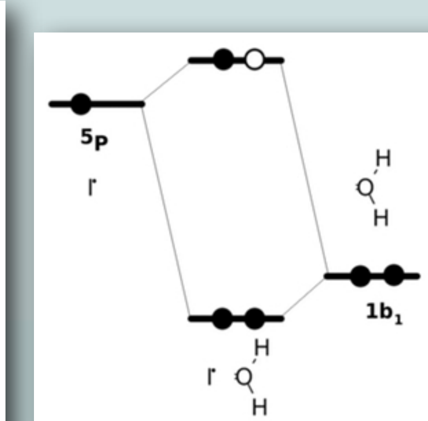
Solvation dynamics: femtosecond timescales

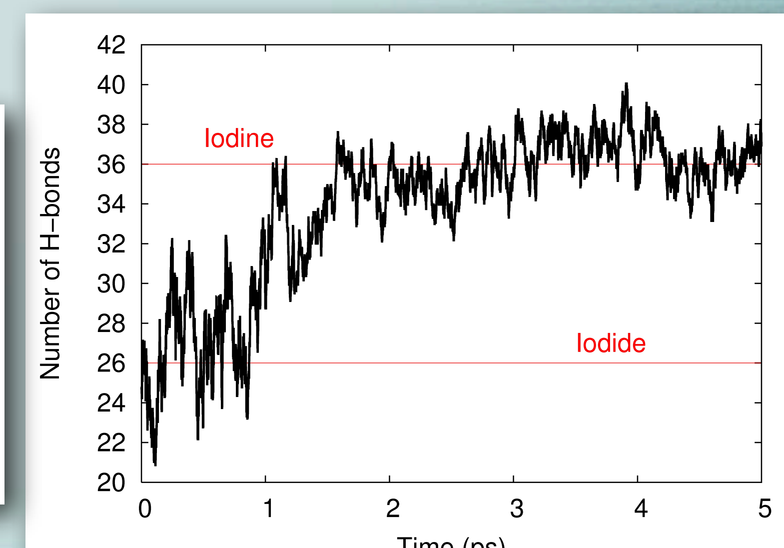
Moving into the femtosecond timescale with sliced x-rays



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





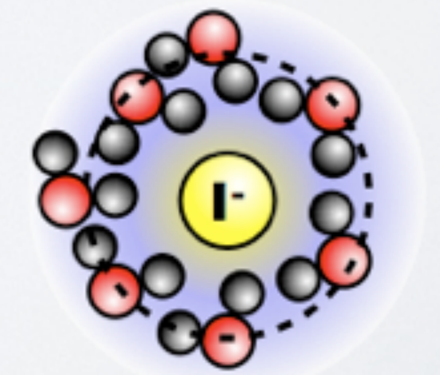


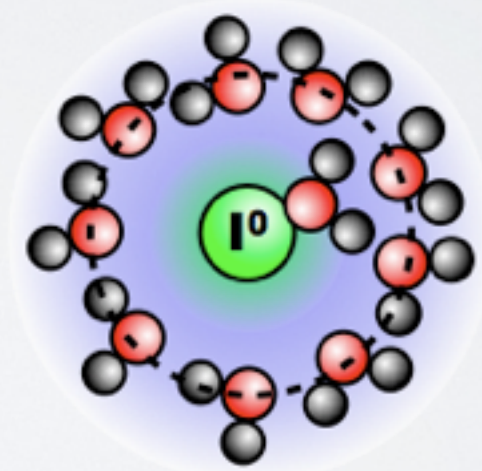
200-300 fs: breakup of first shell, most waters move away but one water moves closer (40% probability)
3-4 ps: the first shell reforms and the lone water recombines with the bulk

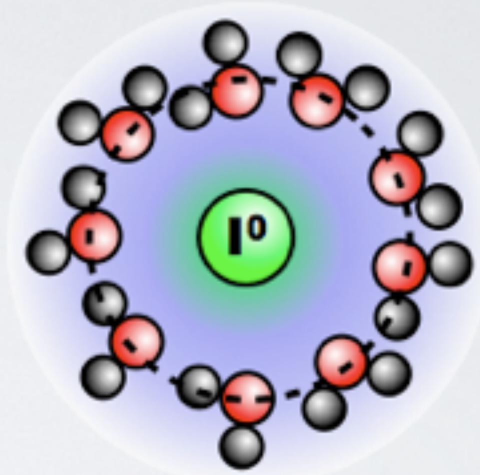
V-T. Pham, T.J. Penfold et al., *JACS*, **133**, 12740 (2011)

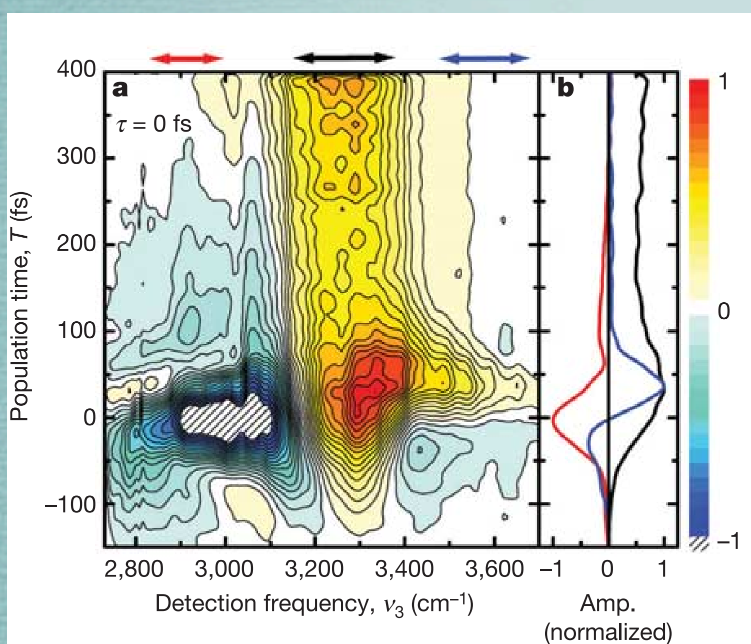
Solvation dynamics: SwissFEL possibilities

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



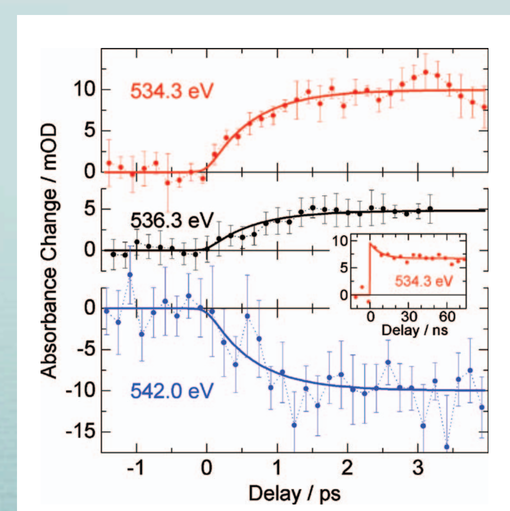






Water is fast
< 50 fs energy redistribution from O-H stretch

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

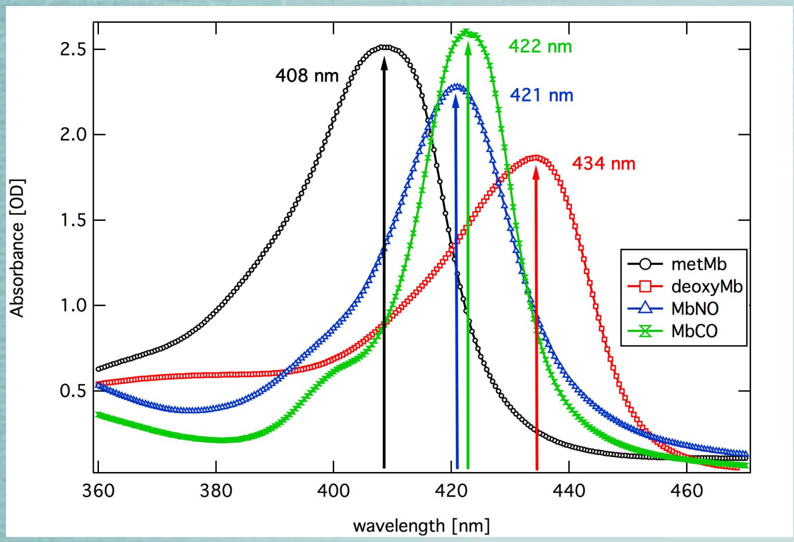


H. Wen et al., *JCP*, **131**, 234505 (2009)

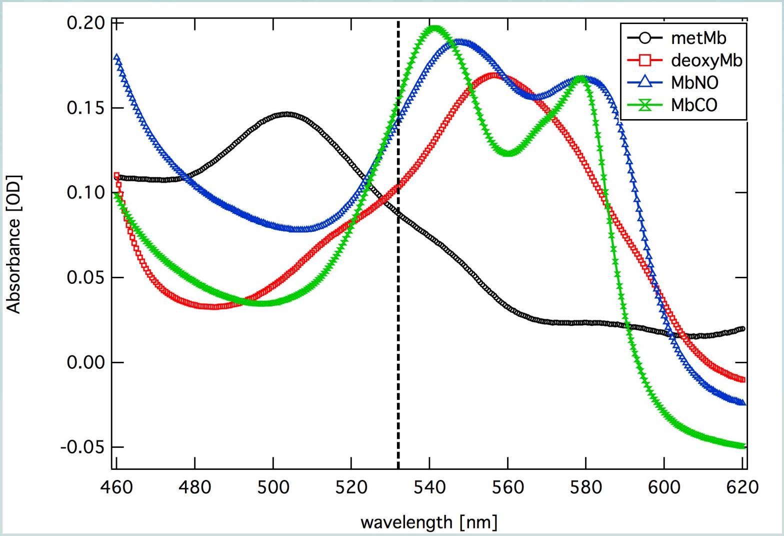
<u>Requirements:</u>
<10 fs time resolution
lots of photons
5.185 keV

Hemoproteins: Investigating biological function

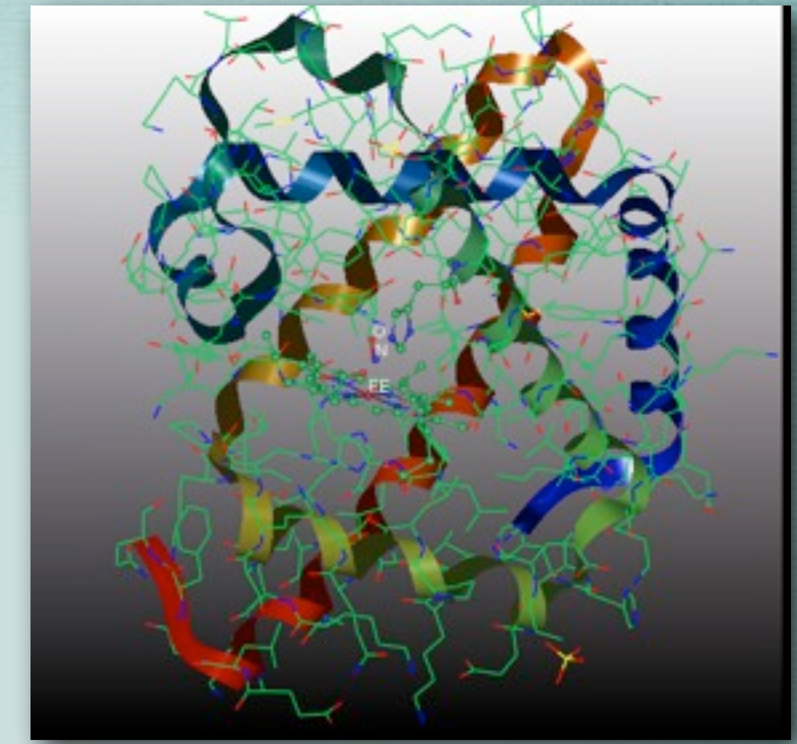
Myoglobin is an oxygen transport protein that has the ability to bind small molecules such as O_2, CO, NO and CN

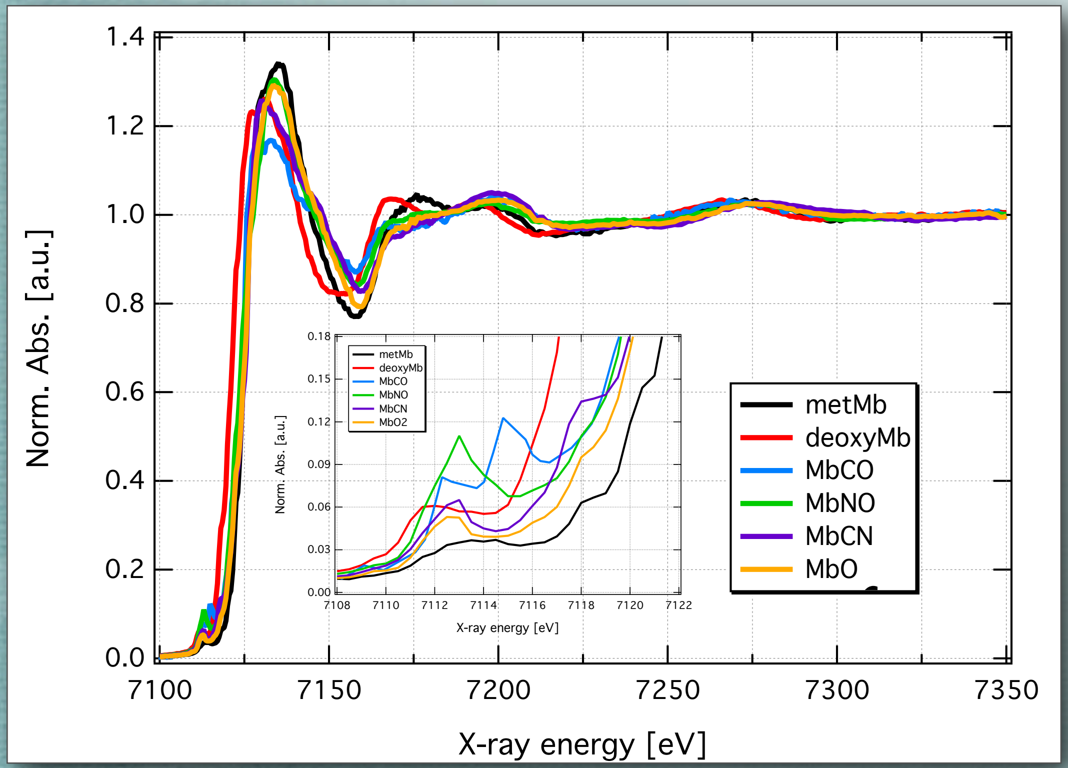


(a) Soret band region



(b) Q-bands region



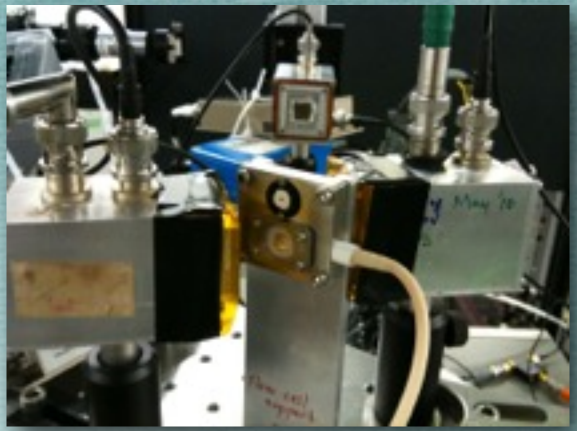


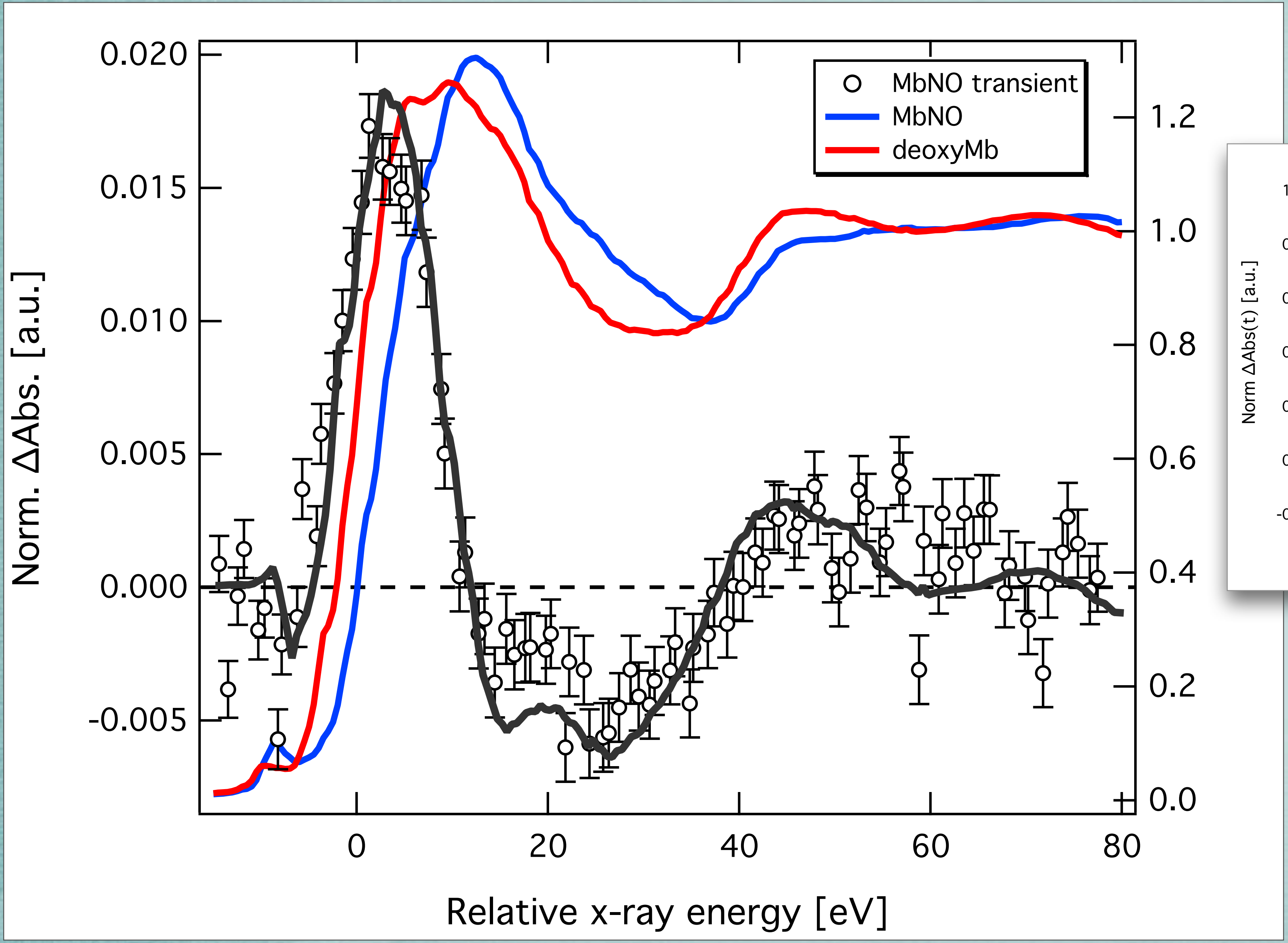
Small changes in the ligand character have profound spectroscopic effects

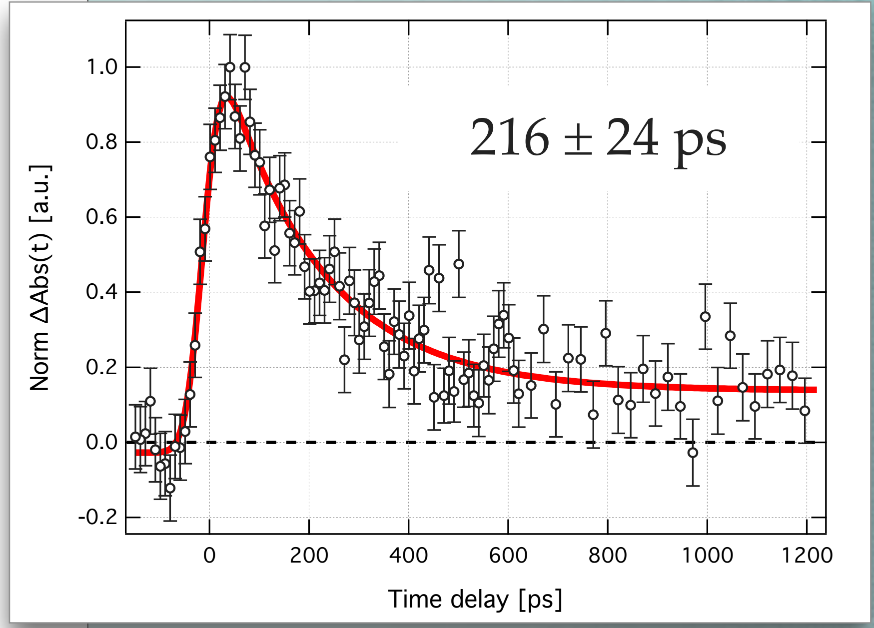
We can knock this ligand off with a photon of green or blue light

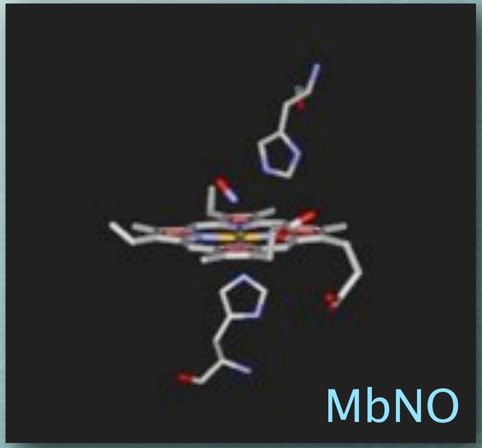
Hemoproteins: MbNO pump-probe XAS

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



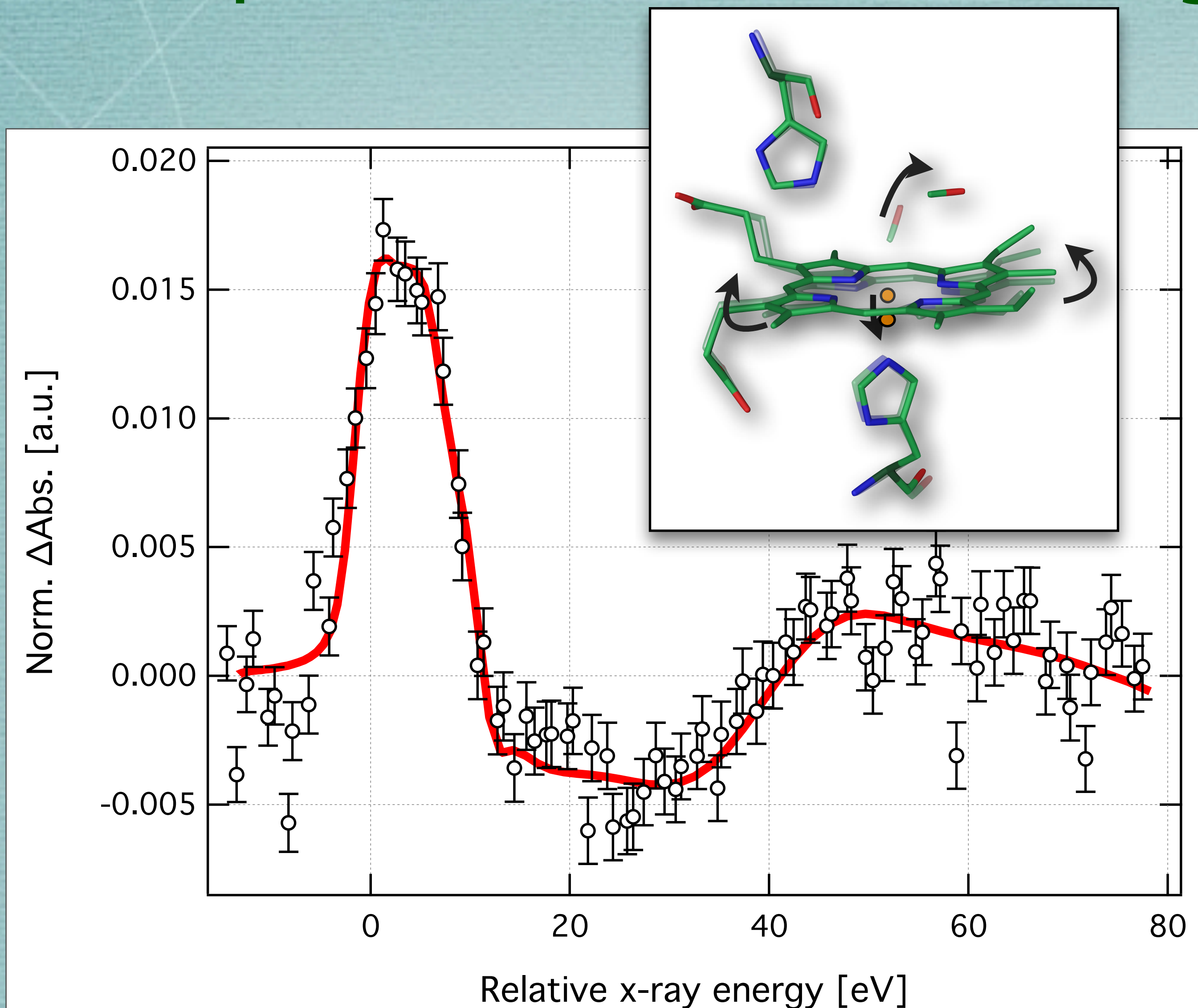






Can we extract further information ?

Hemoproteins: understanding MbNO



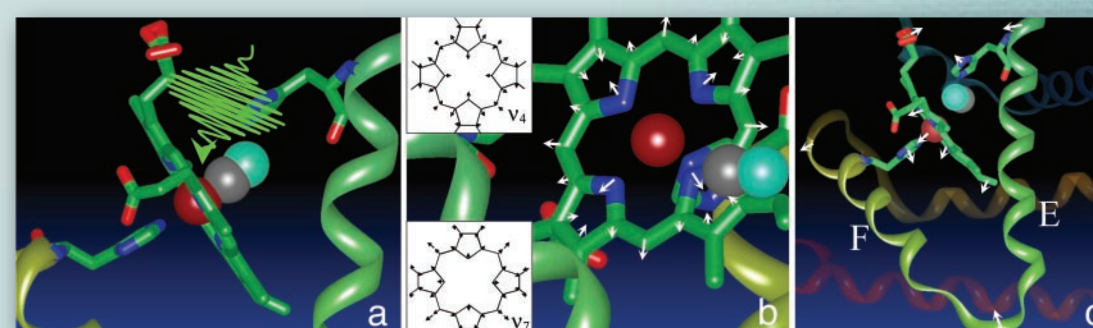
- A domed ligated (6-coordinated) configuration with 30 ps lifetime is possible Kruglik et al. *PNAS* **107**, 13678 (2010)
- We can't distinguish between MbNO and MbON

☑ Fe move down 0.16 ± 0.03 Å

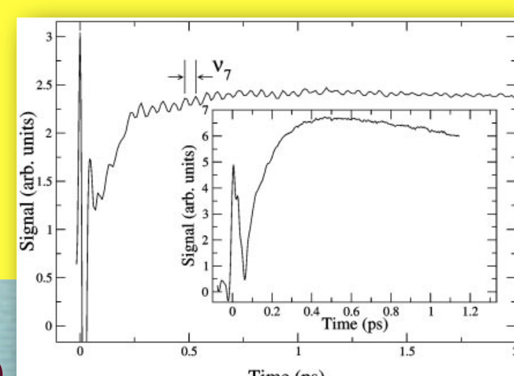
☑ Heme domed ~ 0.03 Å

☑ 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



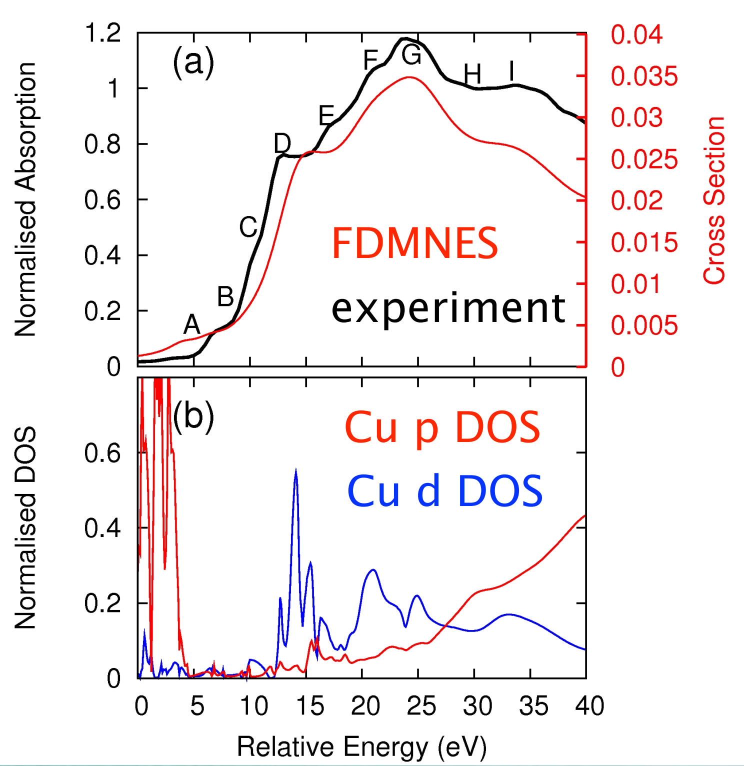
M.R. Armstrong et al., *PNAS*, **100**, 4990 (2003)

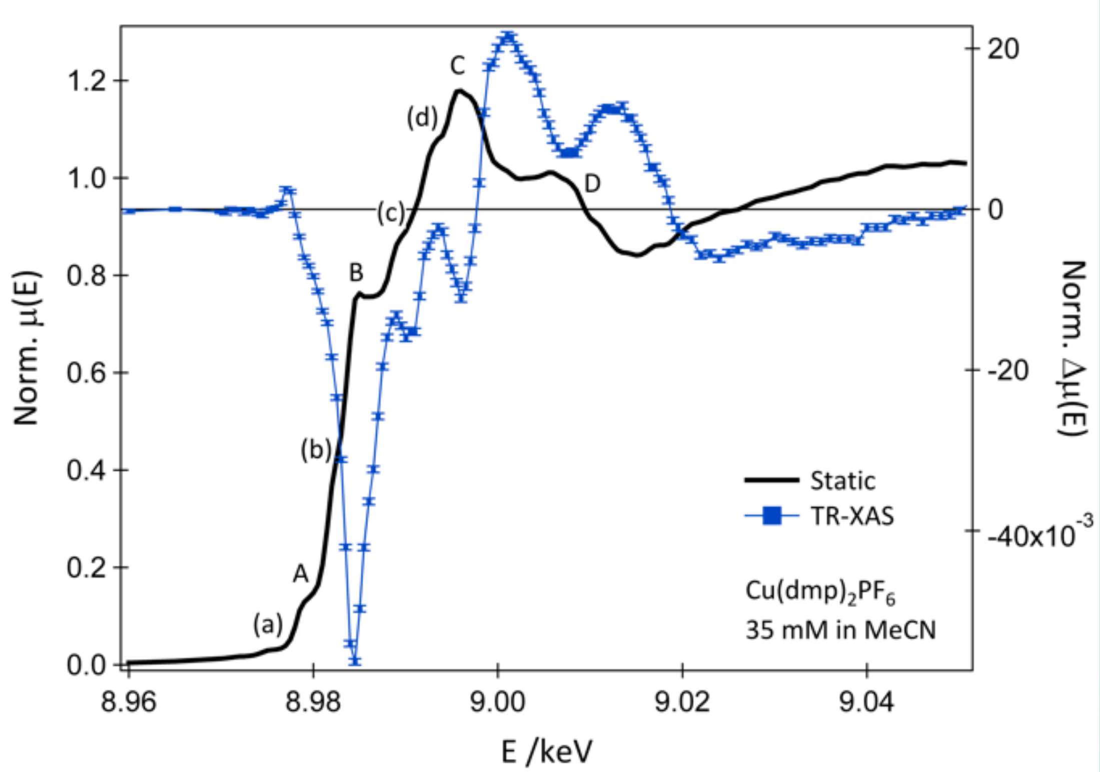
__Requirements:__
<10 fs time resolution
lots of photons
7.125 keV

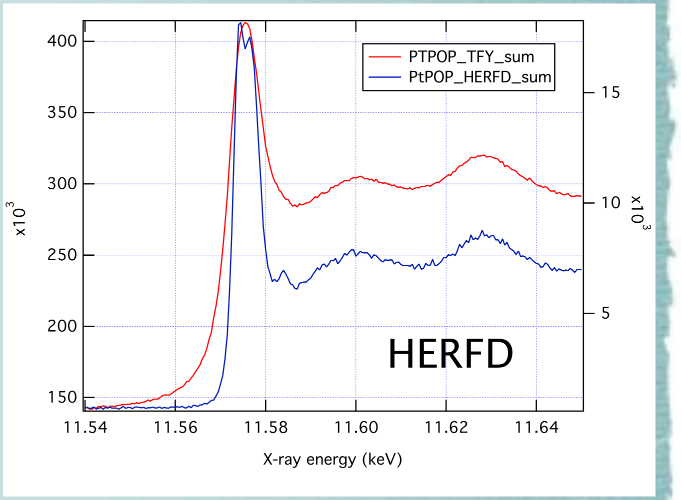
Ultrafast XAS at XFELs: Caveats

- 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)





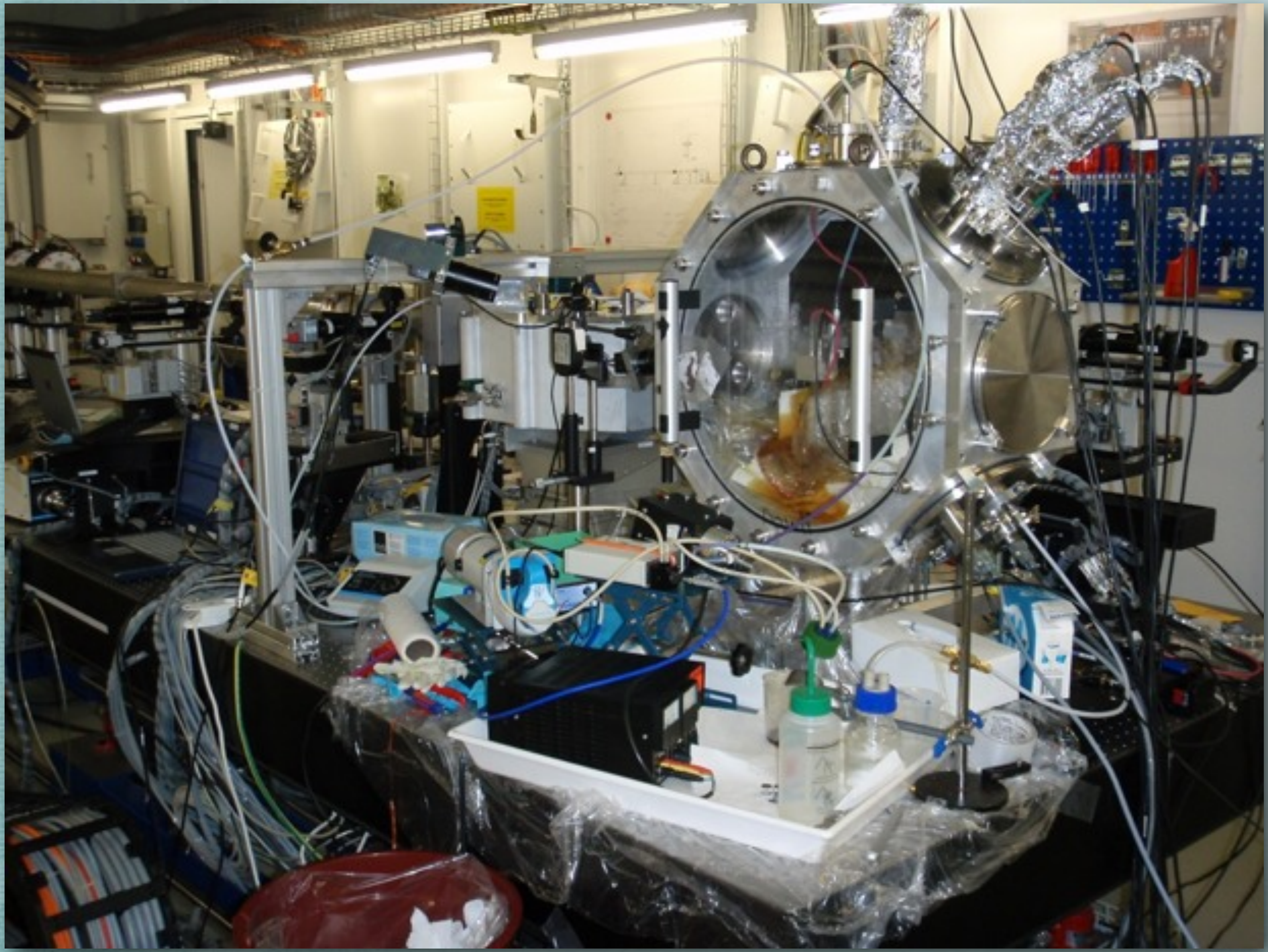


Theory now badly lags experiment for both ground-state and excited-state spectra

PSI seminar: Tom Penfold, Thursday March 15th

microXAS

microXAS beamline
- in-vacuum undulator (4-20 keV)
- Si (111), Ge(111) & Si(311) mono crystals
- micro-focus capability (< 1µm^2)
- 10^{12} photons/second

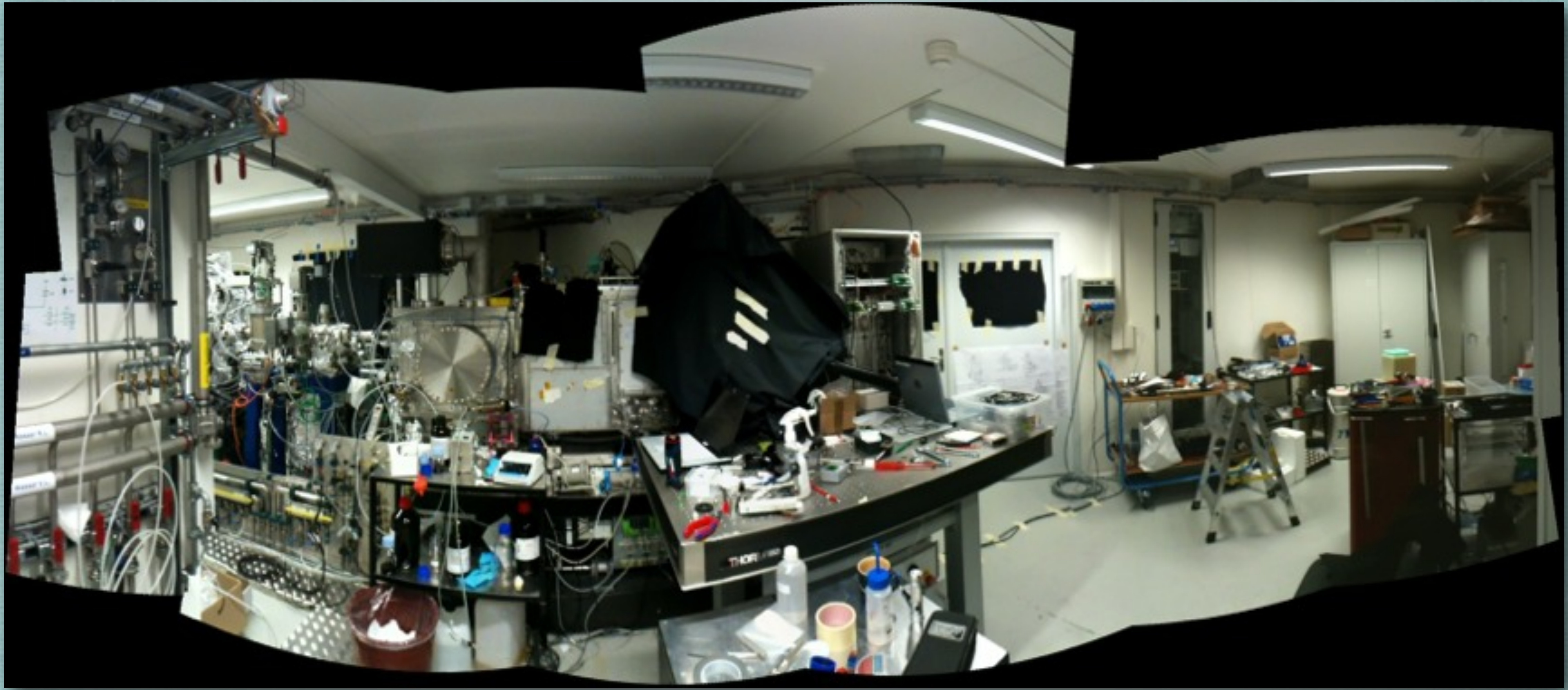


Advantages
- setup flexibility
- micro-focus
- user-selectable energy resolution

Disadvantages
- no permanent setup
- no permanent optical setup
- not ideal sample preparation facilities

PHOENIX

PHOENIX beamline
- in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb mono crystals
- micro-focus capability (< 1 μm^2)
- 10^{11}-10^{12} photons/second



Advantages
- 'tender' x-rays
- micro-focus
- vacuum chamber
- 50% beamtime makes setup easier

Disadvantages
- no permanent setup
- setup in general takes more time
- more difficult to change x-ray energy
- 50% beamtime means less shifts

SuperXAS

SuperXAS
- SuperBend from 4.5 to 35 keV
- Si(111), Si(311) monochromator crystals
- X-ray emission spectrometers
- 10^{11}-10^{12} photons/second

Advantages
- setup flexibility
- broad range of available techniques
- ability to measure XES
- good sample preparation facilities

Disadvantages
- no permanent setup
- no permanent optical setup
- lack of space
- large x-ray focus that isn't terribly stable

What can we learn from the SLS for Aramis ESA ?

Flexibility is key

- Hard x-rays mean you can work in air, take advantage of this by leaving space for setups you can't imagine (but others will !)

Don't waste time

- Beamline commissioning is critically important for the beamline to work well
- Permanent items need to be stable

Permanent but flexible optical setup

- For some reason x-ray users get impatient with laser alignment
- Anticipate users' needs but within reason

Staff are perhaps the most important part of the beamline

- This goes for everyone from technicians, engineers, programmers and beamline scientists
- If only one thing gets copied from the SLS make it the user support

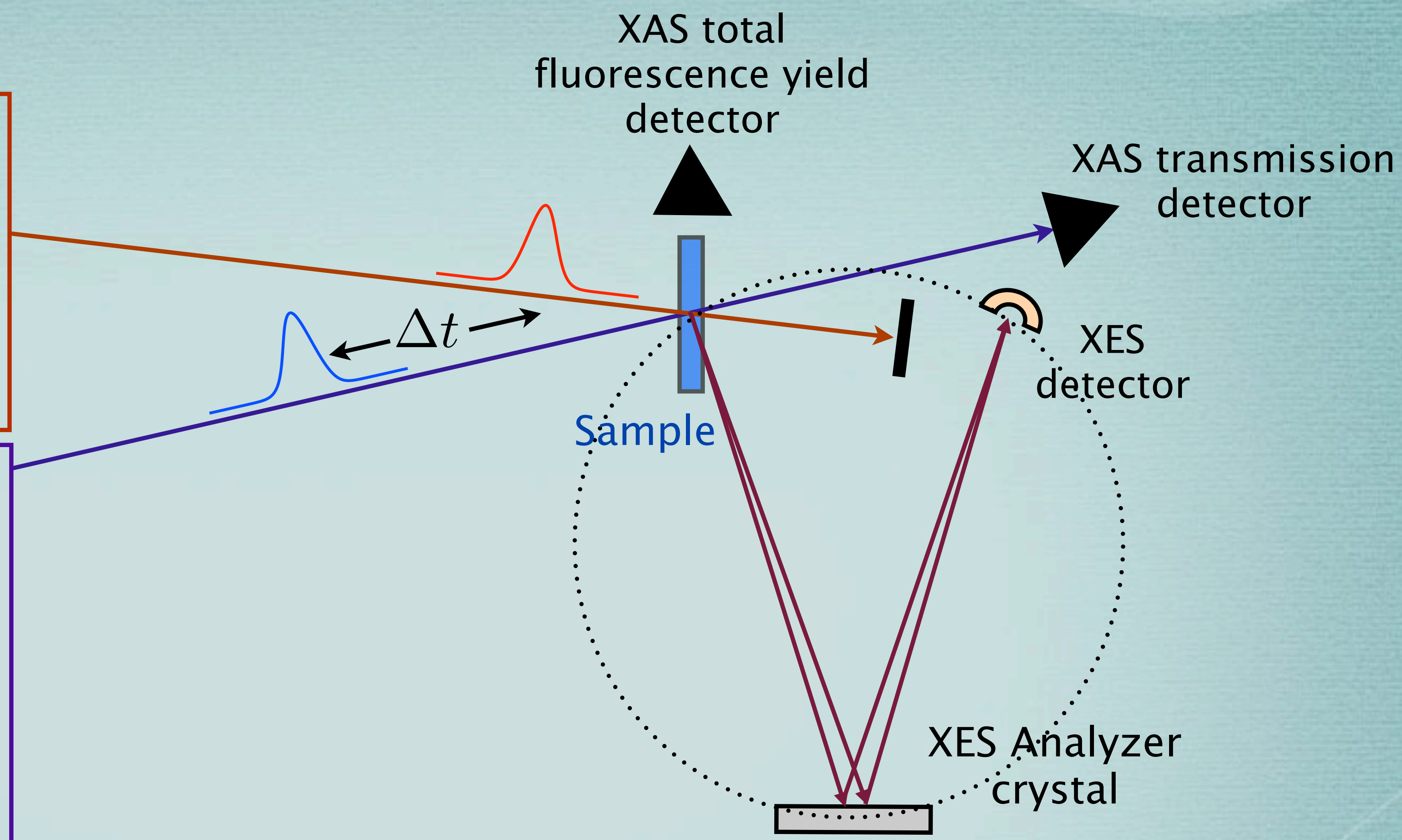
Downtime between shifts is necessary

- No-one can setup an experiment and be running instantaneously and x-rays are precious

SwissFEL Aramis ESA: The default setup

Laser pump
- tuneable from IR to UV
- femtosecond pulses
- possibility to stretch (>1 ps)
- rep rate matched to SwissFEL
- controlled delay (0-1 ns)

X-ray probe
- monochromatic (0.015%)
- scannable within undulator bandwidth
- ability to remove mono
- jitter diagnostic
- focussed spot (<100 μm)
- I_{zero} detector

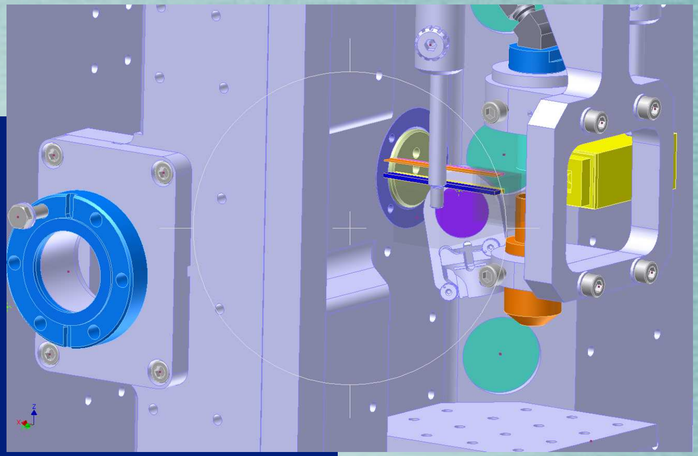
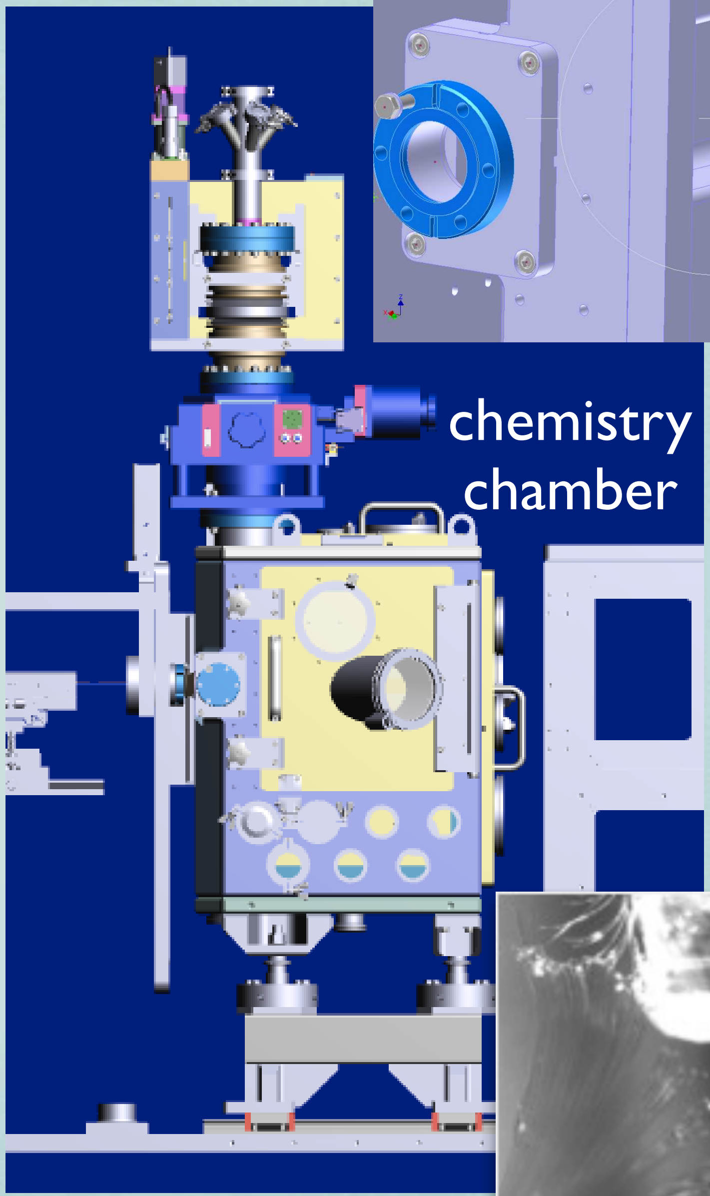


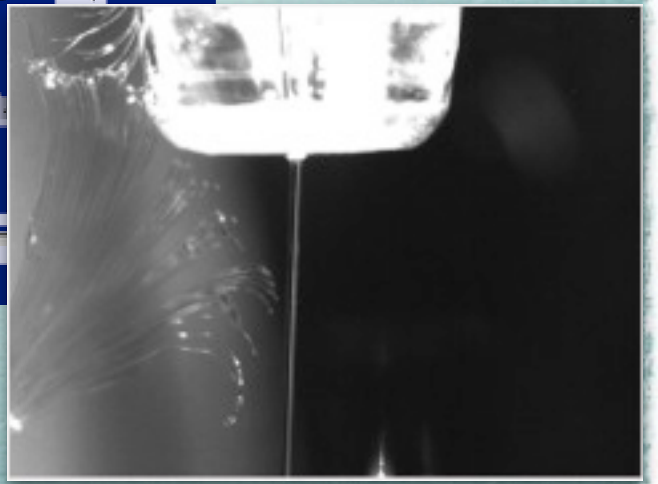
- This is the default setup in air sitting on a sample manipulator
- Detectors are motorized and can be put literally anywhere in space
- Have available a liquid jet for use with a gear or peristaltic pump
- Have available a cryojet and goniometer for crystal mounting
- Also available is a 2D detector for scattering/diffraction measurements
- Ability to measure ‘fast’ differences and record every pulse

SwissFEL Aramis ESA: Increasing complexity

- A portable chamber for measurement under He, vacuum or anaerobic conditions
- The ability to use the chamber with a von Hamos spectrometer (XES) or a 2D detector (scattering)
- Have available a microjet for use in vacuum or with small sample volumes (*Athos*)
- Standard interface for pre-existing chambers (SLS, ESRF, *Athos* etc.)
- Online sample diagnostics (UV/Vis, x-ray fluorescence, IR/Raman)

You can handle the same number of different setups as you have staff members who are interested in using them



SwissFEL Aramis ESA: Conclusions

Focus on strengths

- 100 Hz matches well high pulse energy pump laser sources which means wavelength tunability with excellent excitation possibilities (UV, IR THz)
- Peak fluence will be high
- Reading out detectors will be easy
- Shot-to-shot normalization for all parameters (jitter, energy, focus) should be simpler
- Take advantage of local expertise (detectors, time-resolved XAS/XES/diffraction)

Avoid weaknesses

- Per-pulse flux is high but average flux is low, this means not all photon-starved experiments will be a good idea (e.g. steady-state RIXS, attenuated coherent scattering)
- Scanning x-ray energy is non-trivial so you can't compete with XAS at synchrotrons
- Similarity to other FEL sources means choosing differentiation carefully

Acknowledgements

LSU http://lsu.epfl.ch/

Hannelore Rittman-Frank
Marco Reinhard
Tom Penfold
Jochen Rittmann
Thomas Rossi
Frank van Mourik
Majed Chergui

LSU alumni

Frederico Lima
Wojciech Gawelda
Christian Bressler
Dimali Amarasinghe
Amal El Nahhas
Van-Thai Pham
Renske van der Veen
Andrea Cannizzo
Susanne Karlsson

FEMTO

Paul Beaud
Gerhard Ingold

SwissFEL

Rafael Abela

ETH Zürich

Steve Johnson

University of Basel

Markus Meuwly

EPFL LCBC

Ursula Röthlisberger
Ivano Tavernelli

ETH Zürich

Jeroen van Bokhoven
Matthew Brown

microXAS

Daniel Grolimund
Camelia Borca

PHOENIX

Thomas Huthwelker

SuperXAS

Maarten Nachtegaal
Jakub Szlachetko
Jacinto De Paiva Sa

Funding:
Swiss SNF, PSI, EPFL, NCCR MUST