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

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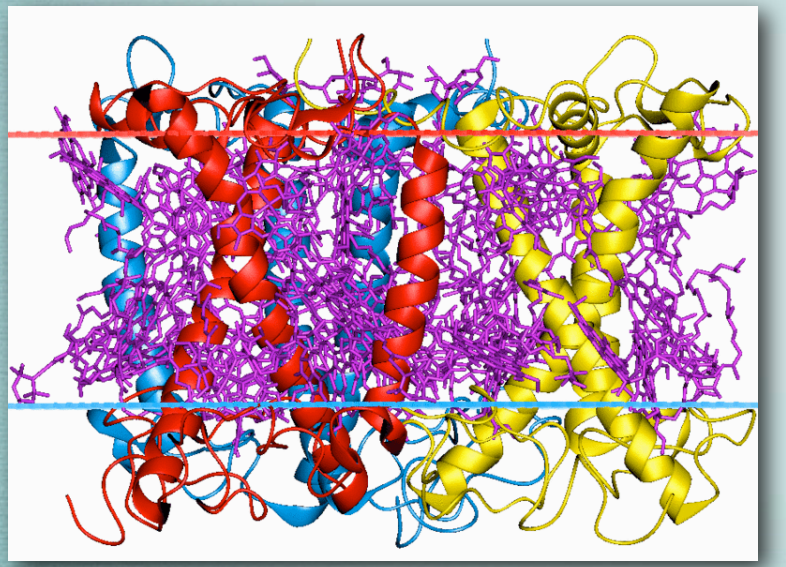
Is function structure or dynamics ?

Structure

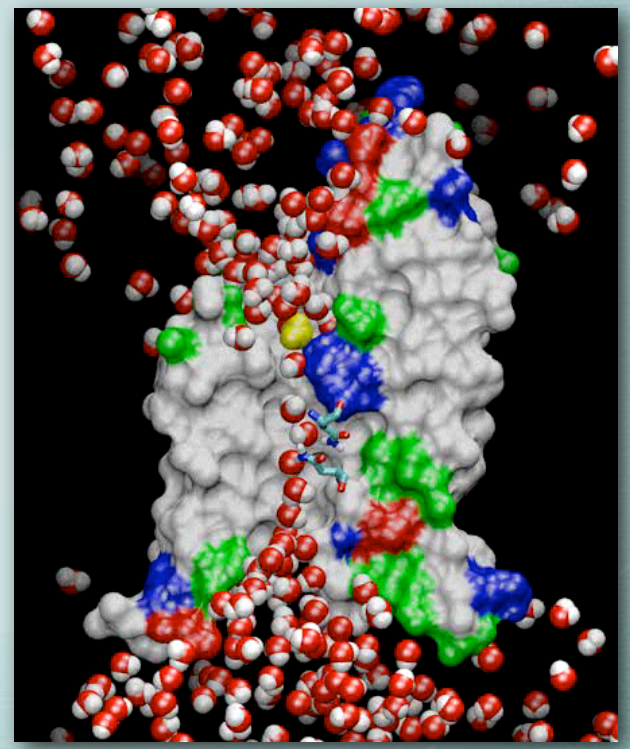
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR



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

Dynamics

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



Water transport through an aquaporin channel in a cell membrane
http://www.ks.uiuc.edu/Research/aquaporins/
Tajkhorshid, E., Nollert, P., Jensen, M.O., Miercke, L.J., O'Connell, J., Stroud, R.M., and Schulten, K. (2002). Science 296, 525-530

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

On what timescale do we want to measure structure ?

X-rays

laser plasma

X-FELs

laser-slicing

synchrotrons

high-harmonic generation

electronics

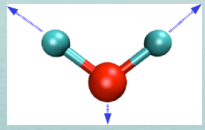
lasers

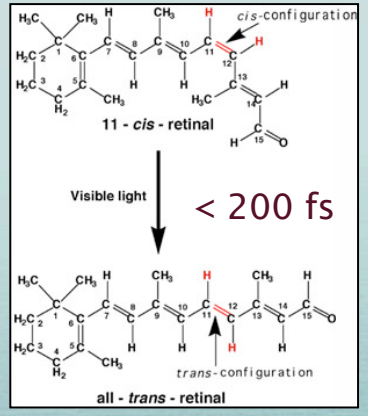
attoseconds 10^{-18} s	femtoseconds 10^{-15} s	picoseconds 10^{-12} s	nanoseconds 10^{-9} s	microseconds 10^{-6} s	milliseconds 10^{-3} s
electron motion core-hole lifetimes	motion of nuclei molecular vibrations optical phonons molecular bond formation	rotation of molecules molecular librations vibrational 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

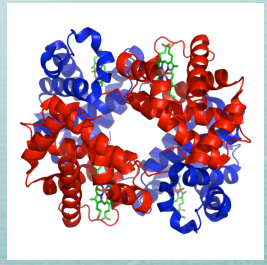
The Fe K-edge core-hole lifetime is 4 fs

period of the symmetric stretch in H_2O is 10 fs





Hemoglobin R->T transition takes microseconds



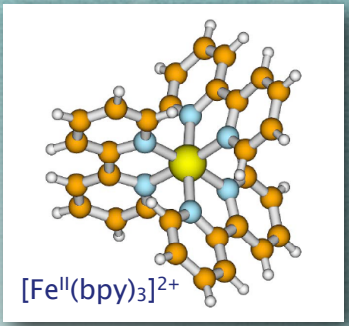
Camera shutter speeds range from ms through to seconds

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Investigating spin-crossover dynamics

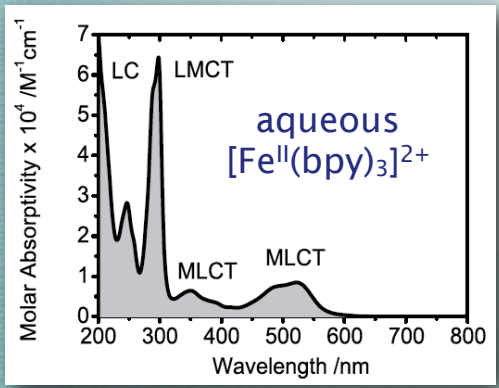
Spin-crossover phenomenon: a transition from a low-spin ground state to a high spin excited state

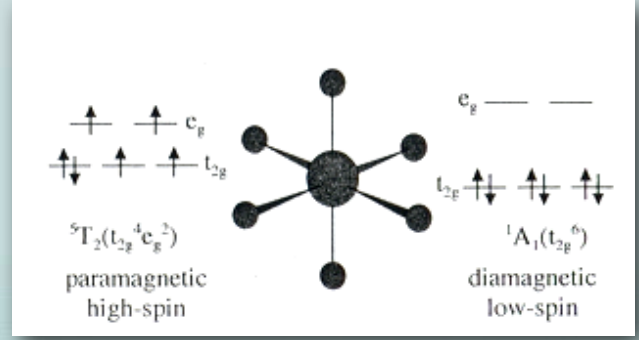
- can be induced by temperature or light
- Fe(II) compounds represent a general class of spin-crossover systems

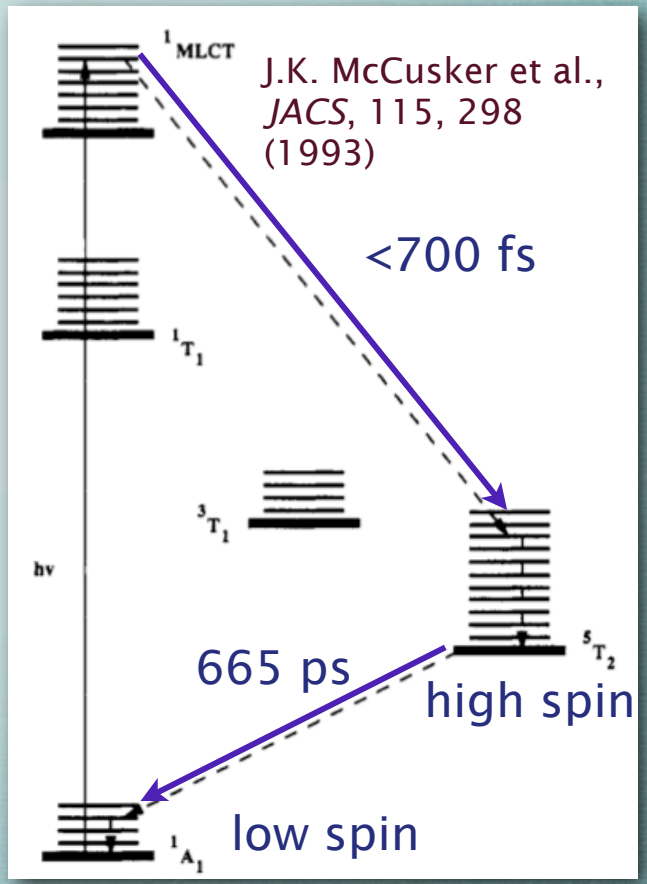


Applications:

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





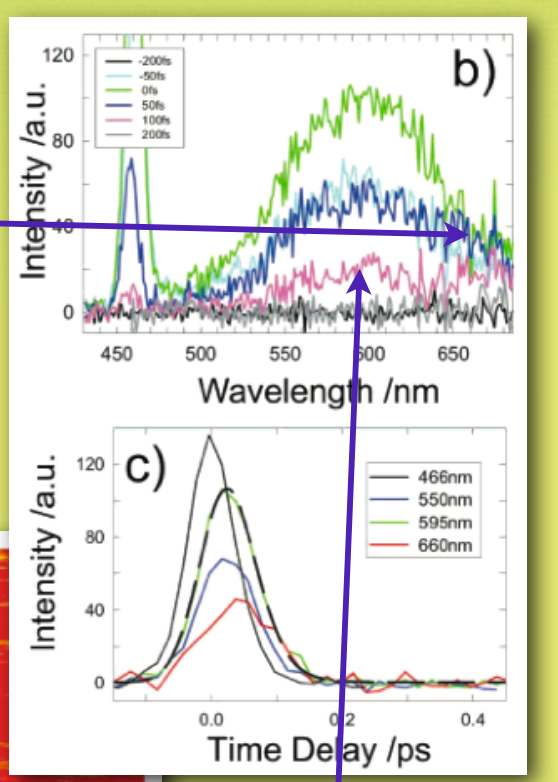


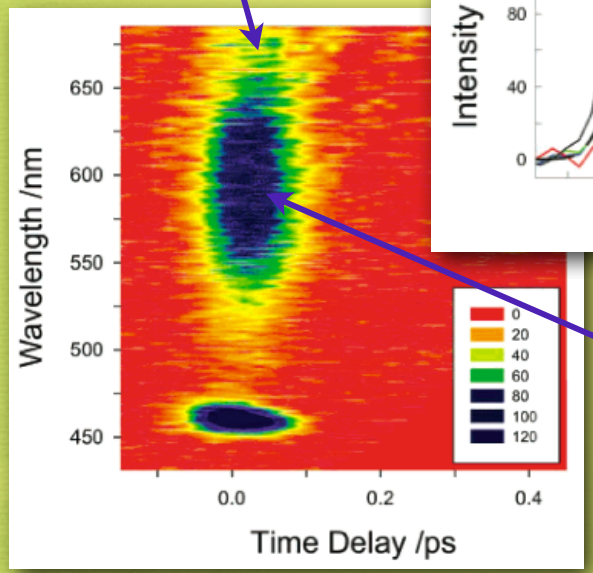
$[Fe^{II}(bpy)_3]^{2+}$ requires optical excitation and shows fs to ns relaxation dynamics

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

Fluorescence upconversion

^{3}MLCT emission ~130 fs

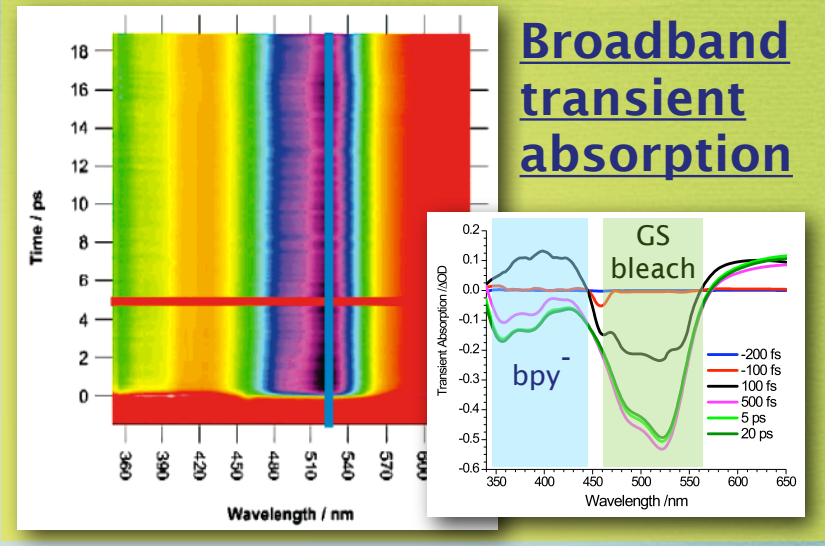


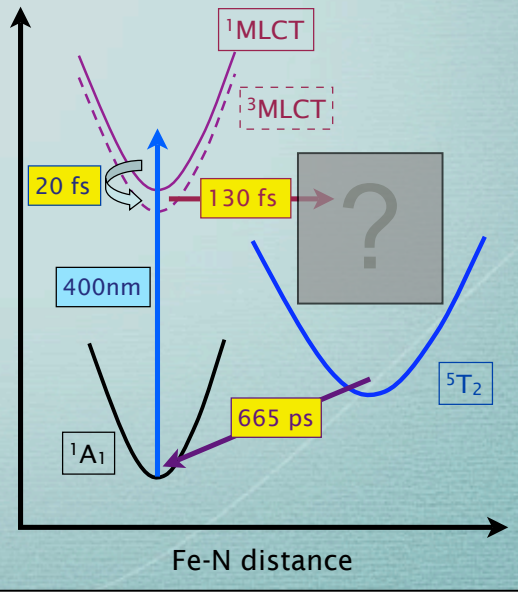


^{1}MLCT emission ~20 fs

W. Gawelda et al. *JACS* 129, 8199 (2007)

Broadband transient absorption

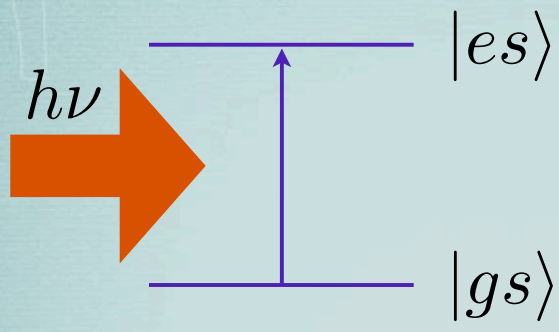




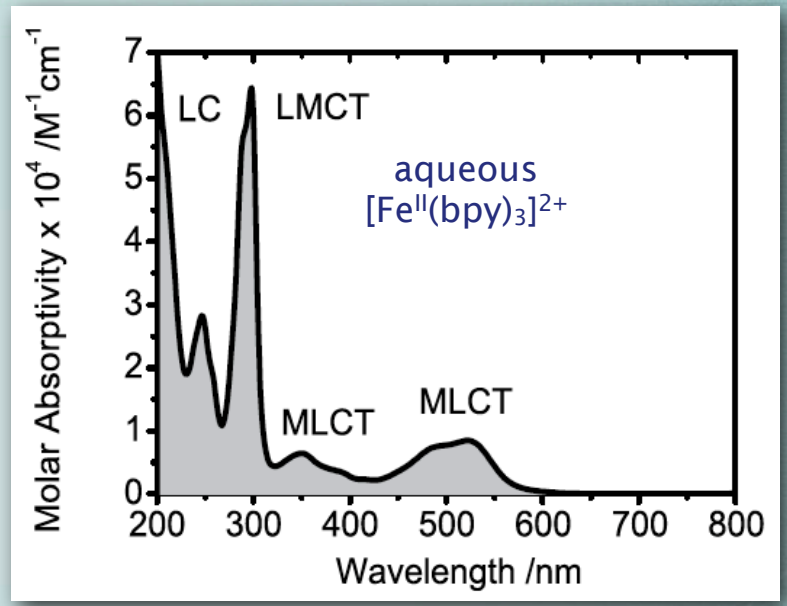
C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Ultrafast laser spectroscopy provides the dynamics

Spectroscopy measures energy transitions between states



We have dynamics but no structural information is directly available

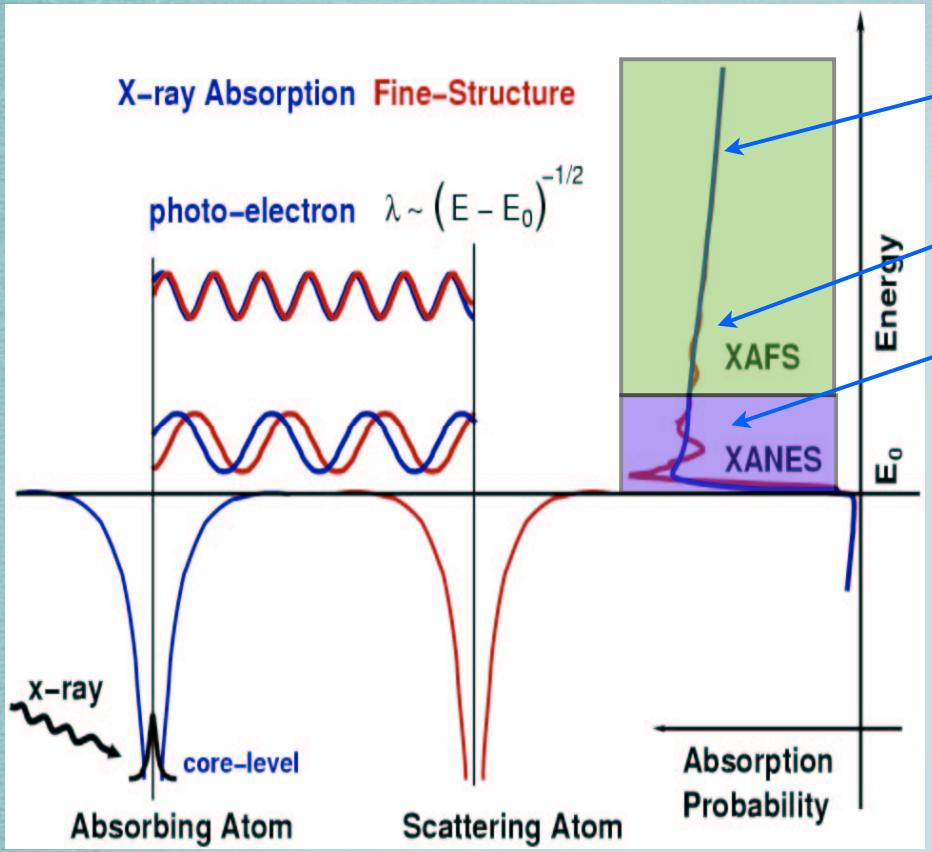


What is the structure of the high-spin state ?

We need a new technique

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

X-ray absorption spectroscopy: Retrieving structure



M. Newville, "Fundamentals of XAFS", pdf available at http://xafs.org/

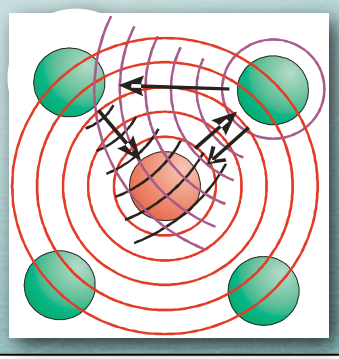
atomic background absorption contribution

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, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

X-ray absorption spectroscopy: Advantages

Any medium: Liquids, solids or gases

Element-specific
- Specific absorption edge
- Can investigate spectroscopically silent species

Electronic structure
- Density and occupancy of states
- Valence orbitals
- Degree of oxidation
- Local symmetry

Bond distances and angles
- Above ionization resonances (multiple and single scattering)

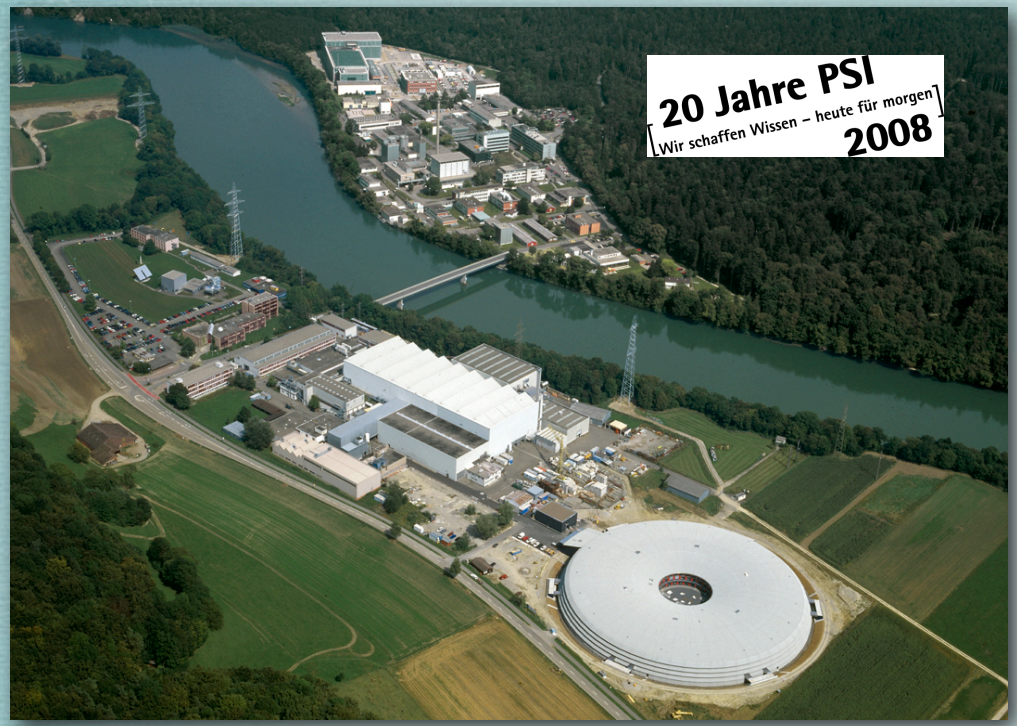
X-ray absorption spectroscopy: Disadvantages

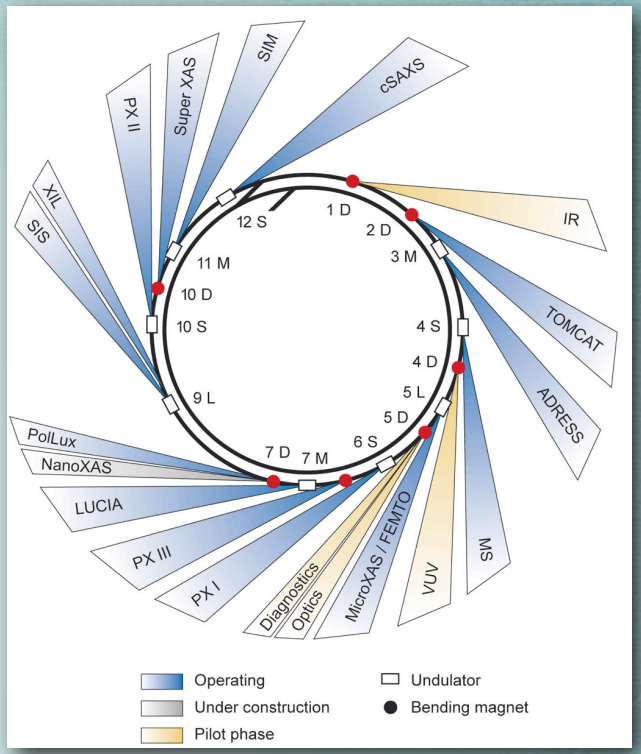
Requires tuneable x-ray source

Only sensitive to local structure within a few Angstroms

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

X-ray source: The Swiss Light Source at the Paul Scherrer Institut

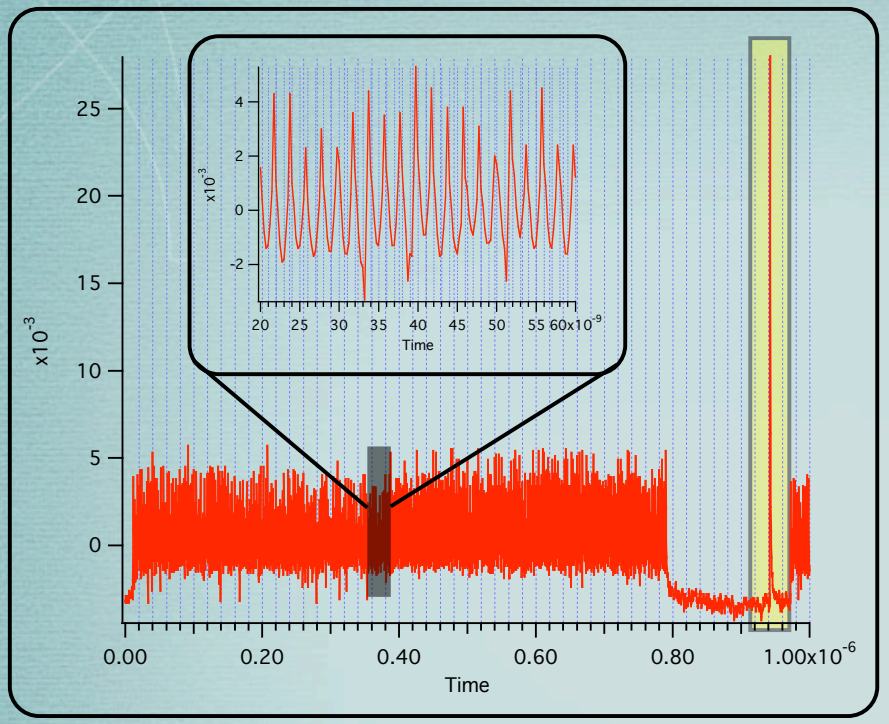




3rd generation synchrotron light source located one hour from Zurich (2.4 GeV)

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Ultrafast x-ray sources: Picosecond

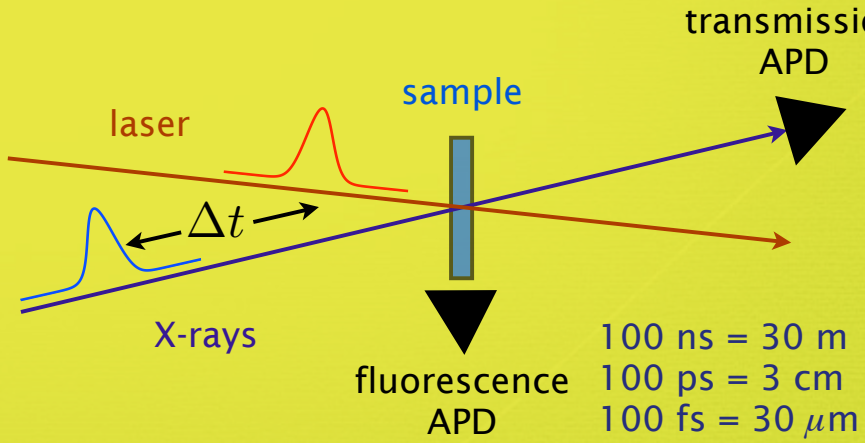


MicroXAS beamline

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

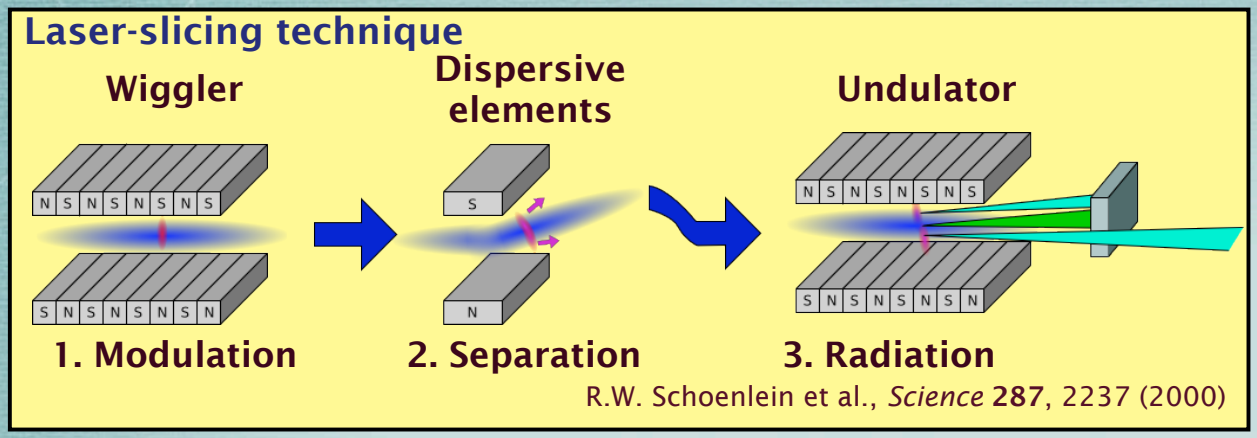
Using fast avalanche photodiodes and boxcar integrators we can selectively measure using only the camshaft pulse giving us 100 ps time resolution

Pump-probe measurements



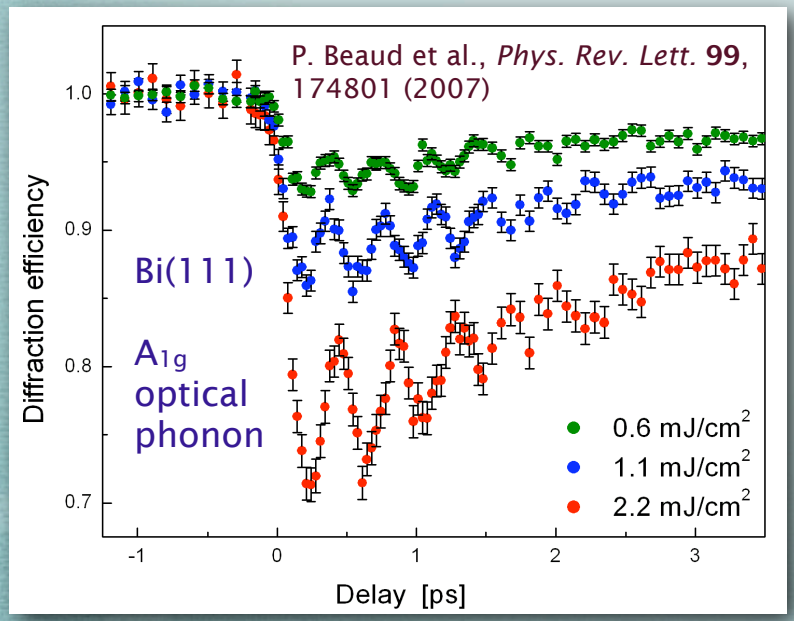
C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

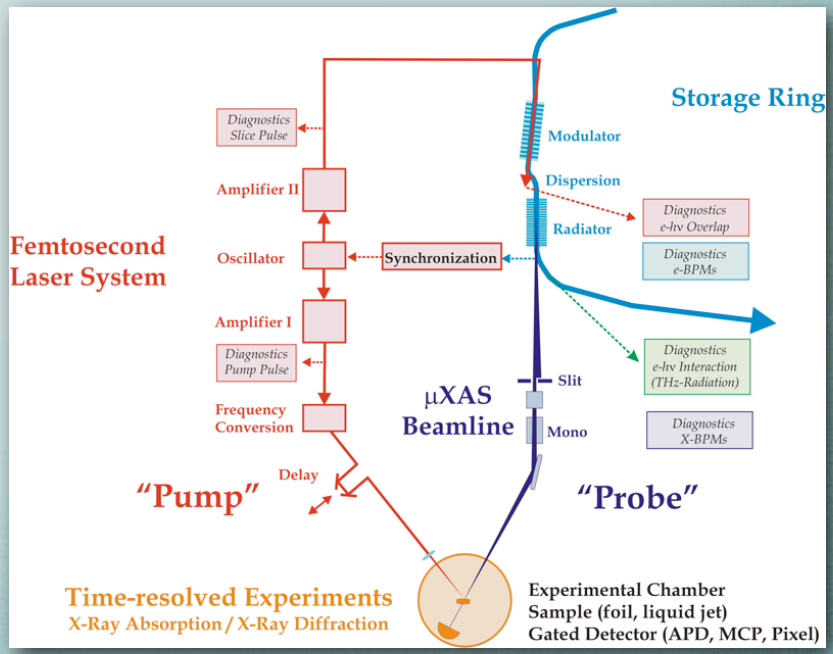
Ultrafast x-ray sources: Femtosecond



The FEMTO slicing source at the SLS

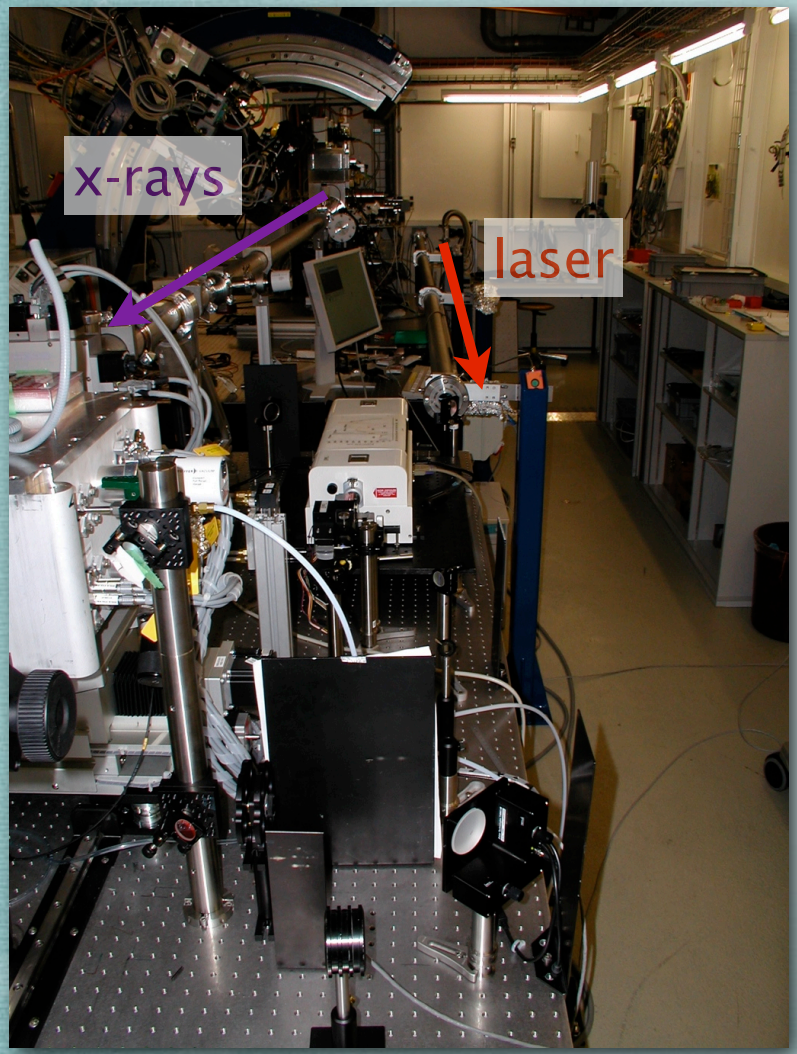
- tuneable from 4 to 14 keV
- 140 ± 30 fs x-ray pulse duration
- timing stability of < 30 fs RMS over days
- 10^5 photons/second



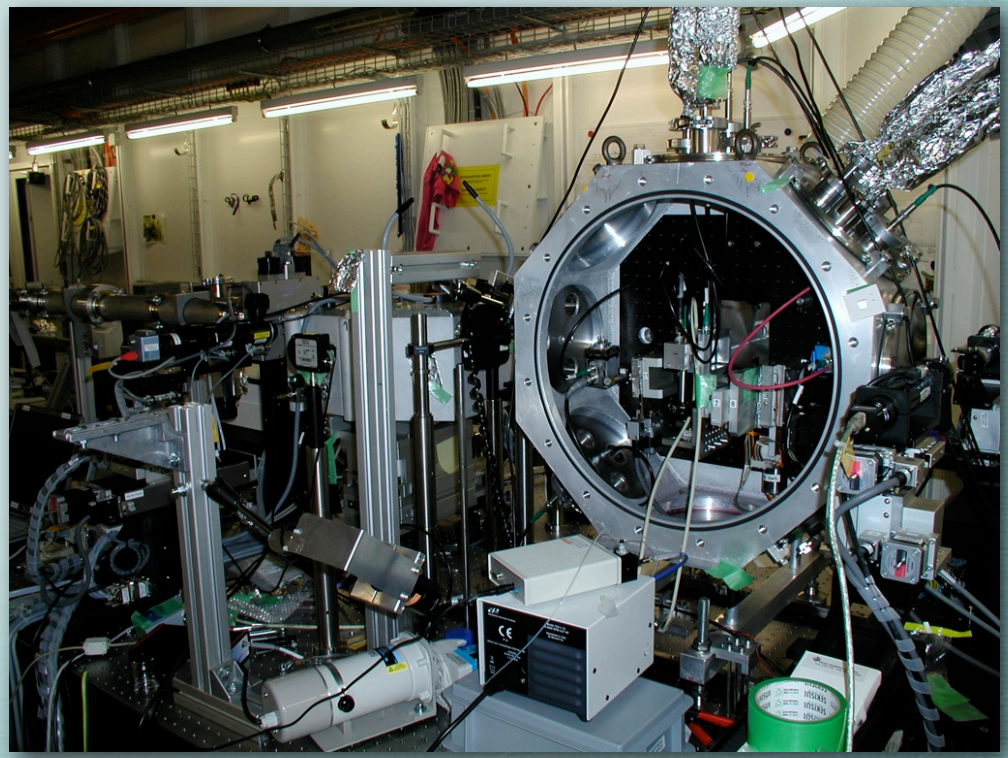


C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Time-resolved XAS experimental setup at the SLS

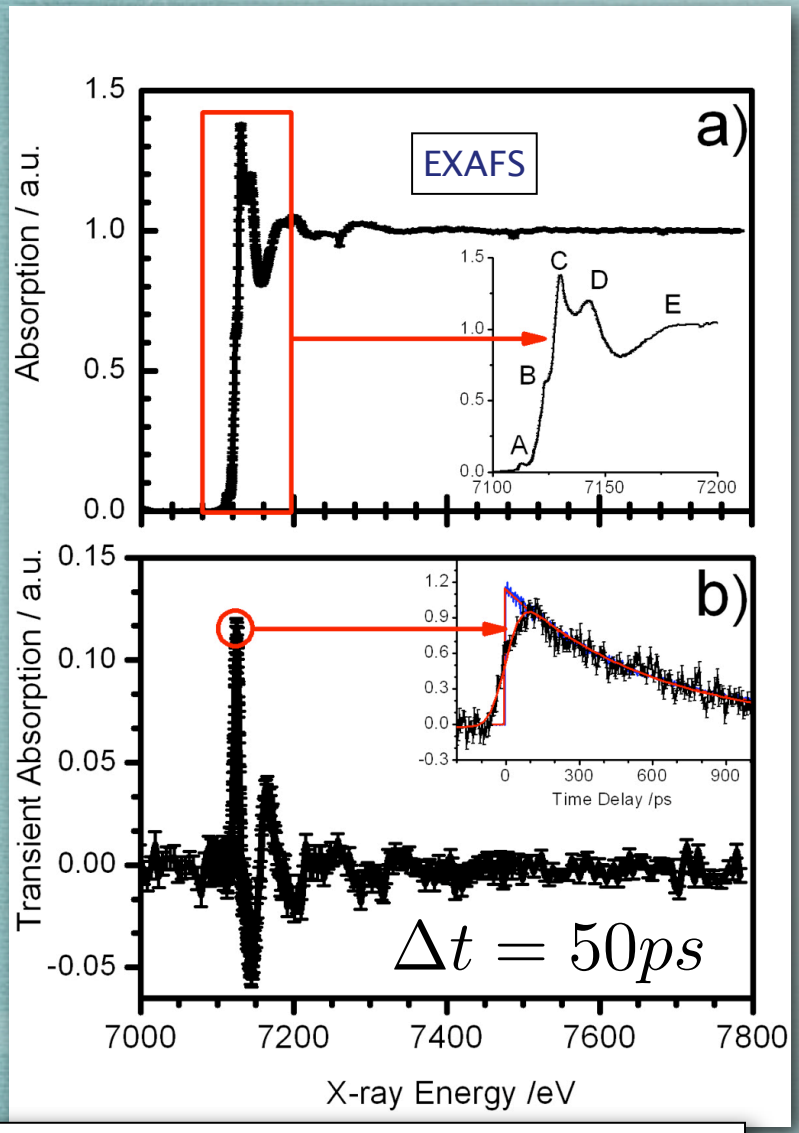


pump laser: 1 kHz, 100 fs tuneable from the UV to the IR using a TOPAS optical parametric amplifier

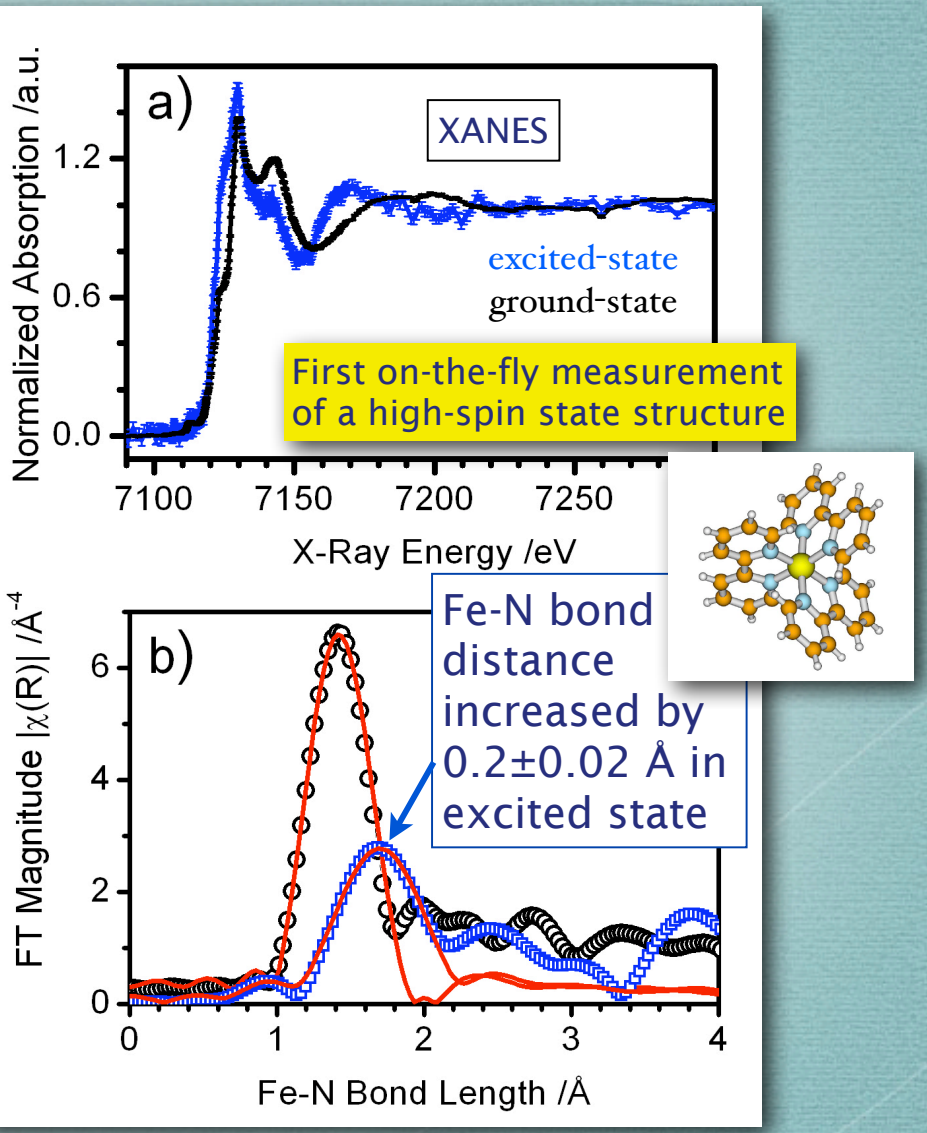


C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

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

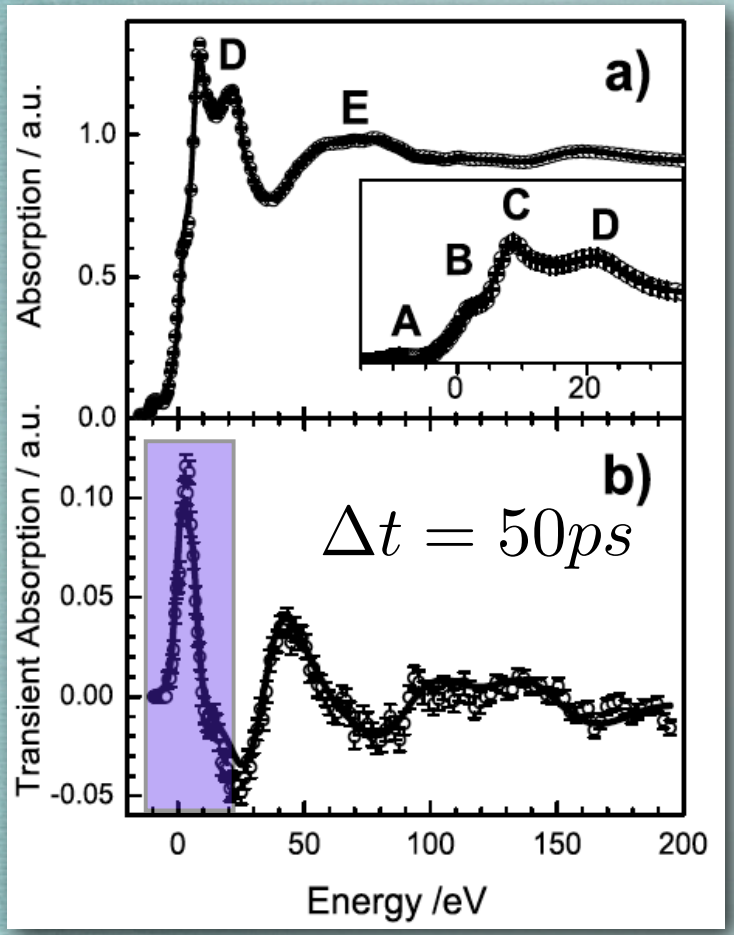


W. Gawelda et al., *Phys. Rev. Lett.*, **98** 057401 (2007)



C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

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

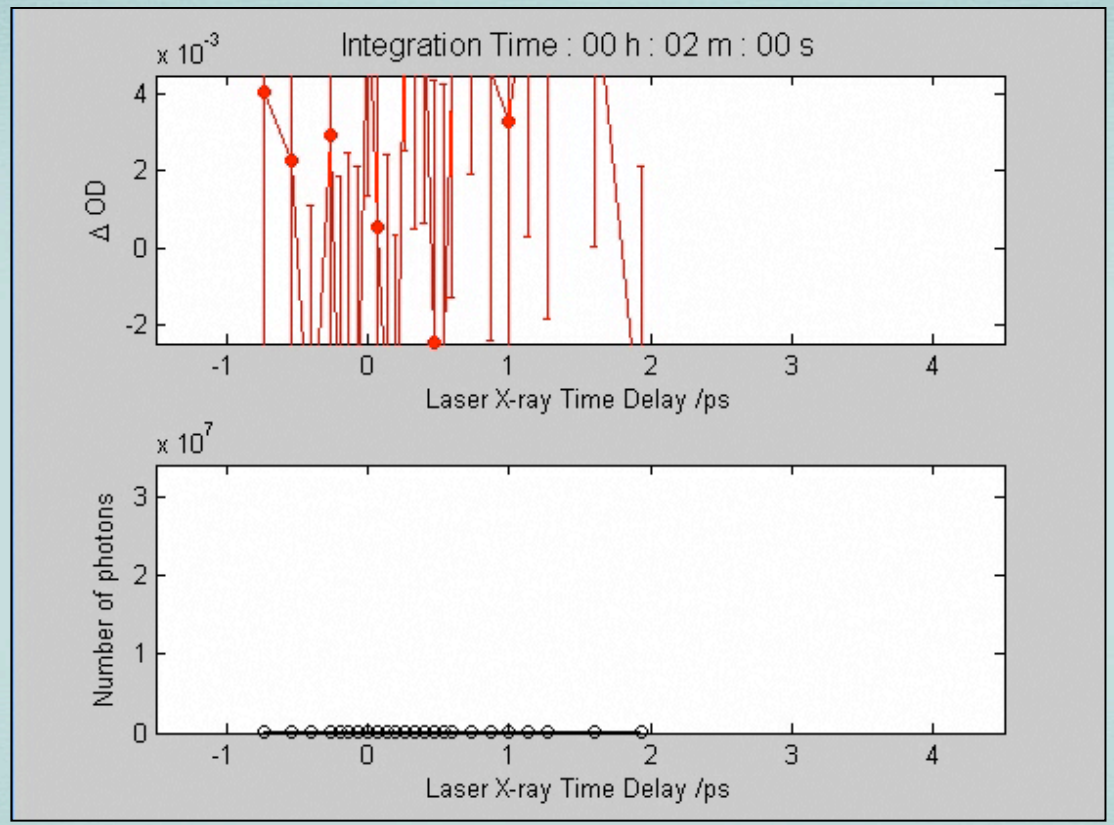
The largest transient signal is at the B feature which is a multiple-scattering feature sensitive to the Fe-N bond distance

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

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

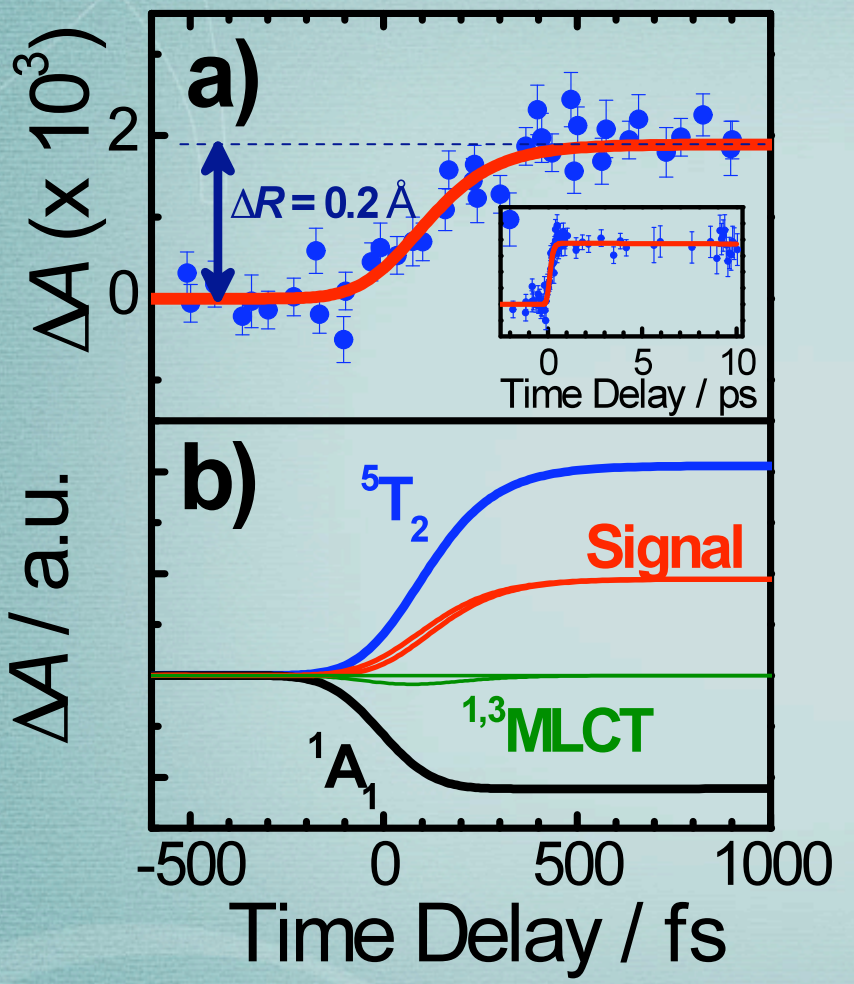
Aqueous $[Fe^{II}(bpy)_3]^{2+}$: First femtosecond timescan



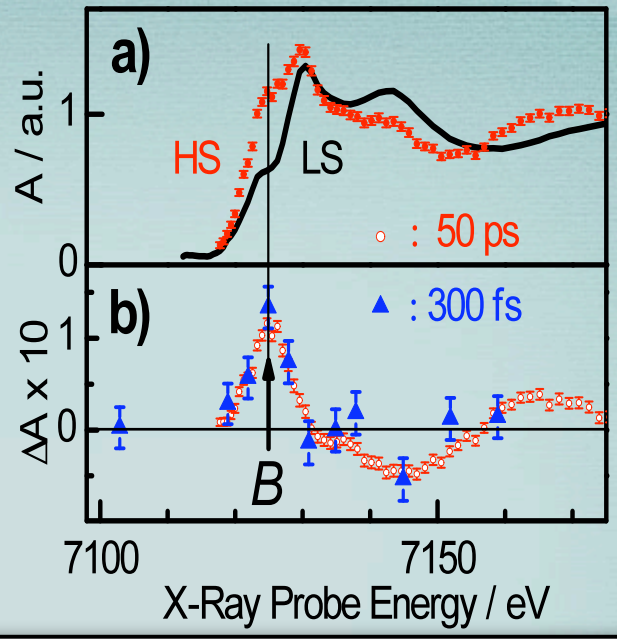
Total data acquisition time: 32 hours

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

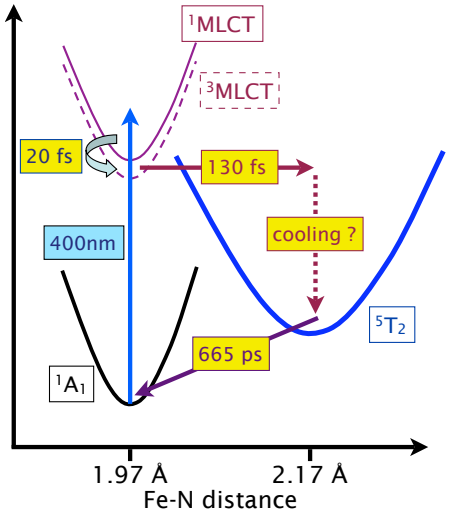
Aqueous $[Fe^{II}(bpy)_3]^{2+}$: Femtosecond XAS results



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

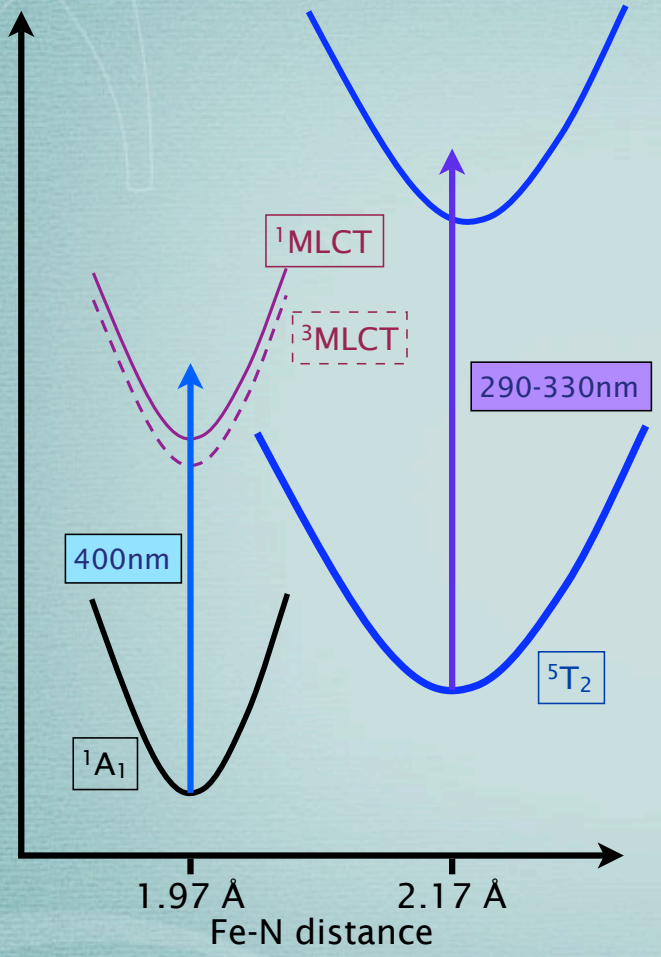


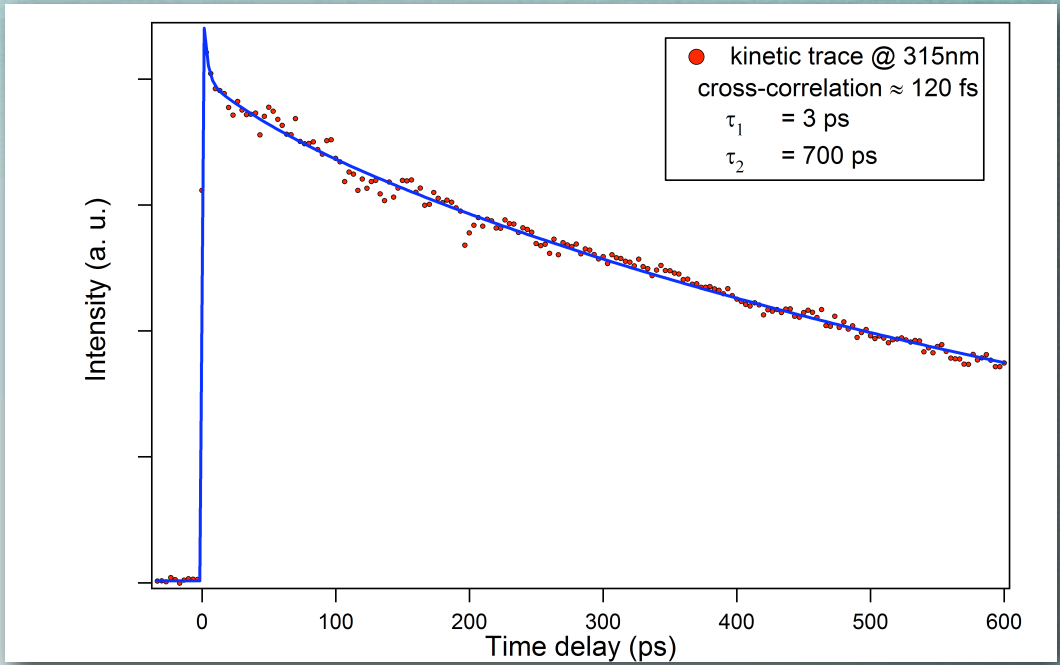
The molecule arrives in the high-spin state directly from the ^{3}MLCT in ~150 fs



C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

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

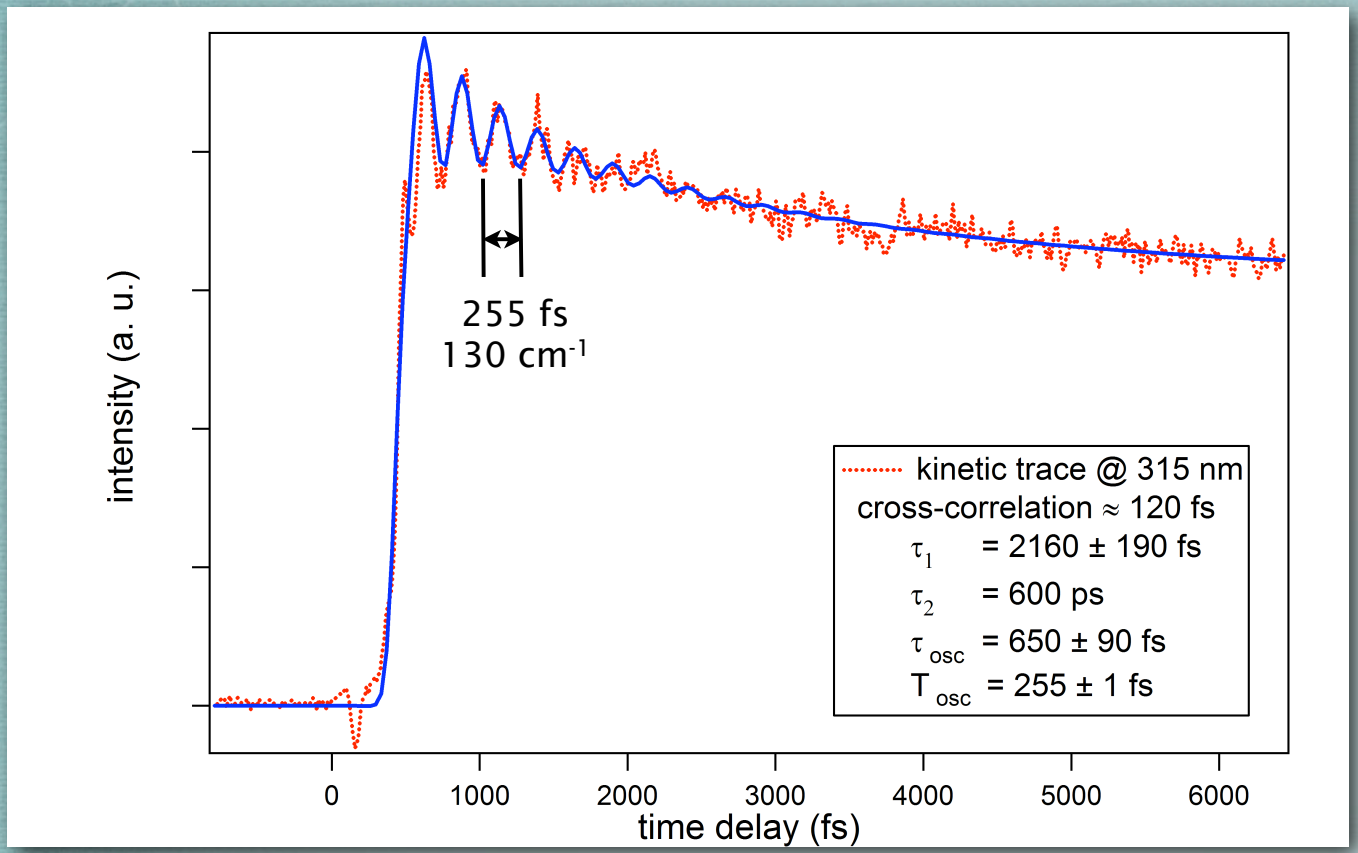




UV probe in the region of 290-330 nm investigates the dynamics of the high-spin state optically

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

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

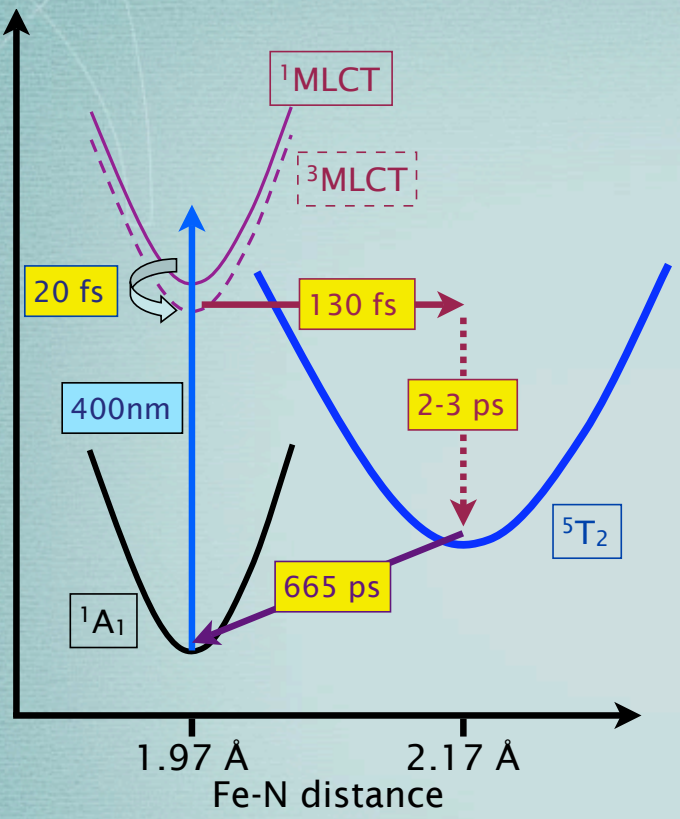


We see wavepacket dynamics with a period of 255 fs and a decay time of 2-3 ps

This corresponds to a low-frequency bending motion of the ligands and is not sensitive to the Fe-N bond distance

C. Consani et al. in preparation (2008)

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

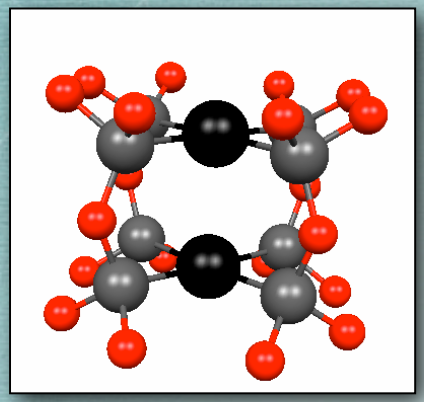
Femtosecond XANES has allowed us to watch the arrival of an excited molecular system in its high-spin state

The potential inherent to the technique is enormous, we can measure structural changes in excited systems on the timescale of atomic motion

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

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Photochemistry and photocatalysis: $Pt_2(P_2O_5H_2)_4^{4-}$

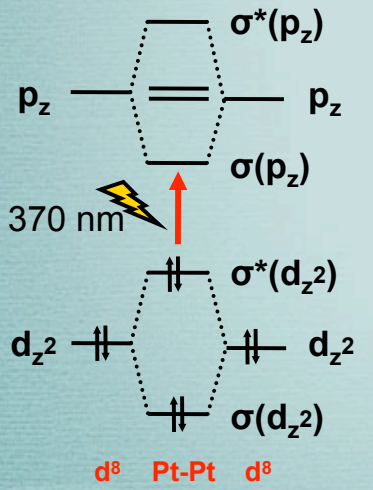


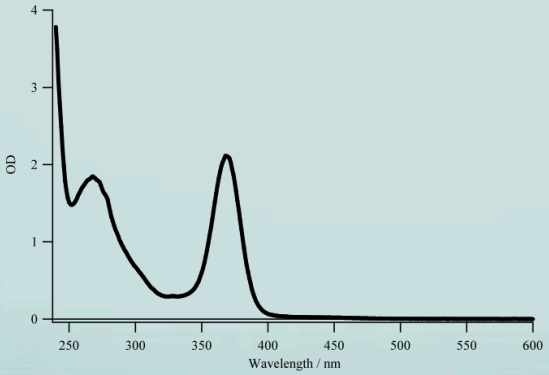
$Pt_2(P_2O_5H_2)_4^{4-}$ is a photocatalyst

$$(CH_3)_2CHOH \xrightarrow[Pt_2(P_2O_5H_2)_4^{4-}]{h\nu = 3.3\ \text{eV}} (CH_3)_2CO + H_2(g)$$

Excitation at 370 nm results in a long-lived (10 μs) triplet state and the formation of a Pt-Pt bond

$$^1A_{1g} \xrightarrow{370\ \text{nm}} {}^1A_{2u} \xrightarrow{\text{ISC}} {}^3A_{2u}$$



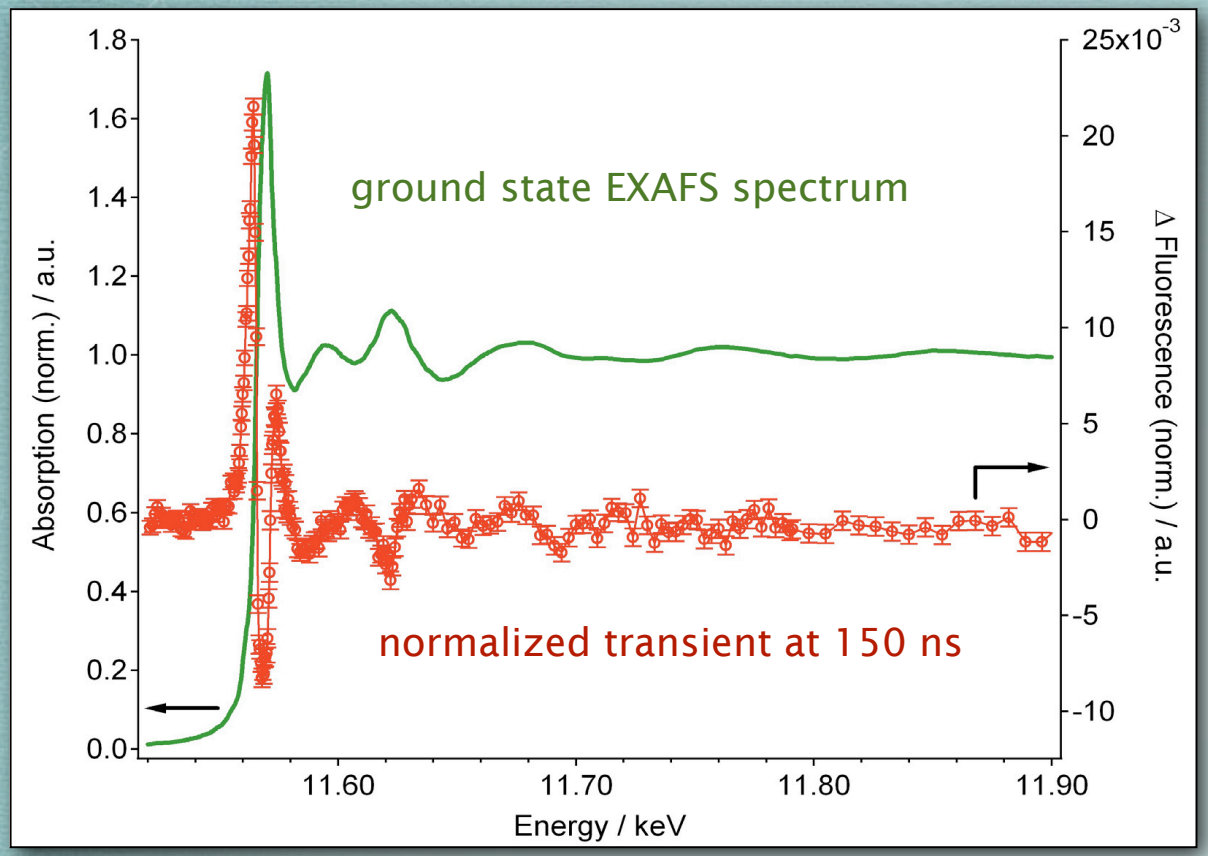


There is substantial disagreement in the literature over this Pt-Pt bond distance change ranging from 0.21 to 0.52 Å

What is the structure of this excited state ?

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

$Pt_2(P_2O_5H_2)_4^{4-}$: ps XAS



Experimental details:

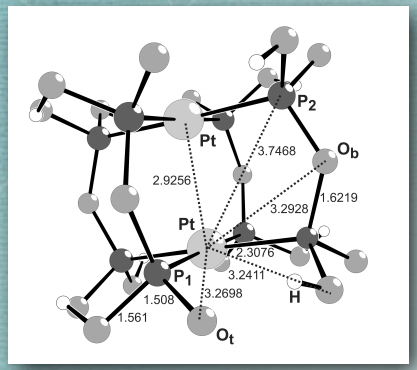
-10 mM $(TBA)_4[Pt_2(P_2O_5H_2)_4]$ solution in degassed ethanol

- pumped at 390 nm (50 mW)
- thin-walled quartz flow capillary with 500 μm diameter was used

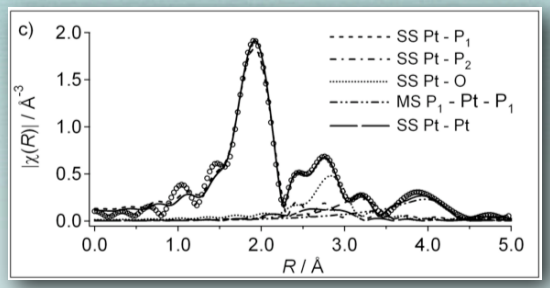
Information about the structure of the triplet excited state is in this transient spectrum, but how do we get it out ?

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

$Pt_2(P_2O_5H_2)_4^{4-}$: Data analysis



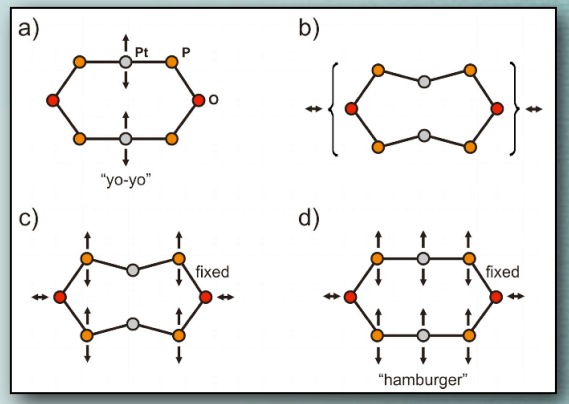
1) optimize ground-state structures and parameters



$$R_{Pt-Pt} = 2.876(28)\text{Å}$$
$$R_{Pt-P_1} = 2.32(4)\text{Å}$$

R.M. van der Veen, et al. *CHIMIA* **62**, 287 (2008)

2) generate a set of EXAFS spectra for a given model by moving specific coordinates



3) Calculate the transient spectrum

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

4) Minimize the reduced chi squared function

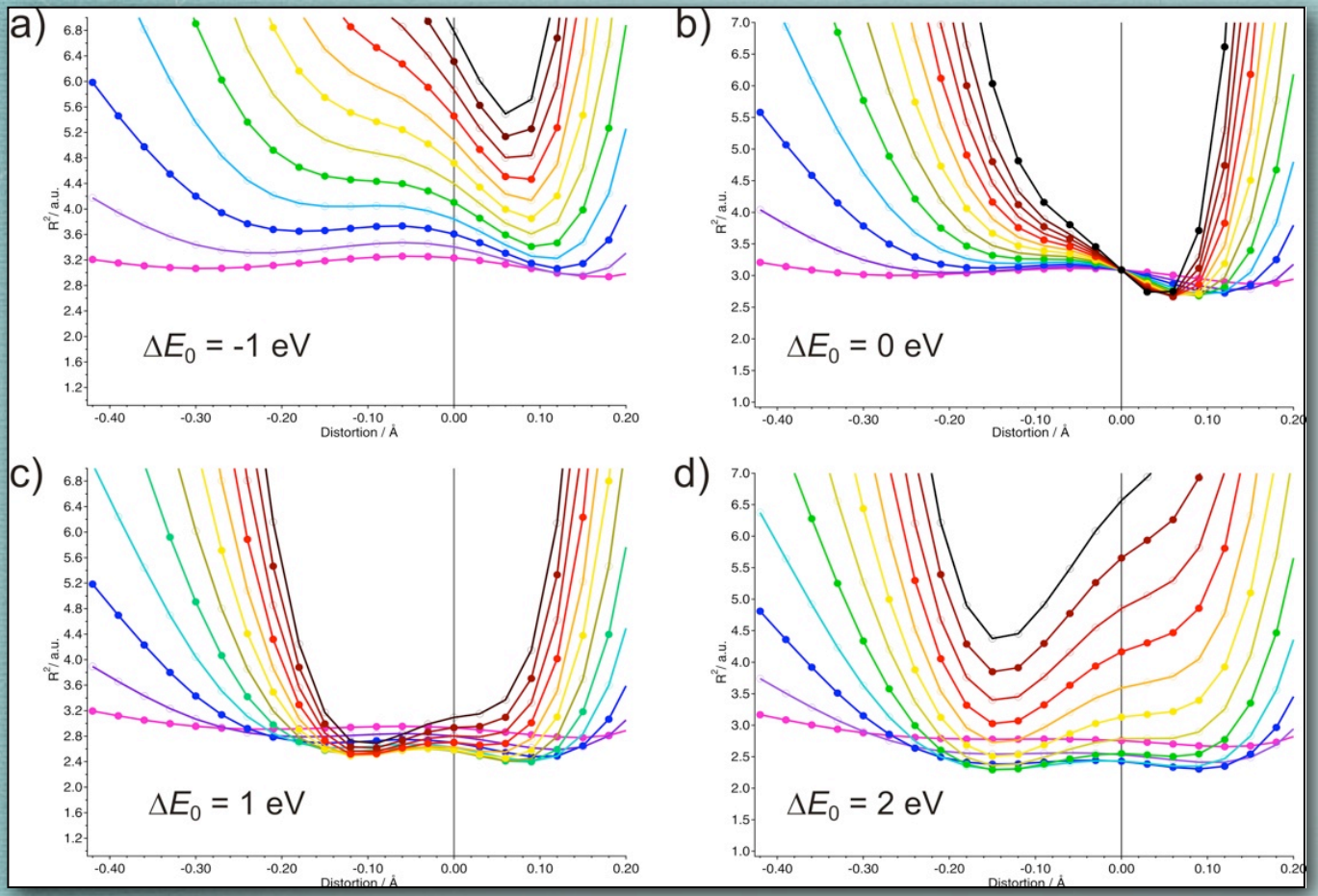
$$\chi_r^2(i, f, \Delta E_0) = \frac{1}{N-1}\sum_{j=1}^{N}\left(\frac{x_j/f - \Delta\chi_{i,j}^{TH}(\Delta R_i, E')}{\sigma_j^x/f}\right)^2$$

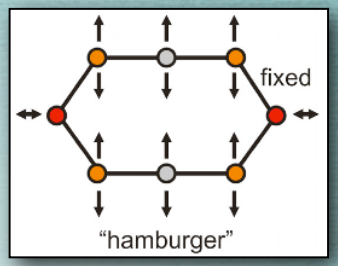
W. Gawelda et al., submitted (2008)

differential EXAFS: Pettifer et al. *Nature* **435**, 78 (2005)

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

$Pt_2(P_2O_5H_2)_4^{4-}$: Data analysis with a poor model





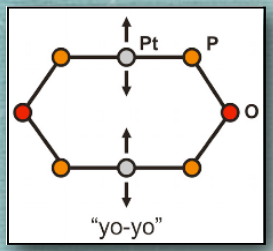
'Hamburger' distortion corresponds to the P-Pt-P planes moving towards each other

D.J. Thiel et al., *Nature* **360**, 40 (1992)

It's clear that this is a poor model which results in large R^2 values and no combination of parameters matches the experimental data

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

$Pt_2(P_2O_5H_2)_4^{4-}$: Data analysis with a better model

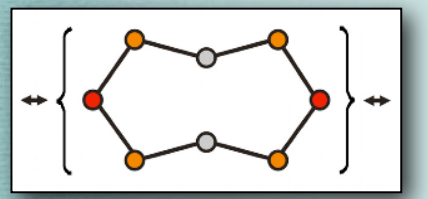


1) start with Pt-Pt distance

$\Delta R_{Pt-Pt} = -0.31\text{Å}$

$f = 8\%$ $\Delta E = -1eV$

$R^2 = 1.67$

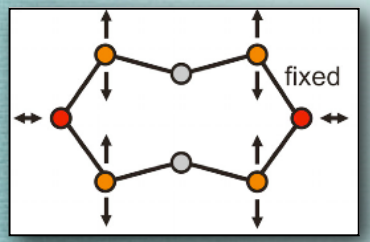


2) fix Pt-Pt distance and distort P-O-P ligands together

$\Delta R = 0.01\text{Å}$

$f = 7\%$ $\Delta E = 0eV$

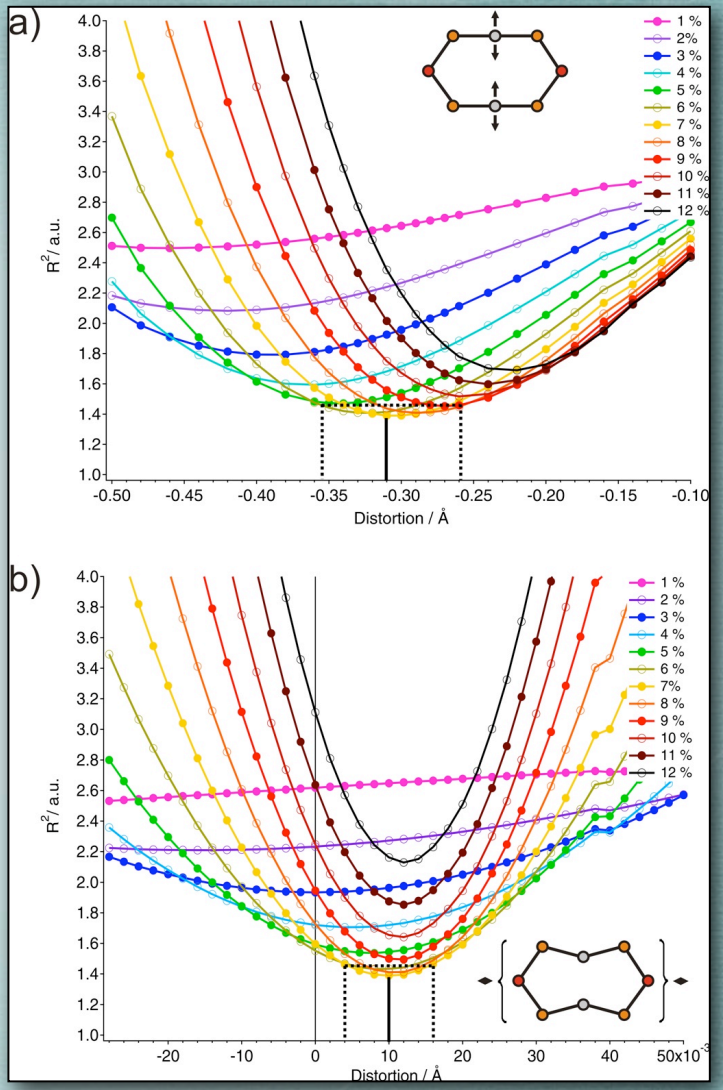
$R^2 = 1.39$



3) allow the P atoms to move seperately from the O atoms

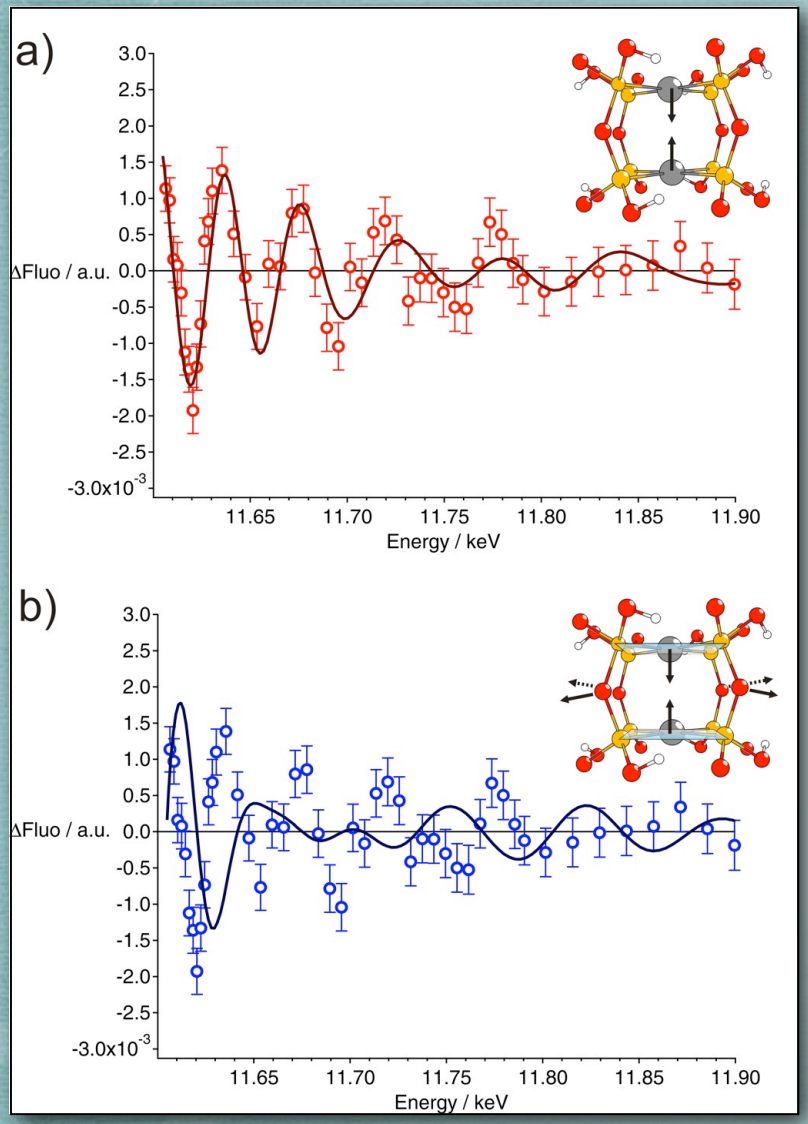
$f = 7\%$ $\Delta E = 0eV$

$R^2 = 1.39$



C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

$Pt_2(P_2O_5H_2)_4^{4-}$: Structural summary



Excitation into the $^3A_{2u}$ state results in a decrease in the Pt-Pt distance and a small increase in the Pt-ligand distance

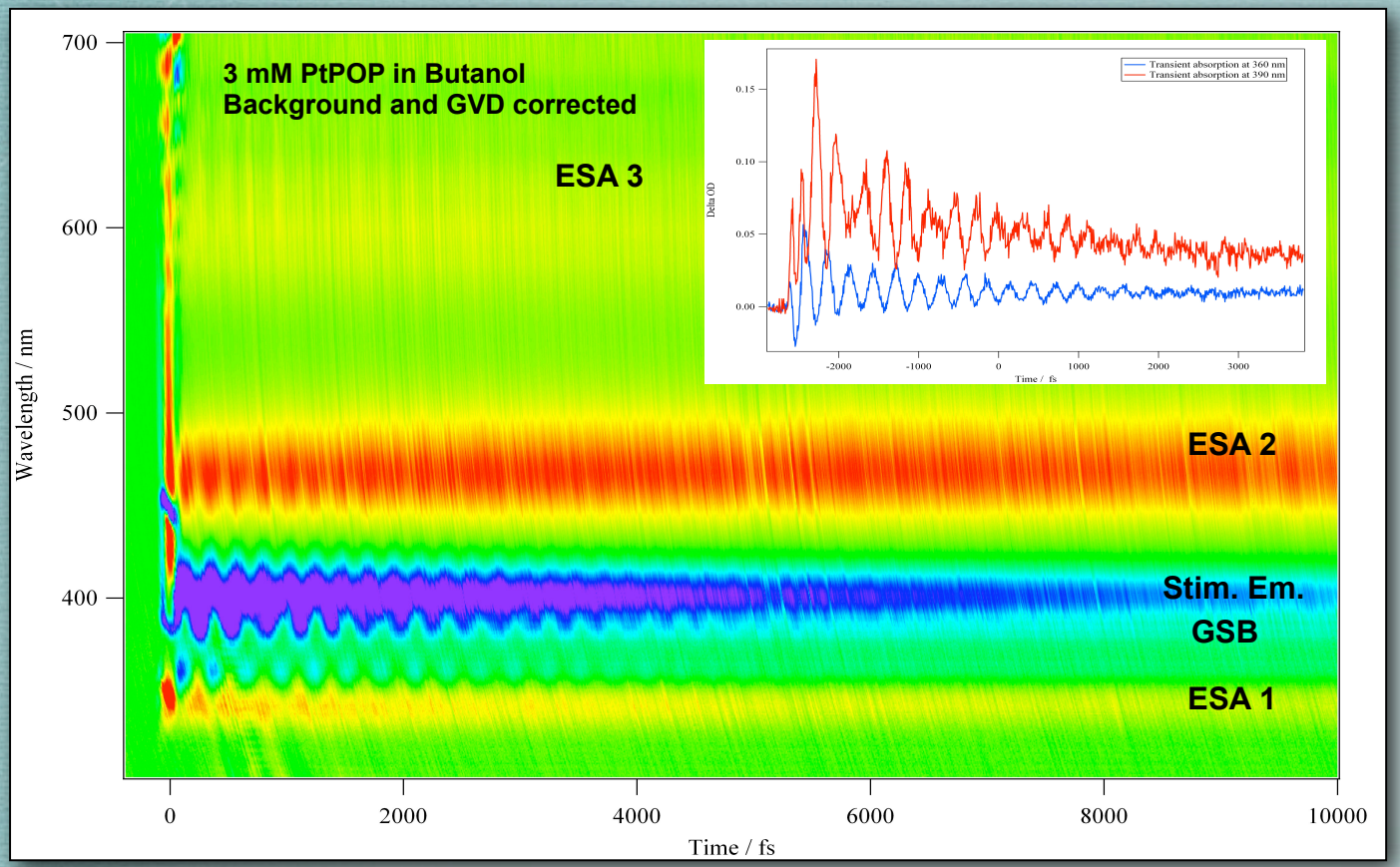
$$\Delta R_{Pt-Pt} = -0.31(5)\text{Å}$$
$$\Delta R_{Pt-P_1} = 0.010(6)\text{Å}$$

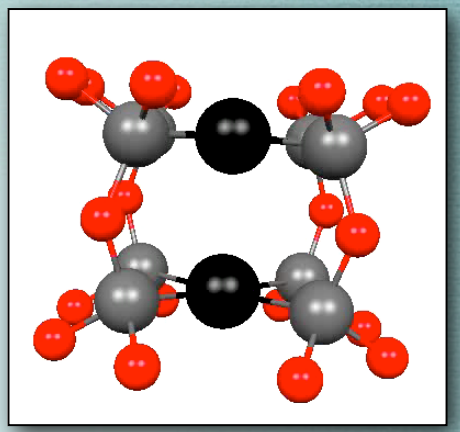
Without any *a priori* knowledge an excitation of 7% was obtained with a 0 eV energy shift both of which make physical sense

This analysis technique is remarkably robust and requires very few assumptions or prior knowledge

R.M. van der Veen, et al., *Angew. Chem. Int. Ed.* (2009)

$Pt_2(P_2O_5H_2)_4^{4-}$: Towards fs XAS



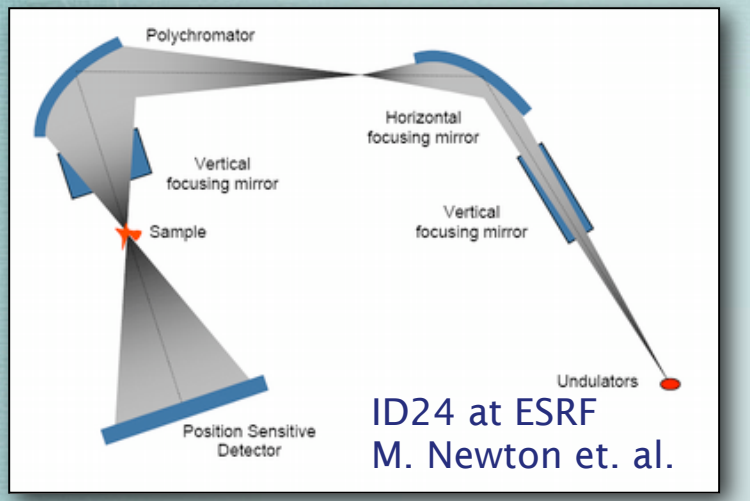


Can we see these 250 fs wavepacket structural oscillations using x-ray absorption spectroscopy ?

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Ultrafast time-resolved EDXAS

How about ultrafast time-resolved energy dispersive XAS ?



-single shot
-very fast
-small beam (< 10 μm)
-no moving parts
-no need to scan the energy
-requires a fast spatial detector
-dispersed flux on detector

T. Matsushita et al., *Japan. J. Appl. Phys.*, **20**, 2223 (1981)

Thoughts:

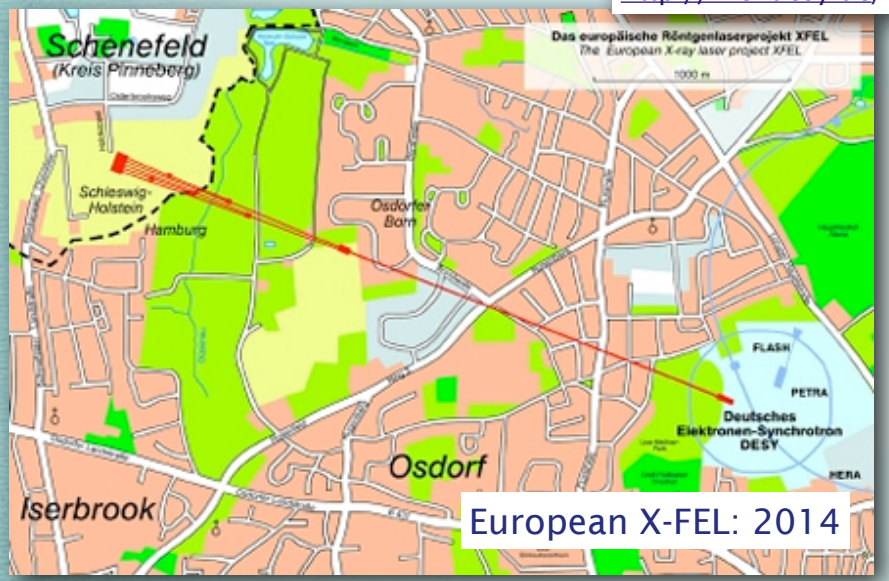
- anything that speeds up data acquisition is good
- flux damage of sample ?
- fast detector ?
- geometrical smearing of time resolution ?

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

Ultrafast XAS: The future

The remaining major restriction is x-ray flux, but with the advent of new x-ray sources (LCLS, European X-FEL, PSI-XFEL) it will soon be possible to perform these types of measurements with both higher time-resolution and in much shorter periods of data acquisition

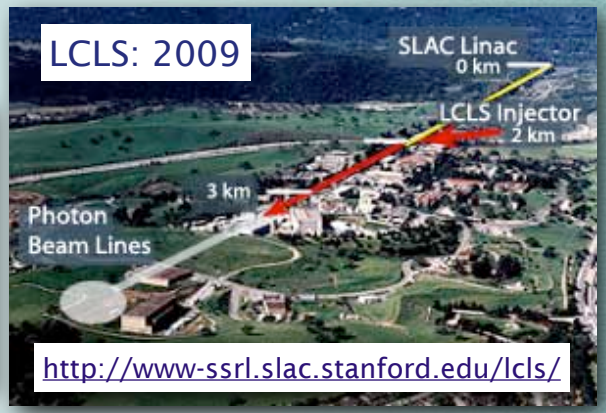
http://xfel.desy.de/



European X-FEL: 2014

10^{12} ph/pulse
10-100 fs

single-shot measurements



http://www-ssrl.slac.stanford.edu/lcls/

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http://fel.web.psi.ch/

In the mean time we have the ability to make significant measurements on solvation dynamics, excited-state structural dynamics and biological systems with current ultrafast x-ray sources

C.J. Milne, *Ultrafast time-resolved XAS: Watching atoms move*, ESRF 2009

EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

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