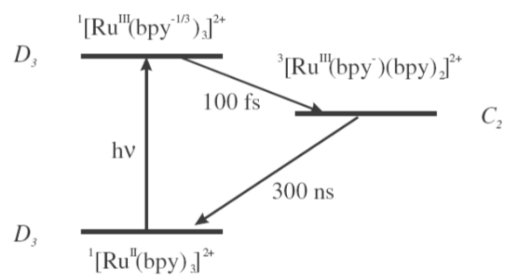
Lecture 4.

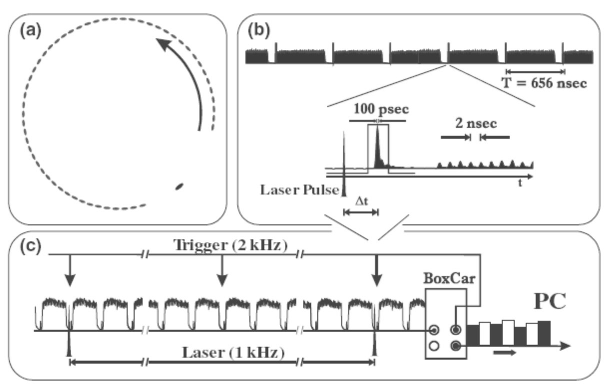
Advanced methods in x-ray spectroscopies

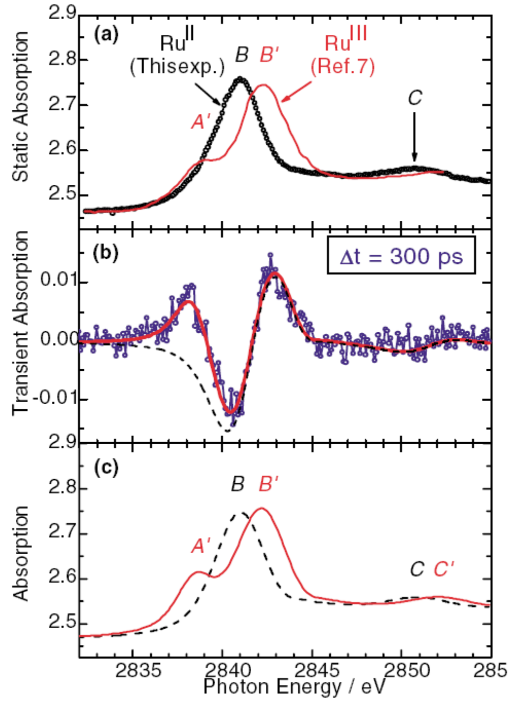
- Ultrafast XAS
- Multiple Excitation
- Diffraction anomalous fine structure – site specific EXAFS
- X-ray magnetic circular dichroism
  - Magnetic imaging
- High-resolution x-ray emission (inelastic x-ray scattering)
- X-ray Raman scattering

Ultrafast XAS

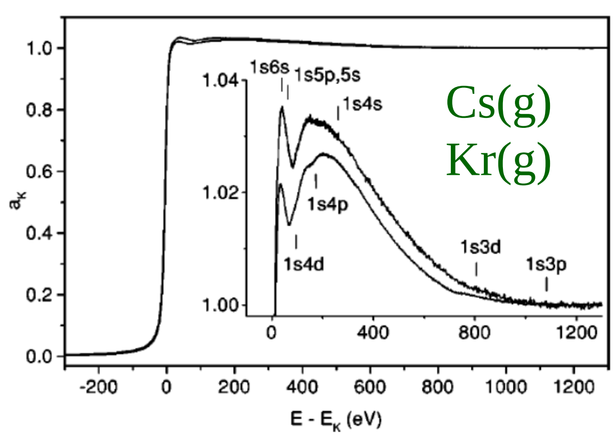


Saes et al., *PRL*, **2003**, *90*, 047403-1



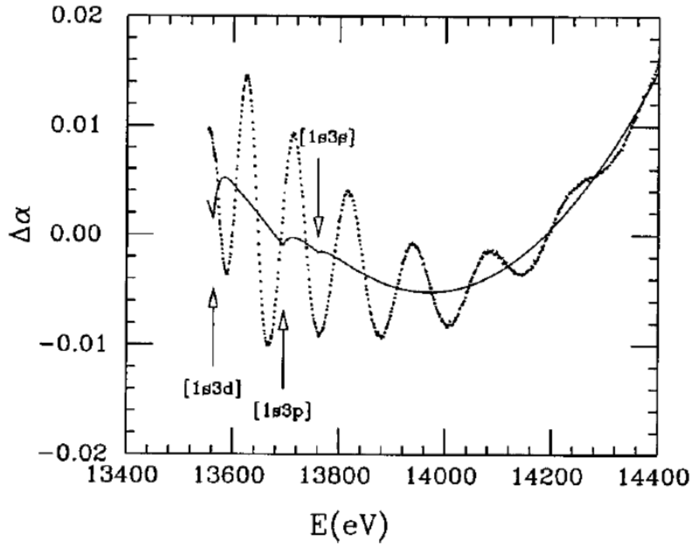


Double Excitation



Padežnik Gomilšek, *Phys Rev. A* **2003**, *68*, 042505

Br_2 EXAFS

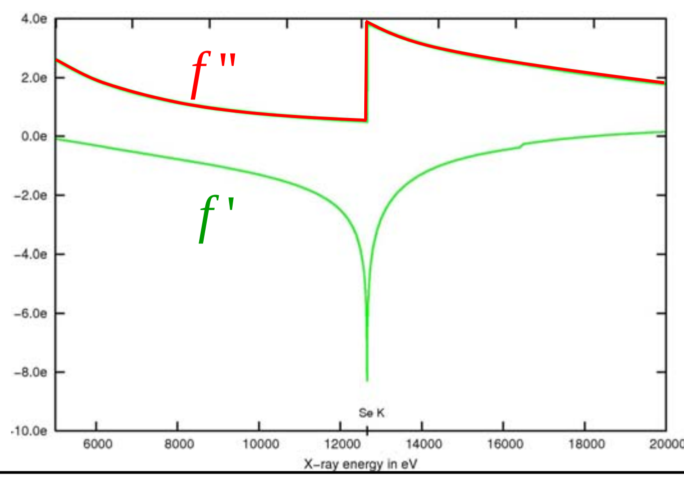


Filipponi and D'Angelo, *J. Chem. Phys.*, **1998**, *109*, 5356

Anomalous scattering

$$F(\mathbf{h}) = \sum_{i=1}^{N} f_i \, e^{2\pi i \mathbf{h} \mathbf{r}_i}$$

$$f(\omega) = f_0 + f'(\omega) + i\, f''(\omega)$$

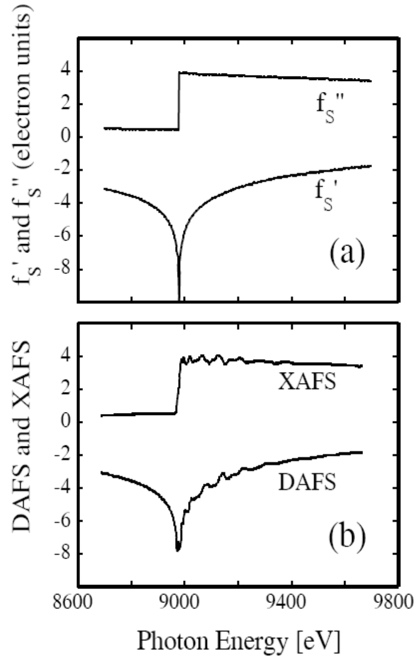


DAFS

Diffraction Anomalous Fine Structure

Kramers-Kronig transformation

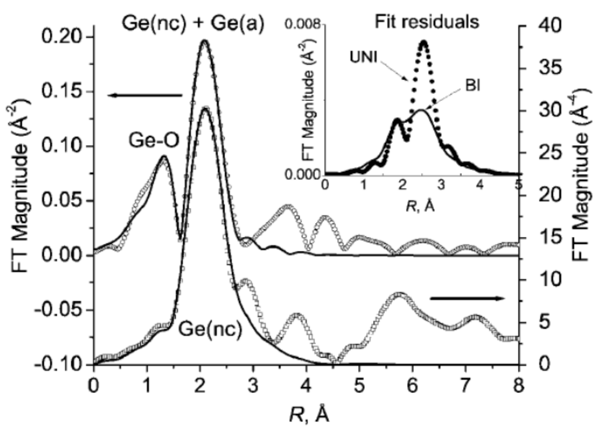
$$f'(\omega) = \frac{2}{\pi}\int_0^{\infty} \frac{\omega' f''(\omega')\partial\omega'}{\omega^2 - \omega'^2}$$



Nano-crystalline Ge in Ge/GeO_2

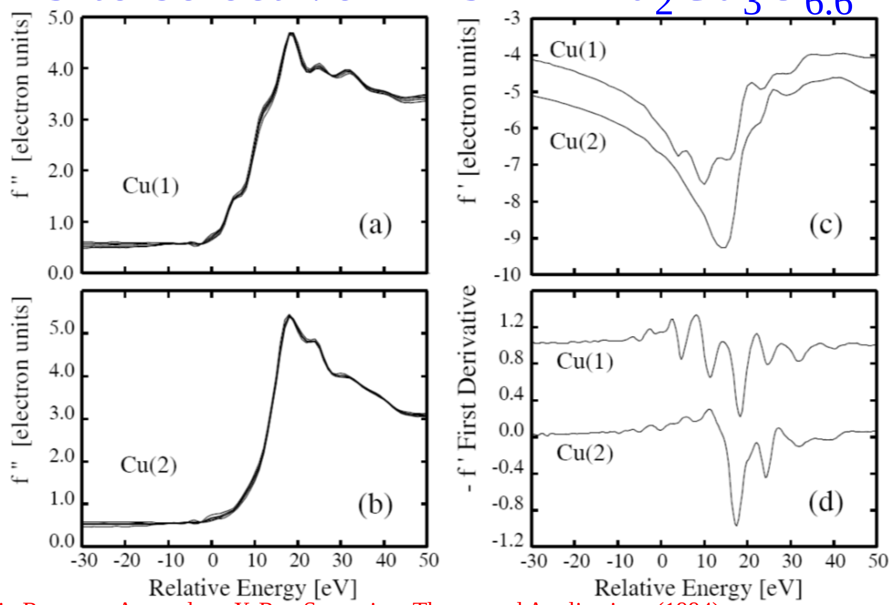
Bulk EXAFS

DAFS



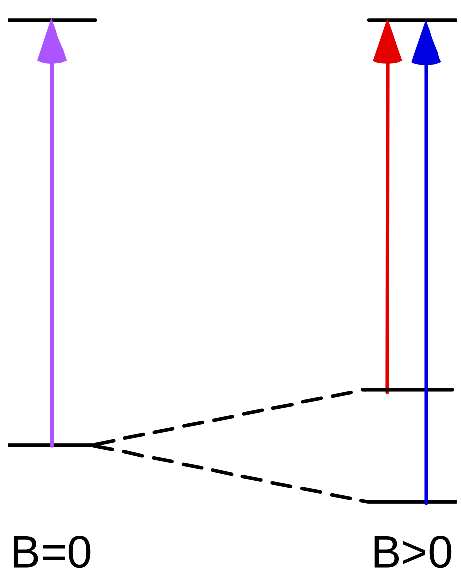
Kolobov et al., *PRL*, *89*, **2002**, 285503-1

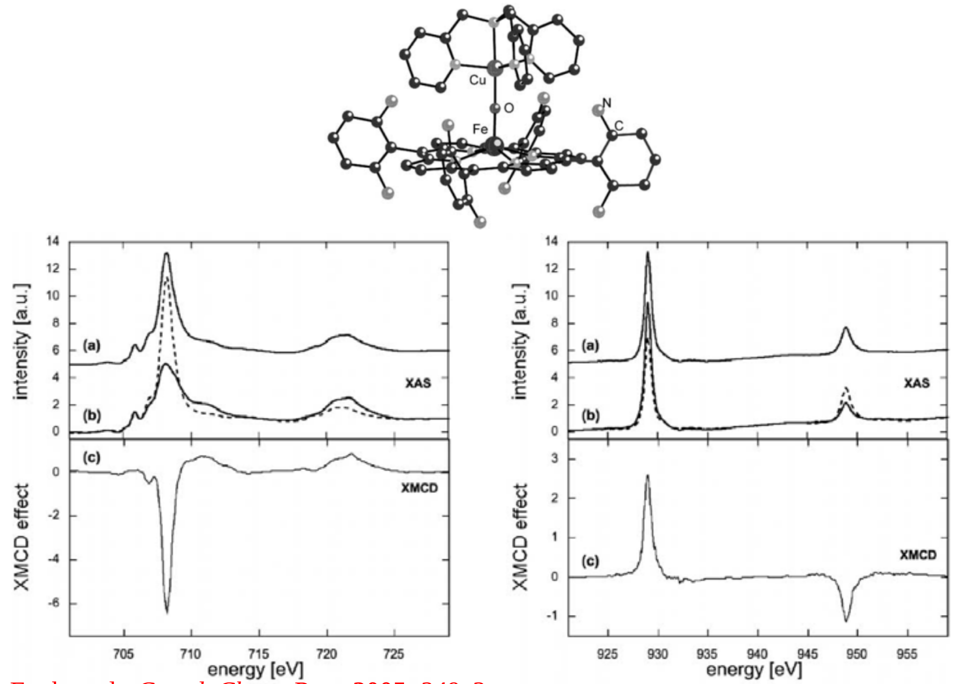
Site-selective XAS – $YBa_2Cu_3O_{6.6}$



in Resonant Anomalous X-Ray Scattering: Theory and Applications,(1994)
Ed. G. Materlik, C. J. Sparks, and K. Fischer, 389-420.

Magnetic Circular Dichroism



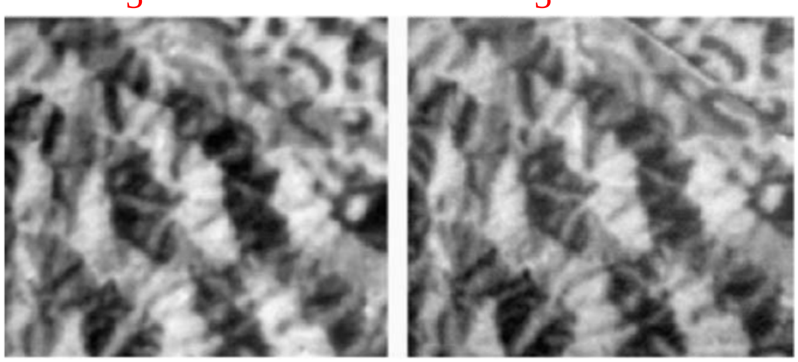


Funk et al., *Coord. Chem. Rev.*, **2005**, *249*, 3

XMCD imaging

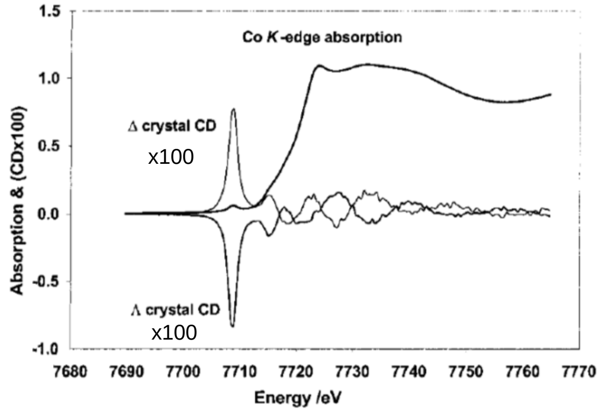
$Co_2Cr_{0.6}Fe_{0.4}Al$

Fe L_3 RCP-LCP   Co L_3 RCP-LCP



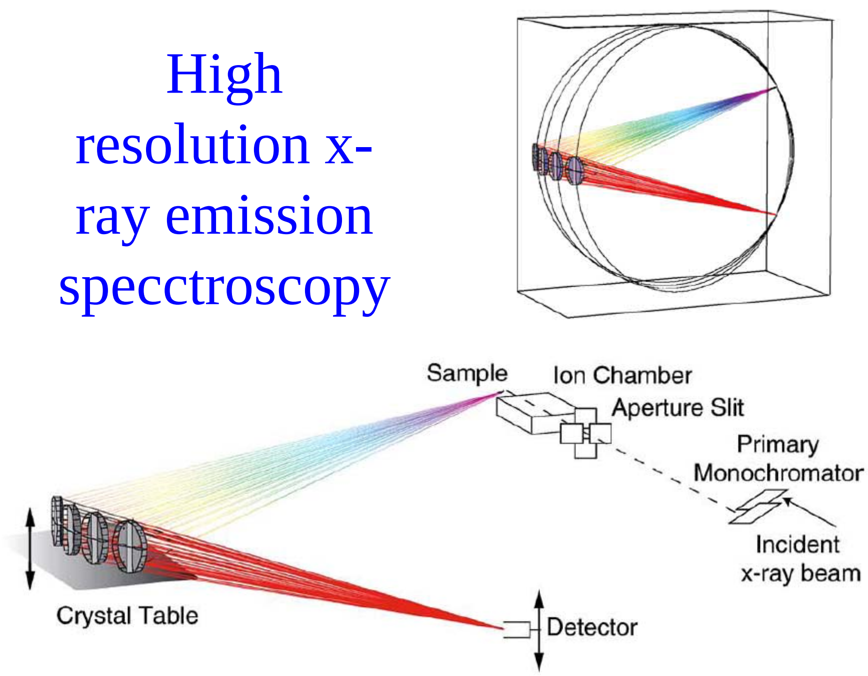
Felser, et al., *J. Phys. Condens. Matter* **2003** *15*, 7019

X-ray Natural CD

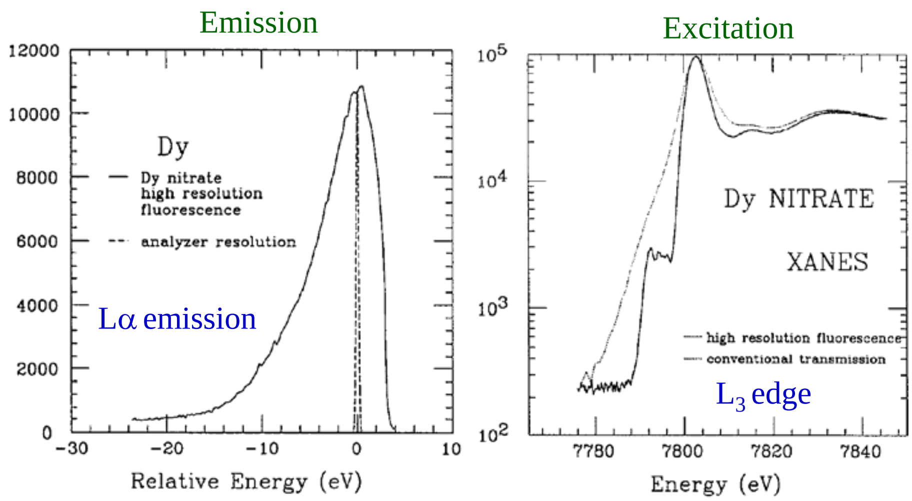


Stewart et al., *J. Am. Chem. Soc.* **1999,** *121*, 10233-10234

High resolution x-ray emission specctroscopy

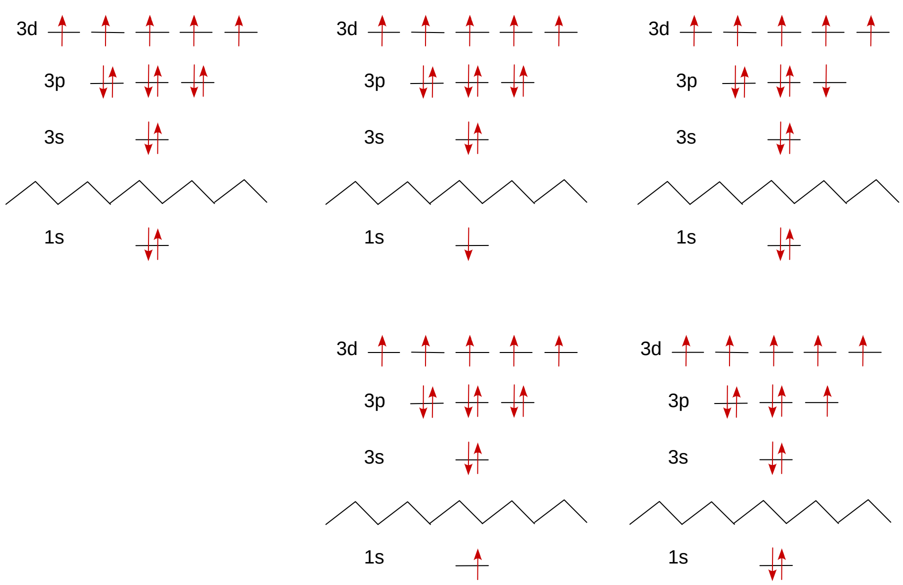


Edge "sharpening"

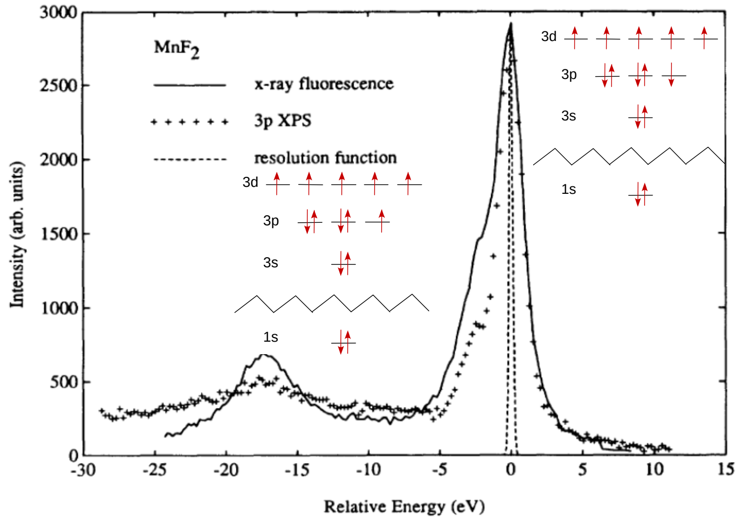


Stojanoff et al., Rev. Sci. Instrum. **1992**, 63, 1125

Spin-resolved XAS

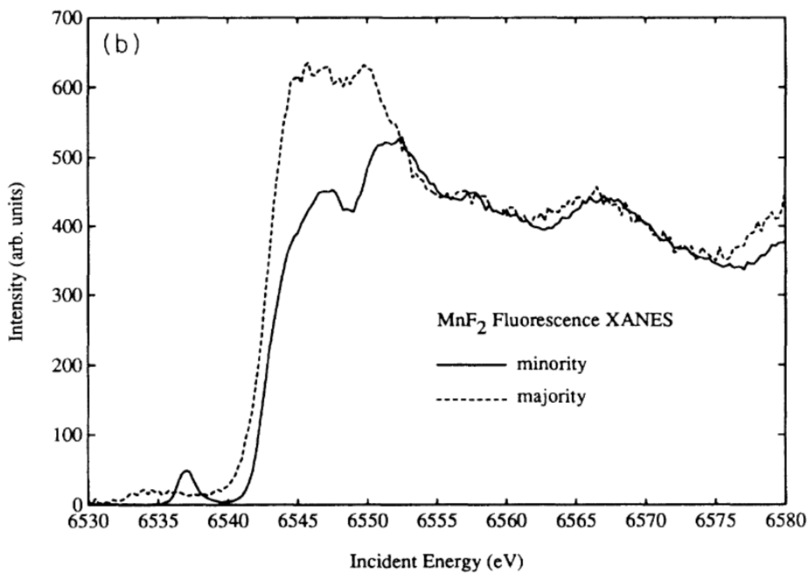


“minority spin” “majority spin”



Hämäläinen, *PRB*, **46**, 14274

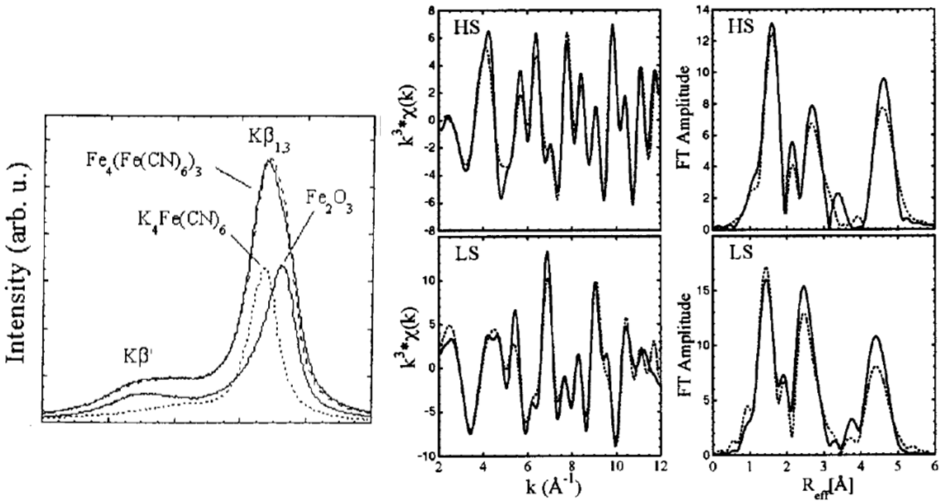
Spin-selective XANES



Prussian Blue

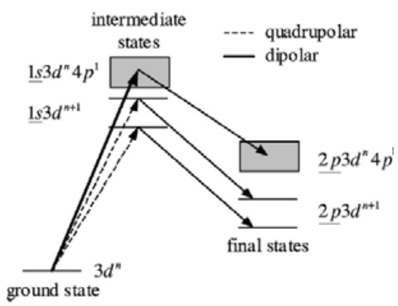
$$Fe_4^{3+}\left[Fe^{2+}(CN)_6\right]_3 \bullet xH_2O$$

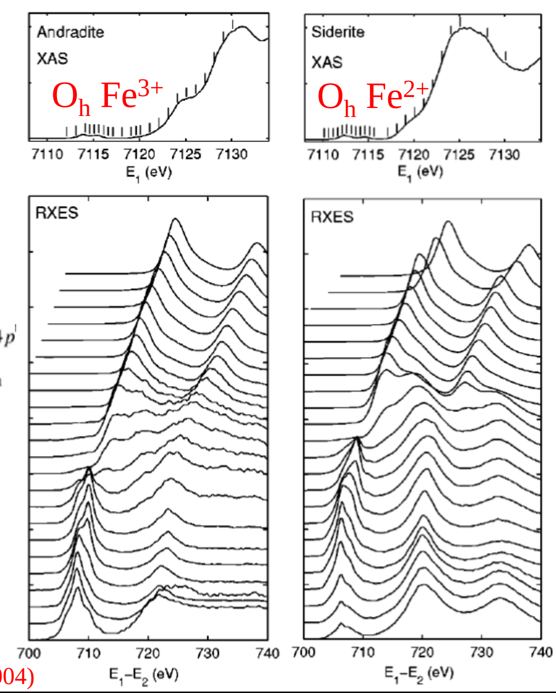
high-spin Fe^{3+} and low-spin Fe^{2+}



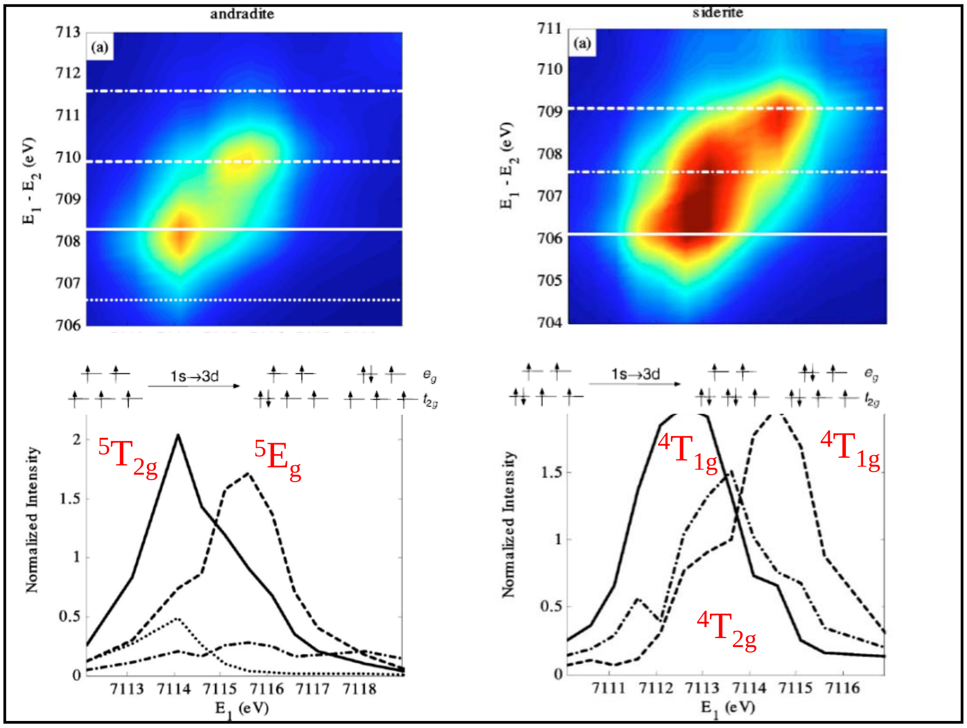
Glatzel *et al.*, *Inorg. Chem.* **2002**, *41*, 3121-3127

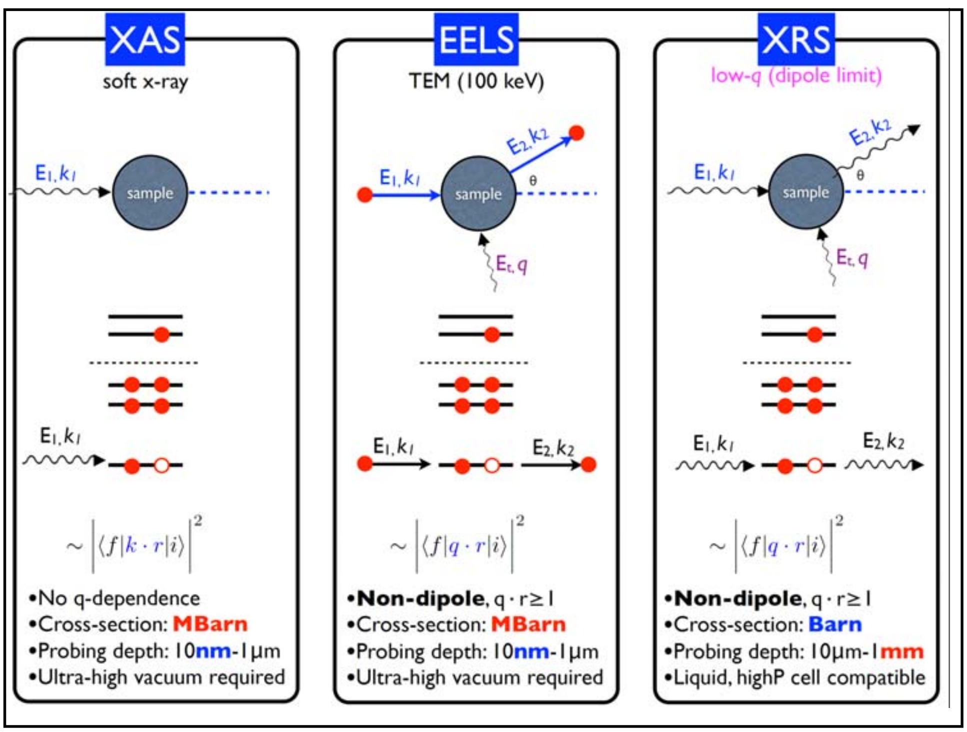
RIXS

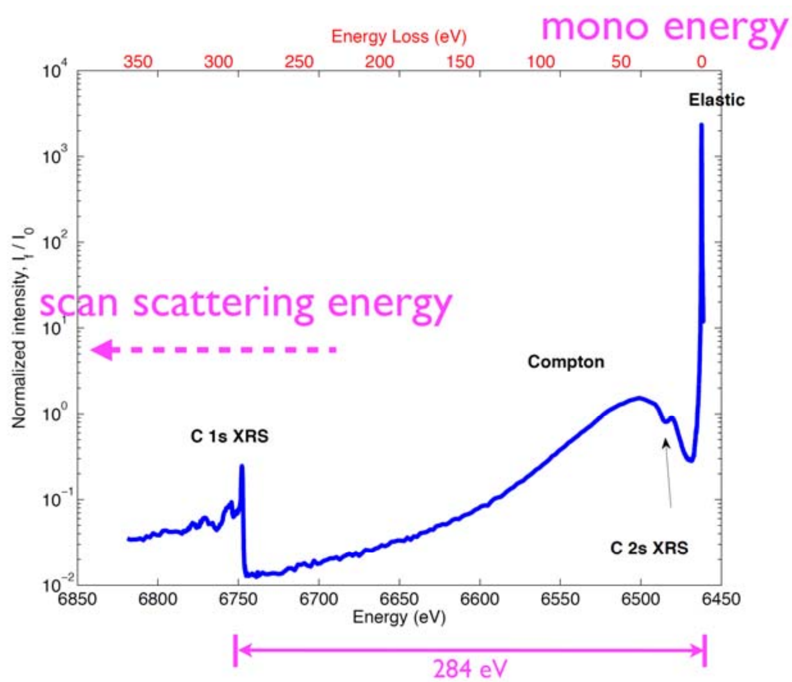




Rueff et al., *Phys Rev. B* **69**, 235107 (2004)

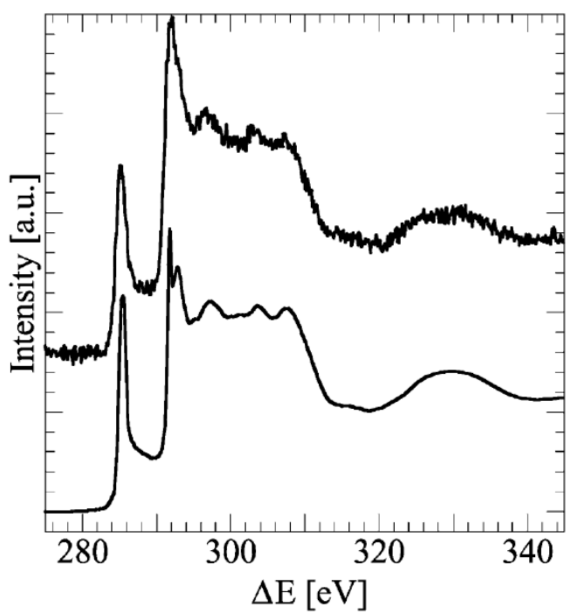

andradite
siderite
E1 - E2 (eV)
Normalized Intensity
E1 (eV)
1s→3d
$^5T_{2g}$
^5E_g
$^4T_{1g}$
$^4T_{1g}$
$^4T_{2g}$


XAS
soft x-ray
EELS
TEM (100 keV)
XRS
low-q (dipole limit)
sample
$\sim |\langle f|k \cdot r|i\rangle|^2$
$\sim |\langle f|q \cdot r|i\rangle|^2$
•No q-dependence
•Cross-section: MBarn
•Probing depth: 10nm-1μm
•Ultra-high vacuum required
•Non-dipole, q · r≥1
•Cross-section: MBarn
•Probing depth: 10nm-1μm
•Ultra-high vacuum required
•Non-dipole, q · r≥1
•Cross-section: Barn
•Probing depth: 10μm-1mm
•Liquid, highP cell compatible



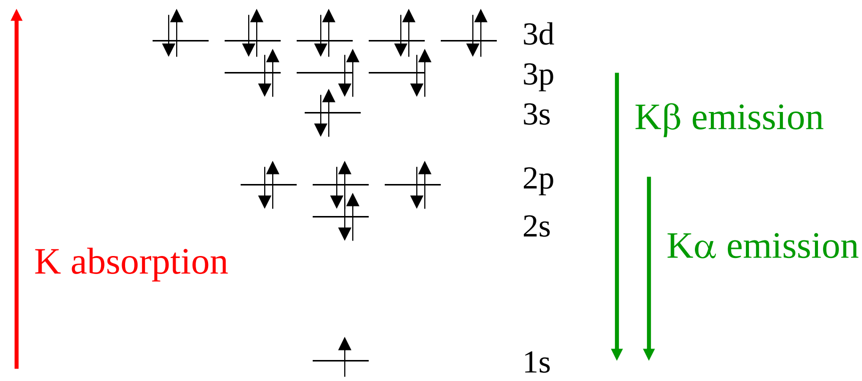
X-ray Raman

Electron-yield detected soft x-ray absorption

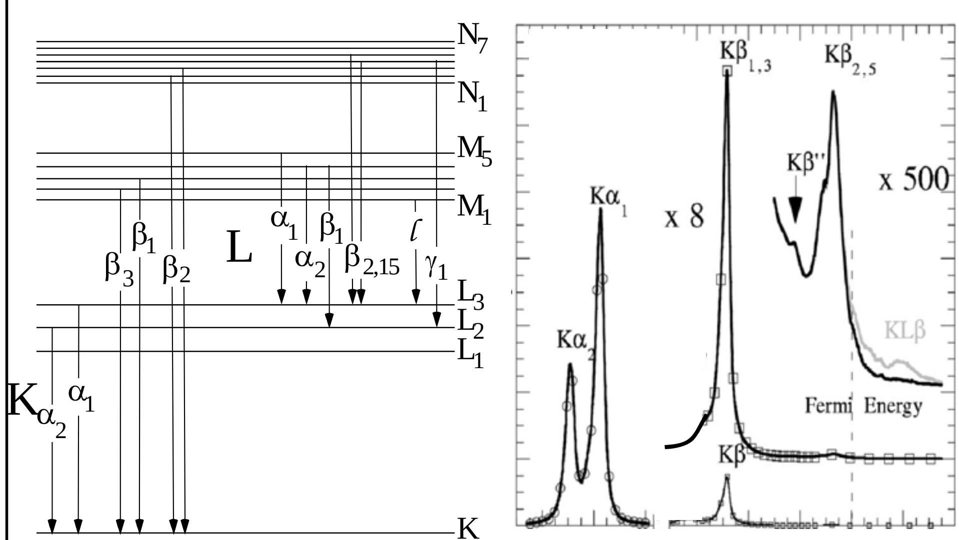


Bergmann et al., *Microchem. J.* **2002**, *71* 221.

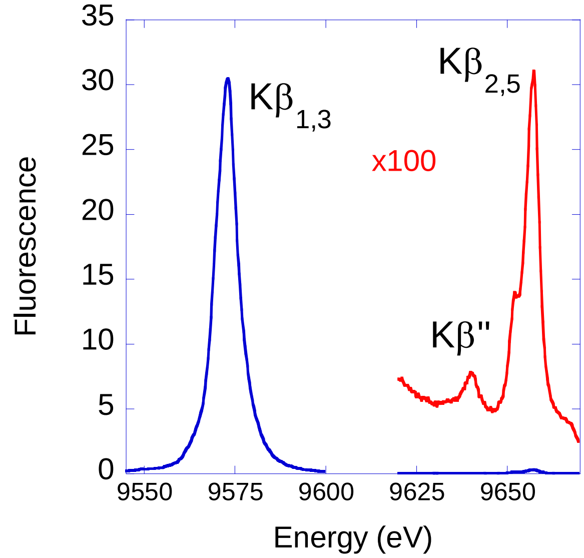
X-ray emission spectroscopy (XES) probes filled orbitals



X-ray fluorescence lines

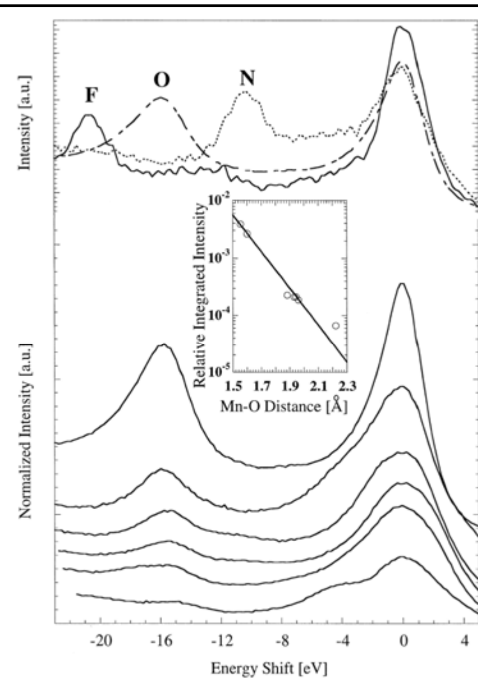


ZnO XES



Ligand identification

"Cross-over" bands (Kβ") are due to ligand-metal charge transfer

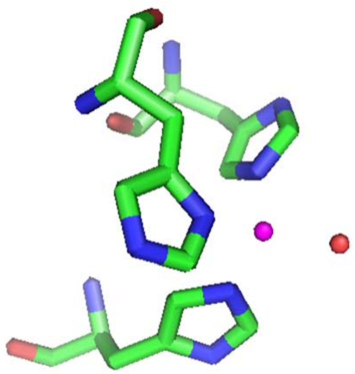


Bergmann et al., *Chem. Phys. Lett*. **1999** *302* 119

Carbonic Anhydrase

$$CO_2 + EZnOH^- \longleftrightarrow EZnHCO_3^- \overset{H_2O}{\longleftrightarrow} EZnH_2O + HCO_3^-$$

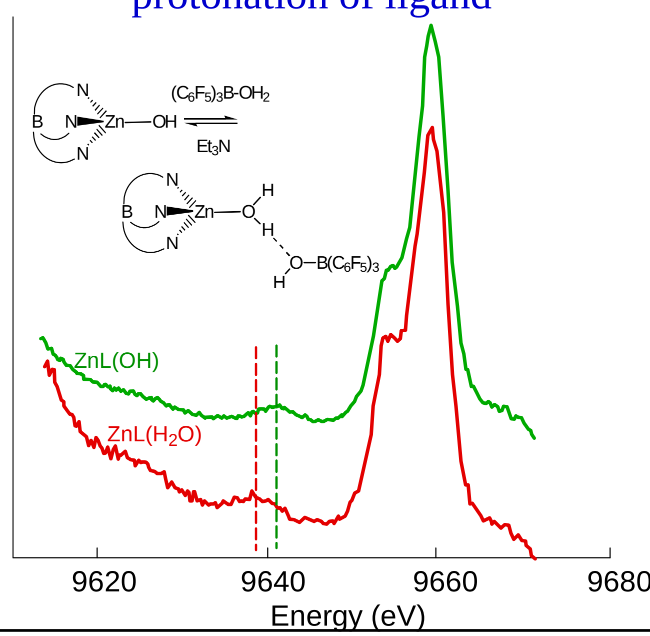
$$EZnH_2O + B \longleftrightarrow EZnOH^- + BH^+$$



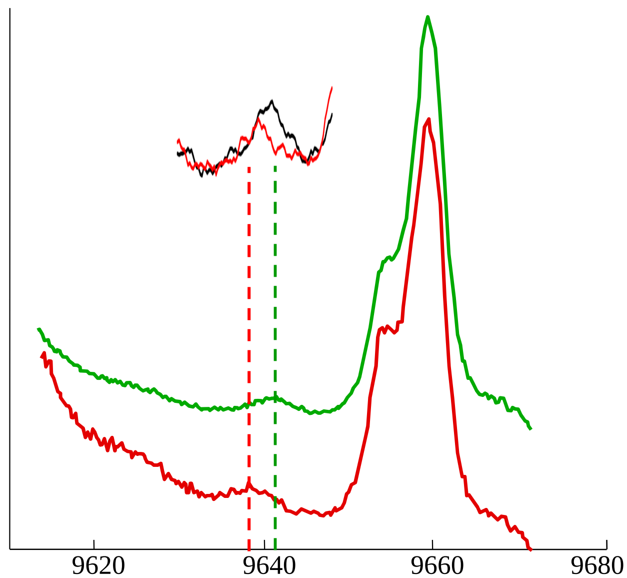
~~Zn-bound water or~~
Zn-bound hydroxide?

Lipton et al., *J. Am. Chem Soc.* (2004), **126**, 4735-4739

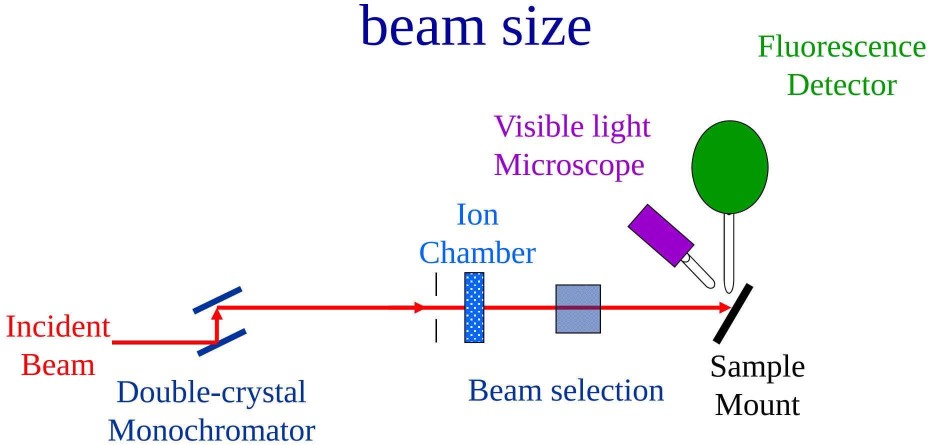
Cross-over band for Zn-O depends on protonation of ligand



CA shows the same pH dependence as the models



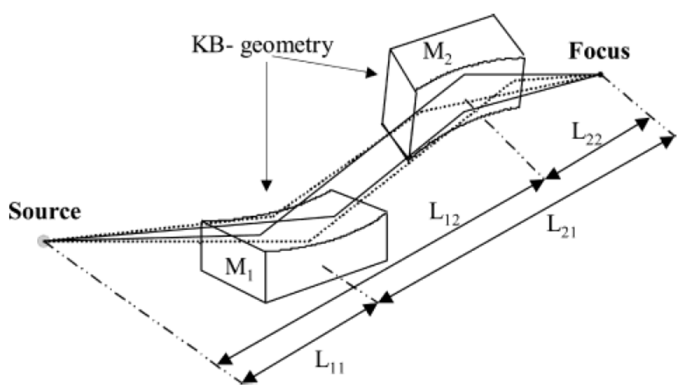
X-ray microprobe provides spatial resolution – defined by beam size



Focusing x-rays

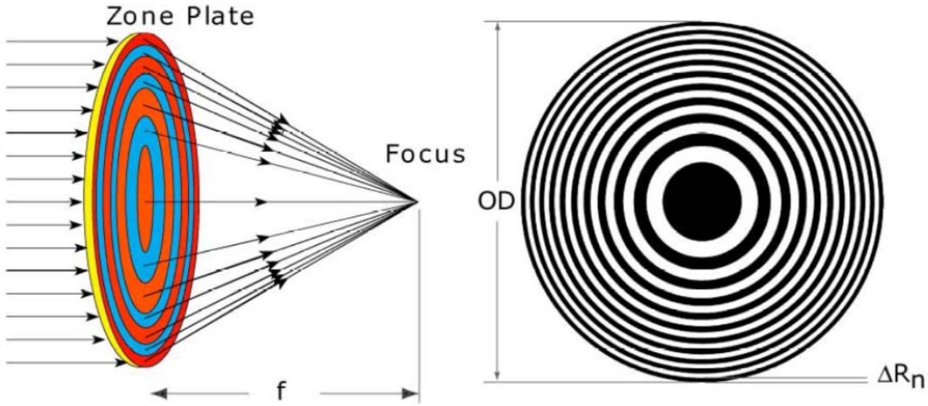
- Total external reflection: Bent mirrors, capillaries
- Bragg reflection from bent single crystals.
- Diffractive focusing elements: Fresnel zone plates
- Refractive focusing elements: Compound refractive lenses

Kirkpatrick-Baez mirrors



~1 μm focus but no chromatic aberration

Zone plate optics – circular diffraction grating



$$f = \frac{OD\,\Delta R_n}{\lambda}$$

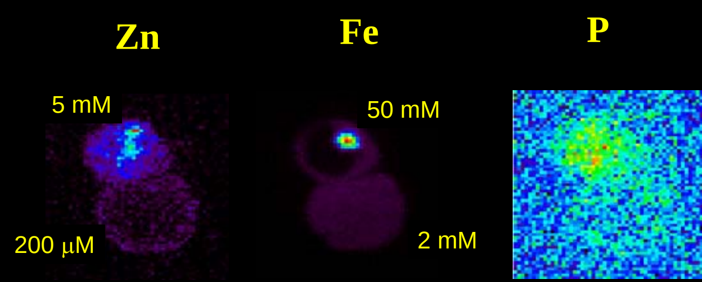
www.xradia.com

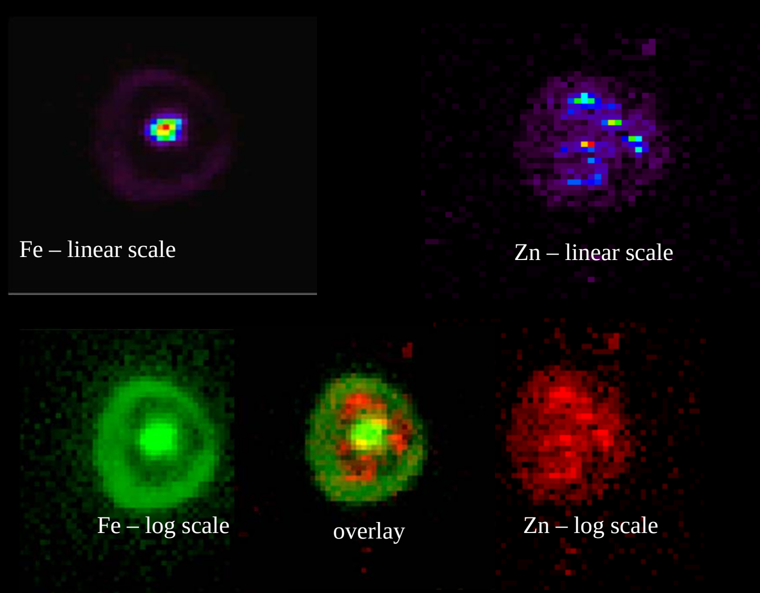
Information from imaging

- Distribution
- Concentration ⟶ Species mapping
- Speciation

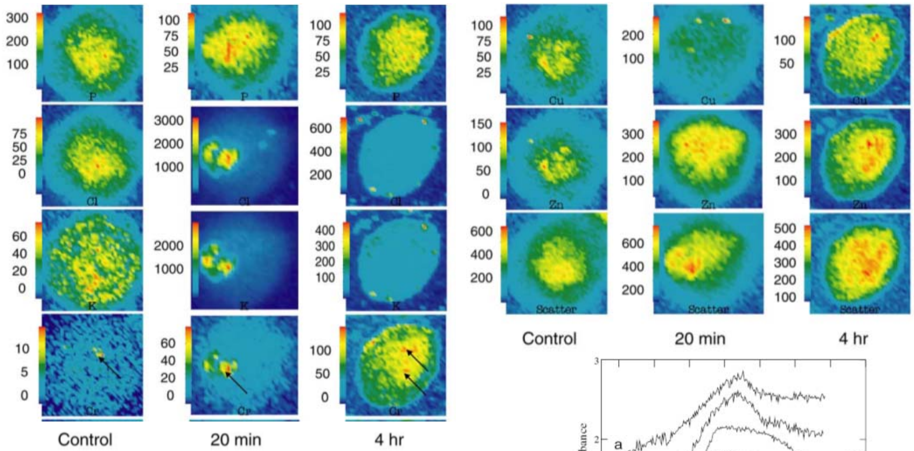
X-ray Fluorescence of RBCs

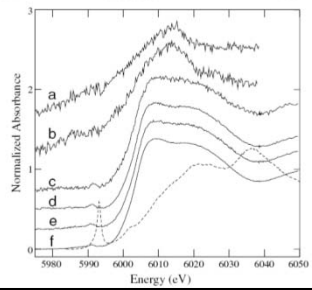
infected cell (top)
uninfected cell (bottom)





Chromate uptake by living cells



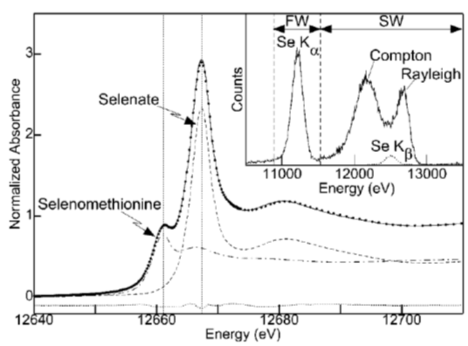


Reduced to Cr(III) in the cell

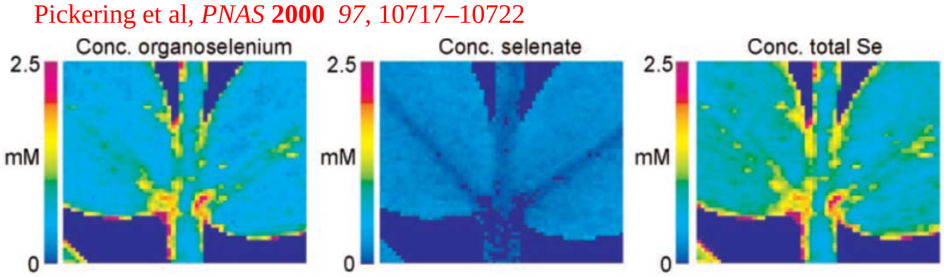
Harris et al., *J Biol Inorg Chem* **2005** *10*,105–118

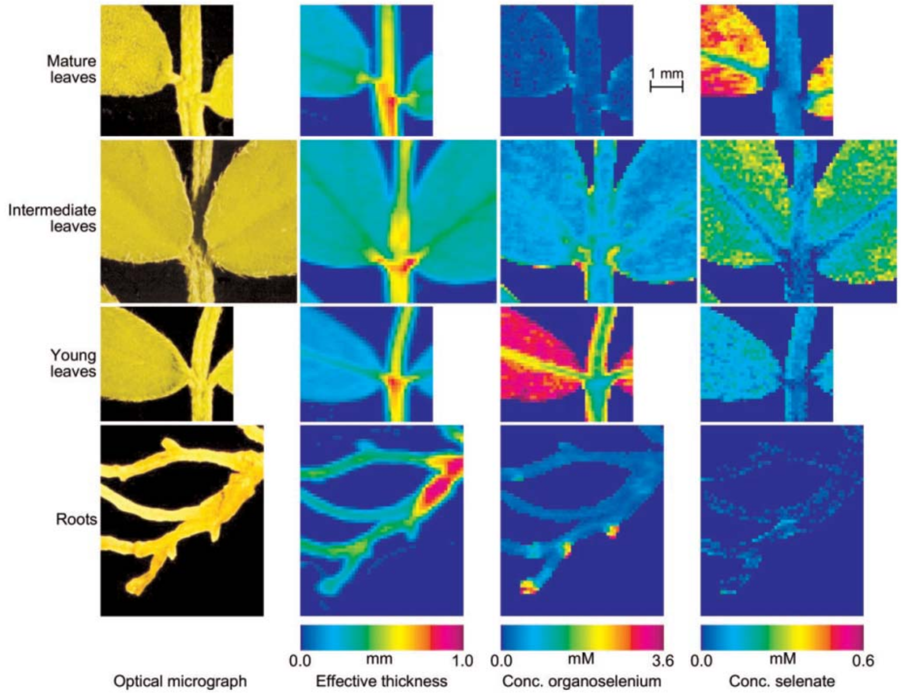
XANES mapping

Multiple images at different excitation energies

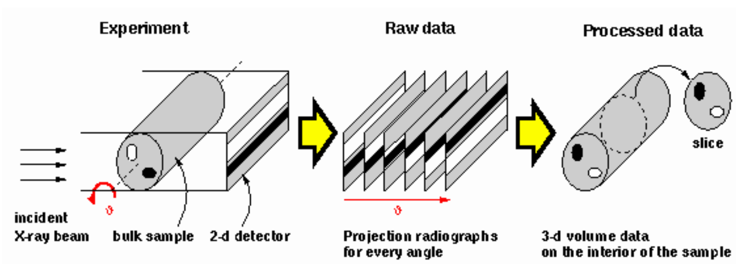


Pickering et al, *PNAS* **2000** *97*, 10717–10722

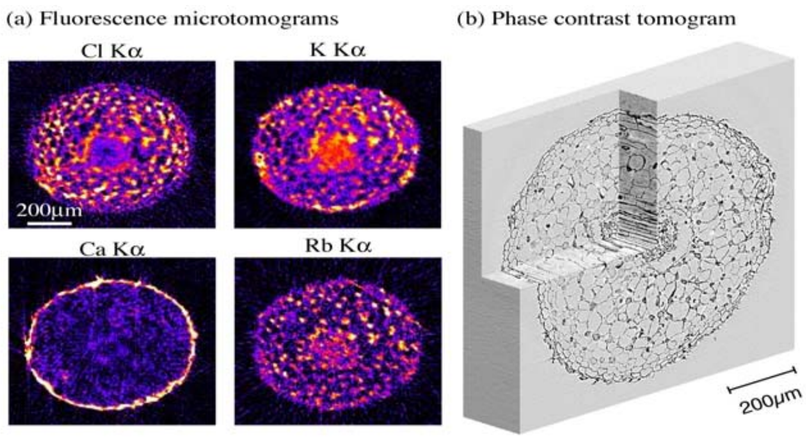




Computer tomography – 3D images



X-ray fluorescence microtomography

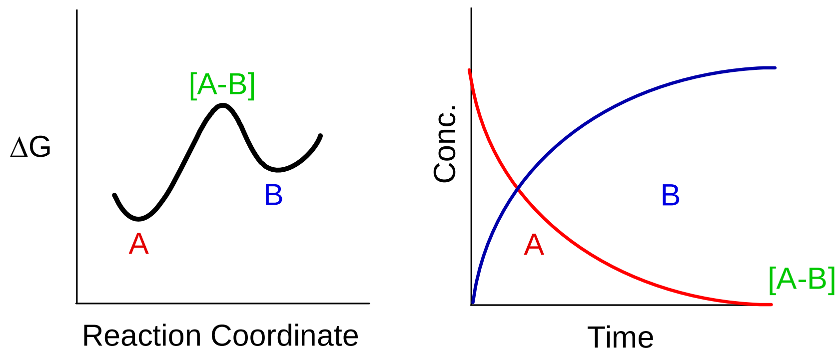


http://www.institut2b.physik.rwth-aachen.de/

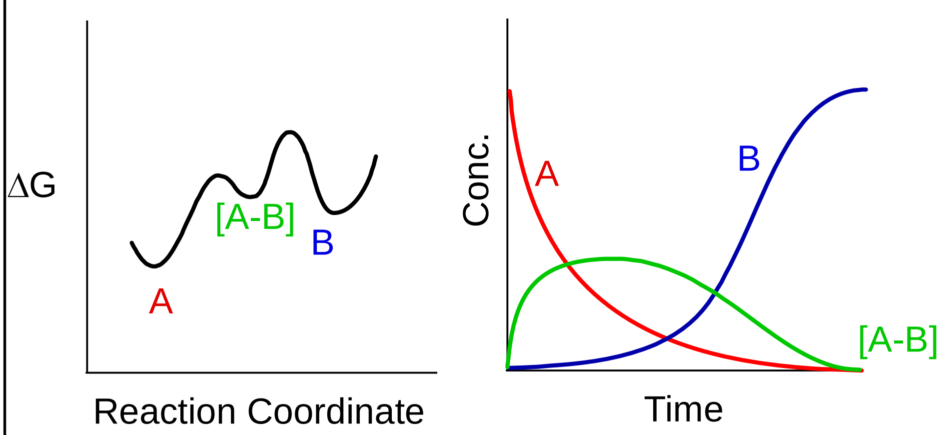
Time-resolved XAS

- Rapid scanning monochromator (“QEXAFS”)
- Dispersive XAS
- Continuous flow
- Rapid freeze quench

Can TR EXAFS be used to determine structure of transition state?

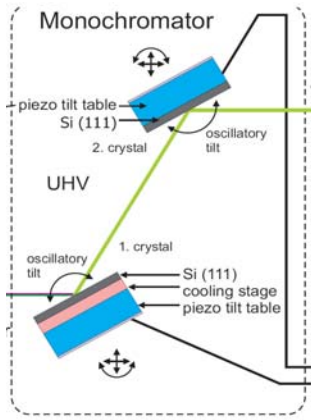


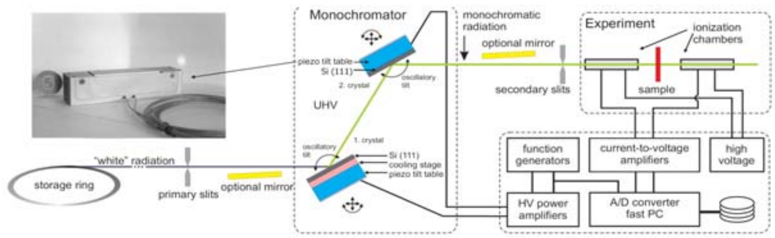
If intermediate builds up to significant concentration, can be studied by XAS



QEXAFS

Piezoelectric tilt for rapid energy scanning (0.1-10 Hz)



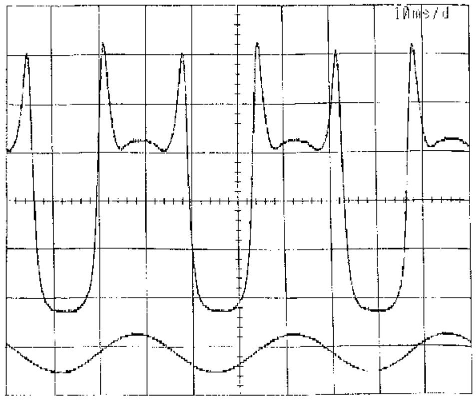


J. Synchrotron Rad. (2001). 8, 354±356

QEXAFS

Absorbance

Piezo voltage



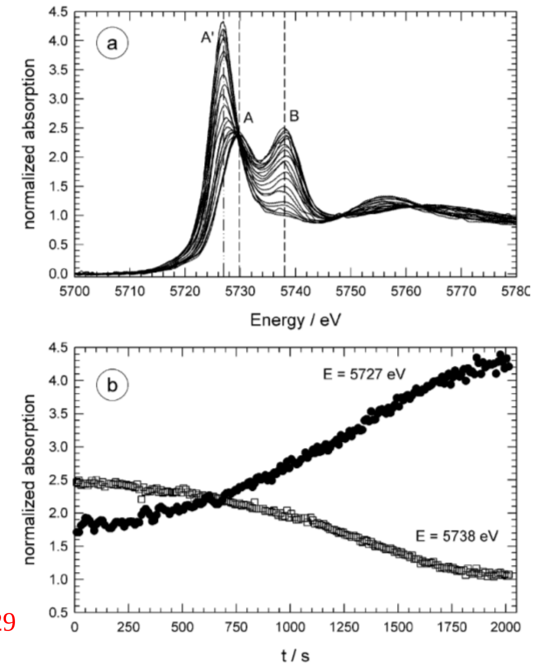
Good time resolution (if recyclable or concentrated)
Compatible with any (fast) detection method

http://schulzeundschultze.anphy.uni-duesseldorf.de/~frahm/QEXAFS/piezo.html

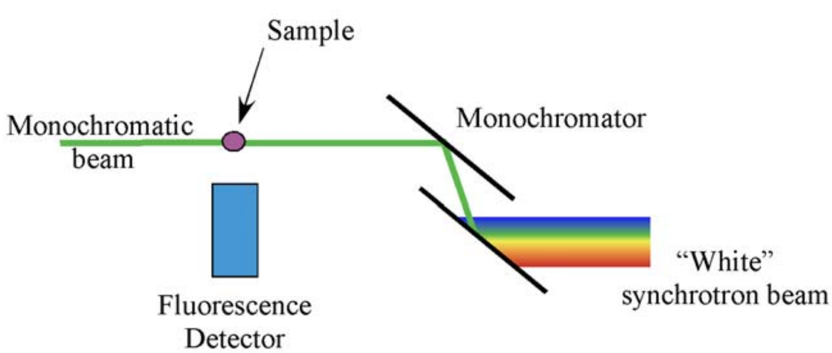
QEXAFS investigation of oxidation of EtOH by Ce(IV)

t=5 sec
[Ce]=0.1 M

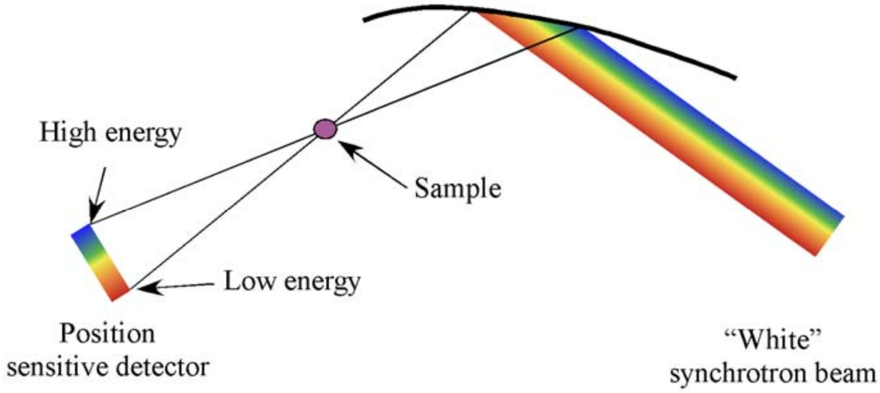
J. Phys. Chem. A **2005,** *109,* 320-329



Conventional XAS geometry



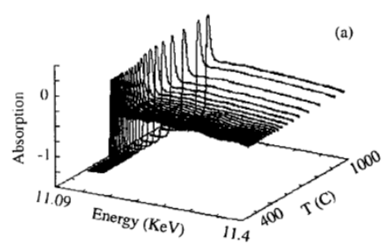
Dispersive XAS geometry



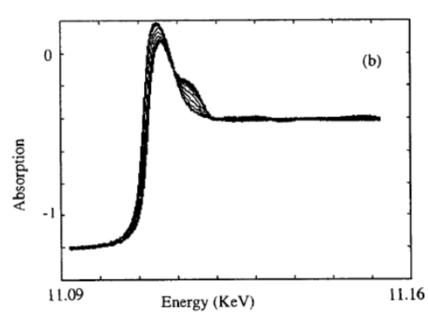
Great time resolution
Only works in transmission mode

Dispersive XAS of Ge solidification

EXAFS – 520 ms/spectrum

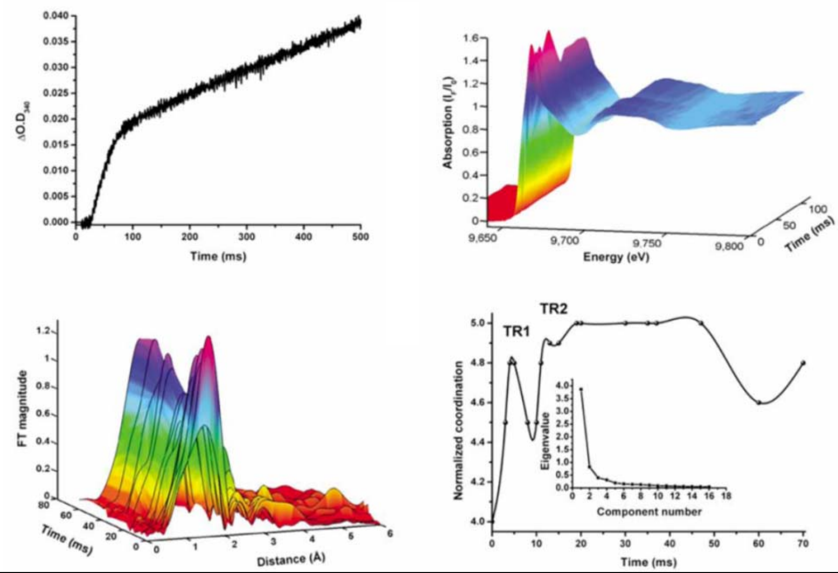


XANES – 120 ms/spectrum

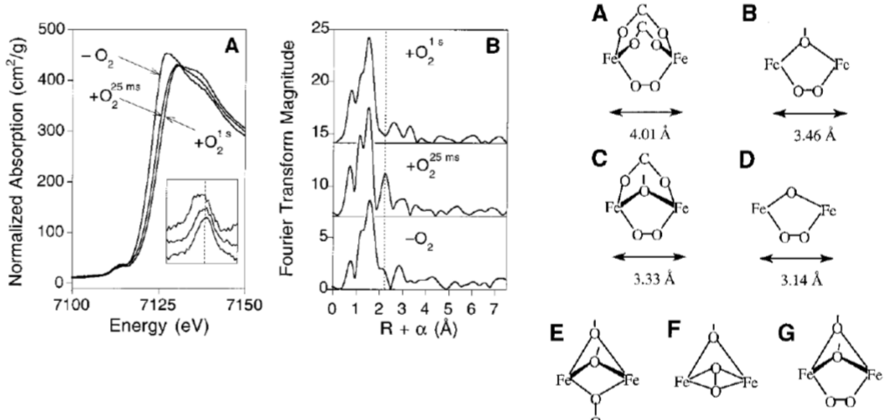


J. Synchr. Rad., **1999** *6* 146

Rapid freeze quench is (the best?) solution to time-resolved EXAFS



Peroxo-diferric ferritin



Hwang et al, *Science*, **2000**, *287*, 122