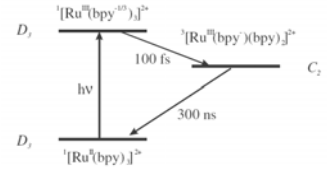
Lecture 6.

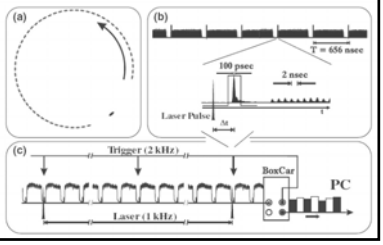
Exotic XAS spectroscopies

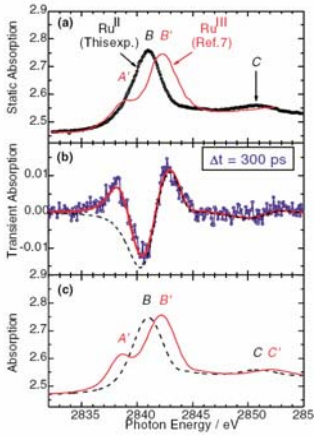
- Ultrafast XAS
- Multiple Excitation
- Diffraction anomalous fine structure – site specific EXAFS
- X-ray magnetic circular dichroism
  - Magnetic imaging
- High-resolution x-ray emission (inelastic x-ray scattering)
- X-ray Raman scattering

Ultrafast XAS

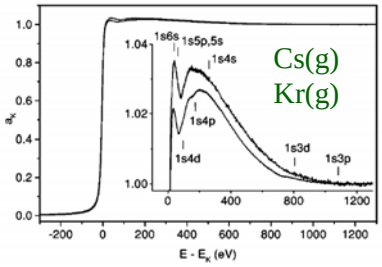


Saes et al., *PRL*, **2003**, *90*, 047403-1



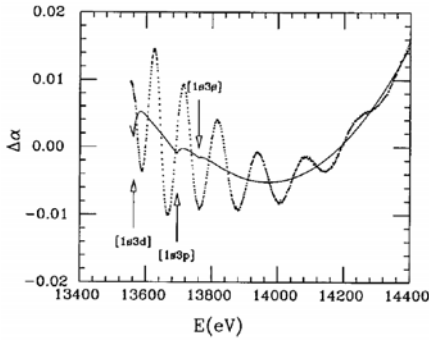


Double Excitation



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

Br_2 EXAFS

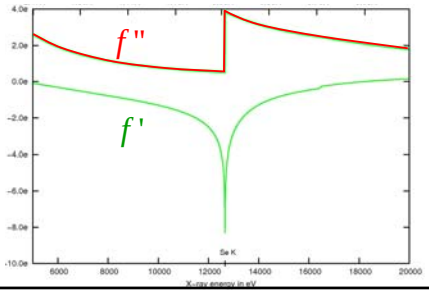


Filipponi and D'Angelo, *J. Chem. Phys.*, **1998**, *109*, 5356

Anomalous scattering

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

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

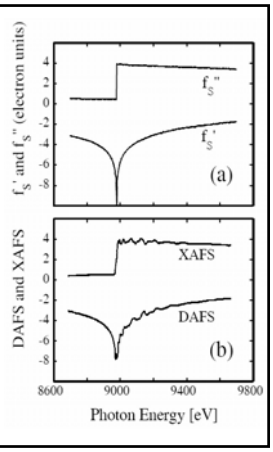


DAFS

Diffraction Anomalous Fine Structure

Kramers-Kronig transformation

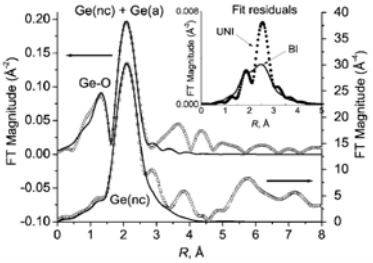
$$f'(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega' f''(\omega')\partial\omega'}{\omega^2 - \omega'^2}$$



Nano-crystalline Ge in Ge/GeO_2

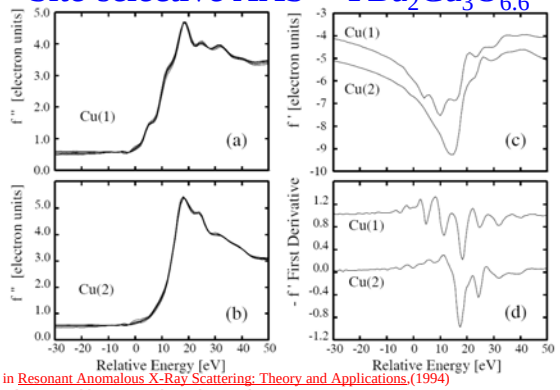
Bulk EXAFS

DAFS



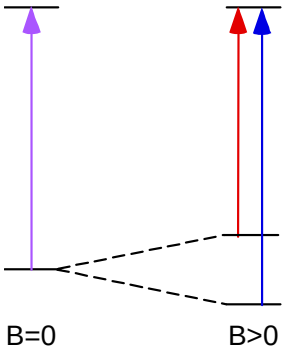
Kolobov et al., *PRL*, *89*, **2002**, 285503-1

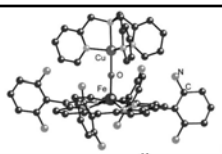
Site-selective XAS – $YBa_2Cu_3O_{6.6}$

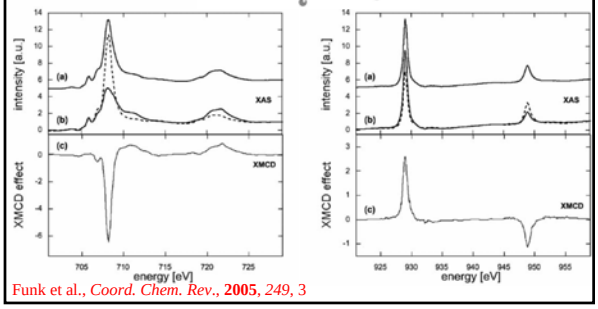


in Resonant Anomalous X-Ray Scattering: Theory and Applications,(1994) Ed. G. Materlik, C. J. Sparks, and K. Fischer, 389-420.

Magnetic Circular Dichroism





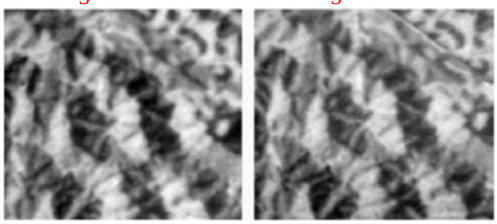


Funk et al., *Coord. Chem. Rev.*, **2005**, *249*, 3

XMCD imaging

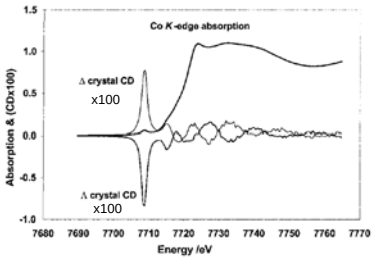
$Co_2Cr_{0.6}Fe_{0.4}Al$

Fe L_3 RCP-LCP Co L_3 RCP-LCP



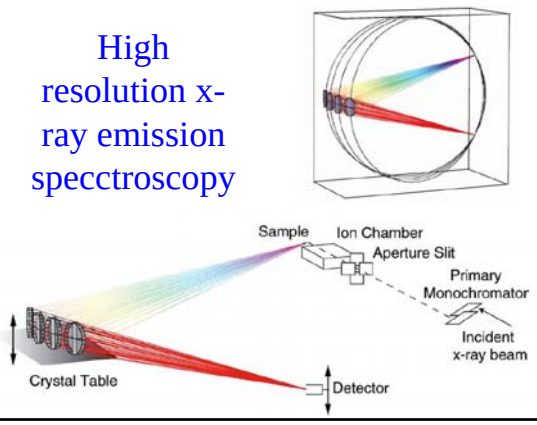
Felser, et al., *J. Phys. Condens. Matter* **2003** *15*, 7019

X-ray Natural CD

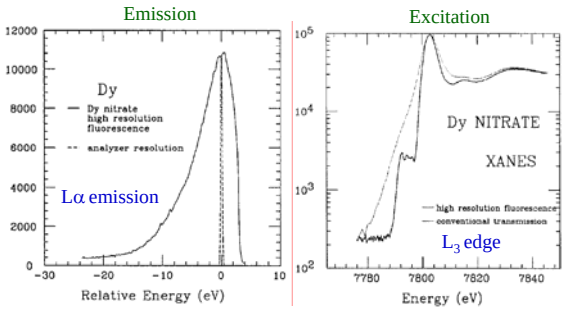


Stewart et al., *J. Am. Chem. Soc.* **1999,** *121*, 10233-10234

High resolution x-ray emission specctroscopy

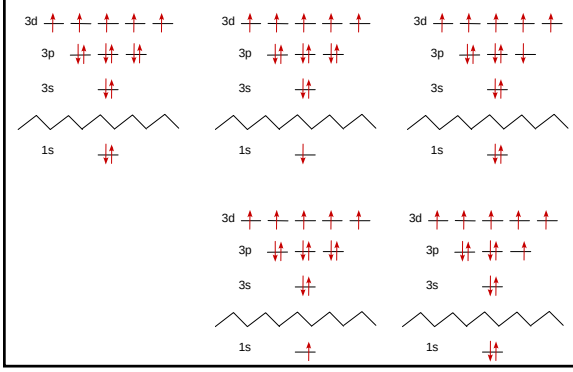


Edge "sharpening"

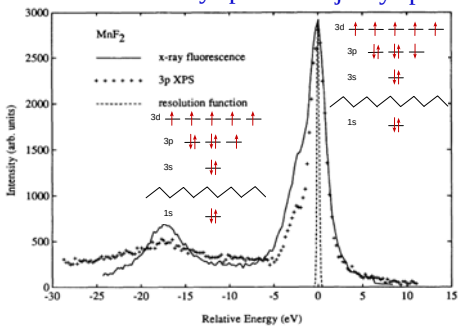


Stojanoff et al., Rev. Sci. Instrum. **1992**, 63, 1125

Spin-resolved XAS

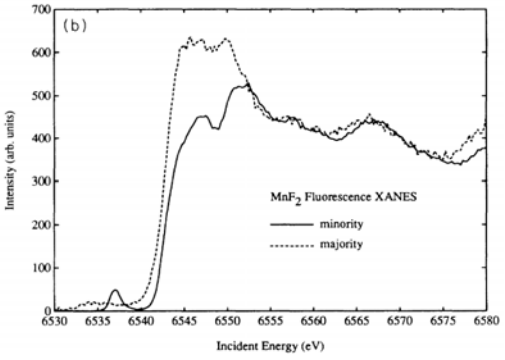


"minority spin" "majority spin"



Hämäläinen, *PRB*, **46**, 14274

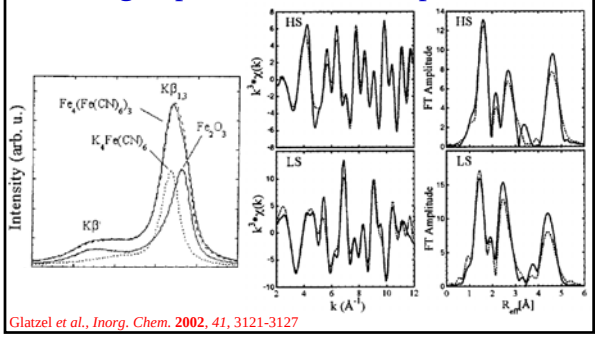
Spin-selective XANES



Prussian Blue

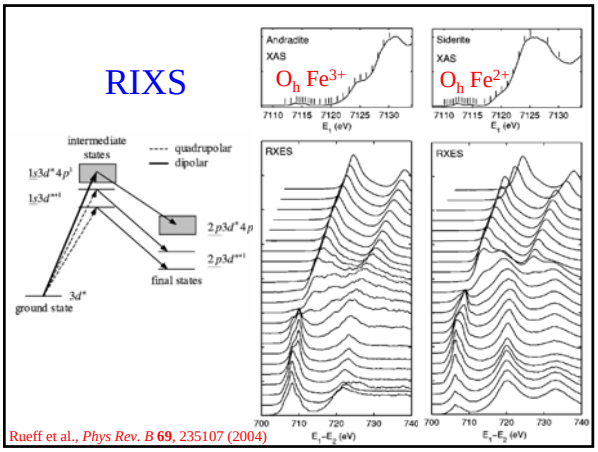
$Fe_4^{3+}[Fe^{2+}(CN)_6]_3 \bullet xH_2O$

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

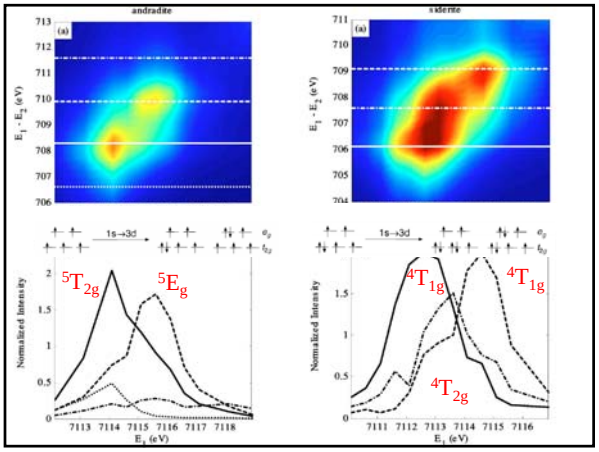


Glatzel *et al.*, *Inorg. Chem.* **2002**, *41*, 3121-3127

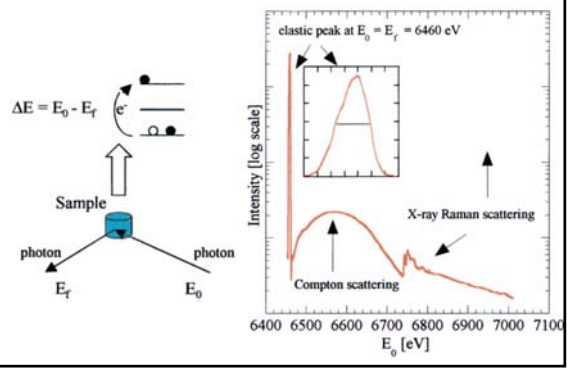
RIXS



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

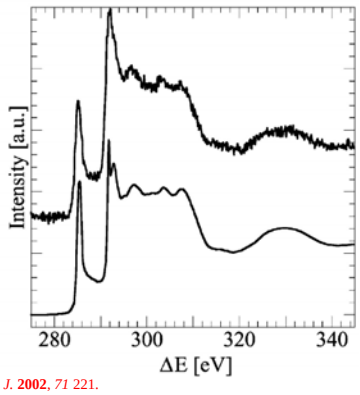


Raman – C edges without UHV



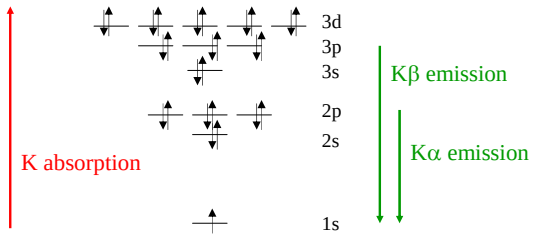
X-ray Raman

Electron-yield detected soft x-ray absorption

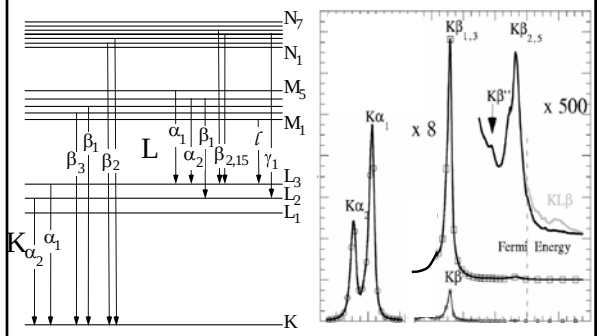


Bergmann et al., *Microchem. J.* **2002**, *71* 221.

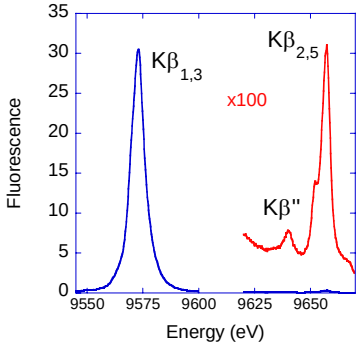
X-ray emission spectroscopy (XES) probes filled orbitals



X-ray fluorescence lines



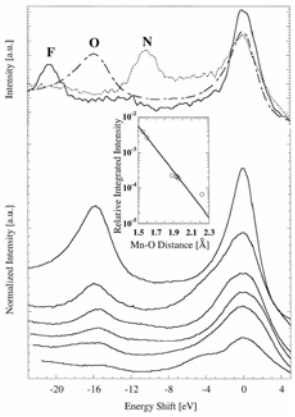
ZnO XES



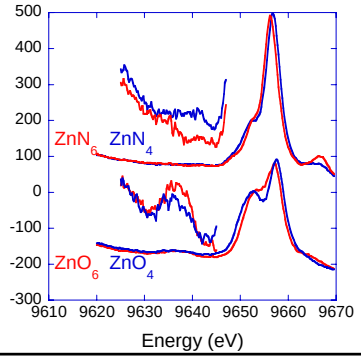
Ligand identification

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

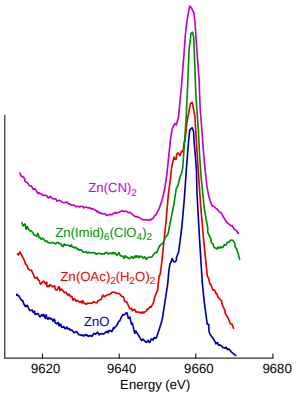
Bergmann et al., *Chem. Phys. Lett*. **1999** *302* 119



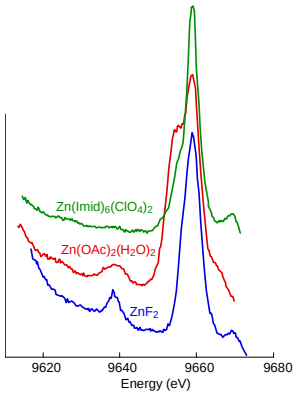
For a single ligand type (acetate or imidazole) cross-over peak is reproducible



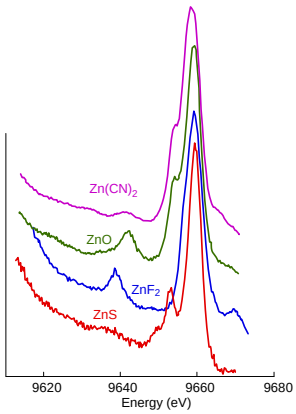
However, there is significant variation for different ligands with the same ligand atom



For octahedral Zn, cross-over energy is nearly independent of ligand identity



However, tetrahedral Zn does not follow the same pattern



Carbonic Anhydrase

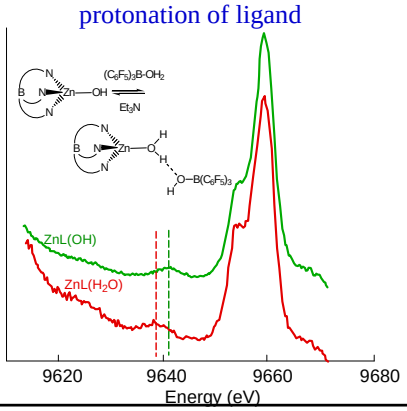
$$CO_2 + EZnOH^- \longleftrightarrow EZnHCO_3^- \overset{H_2O}{\longleftrightarrow} EZnH_2O + HCO_3^-$$

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

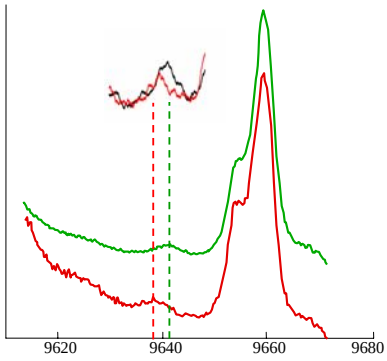
~~Zn-bound water~~ or Zn-bound hydroxide?

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

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

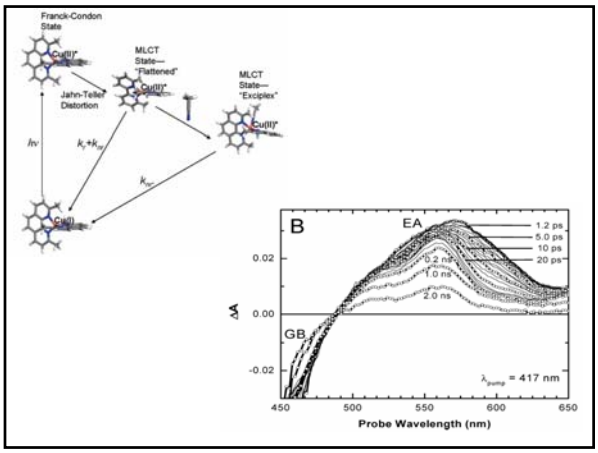


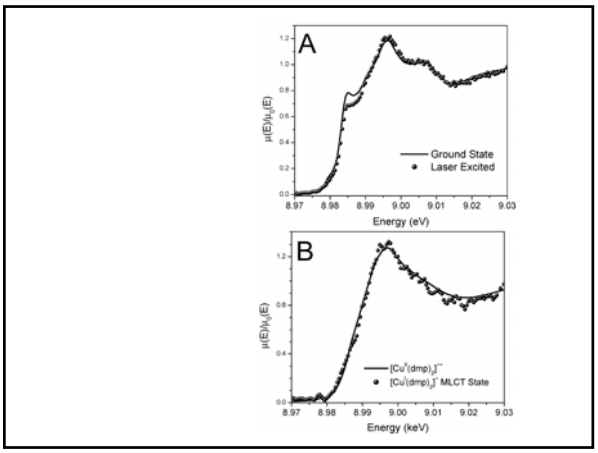
CA shows the same pH dependence as the models



Summary

1. Basic Physical Principles
   - XAS – crystallographic-like information for non-crystalline samples
2. Practical aspects of x-ray absorption
   - Measurement of absorption
   - Energy selection
   - Artifacts (how **NOT** to measure the right signal)
   - Radiation damage
3. Data analysis
   - Probems
     - Least-squares minimization
     - Fourier Filtering
     - Resolution
     - Normalization
   - Methods
     - Multiple scattering
     - PCA
4. Near edge structure
   - Bound state transitions
   - Multiplet structure
   - Oxidation state
   - Multiple scattering and Geometry
   - Ligand K-edge studies
   - Time and concentration dependence - titrations
5. Spatially and temporally resolved methods
   - Methods for focusing x-rays
   - Spatially resolved studies
     - Distribution
     - Concentration
     - Speciation
   - Temporally resolved
     - QEXAFS
     - Dispersive
     - Continuous flow
     - RFQ
6. Exotic x-ray spectroscopies


Franck-Condon State
MLCT State—"Flattened"
MLCT State—"Exciplex"
Jahn-Teller Distortion
hν
B
EA
GB
1.2 ps
5.0 ps
10 ps
20 ps
0.2 ns
1.0 ns
2.0 ns
λpump = 417 nm
ΔA
Probe Wavelength (nm)


A
Ground State
Laser Excited
Energy (eV)
B
[Cu¹(dmp)₂]⁺*
[Cu¹(dmp)₂]⁺ MLCT State
Energy (keV)