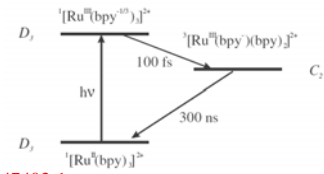


Lecture 6.

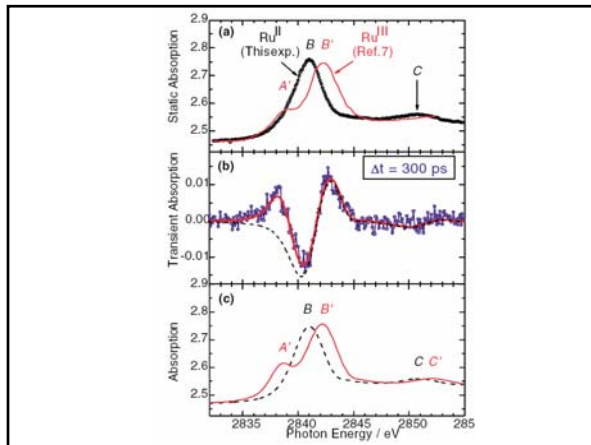
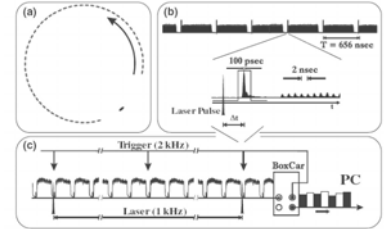
Exotic XAS spectroscopies

- 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

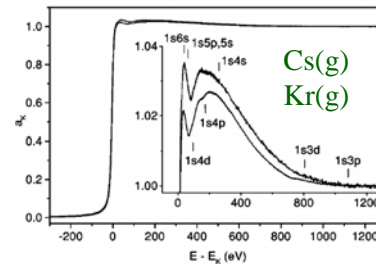
Ultrafast XAS



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

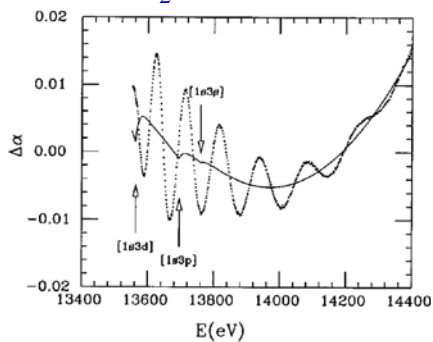


Double Excitation



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

Br₂ EXAFS

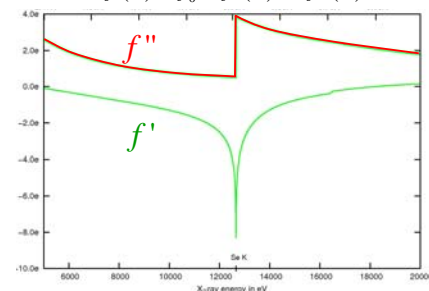


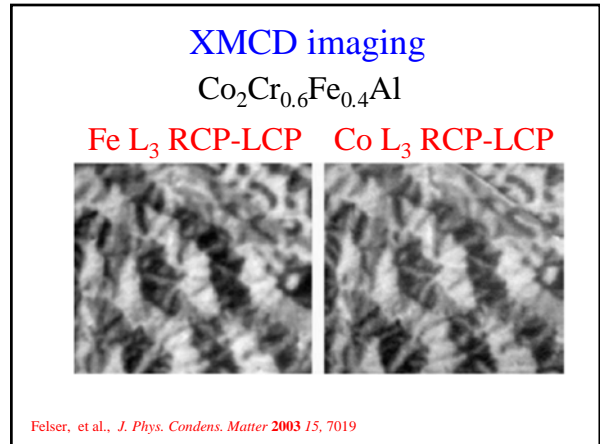
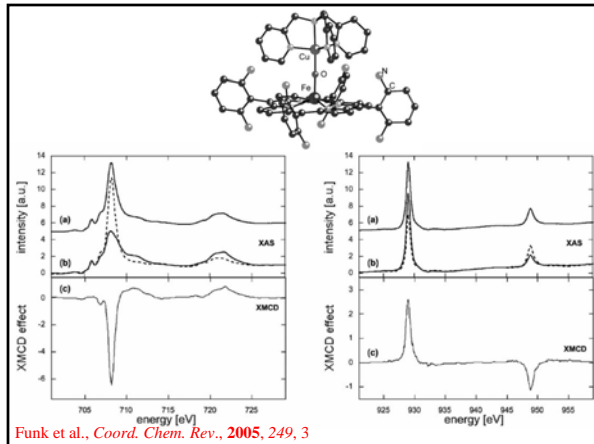
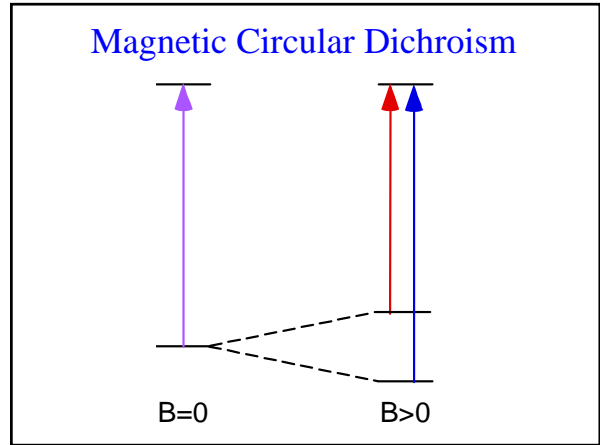
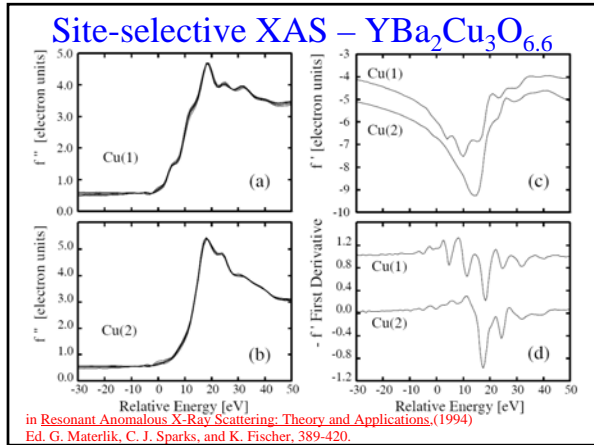
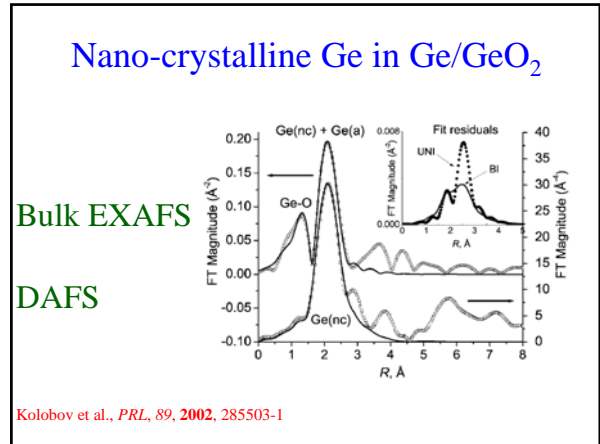
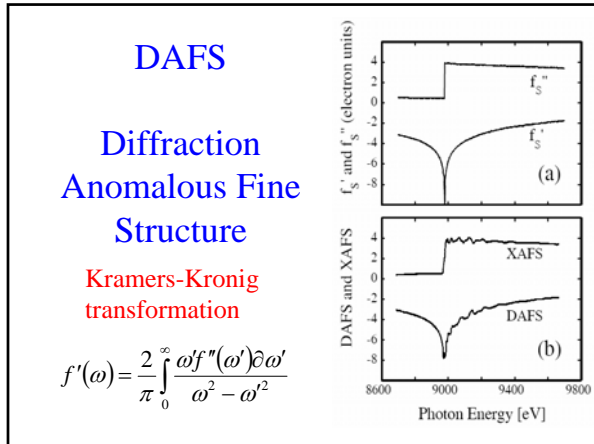
Filipponi and D'Angelo, *J. Chem. Phys.*, 1998, 109, 5356

Anomalous scattering

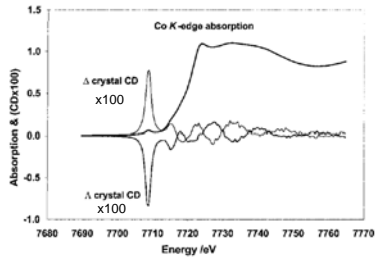
$$F(\mathbf{h}) = \sum_{i=1}^N f_i e^{2\pi i \mathbf{h} \cdot \mathbf{r}_i}$$

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



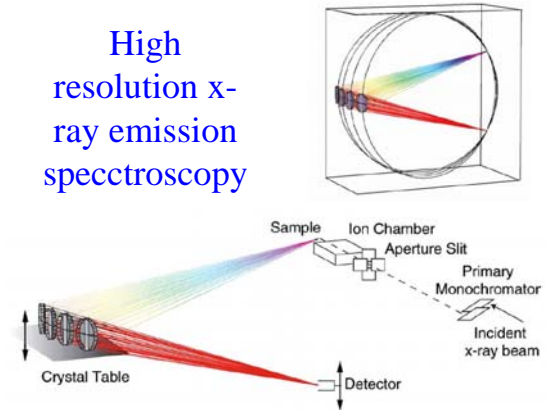


X-ray Natural CD

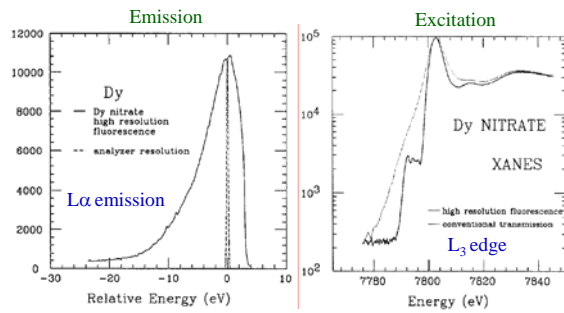


Stewart et al., *J. Am. Chem. Soc.* **1999**, *121*, 10233-10234

High resolution x-ray emission spectroscopy

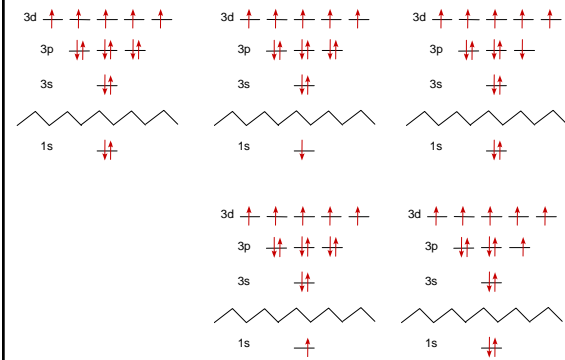


Edge “sharpening”

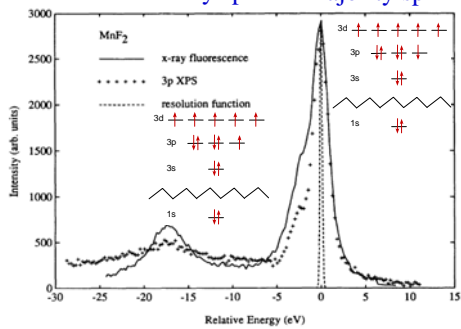


Stojanoff et al., *Rev. Sci. Instrum.* **1992**, *63*, 1125

Spin-resolved XAS

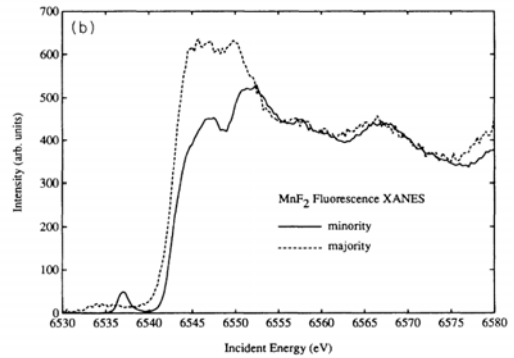


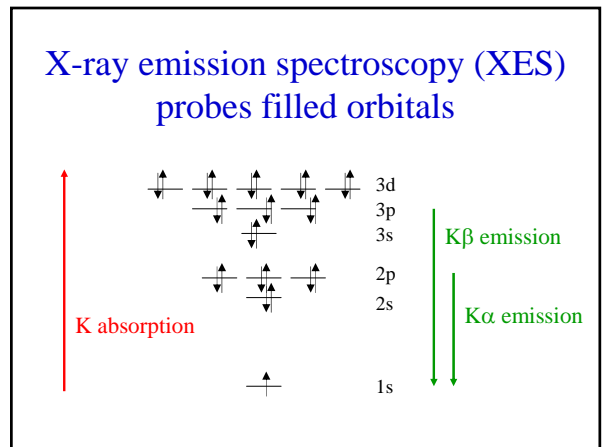
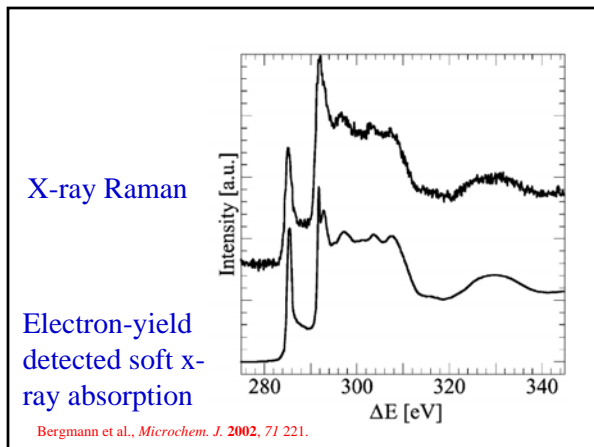
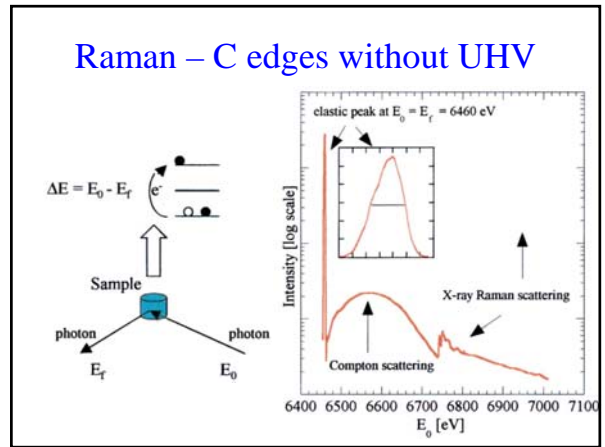
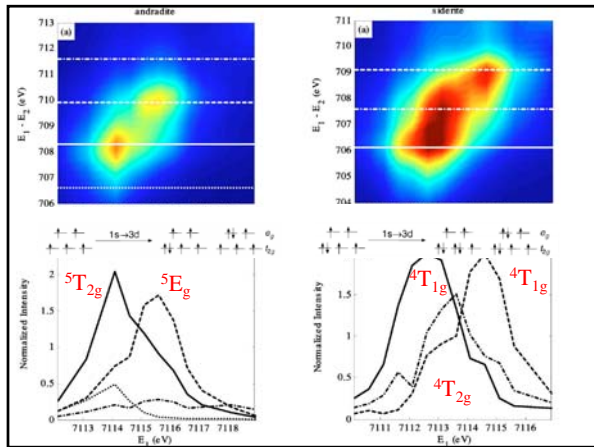
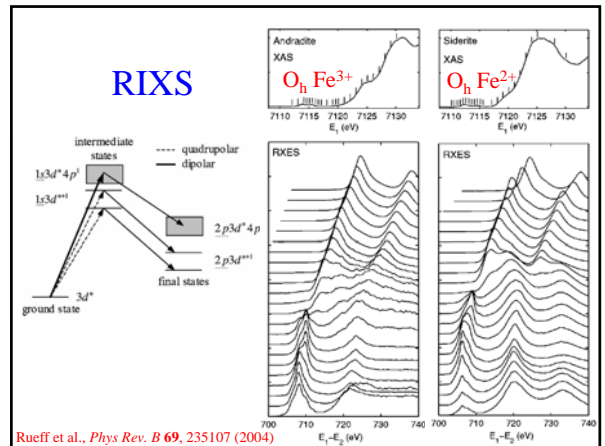
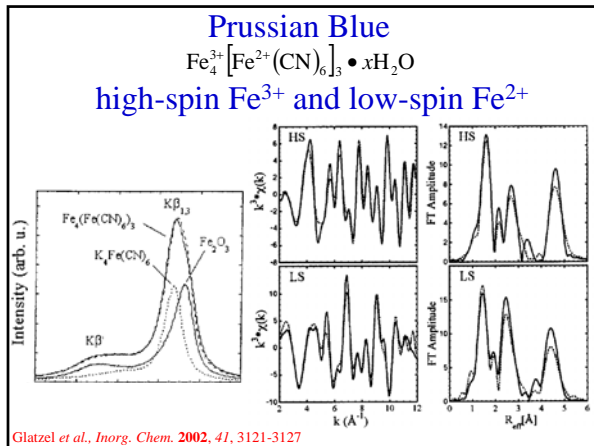
“minority spin” “majority spin”

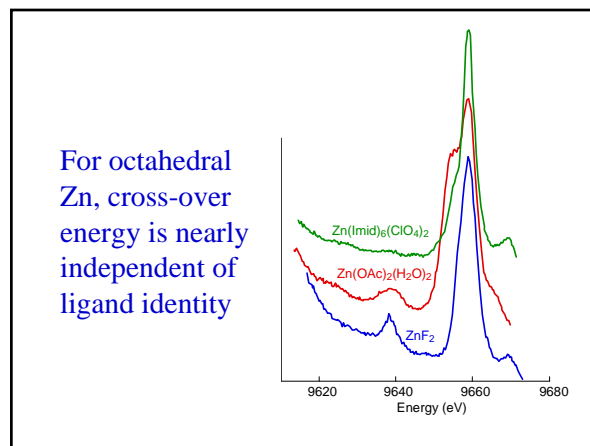
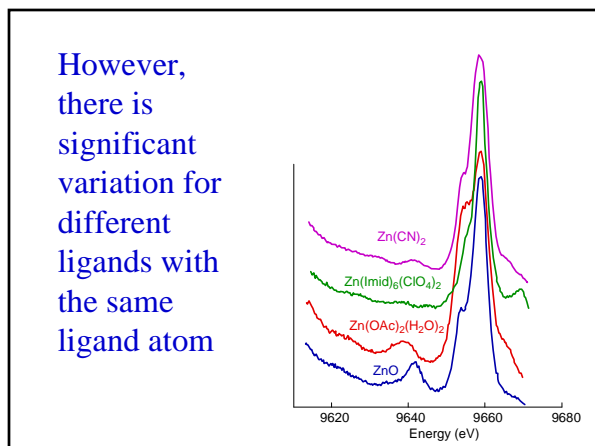
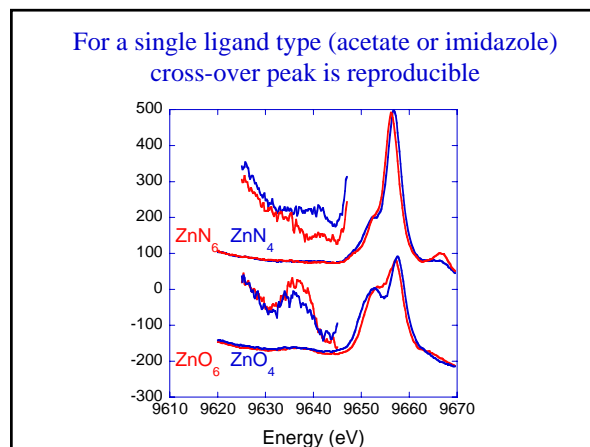
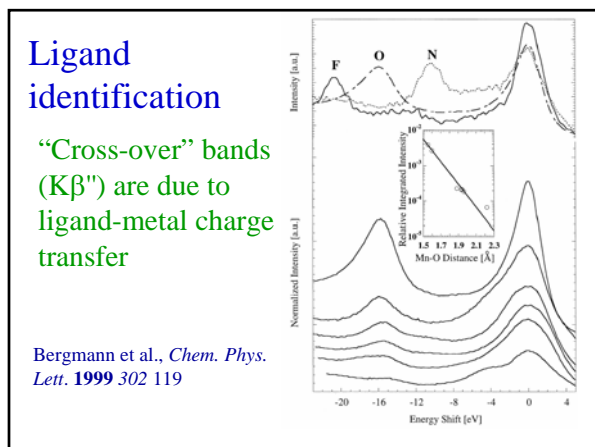
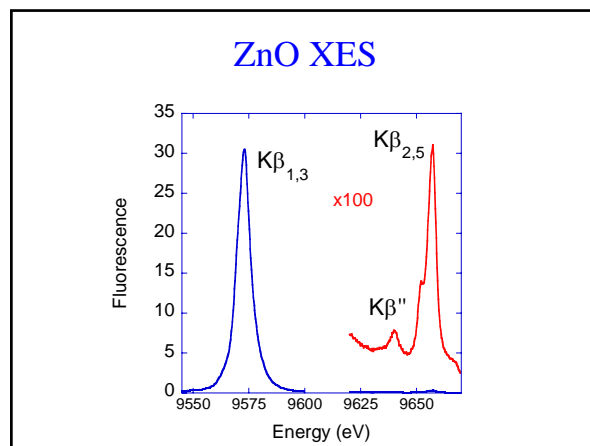
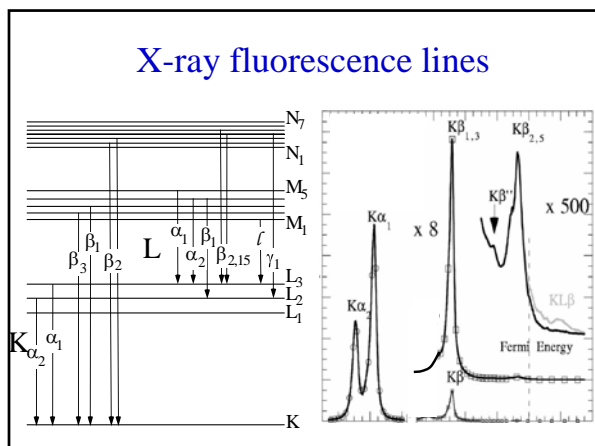


Hämäläinen, *PRB*, **46**, 14274

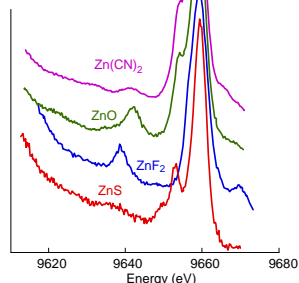
Spin-selective XANES



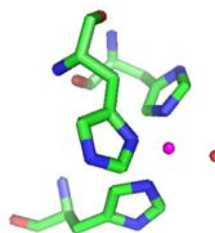
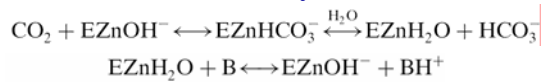




However, tetrahedral Zn does not follow the same pattern



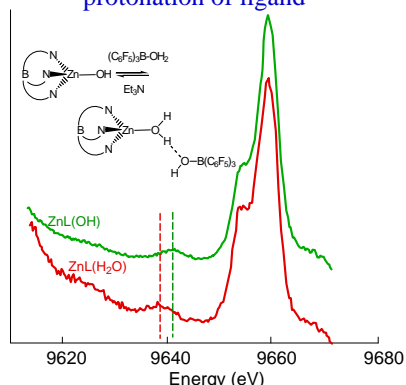
Carbonic Anhydrase



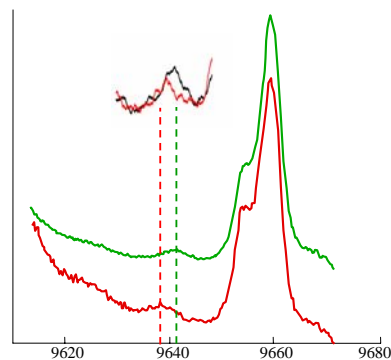
~~Zn-bound water or Zn-bound hydroxide?~~

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

- Basic Physical Principles
 - XAS – crystallographic-like information for non-crystalline samples
- Practical aspects of x-ray absorption
 - Measurement of absorption
 - Energy selection
 - Artifacts (how **NOT** to measure the right signal)
 - Radiation damage
- Data analysis
 - Problems
 - Least-squares minimization
 - Fourier Filtering
 - Resolution
 - Normalization
 - Methods
 - Multiple scattering
 - PCA

- Near edge structure
 - Bound state transitions
 - Multiplet structure
 - Oxidation state
 - Multiple scattering and Geometry
 - Ligand K-edge studies
 - Time and concentration dependence - titrations
- Spatially and temporally resolved methods
 - Methods for focusing x-rays
 - Spatially resolved studies
 - Distribution
 - Concentration
 - Speciation
 - Temporally resolved
 - QEXAFS
 - Dispersive
 - Continuous flow
 - RFQ
- Exotic x-ray spectroscopies

