

Lecture 3.

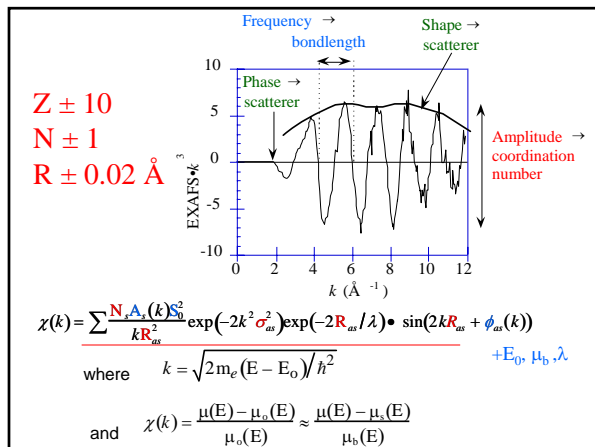
Data Analysis

Tutorials and other Training Material

Bruce Ravel's notes on using FEFFIT for data analysis
 Daresbury Laboratory lectures on data analysis (EXCURV98)
 Grant Bunker's XAFS tutorials
 Frenkel et al on comparing PCA with other methods
 Chantler (Uni. Melbourne) on the absolute determination of x-ray absorption

Programs

ESRF Software catalog
 XFIT
 EXAFSPAK
 Athena and Artemis
 FEFFIT and IFEFFIT
 DL EXCURV
 WinXAS



- The job of a least-squares fitting program is to give you the best (smallest deviation) solution, *not* to give you the right solution.

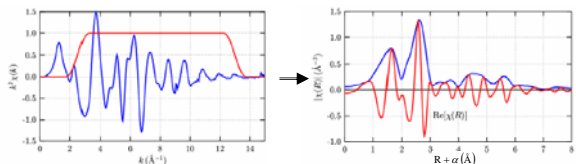
- If you see something, it tells you something; if you see nothing, it tells you nothing.

Fourier transformation can be used to visualize frequencies contributing to EXAFS

$$\chi(k) = \sum \frac{N_i A_i(k) S_i^2}{k R_{oi}^2} \exp(-2k^2 \sigma_{oi}^2) \exp(-2R_{oi}/\lambda) \sin(2kR_{oi} + \phi_{oi}(k))$$

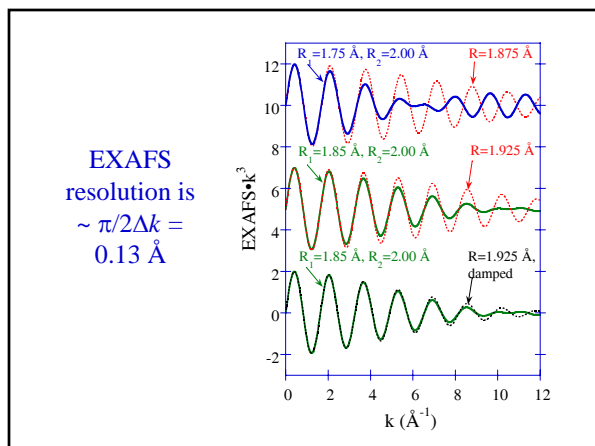
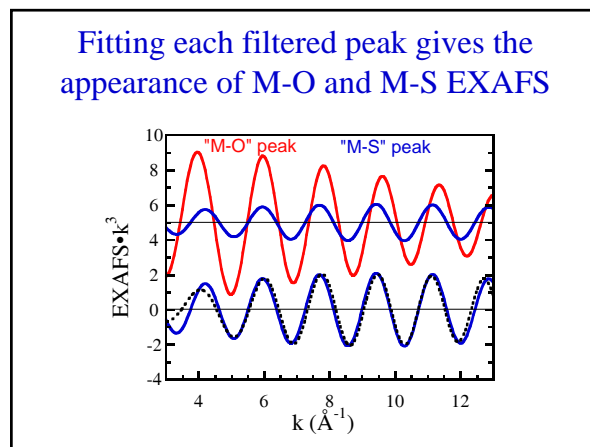
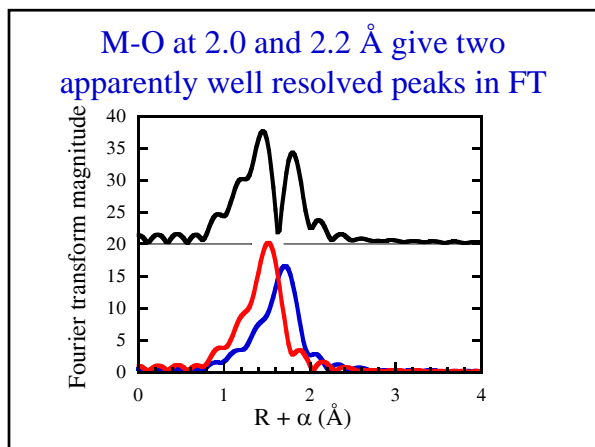
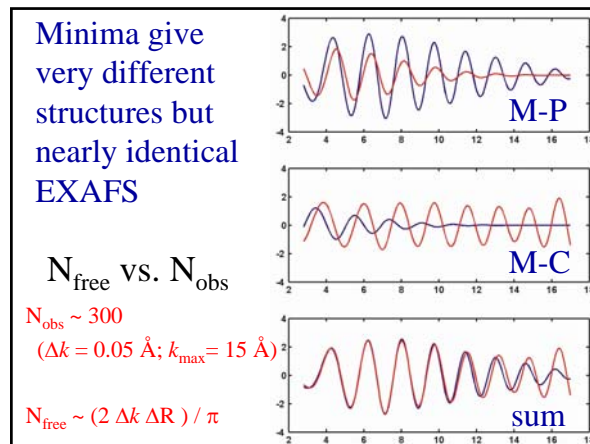
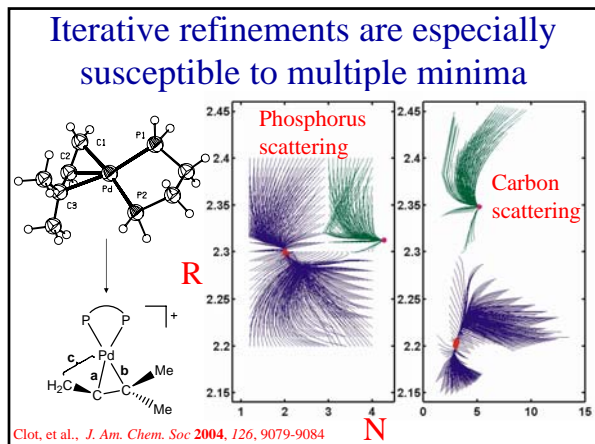
$$\chi(k) = \sum A(k) \sin(2kR + \phi)$$

$$\phi = \phi_0 + R\phi_1 + R^2\phi_2 + \dots$$



Common errors in EXAFS analysis

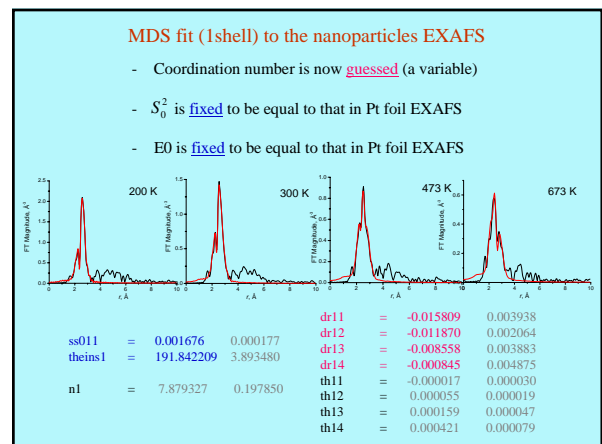
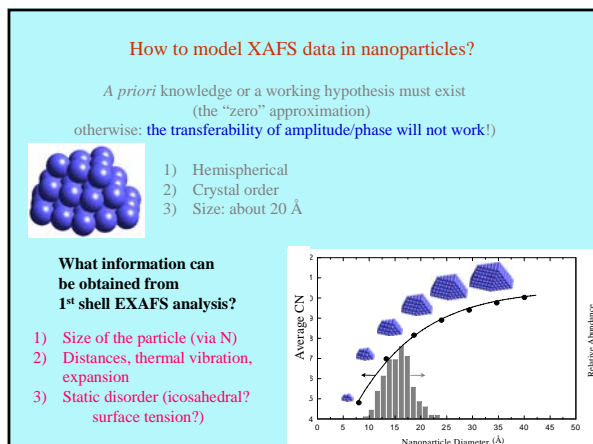
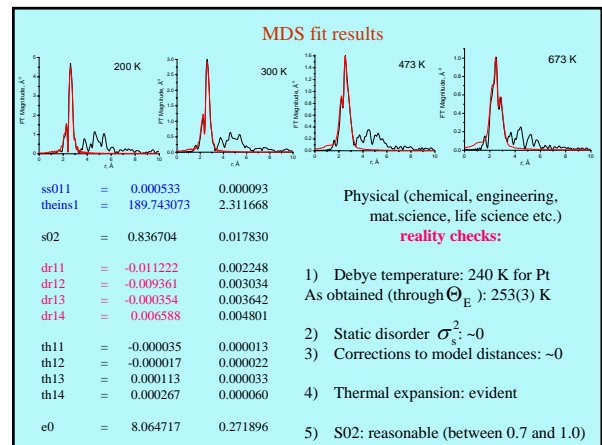
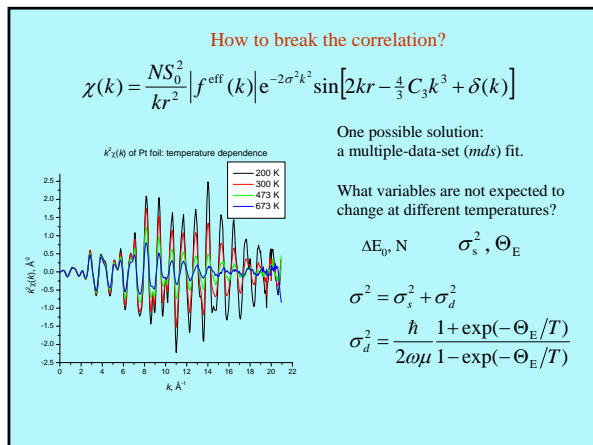
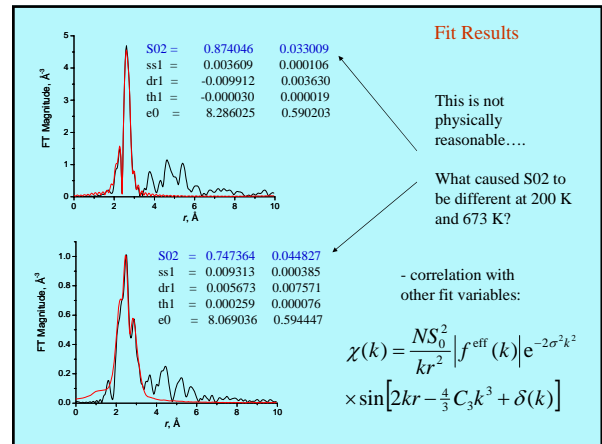
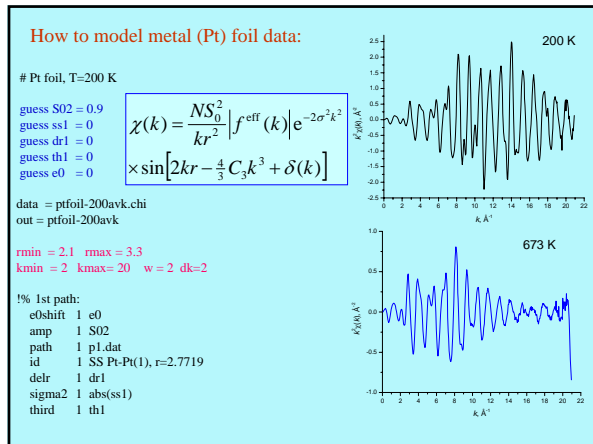
- Least-squares minimization
- Fourier Filtering
- Resolution

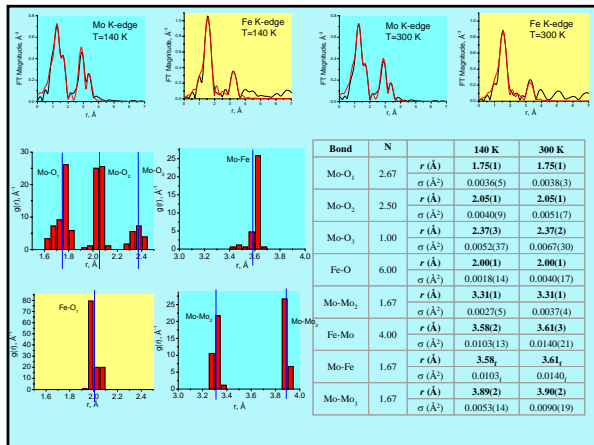
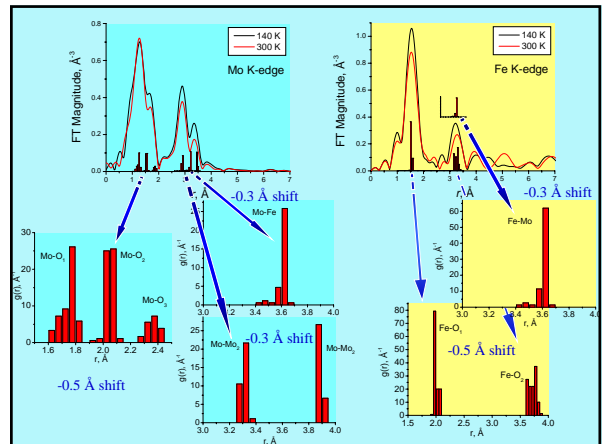
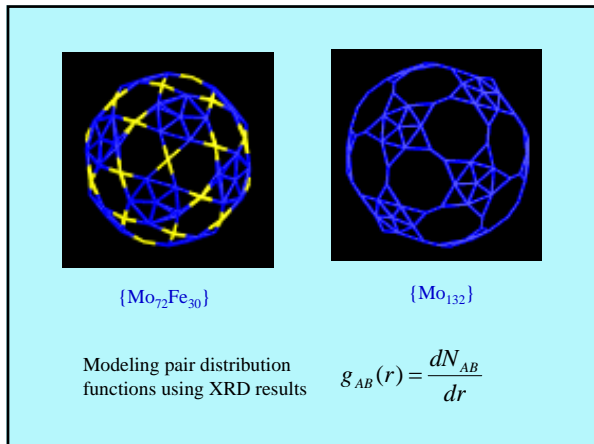


Further explorations of the difficulty of multiple minima

N and σ^2
 R and E_0

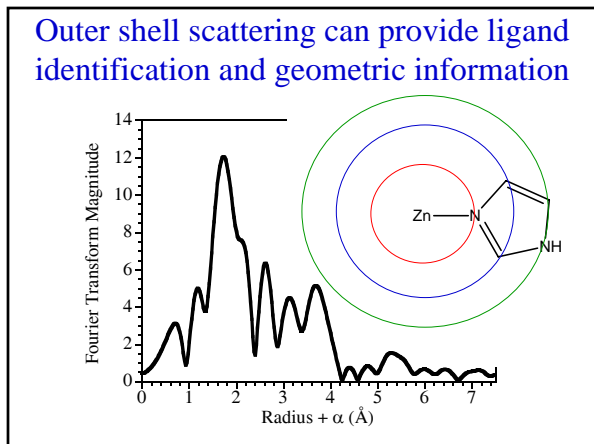
Anatoly Frenkel
 EXAFS Data Collection and Analysis Workshop, NSLS





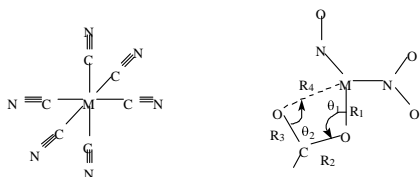
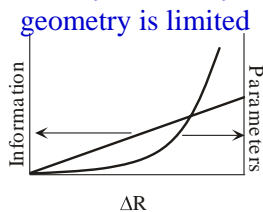
Summary

- The more variables you control, the more likely you are to obtain a unique solution
- Multiple data sets (elements, temperature, concentration, time, etc.) almost always help
- Conclusions are only as good as your model



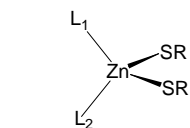
Multiple scattering makes EXAFS sensitive to angular arrangement of ligands

However, ability to reliably determine geometry is limited



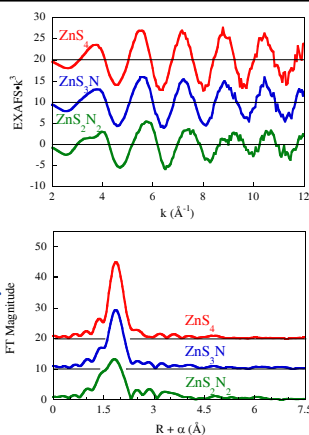
A case study in data under-determination

Clark-Baldwin, et al. "The limitations of X-ray absorption spectroscopy for determining the structure of zinc sites in proteins. When is a tetrathiolate not a tetrathiolate?" *J. Am. Chem. Soc.* **1998**, *120*, 8401-8409.



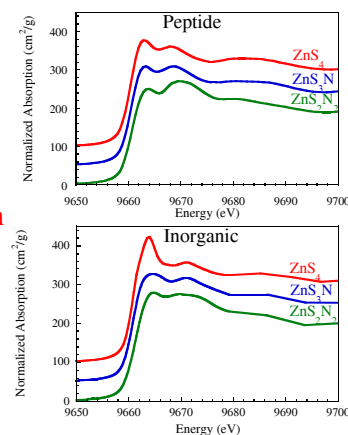
Zn EXAFS is remarkably insensitive to changes in ligation.

$Z \pm 10$???

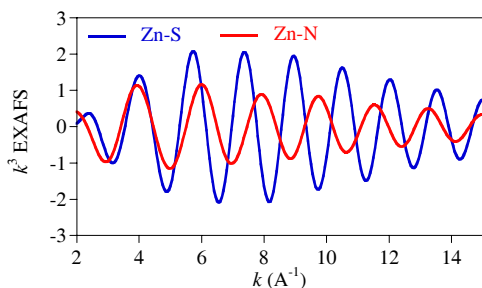


XANES spectra are sensitive to ligation

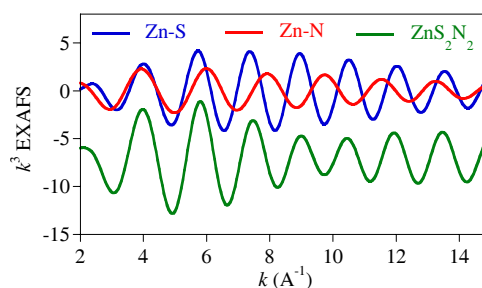
but show greater variation between different compounds than with changes in ligation.



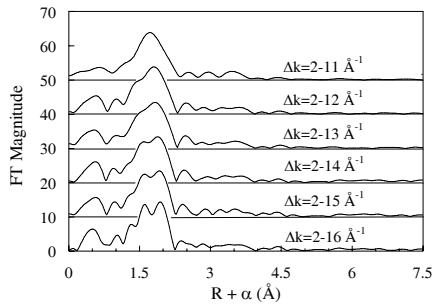
Zn-S and Zn-N EXAFS signals are approximately out of phase



The observed EXAFS for mixed S/N sites is dominated by Zn-S scattering

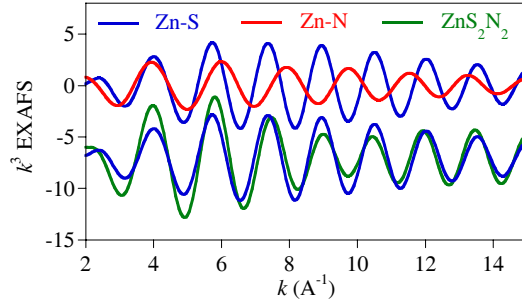


One solution is to measure data over wide k range
(ZnS_2N_2 inorganic)

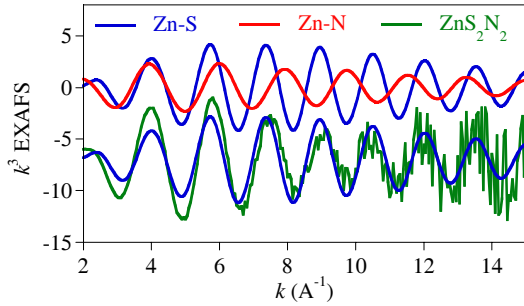


Note - $\Delta R \sim 0.25 \rightarrow \pi/2\Delta k = 0.25 \text{ \AA} \rightarrow \Delta k_{\min} \sim 6.3$

High resolution EXAFS is required to reliably distinguish Zn-S from Zn-N ...



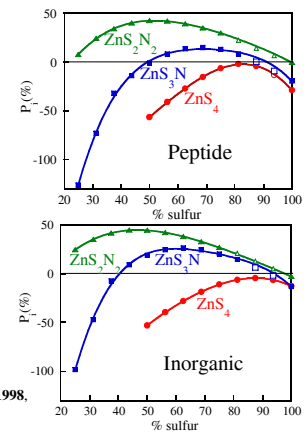
...and even with high resolution data, extremely high signal/noise ratios are required to detect Zn-N in the presence of Zn-S



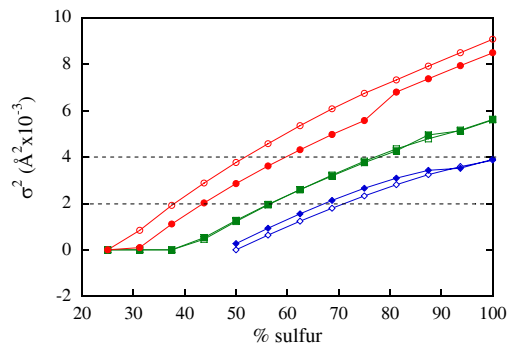
It *is* possible to reliably distinguish between ZnS_4 , ZnS_3N , and ZnS_2N_2 if variable parameters are carefully controlled.

Note that fit quality always improves for mixed ligation fits.

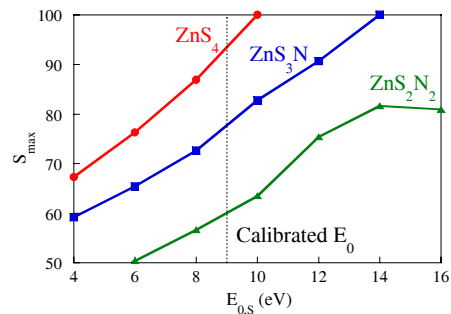
Clark-Baldwin, K et al, *J. Am. Chem. Soc.* **1998**, 120, 8401-8409.



In addition to P_i , σ^2 depends on ligation

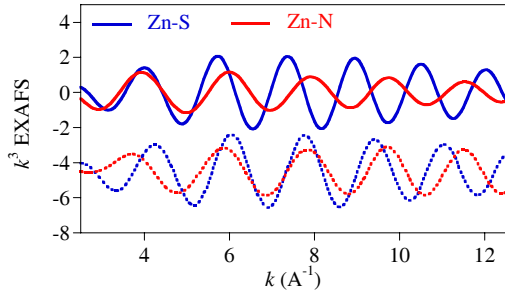


Threshold energy changes apparent ligation



5 eV is enough to change a sulfur into a nitrogen!

Distinction between S and N rests largely on phase, which depends on E_0

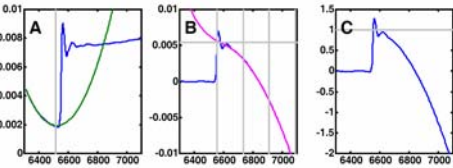


XANES spectra contain useful information regarding structure

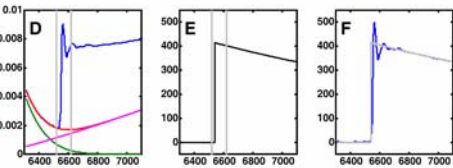
- Quantitative comparisons (e.g., titration) requires accurate normalization.
- Correction for various artifacts (self-absorption) requires accurate normalization.
- Common normalization procedures were developed for extracting EXAFS and do not necessarily work well for XANES.

Normalization Schemes

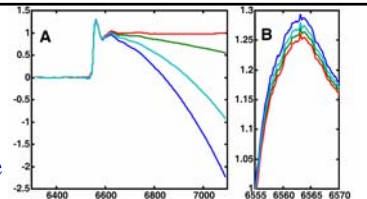
Conventional



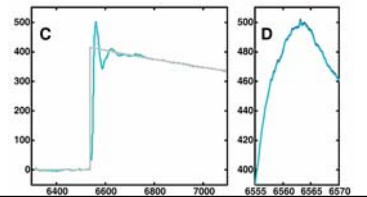
MBACK



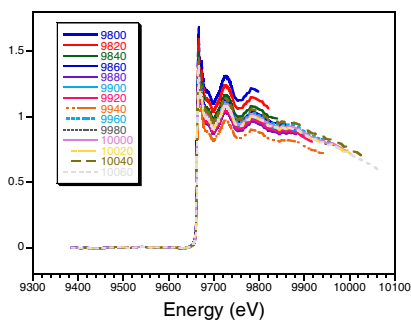
Conventional normalization is sensitive to background shape



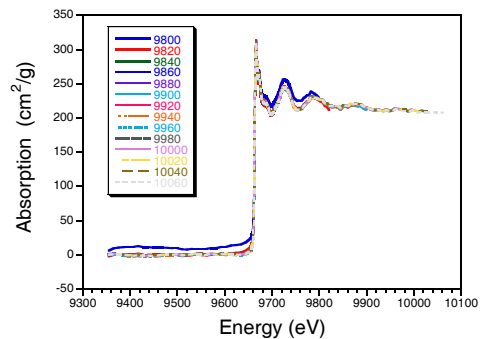
MBACK shows much weaker sensitivity



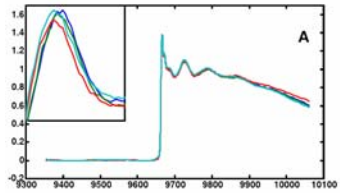
Conventional normalization is sensitive to range of data



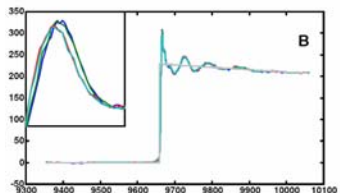
MBACK shows only slight sensitivity for $E_{\max} \geq \sim 150$ eV above edge



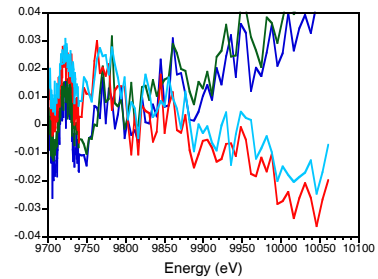
Conventional normalization misses changes in XANES



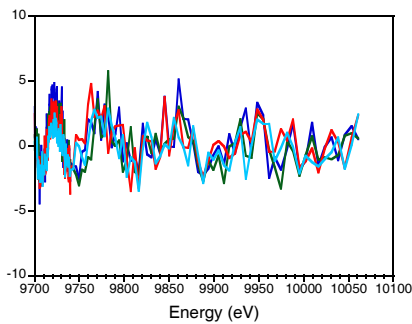
MBACK reveals subtle changes when thiolate is added



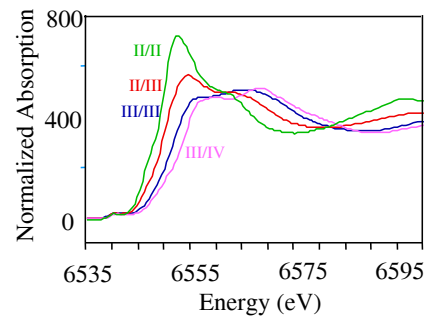
4 possible difference spectra – should all be the same



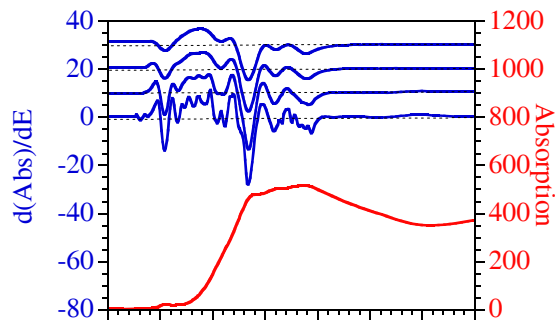
With new normalization, difference signal is detectable



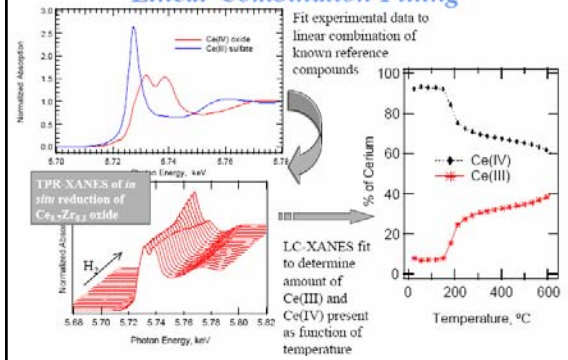
Dependence of XANES on Oxidation State



Edge “energy” is poorly defined



Linear Combination Fitting



Simon Bare, NSLS workshop

Principal Component Analysis

- PCA estimates number of distinct species in a series of spectra.
- Used as a first stage of analysis.
- Based on linear algebra - each spectrum represented as a vector.
- Goal is to find number of components that can reproduce the experimental spectra to within experimental (statistical) error.
- No *a priori* assumptions on number/type of components.

[Factor Analysis in Chemistry](#), 2nd Ed. John Wiley & Sons, NY, 1991

