Lecture 2

How to avoid common errors in EXAFS and XANES analysis

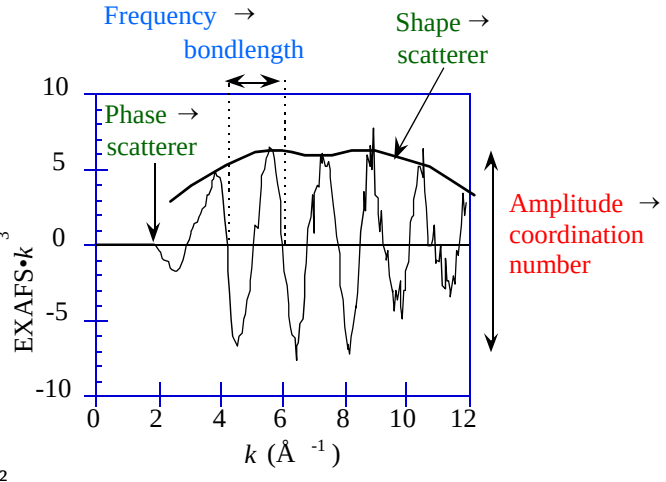
Tutorials and other Training Material

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

Z ± 10
N ± 1
R ± 0.02 Å



$$\chi(k) = \sum \frac{N_s A_s(k) S_0^2}{kR_{as}^2} \exp\left(-2k^2\sigma_{as}^2\right) \exp\left(-2R_{as}/\lambda\right) \bullet \sin\left(2kR_{as} + \phi_{as}(k)\right)$$

where $k = \sqrt{2m_e(E - E_o)/\hbar^2}$

+E_0, μ_b, λ

and $\chi(k) = \frac{\mu(E) - \mu_o(E)}{\mu_o(E)} \approx \frac{\mu(E) - \mu_s(E)}{\mu_b(E)}$

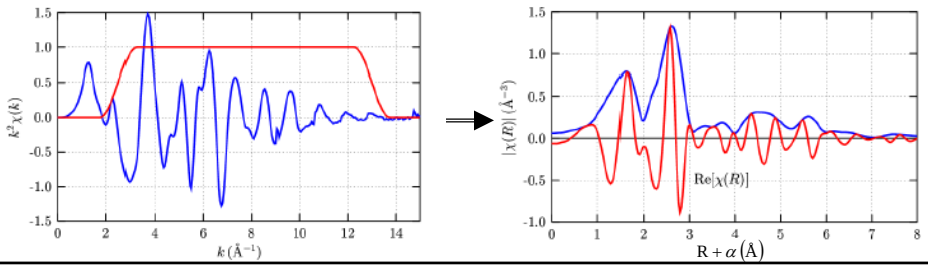
Radial structure only

Fourier transformation can be used to visualize frequencies contributing to EXAFS

$$\chi(k) = \sum \frac{N_s A_s(k) S_0^2}{kR_{as}^2} \exp\left(-2k^2\sigma_{as}^2\right) \exp\left(-2R_{as}/\lambda\right) \bullet \sin\left(2kR_{as} + \phi_{as}(k)\right)$$

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

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



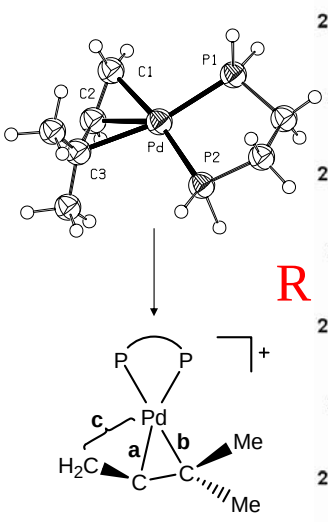
Common errors in EXAFS analysis

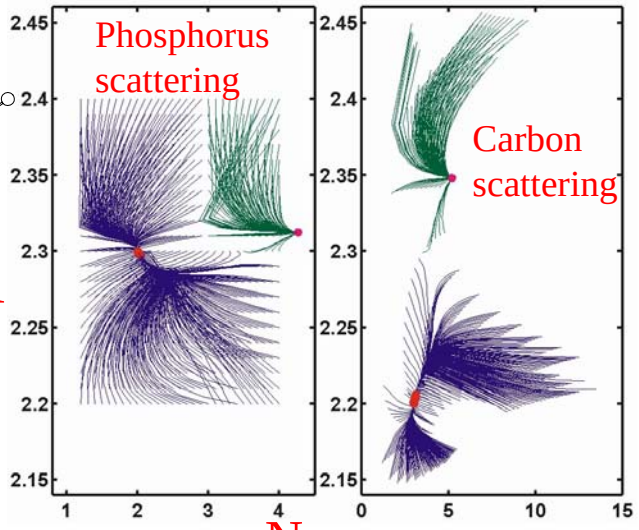
- Least-squares minimization
- Fourier Filtering
- Resolution

- 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.

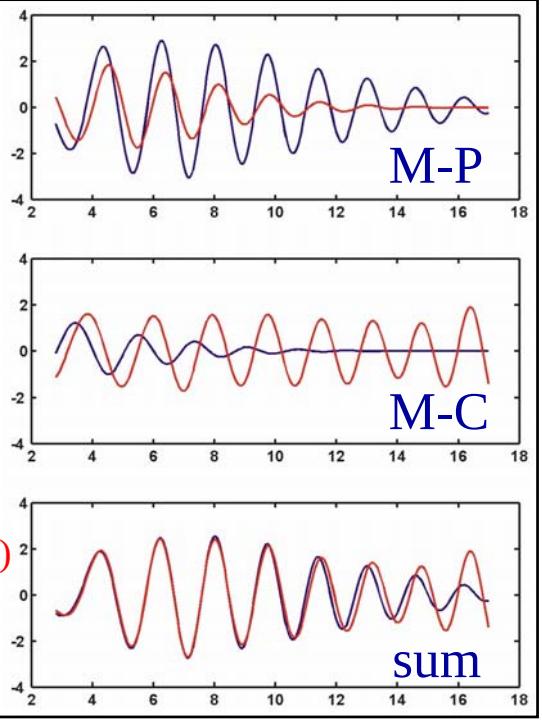
Iterative refinements are especially susceptible to multiple minima





Clot, et al., *J. Am. Chem. Soc* **2004**, *126*, 9079-9084

Minima give very different structures but nearly identical EXAFS



N_{free} vs. N_{obs}

$N_{obs} \sim 300$
($\Delta k = 0.05$ Å; $k_{max} = 15$ Å)

$N_{free} \sim (2\ \Delta k\ \Delta R\ ) / \pi$

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

How to model metal (Pt) foil data:

Pt foil, T=200 K

guess S02 = 0.9
guess ss1 = 0
guess dr1 = 0
guess th1 = 0
guess e0 = 0

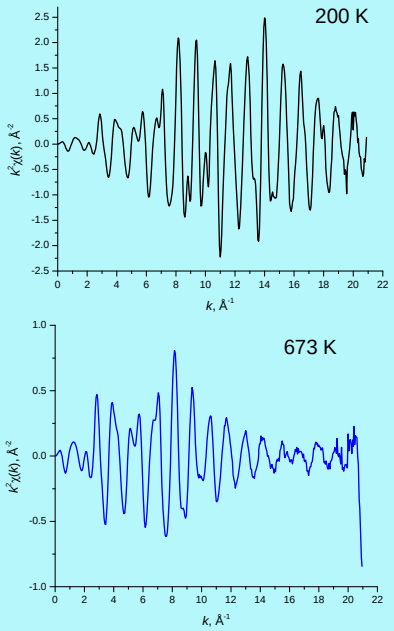
$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

data = ptfoil-200avk.chi
out = ptfoil-200avk

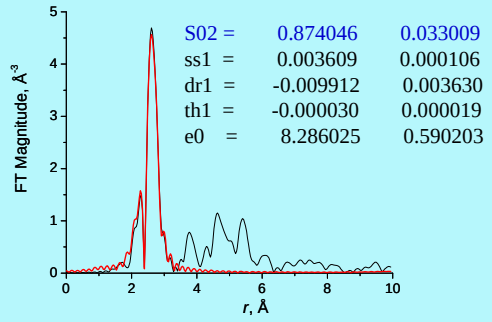
rmin = 2.1 rmax = 3.3
kmin = 2 kmax= 20 w = 2 dk=2

!% 1st path:

e0shift	1	e0
amp	1	S02
path	1	p1.dat
id	1	SS Pt-Pt(1), r=2.7719
delr	1	dr1
sigma2	1	abs(ss1)
third	1	th1

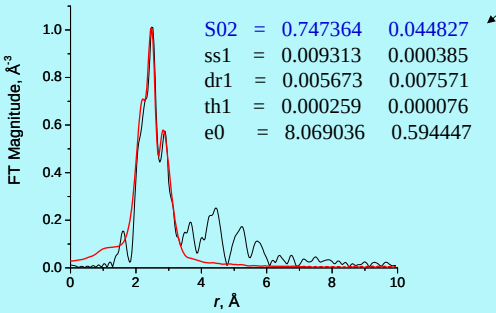


Fit Results



This is not physically reasonable….

What caused S02 to be different at 200 K and 673 K?

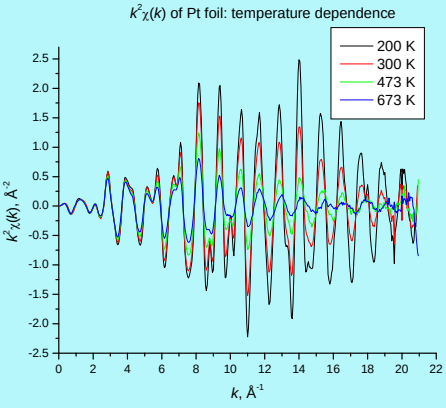


- correlation with other fit variables:

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

How to break the correlation?

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$



One possible solution:
a multiple-data-set (*mds*) fit.

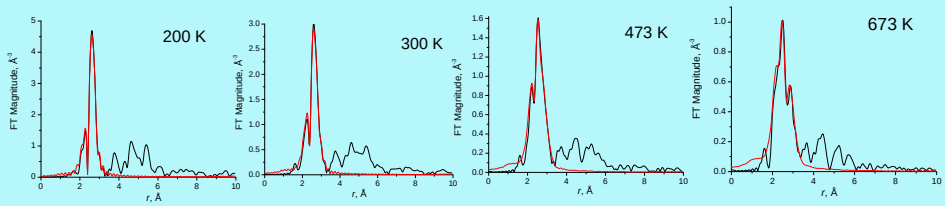
What variables are not expected to change at different temperatures?

ΔE_0, N $\qquad \sigma_s^2$, Θ_E

$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu}\frac{1+\exp(-\Theta_E/T)}{1-\exp(-\Theta_E/T)}$$

MDS fit results



ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

Physical (chemical, engineering, mat.science, life science etc.)
reality checks:

1) Debye temperature: 240 K for Pt
As obtained (through Θ_E): 253(3) K

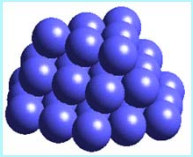
2) Static disorder σ_s^2: ~0
3) Corrections to model distances: ~0

4) Thermal expansion: evident

5) S02: reasonable (between 0.7 and 1.0)

How to model XAFS data in nanoparticles?

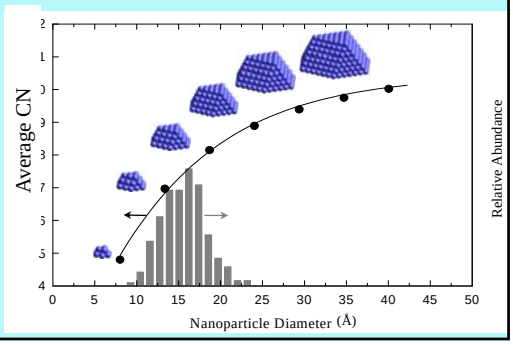
A priori knowledge or a working hypothesis must exist
(the "zero" approximation)
otherwise: the transferability of amplitude/phase will not work!)



1) Hemispherical
2) Crystal order
3) Size: about 20 Å

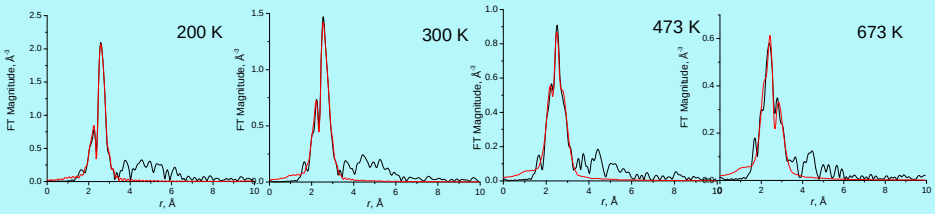
What information can be obtained from 1st shell EXAFS analysis?

1) Size of the particle (via N)
2) Distances, thermal vibration, expansion
3) Static disorder (icosahedral? surface tension?)



MDS fit (1shell) to the nanoparticles EXAFS

- Coordination number is now guessed (a variable)
- S_0^2 is fixed to be equal to that in Pt foil EXAFS
- E0 is fixed to be equal to that in Pt foil EXAFS



ss011	=	0.001676	0.000177
theins1	=	191.842209	3.893480
n1	=	7.879327	0.197850

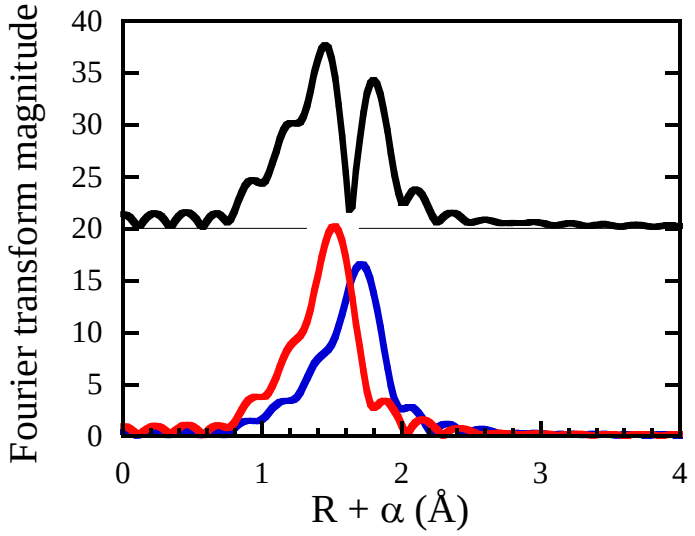
dr11	=	-0.015809	0.003938
dr12	=	-0.011870	0.002064
dr13	=	-0.008558	0.003883
dr14	=	-0.000845	0.004875
th11	=	-0.000017	0.000030
th12	=	0.000055	0.000019
th13	=	0.000159	0.000047
th14	=	0.000421	0.000079

Summary

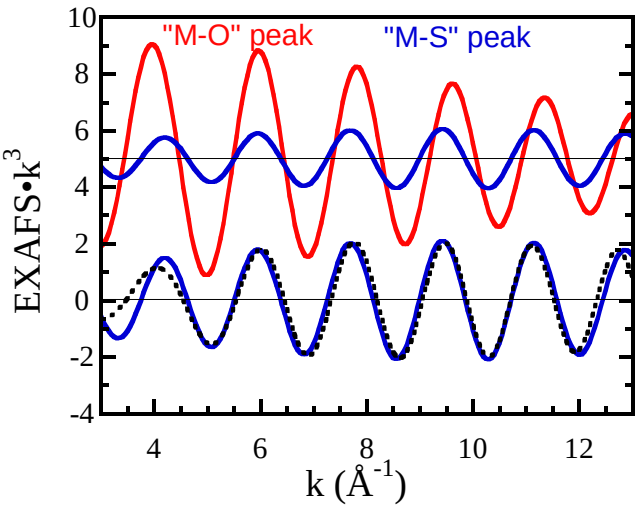
- The more variables you control, the more likely you are to obtain a unique solution
- Multiple data sets (elements, temperature, concentration, time, etc.) almost always help
- Conclusions are only as good as your model

Fourier filtered data can be distorted

M-O at 2.0 and 2.2 Å give two apparently well resolved peaks in FT

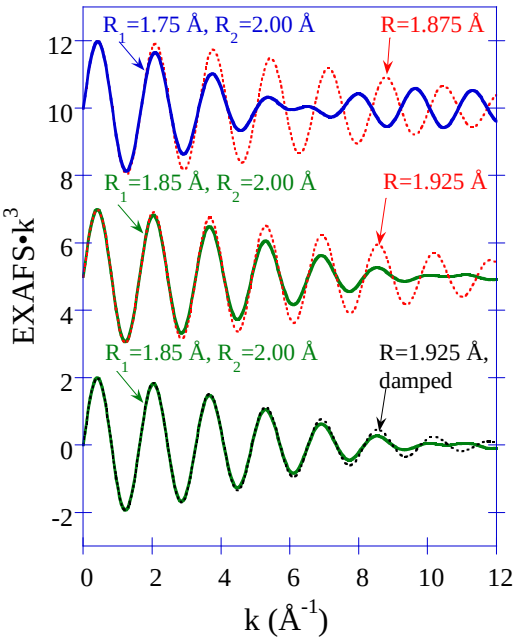


Fitting each filtered peak gives the appearance of M-O and M-S EXAFS



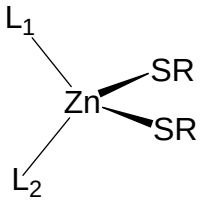
Effect of limited resolution on EXAFS

EXAFS resolution is ~ $\pi/2\Delta k$ = 0.13 Å



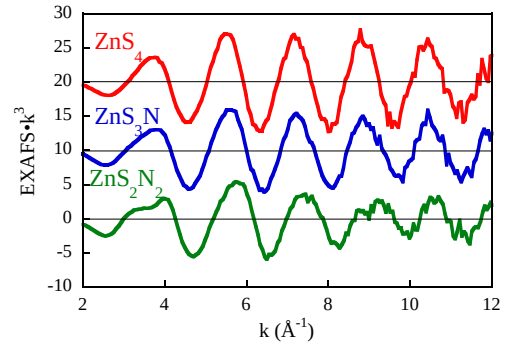
A case study in data under-determination

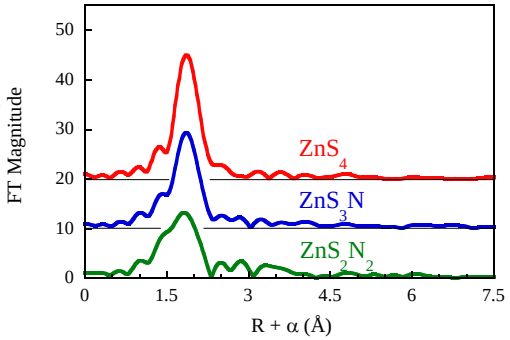
Clark-Baldwin, et al. "The limitations of X-ray absorption spectroscopy for determining the structure of zinc sites in proteins. When is a tetrathiolate not a tetrathiolate?" *J. Am. Chem. Soc.* **1998**, *120*, 8401-8409.



Zn EXAFS is remarkably insensitive to changes in ligation.

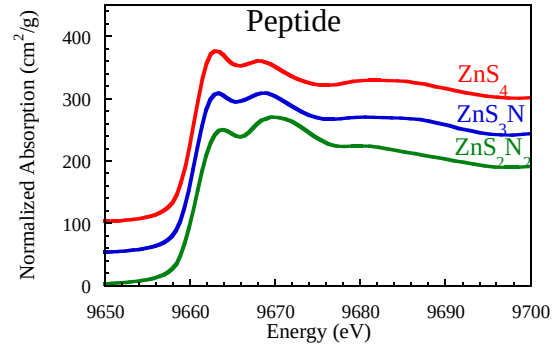
Z ± 10 ???

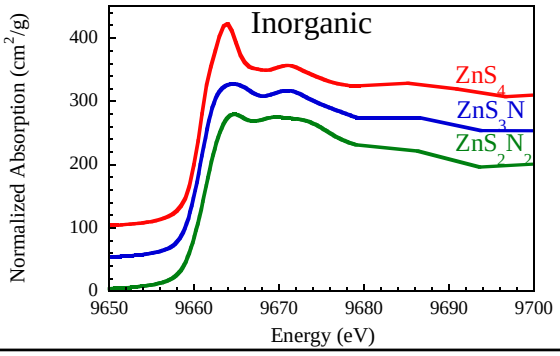




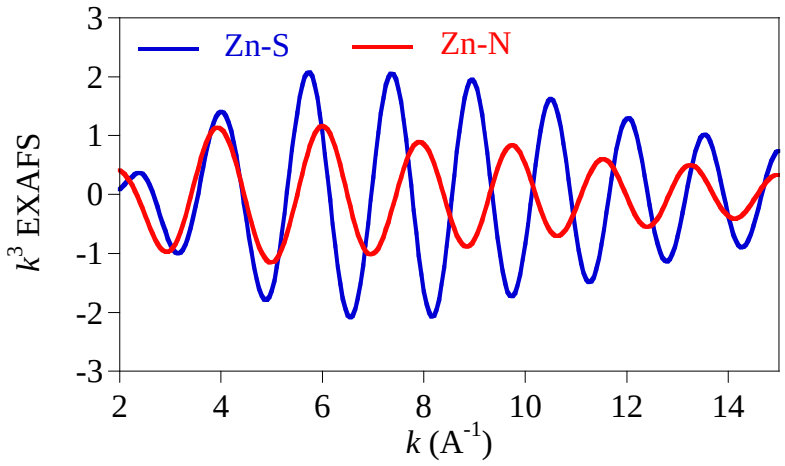
XANES spectra *are* sensitive to ligation

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

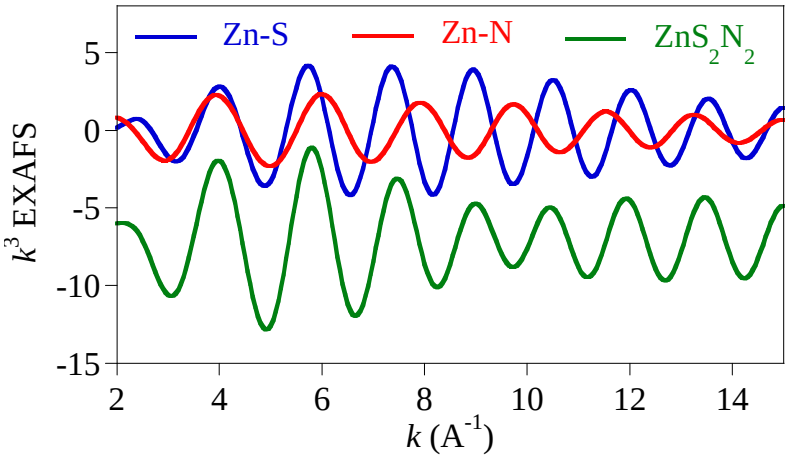




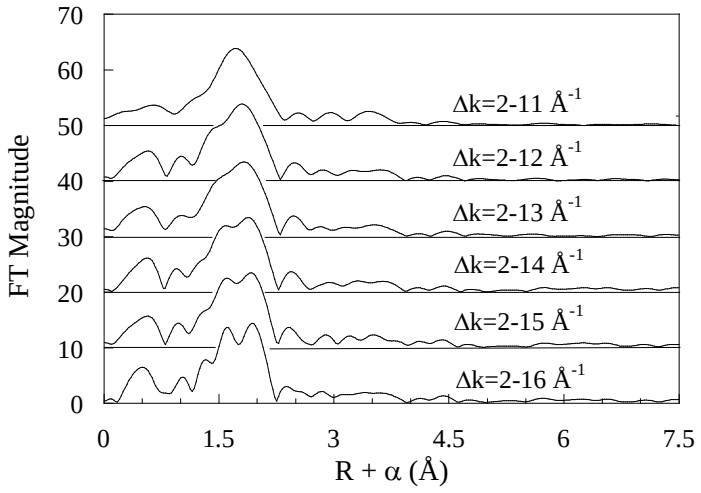
Zn-S and Zn-N EXAFS signals are approximately out of phase



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

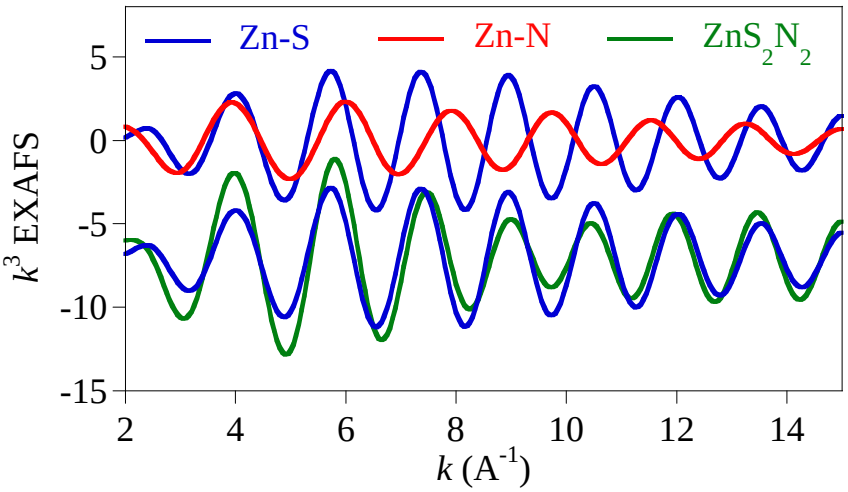


One solution is to measure data over wide *k* range (ZnS_2N_2 inorganic)

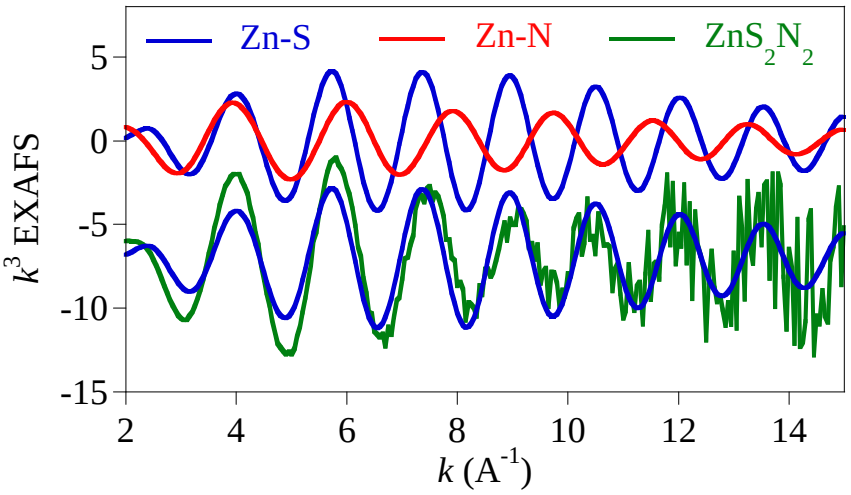


Note – $\Delta R \sim 0.25 \rightarrow \pi/2\Delta k = 0.25$ Å $\rightarrow \Delta k_{min} \sim 6.3$

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

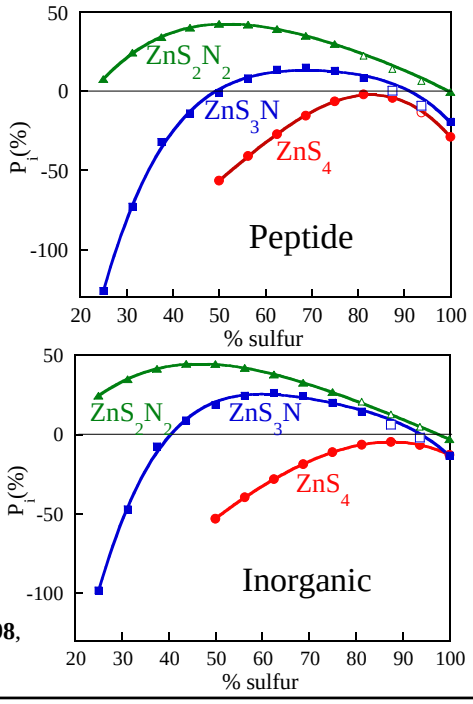


…and even with high resolution data, extremely high signal/noise ratios are required to detect Zn-N in the presence of Zn-S



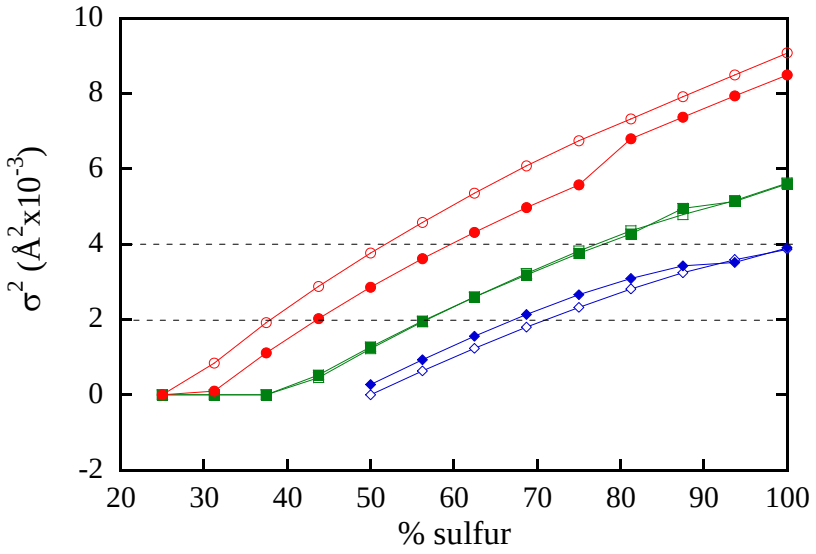
It *is* possible to reliably distinguish between ZnS_4, ZnS_3N, and ZnS_2N_2 if variable parameters are carefully controlled.

Note that fit quality always improves for mixed ligation fits.

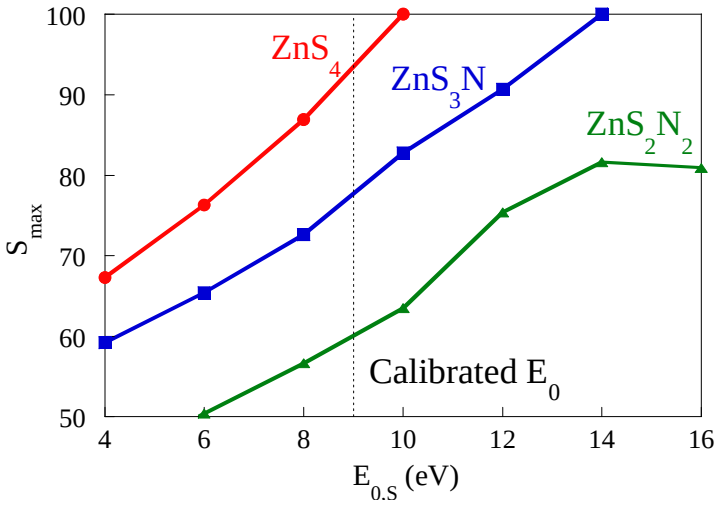


Clark-Baldwin, K et al, *J. Am. Chem. Soc.* **1998**, *120*, 8401-8409.

In addition to P_i, σ^2 depends on ligation

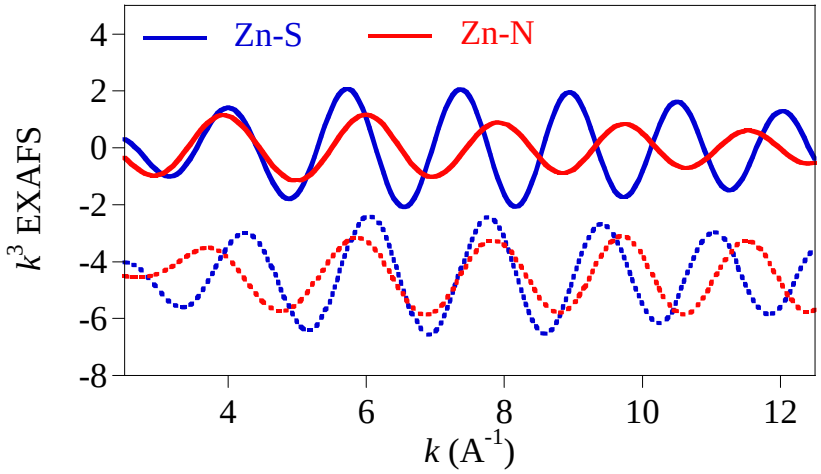


Threshold energy changes apparent ligation



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

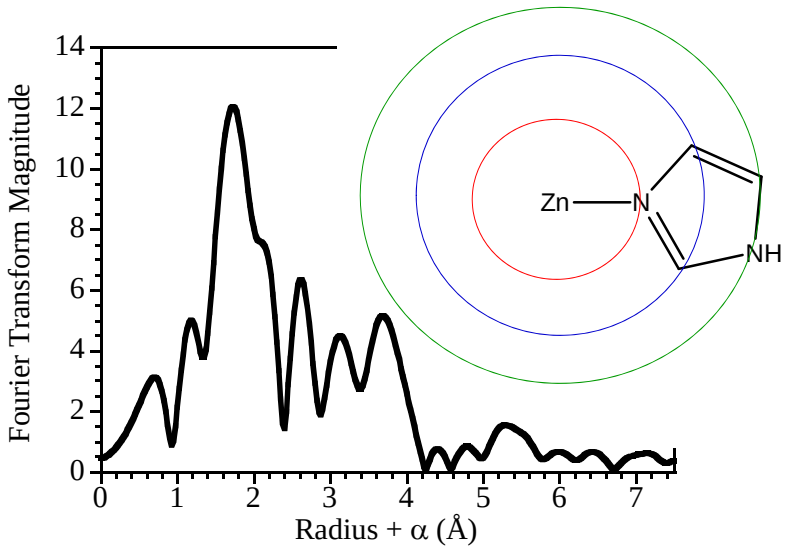
Distinction between S and N rests largely on phase, which depends on E_0



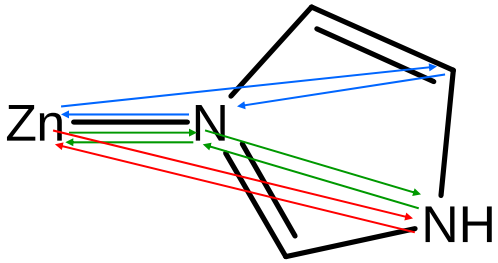
Geometry determination

Multiple scattering in EXAFS

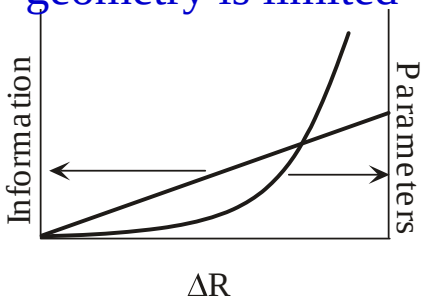
Outer shell scattering can provide ligand identification and geometric information

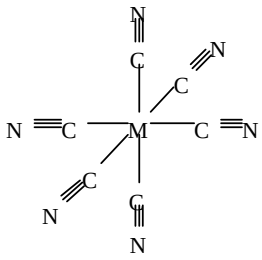


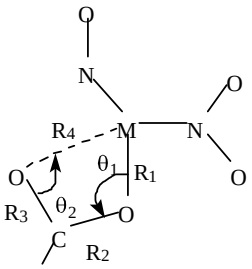
Multiple scattering makes EXAFS sensitive to angular arrangement of ligands



However, ability to reliably determine geometry is limited





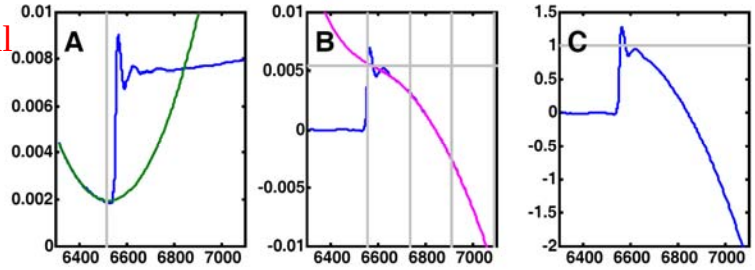


XANES spectra contain useful information regarding structure

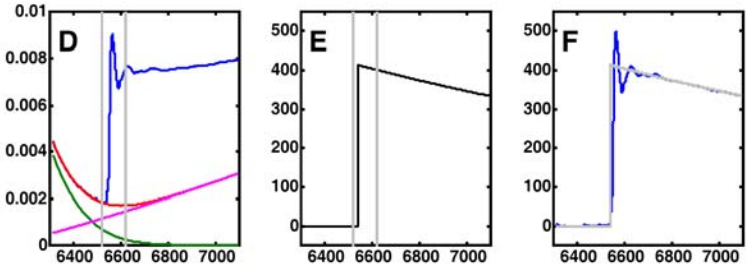
- Quantitative comparisons (e.g., titration) requires accurate normalization.
- Correction for various artifacts (self-absorption) requires accurate normalization.
- Common normalization procedures were developed for extracting EXAFS and do not necessarily work well for XANES.

Normalization Schemes

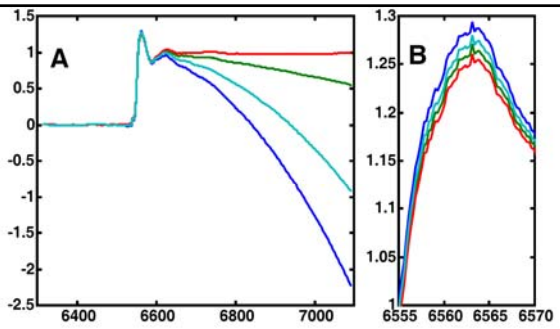
Conventional



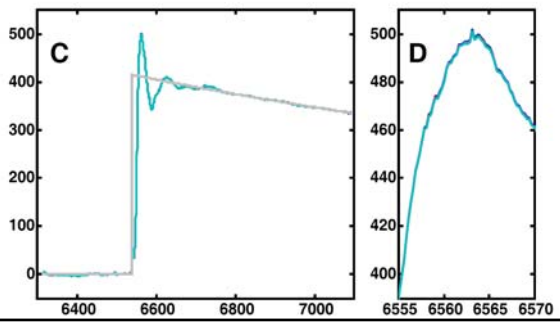
MBACK



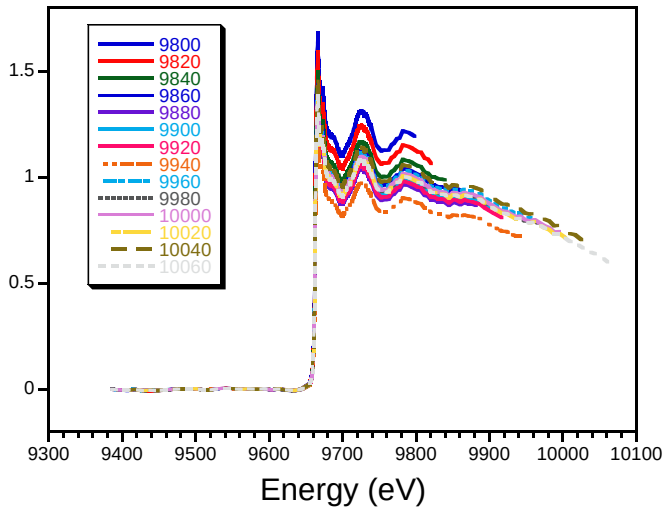
Conventional normalization is sensitive to background shape



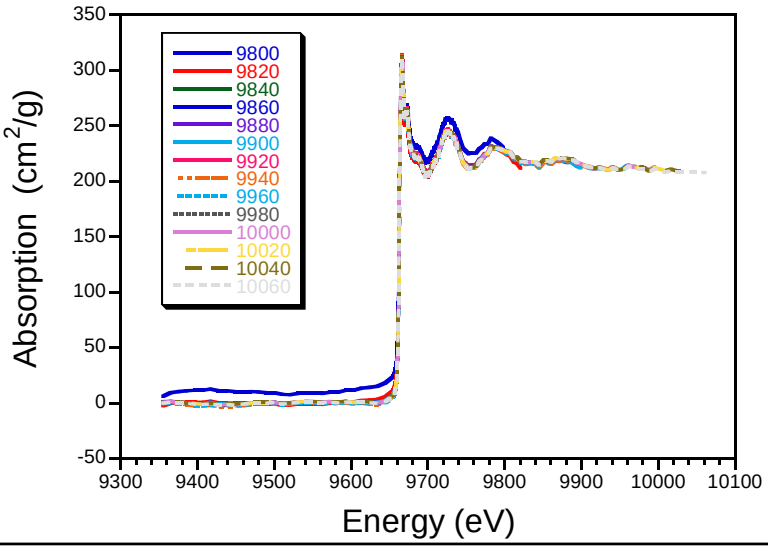
MBACK shows much weaker sensitivity



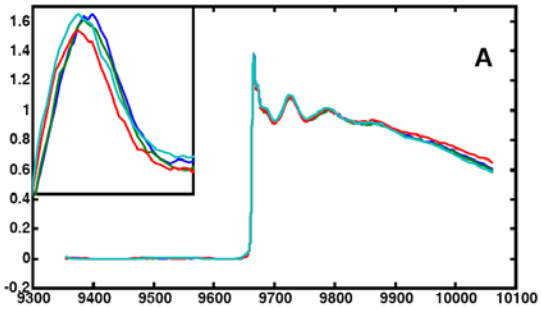
Conventional normalization is sensitive to range of data



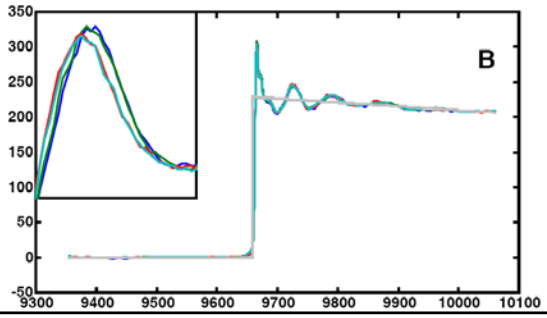
MBACK shows only slight sensitivity for $E_{max} \geq \sim 150$ eV above edge



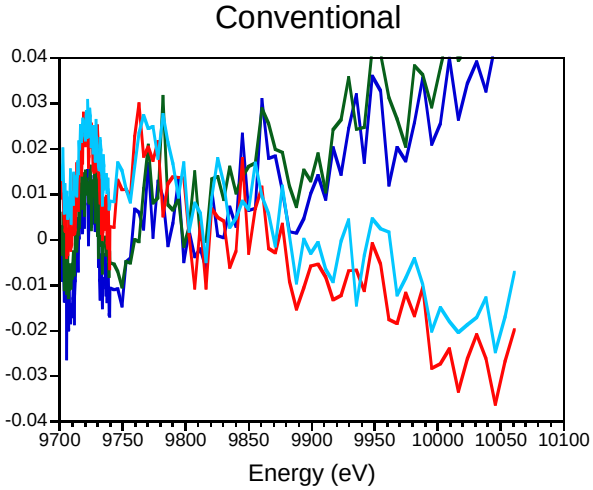
Conventional normalization misses changes in XANES



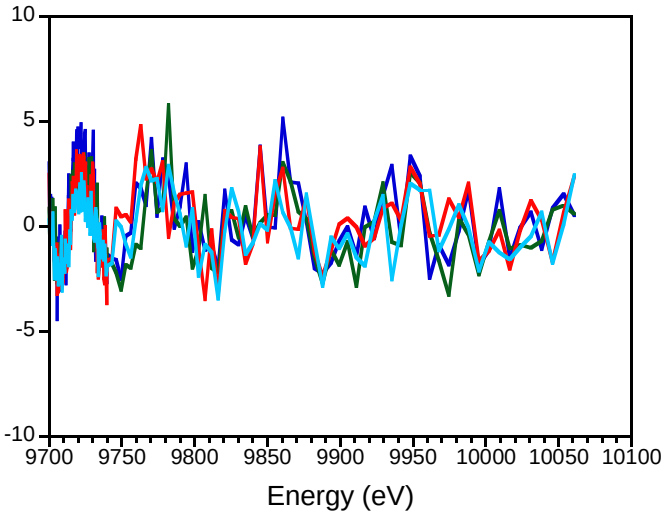
MBACK reveals subtle changes when thiolate is added



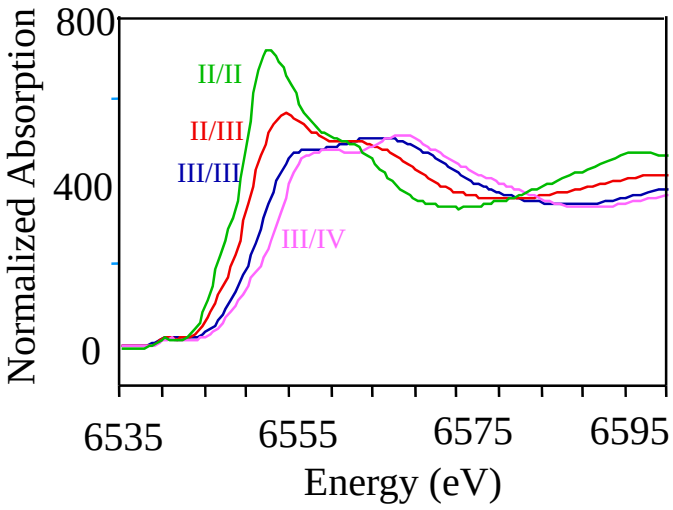
4 possible difference specta – should all be the same



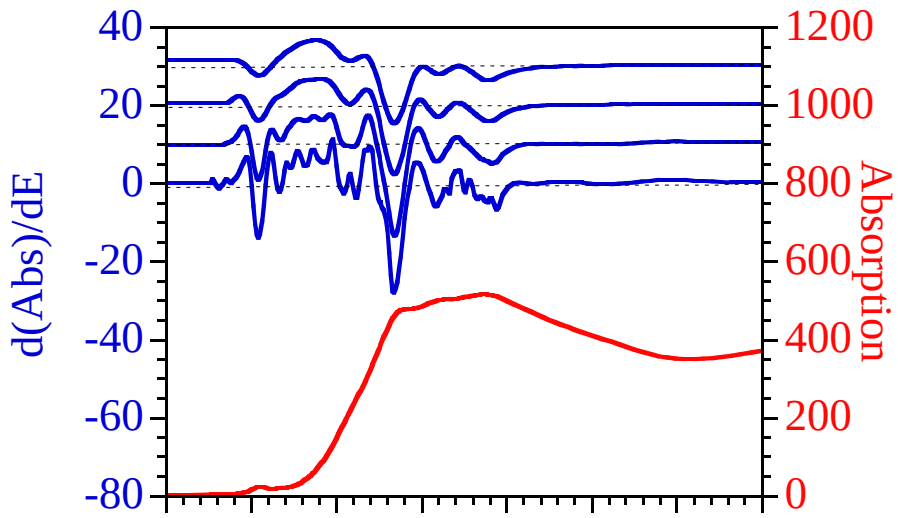
With new normalization, difference signal is detectable



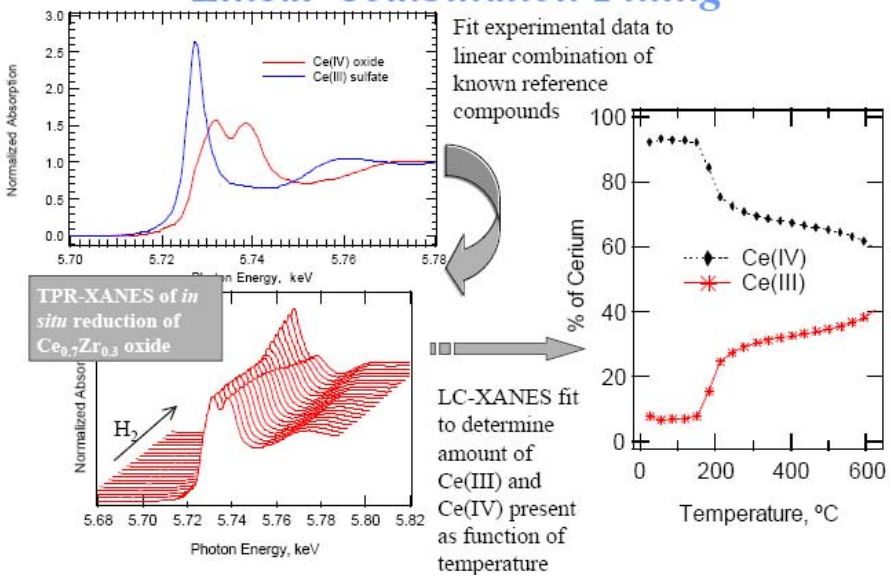
Dependence of XANES on Oxidation State



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.

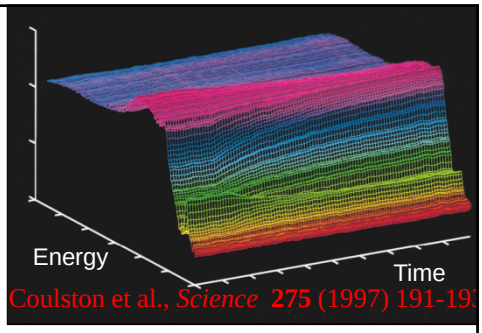
Factor Analysis in Chemistry, 2nd Ed. John Wiley & Sons, NY, 1991

$$X = U S V^{\mathrm{T}}$$

$$X^{(l)} = \sum_{k=1}^{l} \mathbf{u}_k s_k \mathbf{v}_k^{\mathrm{T}}$$

is the closest l-rank matrix to X

(see http://public.lanl.gov/mewall/kluwer2002.html)



Coulston et al., *Science* **275** (1997) 191-19