The linear combination approach for XANES data treatment

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Outline

What is XANES?
How to interpret XANES?
Why are we interested in XANES?
Advantages of XANES vs. EXAFS

Analysis of Mixtures
Linear combinations
An example from literature

Conclusions: take away messages

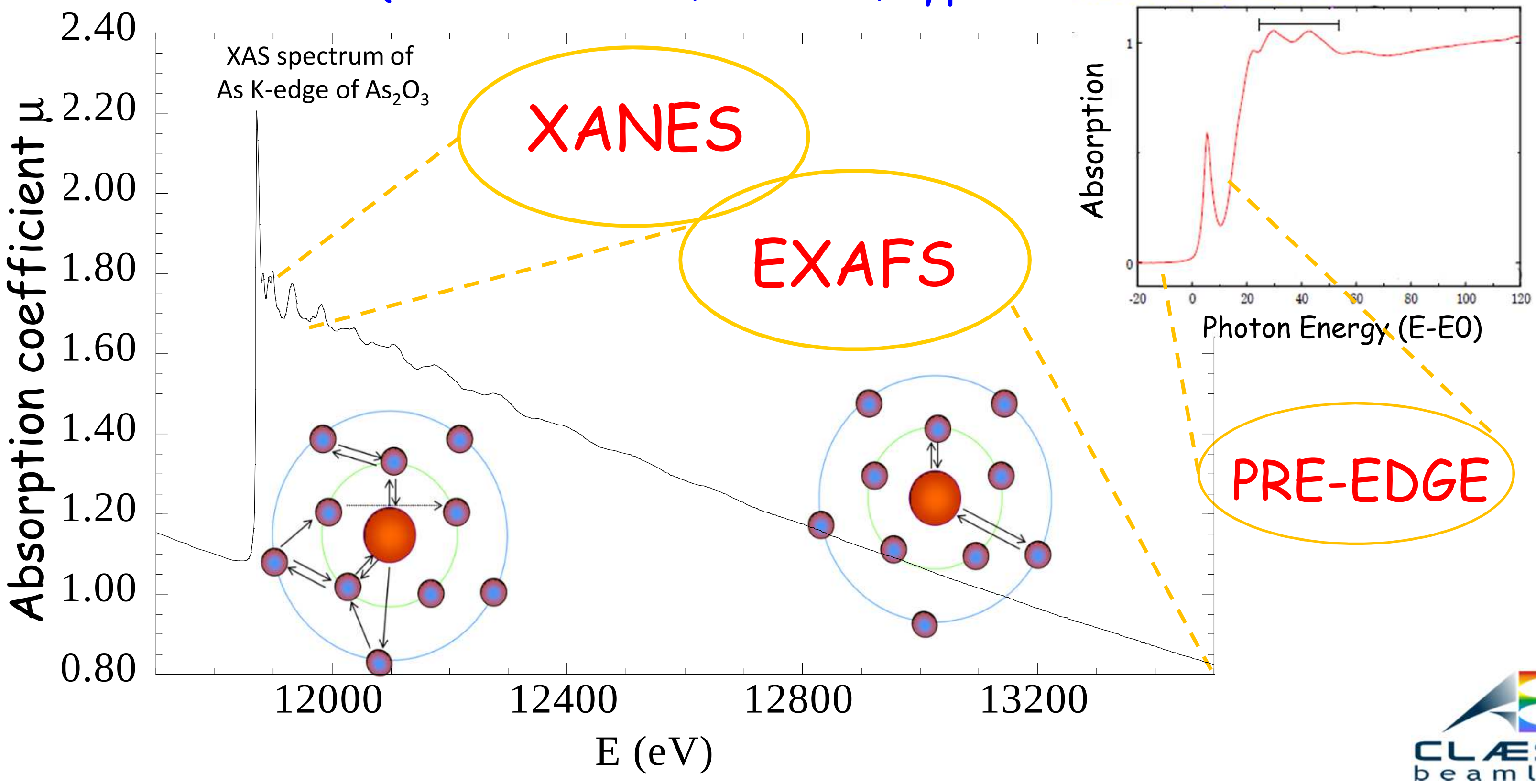
What is XANES?

XANES: transitions to unfilled bound states, nearly bound states, continuum

→ local site symmetry, charge state, orbital occupancy

EXAFS: 50 - 1000 eV after edge due to transitions to continuum

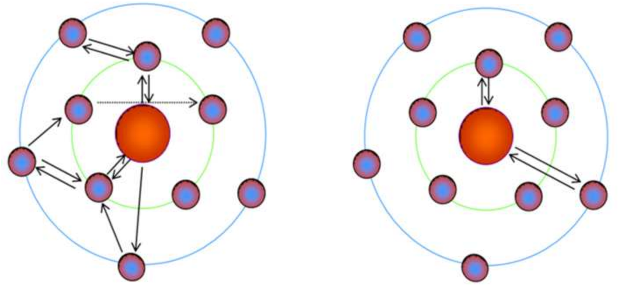
→ local structure (bond distance, number, type of neighbors….)



How to interpret XANES?

EXAFS equation:

$$\chi(k) = \sum_i \frac{N_i S_0^2}{kR_i^2} f_i(k, R_i) e^{-\frac{2R_i}{\lambda}} e^{-2k^2\sigma_i^2} \sin[2kR_i + \delta_i(k)]$$



where for each coordination shell :

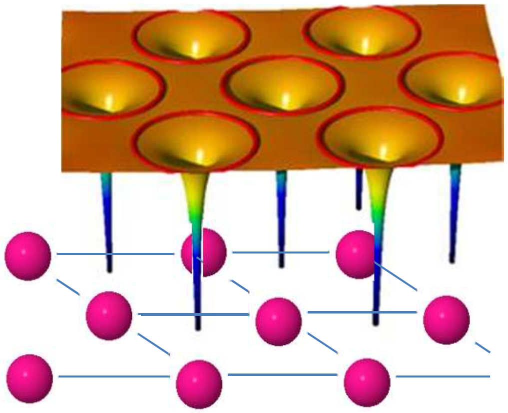
R_i, N_i, σ^2_i are the structural parameters (distance, coord. number and distance variance)

$\delta_i(k)$ is the phase shift due to the central atom

$f_i(k, R_i)$ is the global scattering factor

λ_i is the penetration depth

$\delta_i(k)$, $f_i(k, R_i)$, and λ_i must be calculated from the local structure around the absorber by means of muffin tin approximation for the atomic potentials

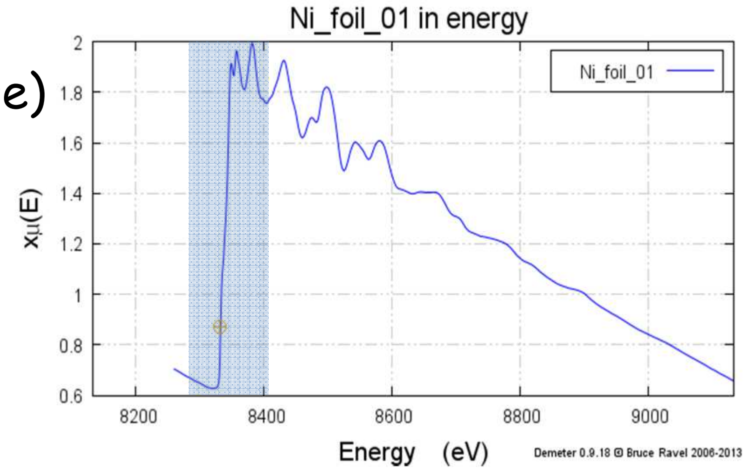


muffin tin potential

Unfortunately this approximation breaks down at low-*k* (XANES region), where multiple scattering effects became important.

We do not have a simple equation for XANES.

XANES vs EXAFS?



1. XANES simpler than EXAFS (small energy range)
   Faster to measure than full spectrum: t < ms

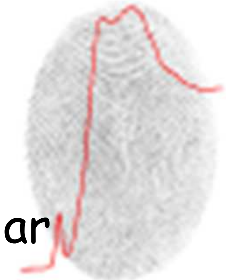
2. Weak temperature dependence:
(in situ measurements)

$$\boxed{e^{-k^2\sigma^2} = e^{-(0.5)^2\,(0.003)^2} \Rightarrow 1}$$

3. Sensitive to chemical information: valence, charge transfer.

4. Probes unoccupied electronic states: important in chemistry.

5. Often used as simple “fingerprint” to identify presence of a particular chemical species.



…which information?

XANES can be described ***qualitatively*** (and nearly ***quantitatively***) in terms of:

Coordination chemistry	regular, distorted octahedral, tetrahedral
molecular orbitals	p-d hybridization, crystal field theory
band structure	the density of available occupied electronic states
multiple scattering	multiple bounces of the photoelectron

Now several software are available for XANES simulation: FEFF, FDMNES…

Phys. Chem. Chem. Phys., 12-5503 (2010).

Phys. Rev. B 63, 125120 (2001).

XANES transition

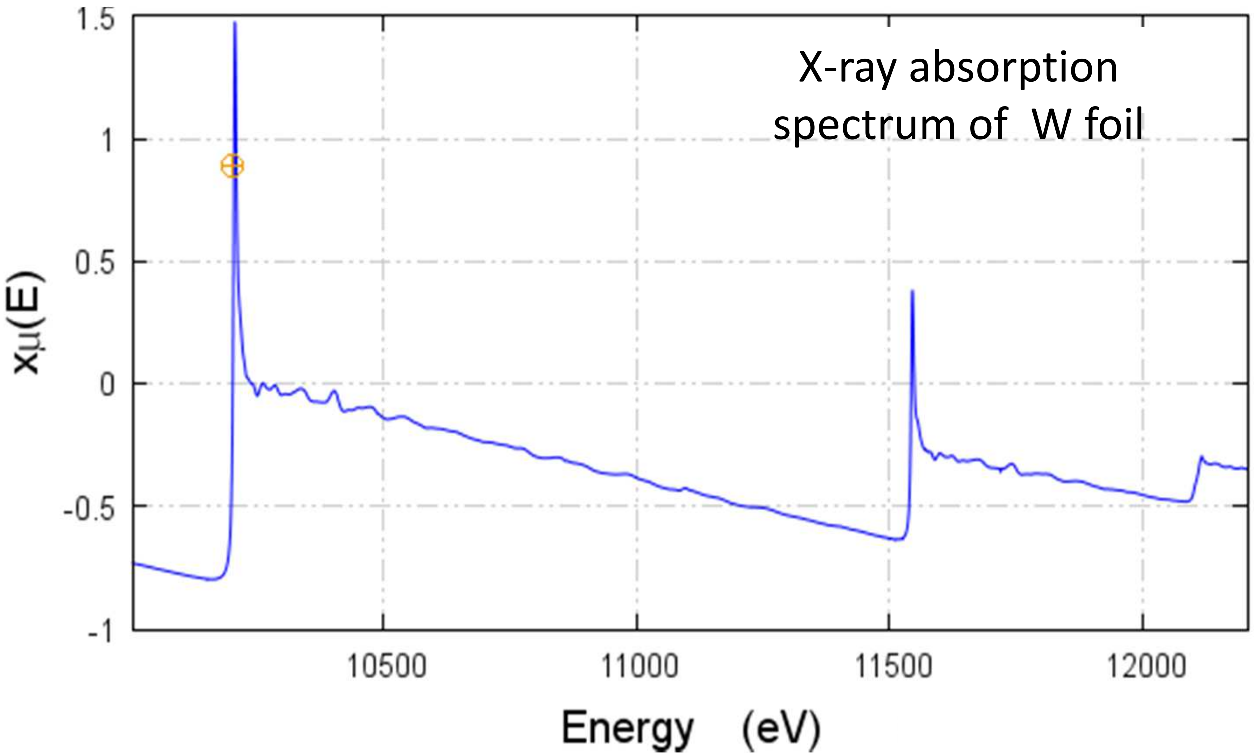
- XANES directly probes the angular momentum of the unoccupied electronic states: these may be bound or unbound, discrete or broad, atomic or molecular.
- Dipole selection rules apply: $\Delta l = \pm 1$, $\Delta j = \pm 1$, $\Delta s = 0$.
- Primary transition will be:
  - $s \rightarrow p$ for K ($1s$ core electron) and L_1 ($2s$ core electron initial state) edges
  - $p \rightarrow d$ for L_2 ($2p_{\frac{1}{2}}$) and L_3($2p_{3/2}$) edges

But…..final state usually not atomic-like and may have mixing (hybridization) with other orbitals.

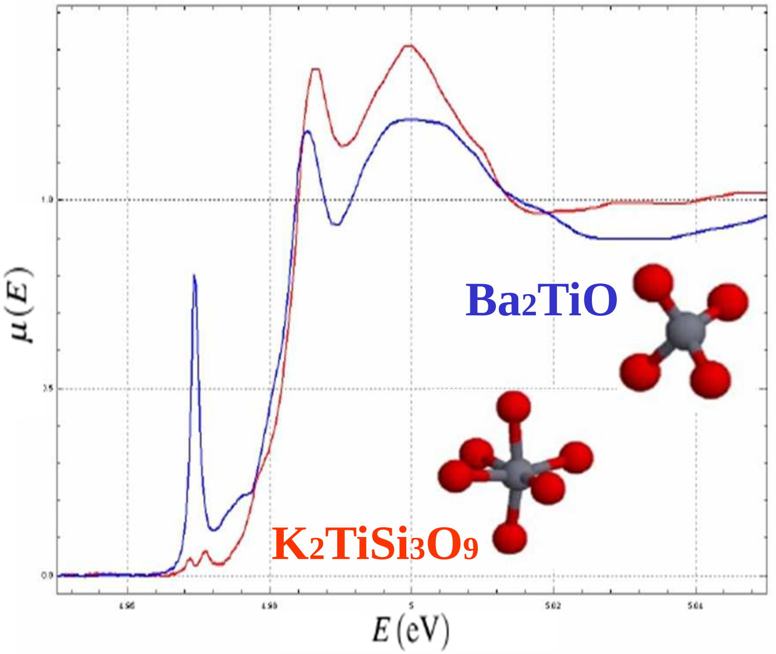
This makes XANES interesting!

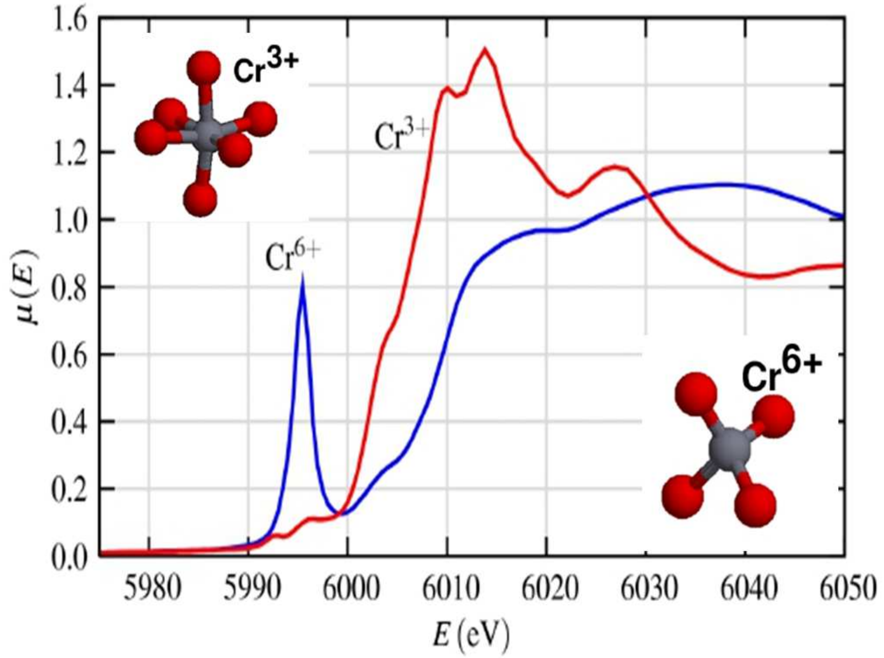
XANES – white line

- In years past x-ray absorption spectra were taken with use of photographic plates. Absorption edges appeared as unexposed bands on the plate (developed in negative), or “white lines”.
- Very prominent for L-edges of transition metals in high oxidation states.
- Intensity can be associated to occupancies of states. PRB-47-8471(1993)



Why are we interested in XANES? Local Coordination

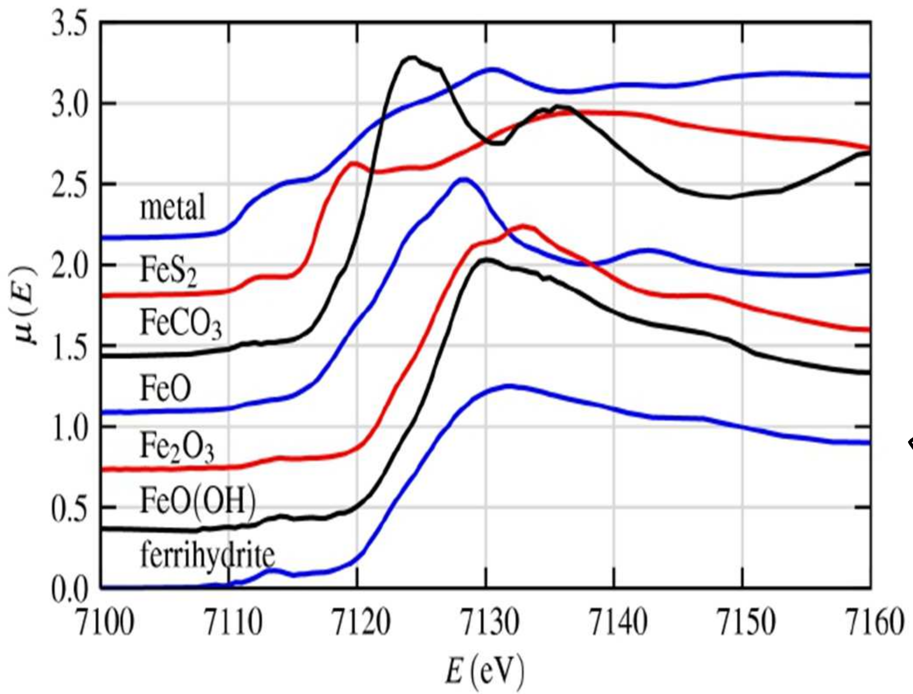


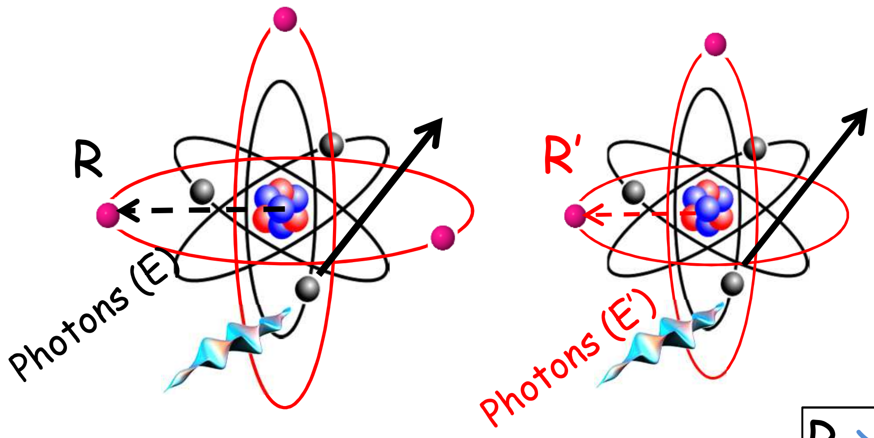


- Ti K-edge XANES shows dramatic dependence on the local coordination chemistry.
- In Cr and Ti compounds the p-d hybridization changes dramatically depending on the local environment of the metallic atoms (octahedral and tetrahedral)

for a detailed discussion refer to J. Phys.: Condens. Matter 21-104207(2009)

Why are we interested in XANES?
Oxidation state





R > R'
E < E'

- Many edges of many elements show significant edge shift (binding energy shifts) with oxidation state.
- First observation was by Berengren for phosphorus in 1920

Ann. Phys. Fr. 14-4(1989)

- XANES analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components. (see below)

Summing up…

XANES is strongly sensitive to the chemistry (formal oxidation state and geometry) of the absorbing atom.

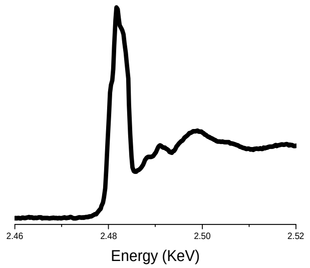
Region	Transitions	InformationContent
Pre-edge	Features caused by electronic transitions to empty bound states. transition probability controlled by dipolar selection rules.	Local geometry around absorbing atom. Dependence on oxidation state and bonding Characteristics (chemical shift). The heights and positions of pre-edge peaks can also be sometimes used to determine Fe3+/Fe2+ ratios.
Edge	Defines ionization threshold to continuum states.	Dependence on oxidation state (chemical shift),main edge shifts to high energy with increased oxidation state.(as much as 5eV per one unit change).
XANES	Features dominated by multiple-scattering resonances of the photoelectrons ejected at low kinetic energy. Large scattering cross section.	Atomic position of neighbors : interatomic distances and bond angles. Multiple Scattering dominates but *ab initio* calculations providing accessible insight (e.g. FEFF8).

Analysis of mixtures…

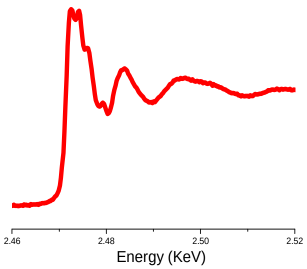
- XANES useful technique to quantitatively determine composition of a mixture of species.
- Useful for following time evolution of species during a chemical reaction.
- Two most common methods:
  - Least squares linear combination fitting (this talk)
  - Principal component analysis (Kostantin’s talk…)

Least Squares Linear Combination Fitting

a



+ b



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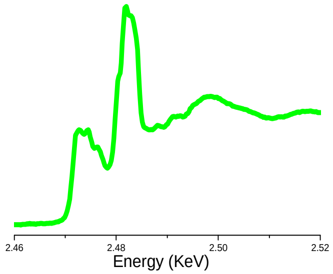
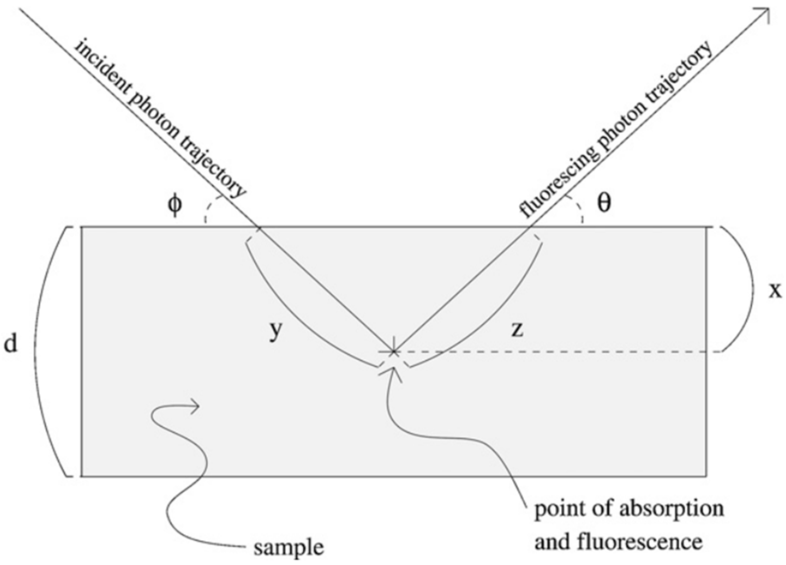


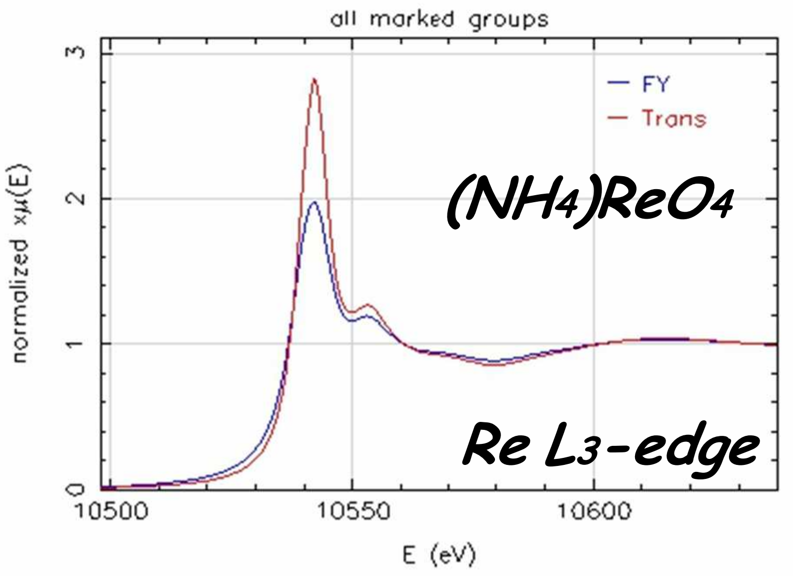
- Use a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum.
- Simple method, easy to implement.
- **Must have good quality spectra of the reference compounds recorded under similar conditions – energy alignment is critical.**

A possible (easy) mistake…

FLUORESCENCE MODE:
thick or concentrated samples
SELF ABSORPTION EFFECT



Need to be cautious about collecting XANES data of bulk reference compounds in fluorescence – will get incorrect answer in quantitative fitting!



$(NH_4)ReO_4$

Re L_3-edge

White line of spectrum collected in fluorescence is severely attenuated.

How to choose the references?

Gravimetry, the sample is dissolved and then the element of interest is precipitated

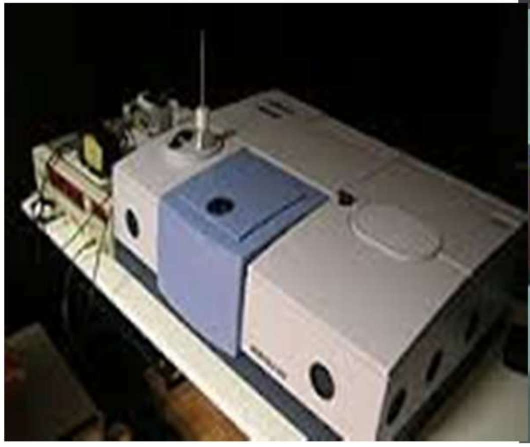
Optical spectroscopy, such IR absorption, Raman

Neutron activation analysis, which involves the activation of a sample matrix through the process of neutron capture.

Mass spectrometry

X ray diffraction pattern

…



Never come to a synchrotron before having a characterization of the sample with laboratory techniques!!!

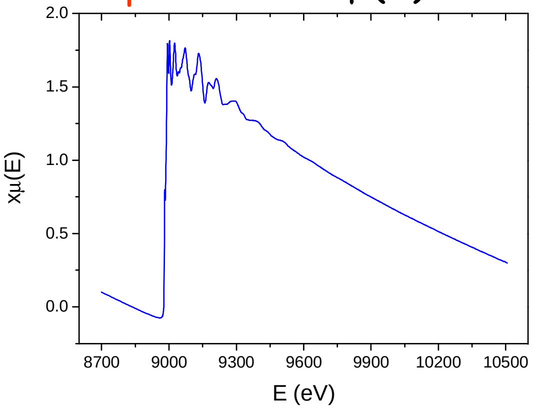
Checklist:

- ☑ Sample (well characterized!)
- ☑ References
- ☑ Correctly measured spectra

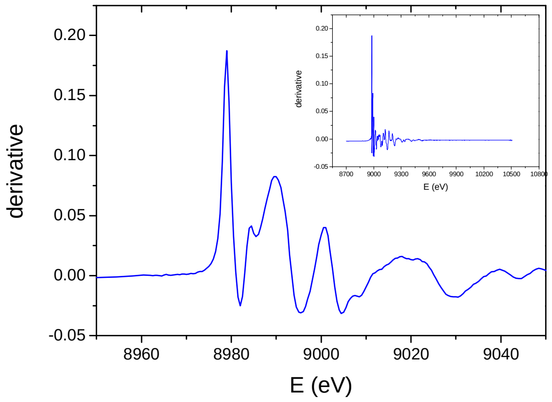
Let’s start with Linear combination!

Data normalization (1)

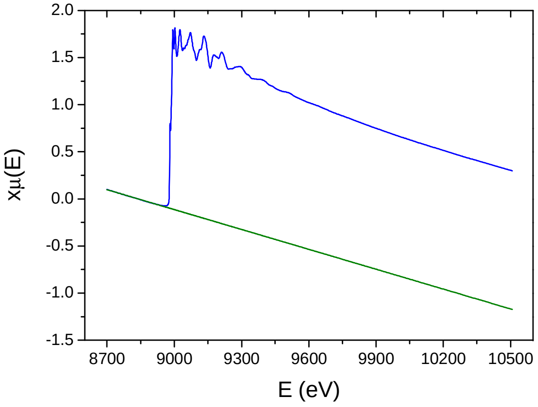
1. Import and plot the raw absorption data xμ(E)



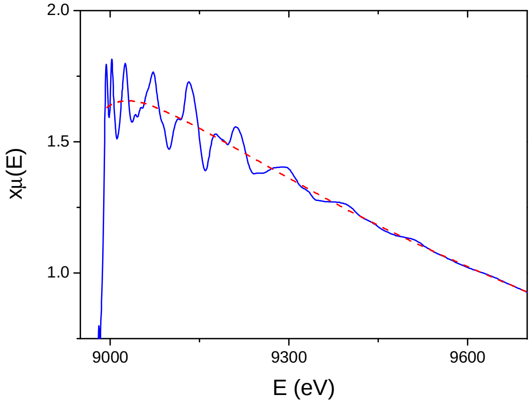
2. Select the E_{edge} arbitrarily as the maximum of the first derivative



3. Fit linearly the pre-edge region in xm(E) and subtract it

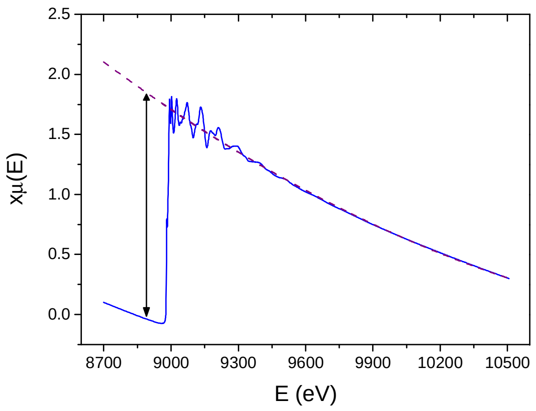


4. Find a smooth adjustable spline to guess the background $\mu_0(E)$

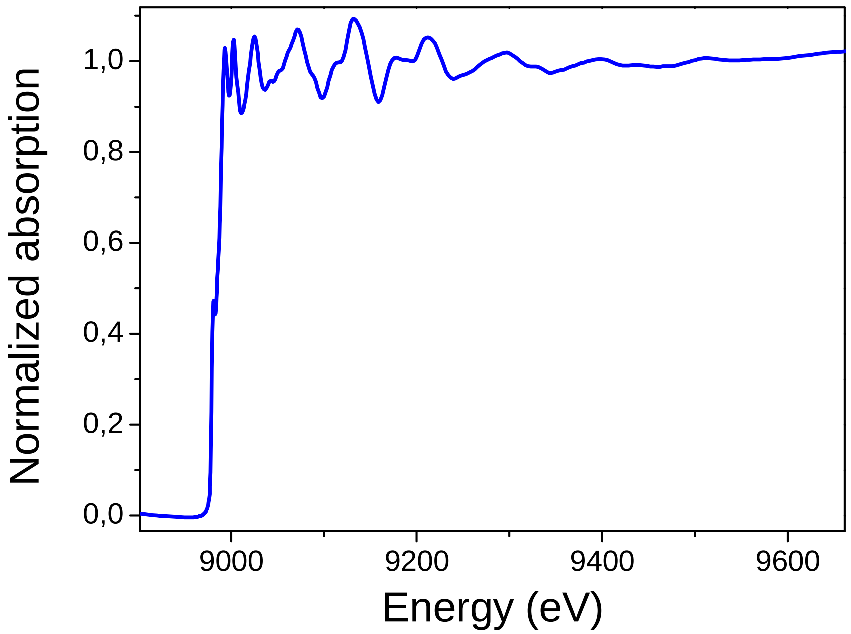


Data normalization (2)

5. Estimate the edge-jump from the post-edge interpolation

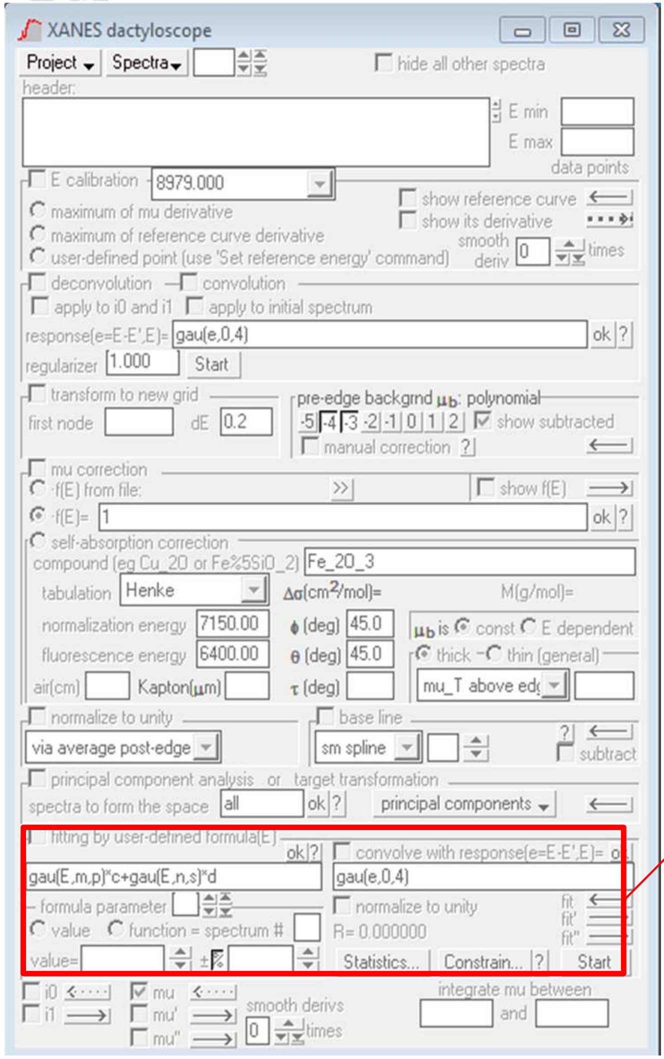


Normalized spectrum



See the talk of Mariaangels

Linear combination fit in XANDA


XANES dactyloscope

Project, Spectra

☐ hide all other spectra

header:

E min, E max, data points

☐ E calibration 8979.000

○ maximum of mu derivative
○ maximum of reference curve derivative
○ user-defined point (use 'Set reference energy' command)

☐ show reference curve
☐ show its derivative
smooth deriv 0 times

☐ deconvolution ☐ convolution
☐ apply to i0 and i1 ☐ apply to initial spectrum
response(e=E-E',E)= gau(e,0,4) ok ?
regularizer 1.000 Start

☐ transform to new grid
first node, dE 0.2

pre-edge backgrnd μ_b: polynomial -5 -4 -3 -2 -1 0 1 2 ☑ show subtracted
☐ manual correction ?

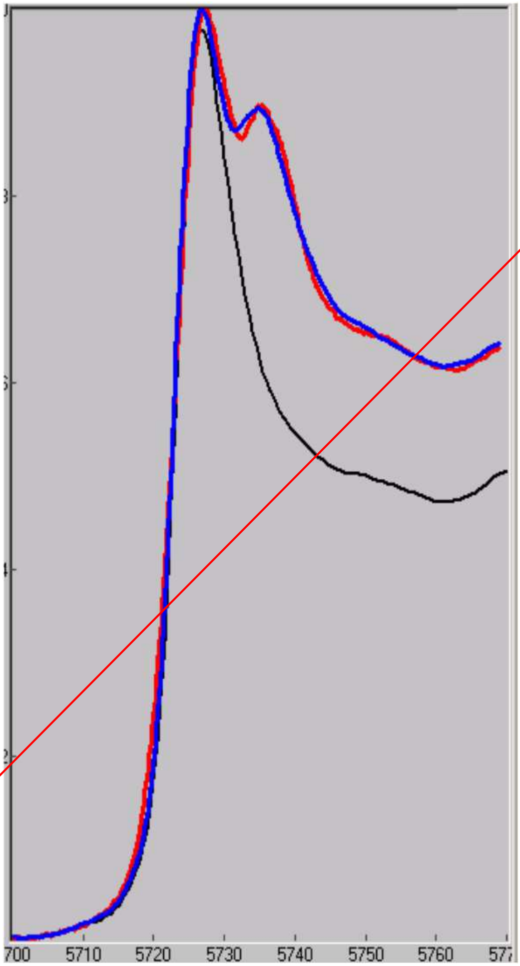
☐ mu correction
○ f(E) from file: ☐ show f(E)
● f(E)= 1 ok ?
○ self-absorption correction
compound (eg Cu_20 or Fe%5Si0_2) Fe_20_3
tabulation Henke, $\Delta\sigma$(cm²/mol)=, M(g/mol)=
normalization energy 7150.00, ϕ (deg) 45.0, μ_b is ● const ○ E dependent
fluorescence energy 6400.00, θ (deg) 45.0, ● thick ○ thin (general)
air(cm), Kapton(μm), τ (deg), mu_T above edge

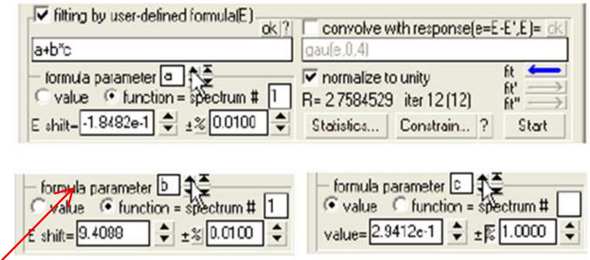
☐ normalize to unity: via average post-edge
☐ base line: sm spline, ☐ subtract

☐ principal component analysis or target transformation
spectra to form the space all ok ? principal components

☐ fitting by user-defined formula(E) ok ?
gau(E,m,p)*c+gau(E,n,s)*d
☐ convolve with response(e=E-E',E)= ok
gau(e,0,4)
formula parameter
○ value ○ function = spectrum #
value= ±%
☐ normalize to unity
R= 0.000000
Statistics... Constrain... ? Start

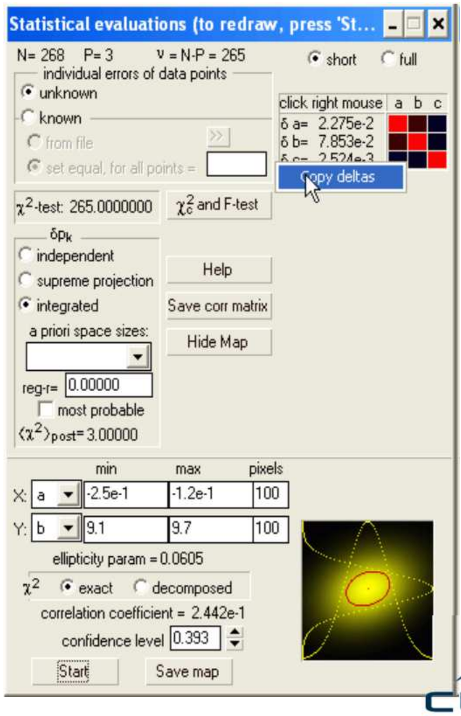
☐ i0 ☐ i1 ☑ mu ☐ mu' ☐ mu''
smooth derivs 0 times
integrate mu between and




☑ fitting by user-defined formula(E) ok ?
a+b*c
☐ convolve with response(e=E-E',E)= ok
gau(e,0,4)
formula parameter a
○ value ● function = spectrum # 1
E shift= -1.8482e-1 ±% 0.0100
☑ normalize to unity
R= 2.7584529 iter 12(12)
Statistics... Constrain... ? Start

formula parameter b
○ value ● function = spectrum # 1
E shift= 9.4088 ±% 0.0100

formula parameter c
● value ○ function = spectrum #
value= 2.9412e-1 ±% 1.0000


Statistical evaluations (to redraw, press 'St...

N= 268 P= 3 ν = N-P = 265
● short ○ full

individual errors of data points
● unknown
○ known
○ from file
○ set equal, for all points =

click right mouse	a	b	c
δ a= 2.275e-2	🟥	■	■
δ b= 7.853e-2	■	🟥	■
δ c= 2.524e-3	■	■	🟥

Copy deltas

χ^2-test: 265.0000000
χ^2_c and F-test

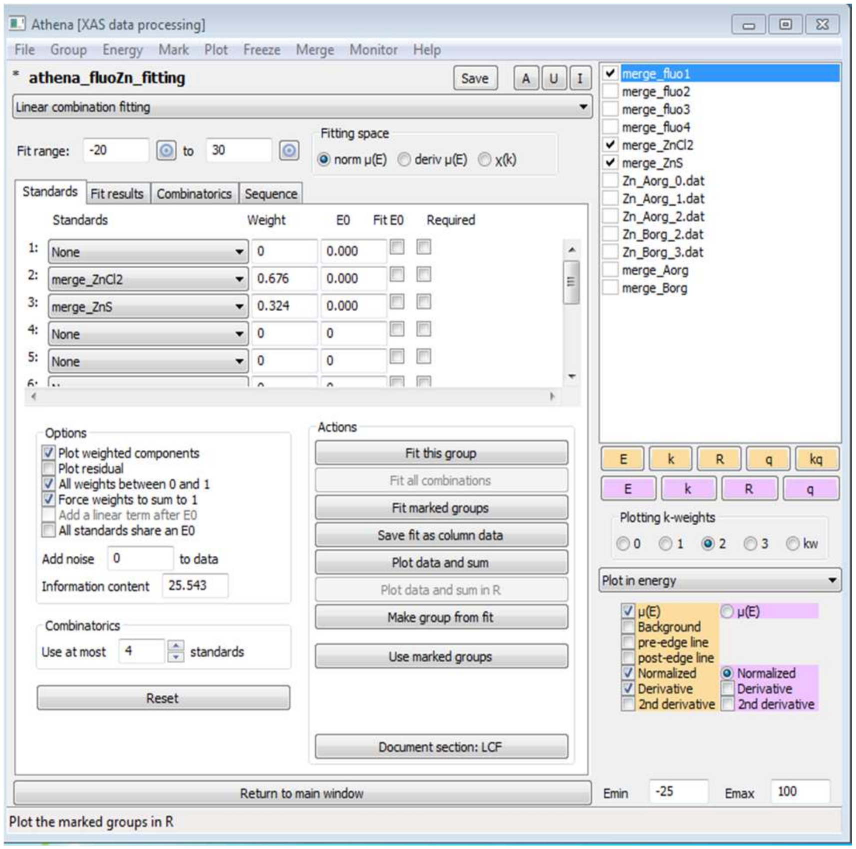
δp_k
○ independent
○ supreme projection
● integrated
a priori space sizes:
reg-r= 0.00000
☐ most probable
$\langle\chi^2\rangle_{post}$= 3.00000

Help
Save corr matrix
Hide Map

		min	max	pixels
X:	a	-2.5e-1	-1.2e-1	100
Y:	b	9.1	9.7	100

ellipticity param = 0.0605
χ^2 ● exact ○ decomposed
correlation coefficient = 2.442e-1
confidence level 0.393
Start Save map

Linear combination fit in Athena



athena_fluoZn_fitting

Linear combination fitting

Fit range: -20 to 30

Fitting space: ● norm μ(E) ○ deriv μ(E) ○ χ(k)

	Standards	Weight	E0	Fit E0	Required
1:	None	0	0.000	☐	☐
2:	merge_ZnCl2	0.676	0.000	☐	☐
3:	merge_ZnS	0.324	0.000	☐	☐
4:	None	0	0	☐	☐
5:	None	0	0	☐	☐

Options
- ☑ Plot weighted components
- ☐ Plot residual
- ☑ All weights between 0 and 1
- ☑ Force weights to sum to 1
- ☐ Add a linear term after E0
- ☐ All standards share an E0

Add noise 0 to data

Information content 25.543

Combinatorics: Use at most 4 standards

- ☑ merge_fluo1
- ☐ merge_fluo2
- ☐ merge_fluo3
- ☐ merge_fluo4
- ☑ merge_ZnCl2
- ☑ merge_ZnS
- ☐ Zn_Aorg_0.dat
- ☐ Zn_Aorg_1.dat
- ☐ Zn_Aorg_2.dat
- ☐ Zn_Borg_2.dat
- ☐ Zn_Borg_3.dat
- ☐ merge_Aorg
- ☐ merge_Borg

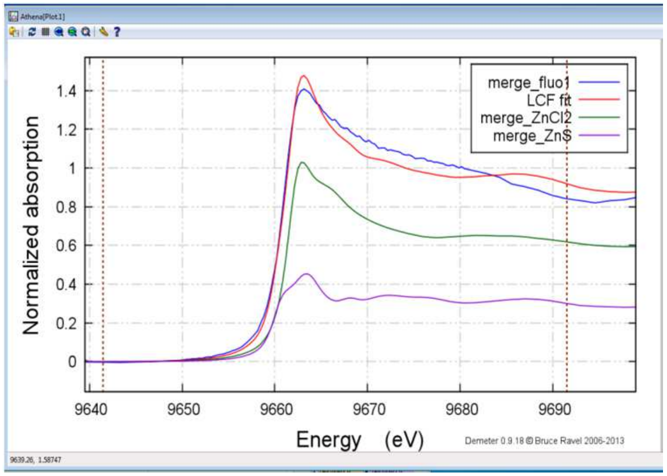
Plotting k-weights: ○ 0 ○ 1 ● 2 ○ 3 ○ kw

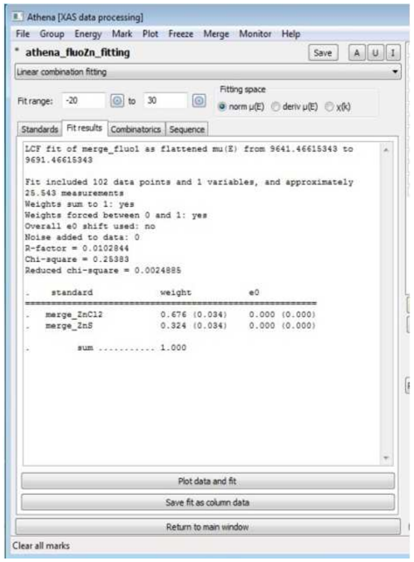
Plot in energy

- ☑ μ(E) ○ μ(E)
- ☐ Background
- ☐ pre-edge line
- ☐ post-edge line
- ☑ Normalized ● Normalized
- ☑ Derivative ☐ Derivative
- ☐ 2nd derivative ☐ 2nd derivative

Emin -25 Emax 100

Plot the marked groups in R





athena_fluoZn_fitting

Linear combination fitting

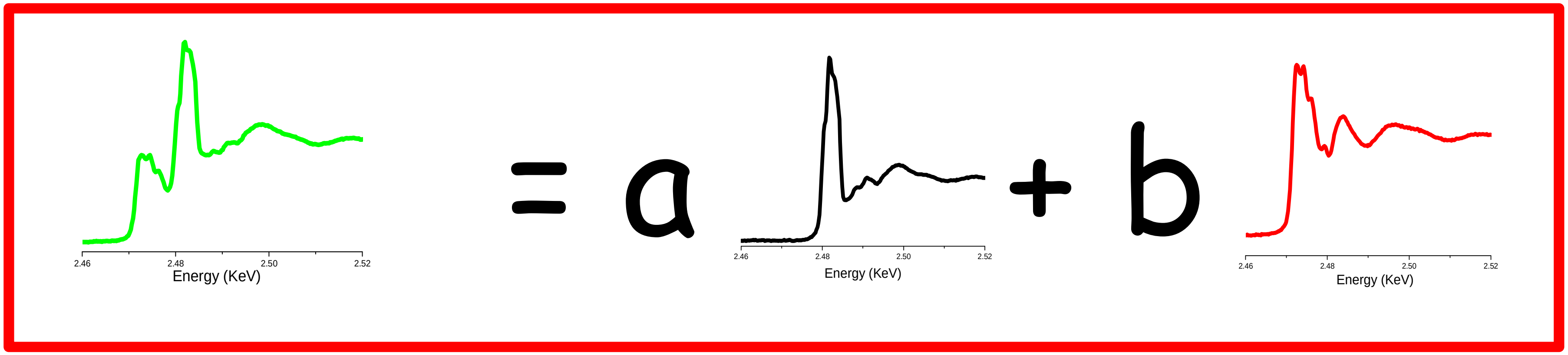
Fit range: -20 to 30

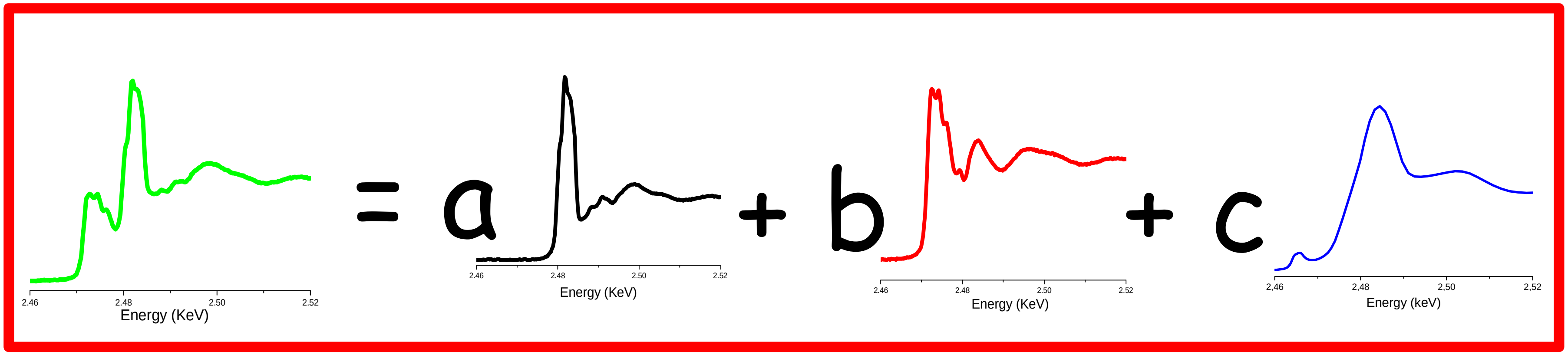
Fitting space: ● norm μ(E) ○ deriv μ(E) ○ χ(k)

```
LCF fit of merge_fluo1 as flattened mu(E) from 9641.46615343 to
9691.46615343

Fit included 102 data points and 1 variables, and approximately
25.543 measurements
Weights sum to 1: yes
Weights forced between 0 and 1: yes
Overall e0 shift used: no
Noise added to data: 0
R-factor = 0.0102844
Chi-square = 0.25383
Reduced chi-square = 0.0024885

.    standard              weight           e0
==================================================================
.   merge_ZnCl2            0.676 (0.034)    0.000 (0.000)
.   merge_ZnS              0.324 (0.034)    0.000 (0.000)

.        sum ........... 1.000
```

Clear all marks

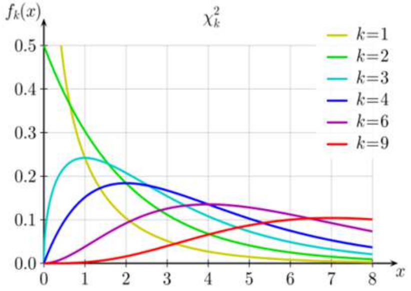
Discriminating between two models (1)





Discriminating between two models (2)

From χ^2 to…



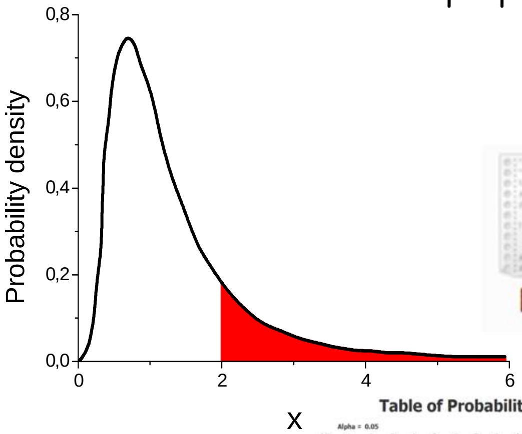
$$\chi^2 = \sum_i^N \left(\frac{d_i - t_i(k,p)}{\sigma_i}\right)^2$$

d_i = experimental data
t_i (k,p) = theoretical model
k = number of parameter
p = parameters

… **or F test:**

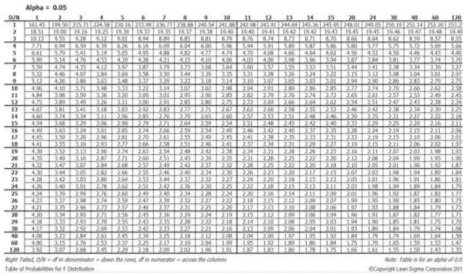
Let χ_1^2 and χ_2^2 follow the χ^2-distribution law with $\nu_1 = N^{ind}-k_1$ *and* $\nu_2 = N^{ind}-k_2$ *degrees of freedom . Then*

$$f = \frac{\left(\chi_1^2 - \chi_2^2\right)/\left(\upsilon_1 - \upsilon_2\right)}{\chi_2^2 / \upsilon_2}$$



Ftest

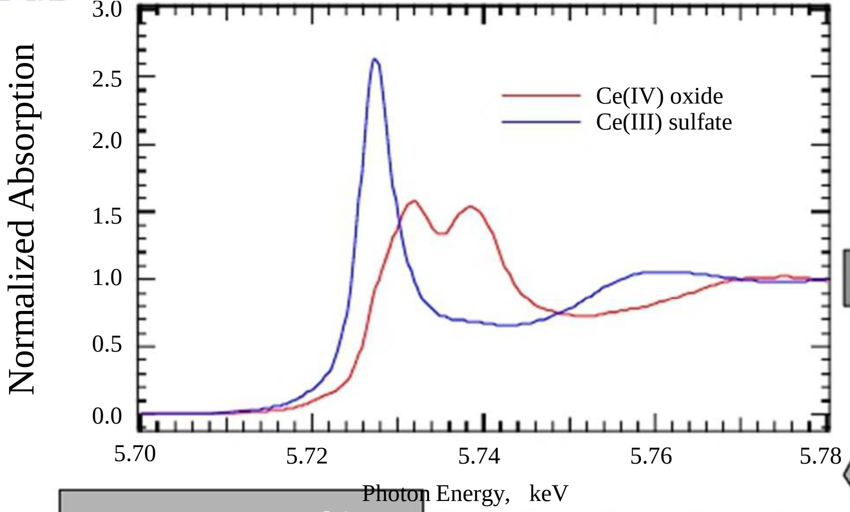
Table of Probabilities for the F Distribution



obeys the Fisher-Snedecor F-distribution . Thus calculating the cumulative probability function of f, it is possible to answer to the question:

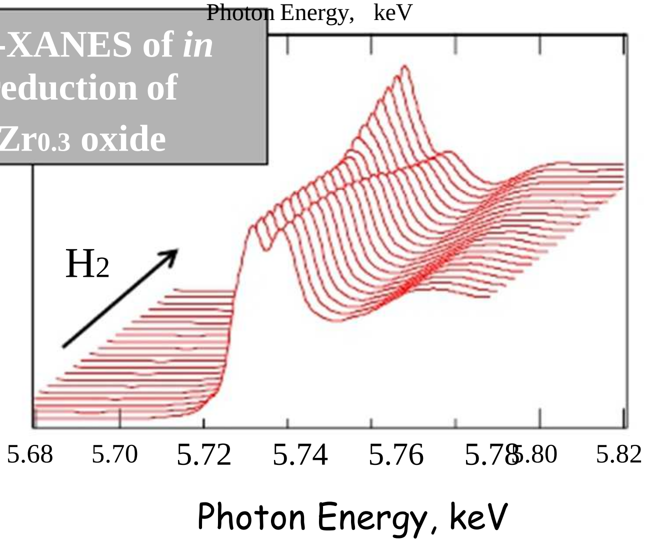
"what is the probability that the model 2 is better than the model 1 at the specified (P1, ν1) and (P2, ν2)?"

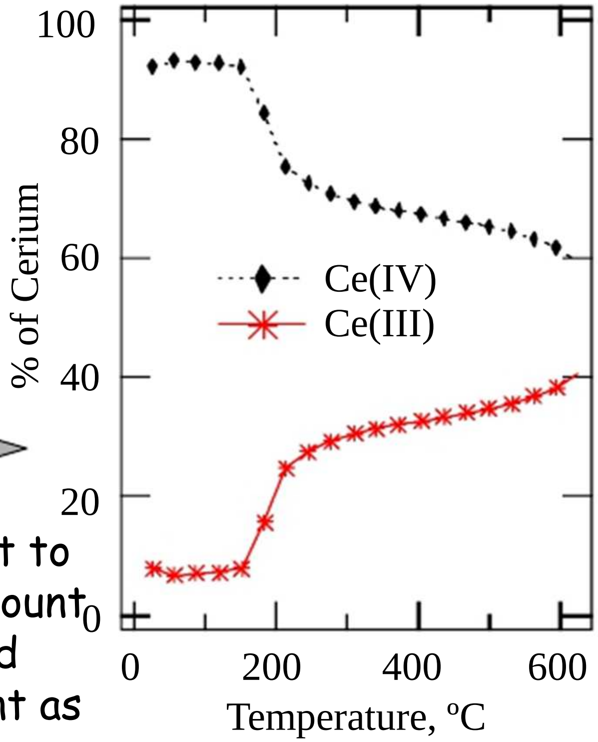
Linear Combination Fitting: an examples from literature…



Fit experimental data to linear combination of known reference compounds

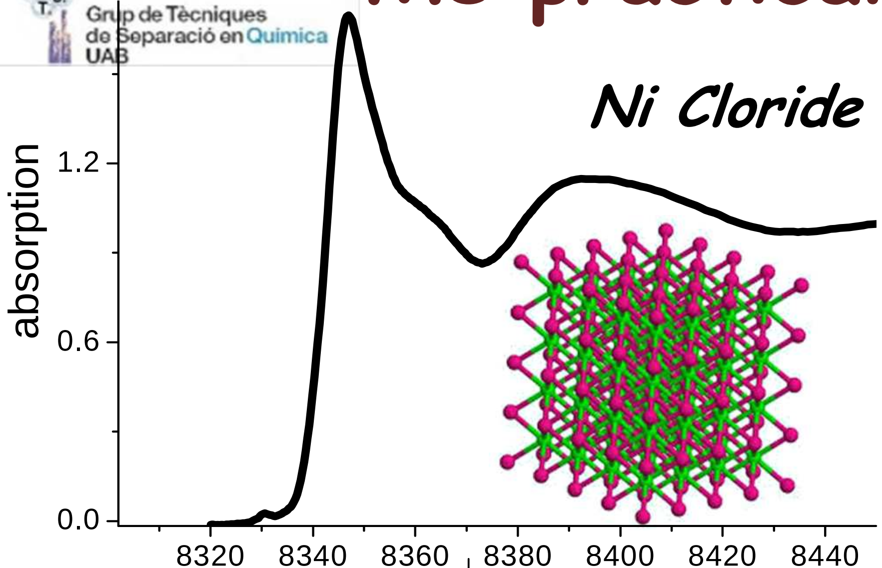
TPR-XANES of *in situ* reduction of $Ce_{0.7}Zr_{0.3}$ oxide

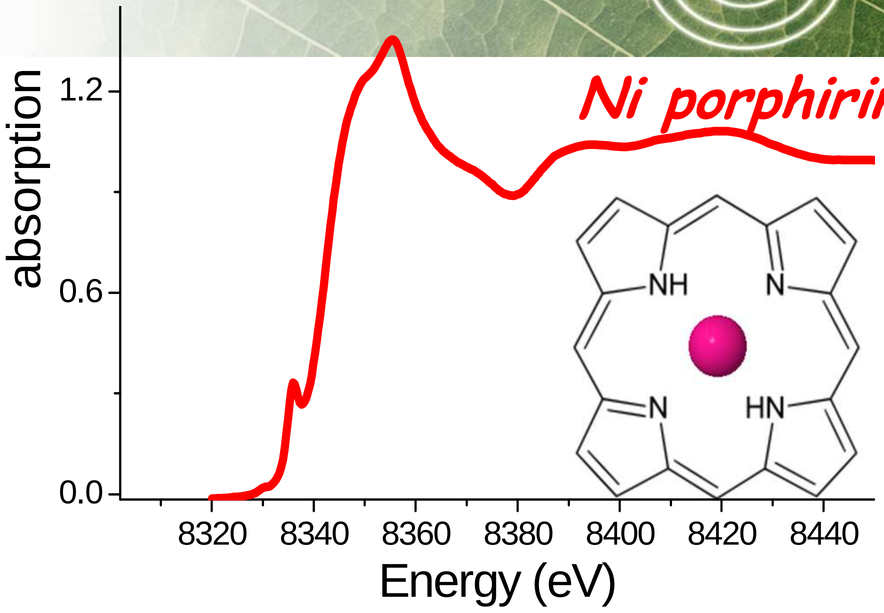


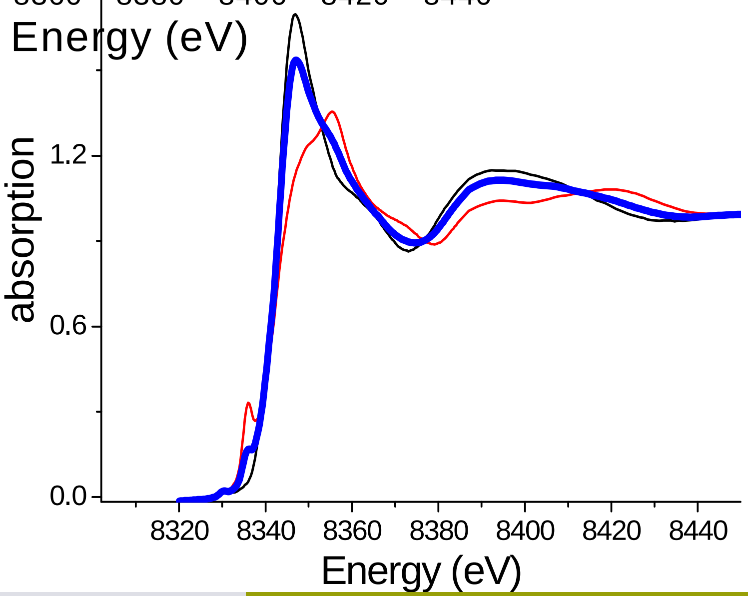


LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature

…and now what about the practical section…



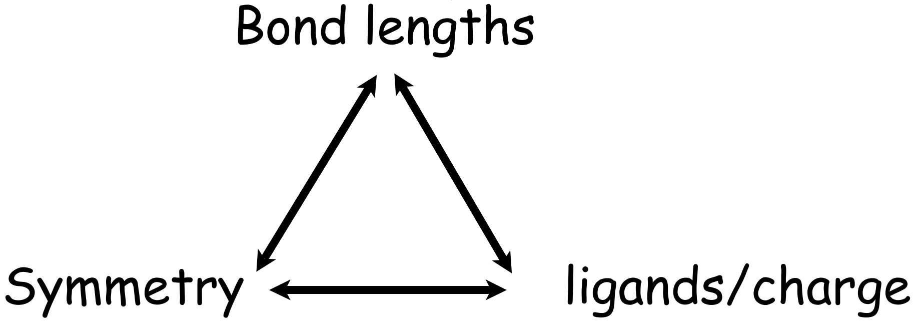




…which is the fraction of $NiCl_2$ inside the mixture?

Take away messages…

XANES can be described *qualitatively* in terms of coordination chemistry, molecular orbitals, band-structure, multiple-scattering



Quantitative XANES analysis using Linear combination, PCA, Target transformation methods and first-principles calculations are now day possible…

LC is an easy, reliable and widely used technique for identification and quantification of the different chemical species present in a sample (SPECIATION). It can be done both in the XANES and EXAFS regions. But analyzing the complex structure containing number of species using EXAFS is difficult and the parametrical analysis becomes practically impossible. In such cases, the analysis of XANES plays an important role.

…and now from here to…

International XAFS Society:

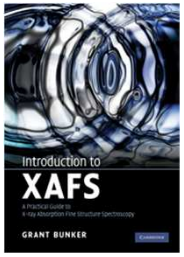
http://ixs.iit.edu/

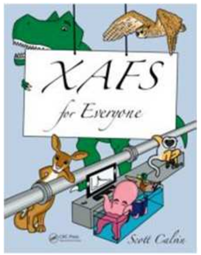
Books and Review Articles:

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, in Chemical Analysis 92, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.

"Introduction to XAFS", G.Bunker (2010)

"XAFS for everyone" S. Calvin (2011)





Tutorials and other Training Material:

http://gbxafs.iit.edu/training/tutorials.html Grant Bunker's tutorials
http://srs.dl.ac.uk/XRS/courses/ Tutorial from Daresbury Lab, UK
http://leonardo.phys.washington.edu/~ravel/course/ (Bruce Ravel's Course on Advanced EXAFS Analysis).
http://cars.uchicago.edu/xafs/.

Software Resources:

http://www.esrf.fr/computing/scientific/exafs/
http://cars9.uchicago.edu/IXS-cgi/XAFS Programs
http://leonardo.phys.washington.edu/feff
www.cells.es/Beamlines/CLAESS VIPER

Thank you for your attention