Introduction to the EXAFS data analysis

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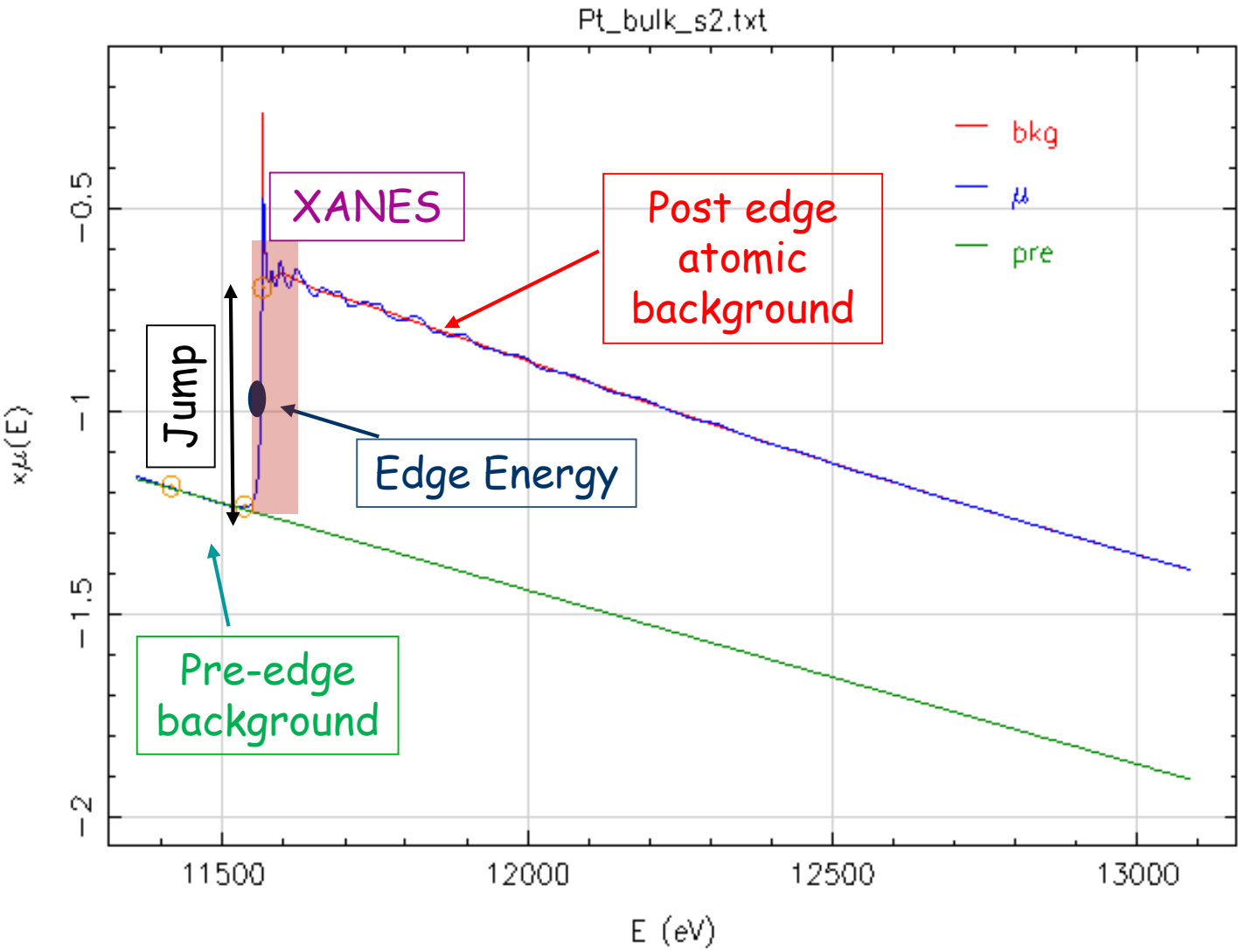
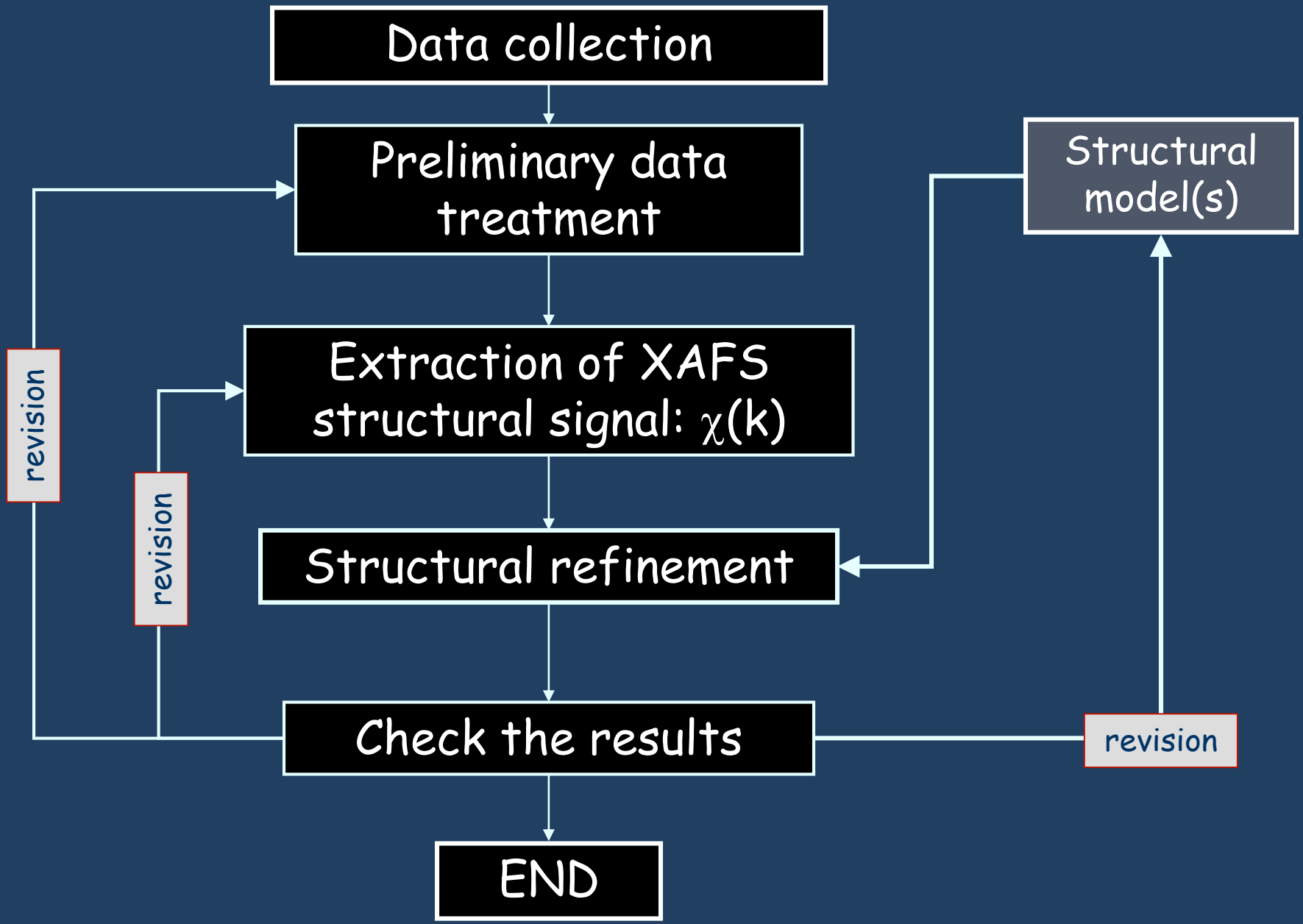
Elettra – Sincrotrone Trieste

Material almost integrally taken from Carlo Meneghini: EXAFS tutorial at Synchrotron Radiation school of Duino 2011

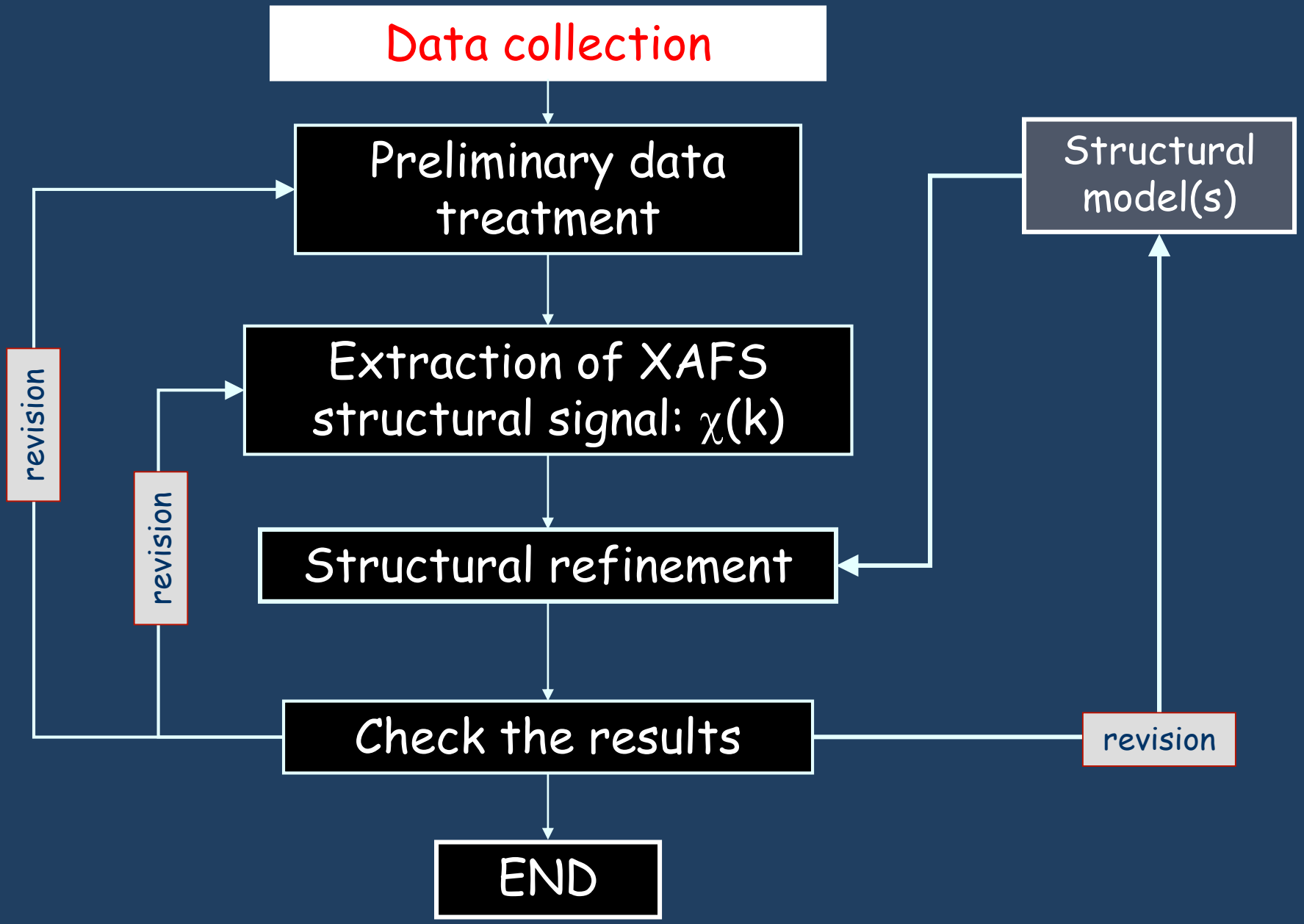
Characteristics of a XAS spectrum



XAFS study: from experiment to results



XAFS study: from experiment to results

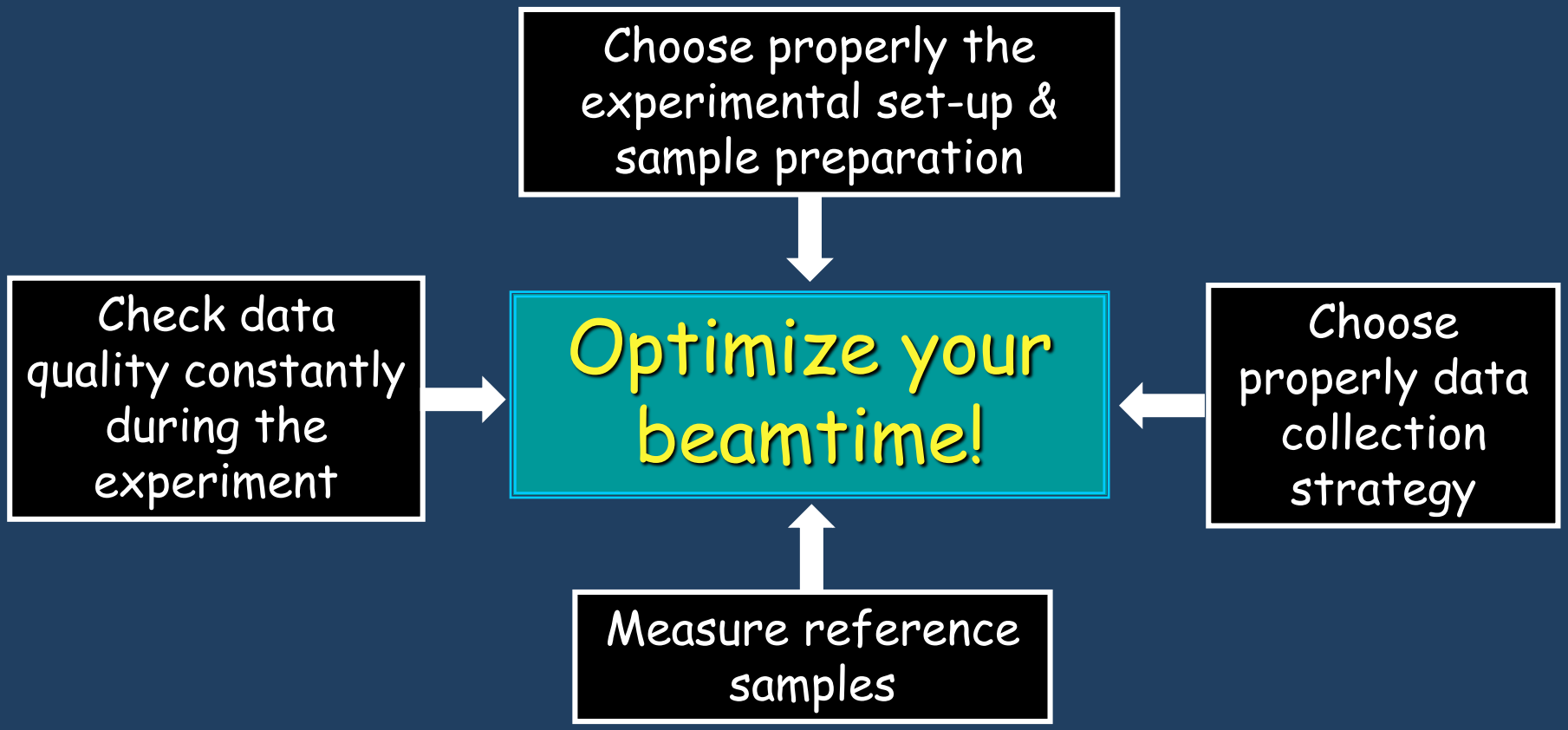


Data collection

Considerations:

1) Proposal submission + proposal evaluation + beamtime scheduling = 6 to 12 months
2) Difficult to have new beamtime in case of proposal failure

- Check the proposal submission deadlines
- discuss your experiment with local contacts



Data collection

Choose properly the experimental set-up & sample preparation

- For massive concentrated samples: **TRANSMISSION**

Jump $0.5 \leq \Delta\mu t \leq 1.5$

Total absorption $\mu t \leq 2.$

inhomogeneities, holes, not parallel surfaces, etc...

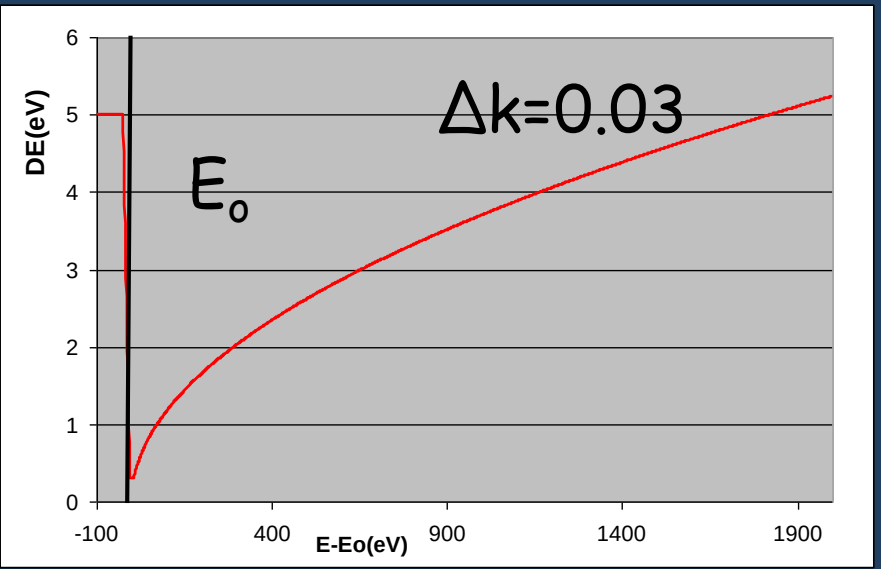
- For thin concentrated or thin diluted samples: **FLUORESCENCE**

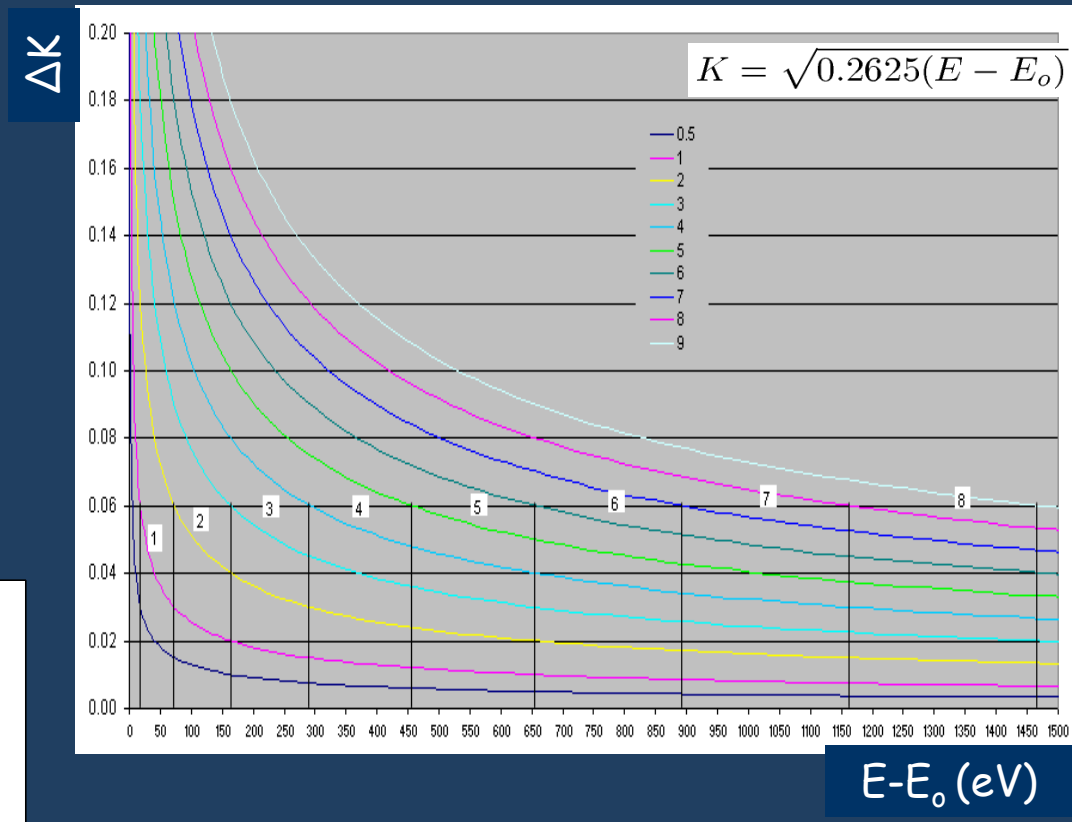
Self absorption, detector linearity, Bragg reflections

Data collection

Choose properly the data collection strategy

- Acquisition time per point
- Single scan or repeated scans
- ΔE or Δk step



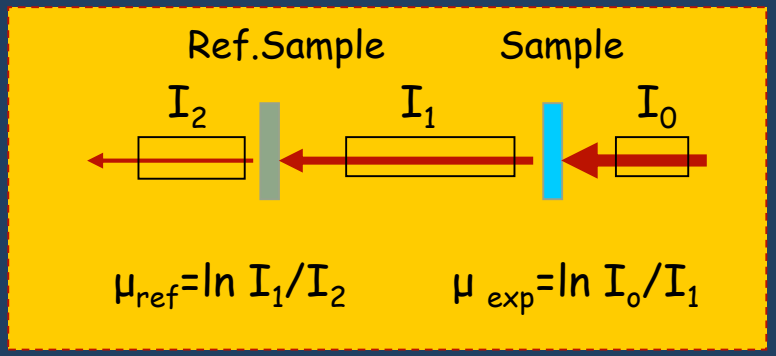


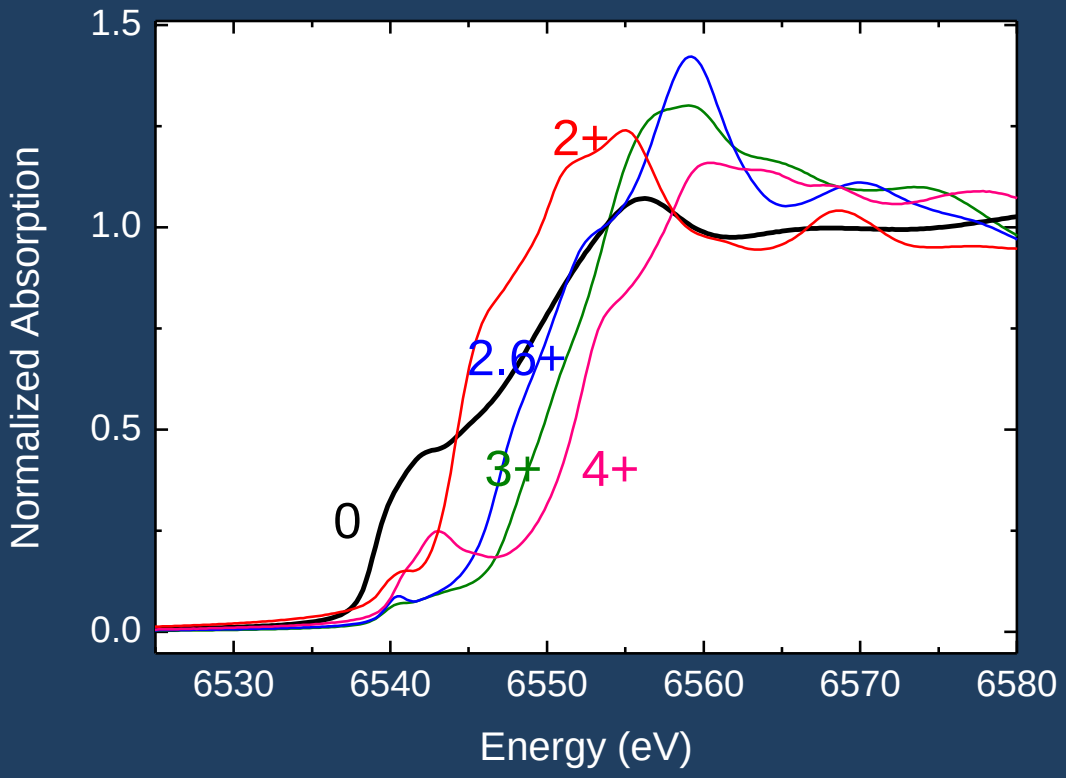
Constant Δk acquisition

- Optimizes the number of collected points
- More efficient
- Faster

Data collection

Measure reference samples

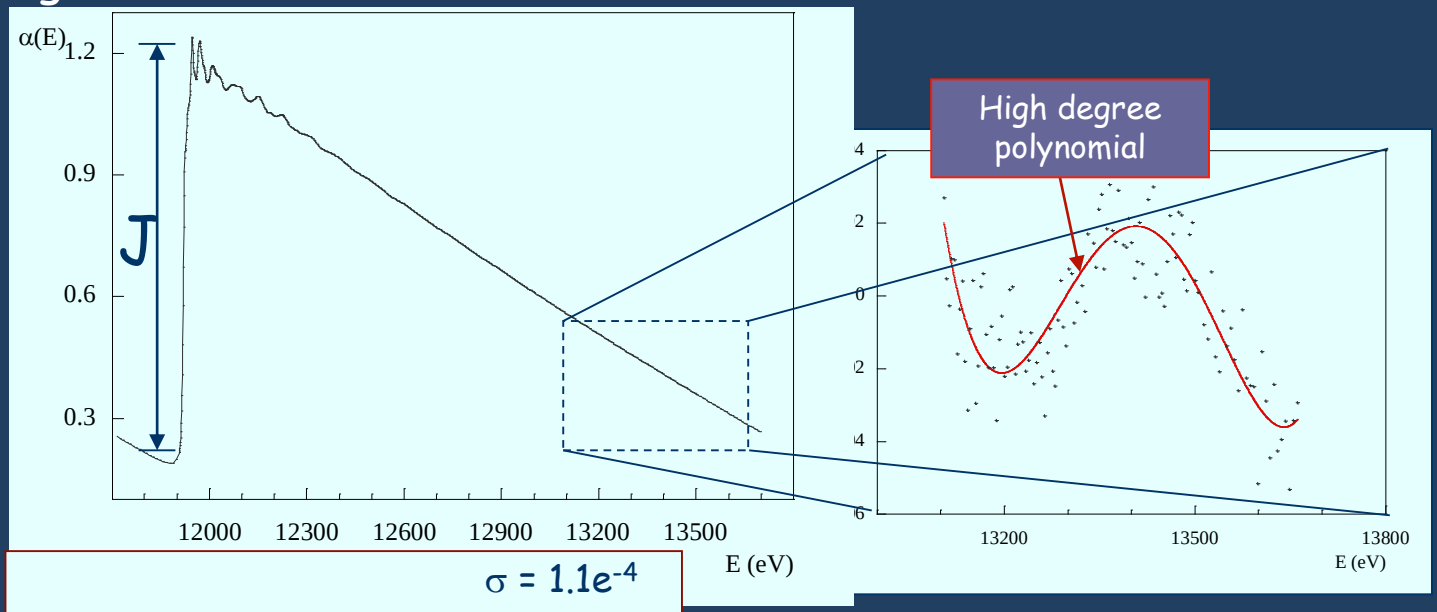


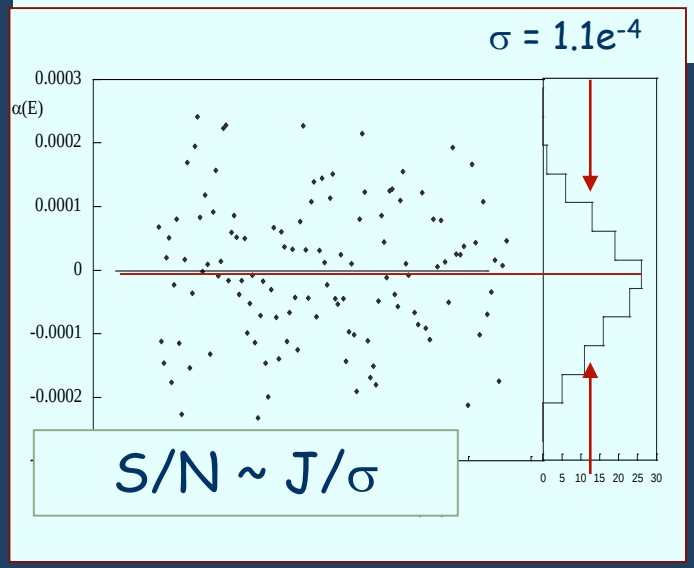


Data collection

Check data quality constantly during the experiment

- Evaluate signal/noise ratio





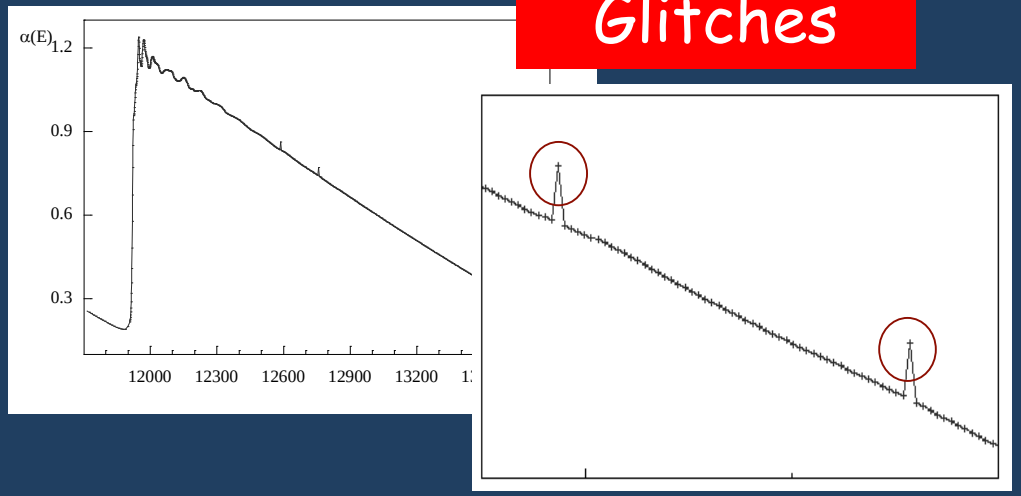
S/N ratio should be less than 10^{-3}

Data collection

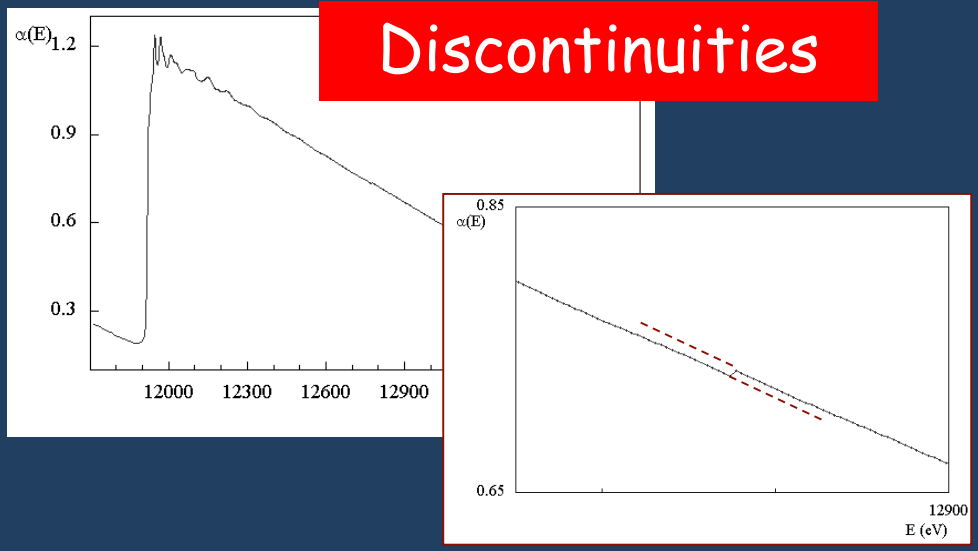
Check data quality constantly during the experiment

- Check for:

Glitches

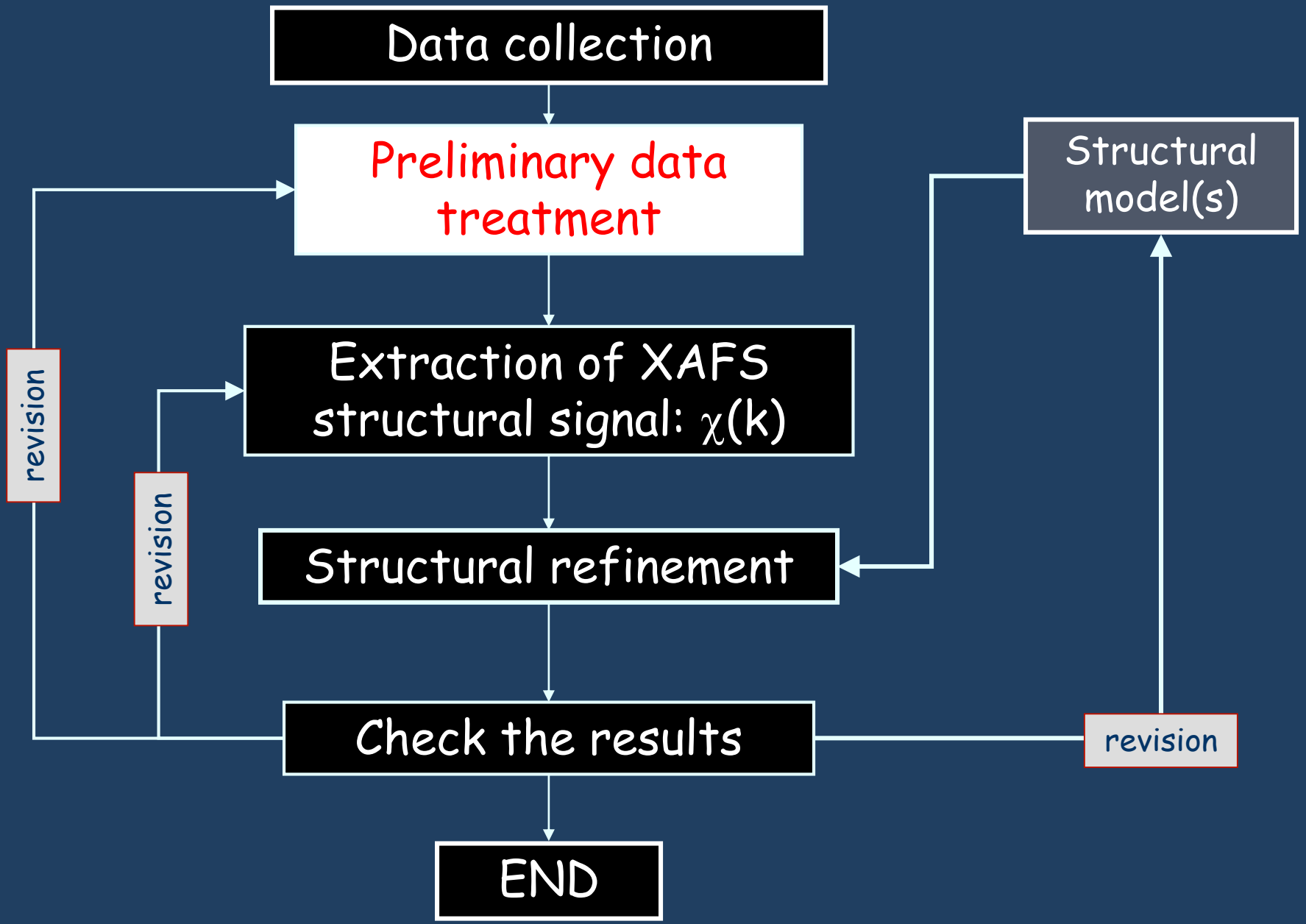


Discontinuities



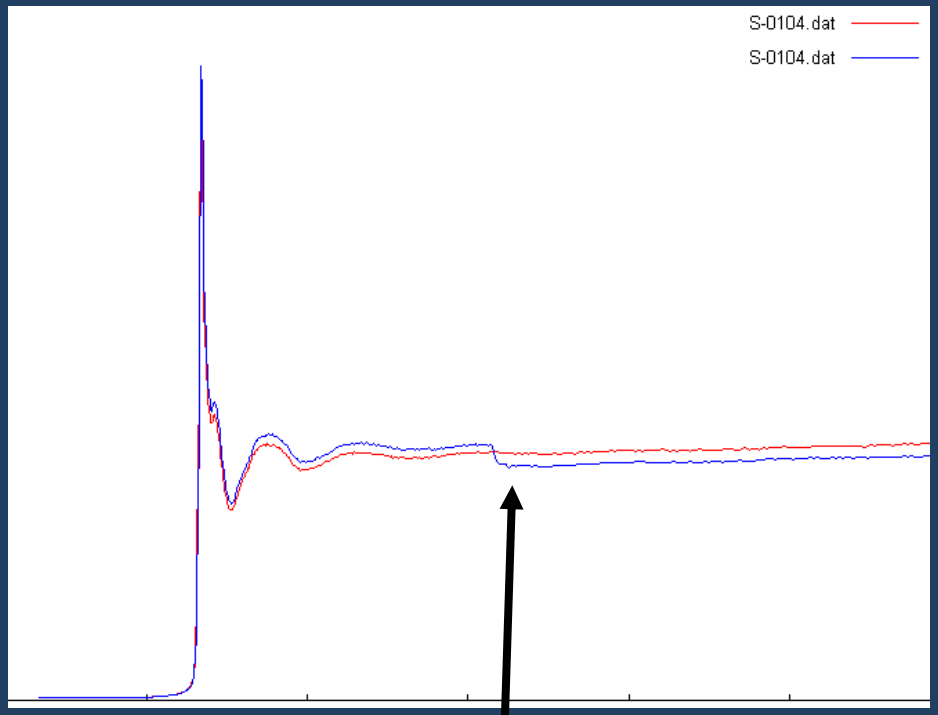
edge shift

XAFS analysis: from experiment to results

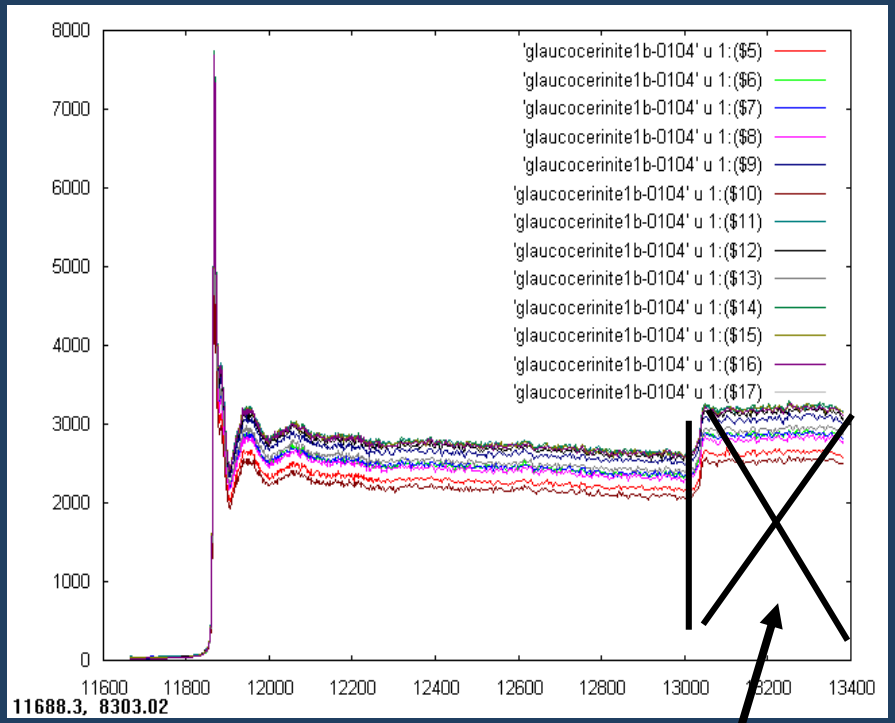


Preliminary data treatment

Choose the best spectra and useful data regions



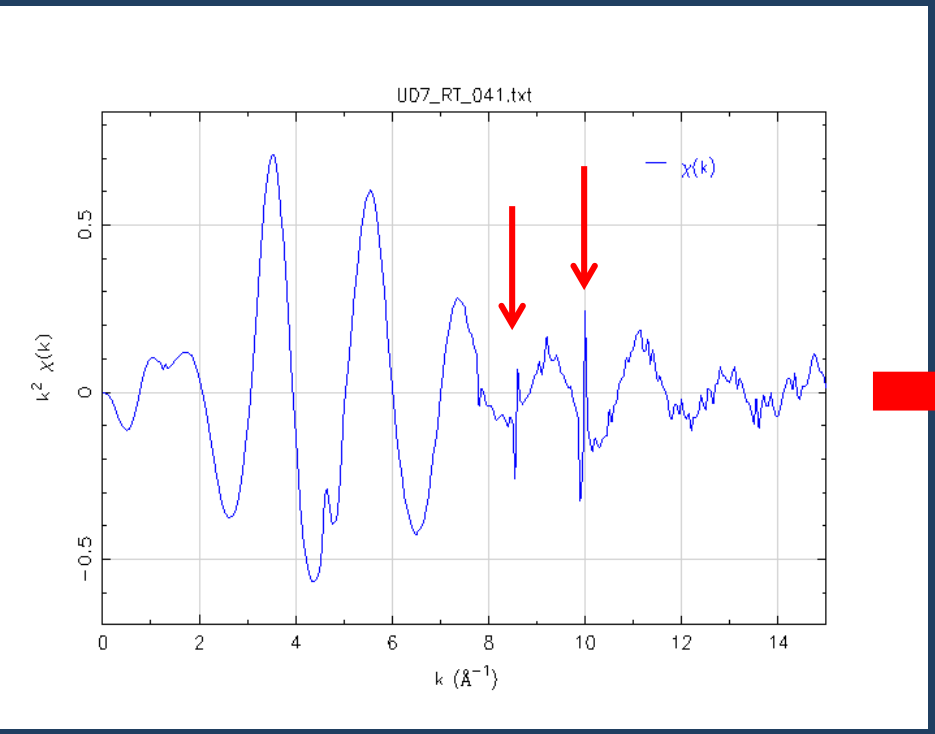
do not use the blue one!

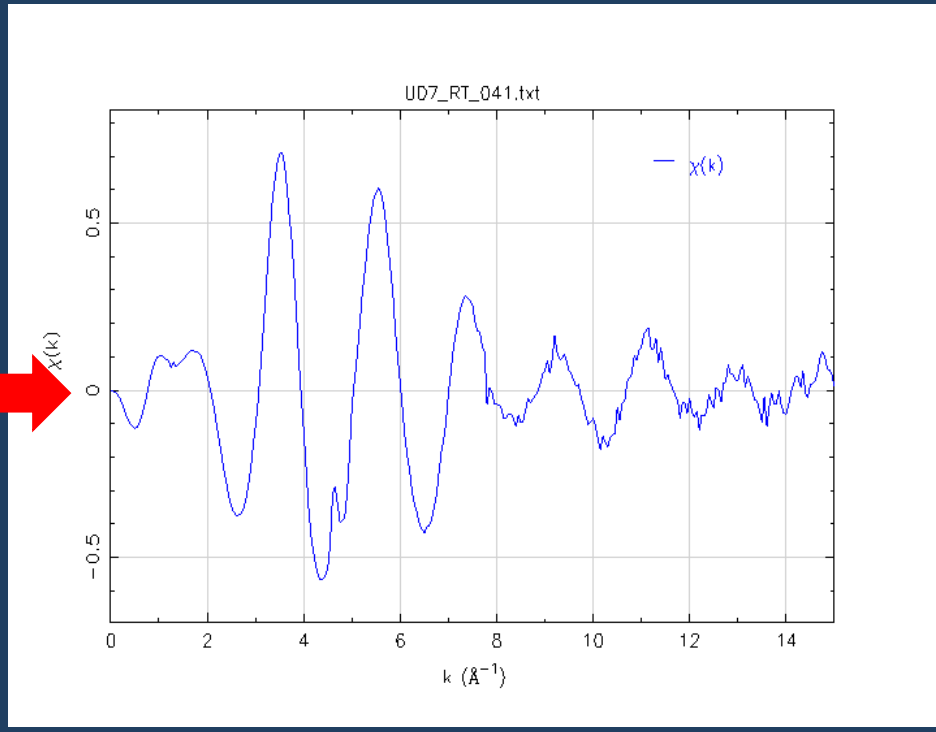


do not use data beyond 13000 eV !

Preliminary data treatment

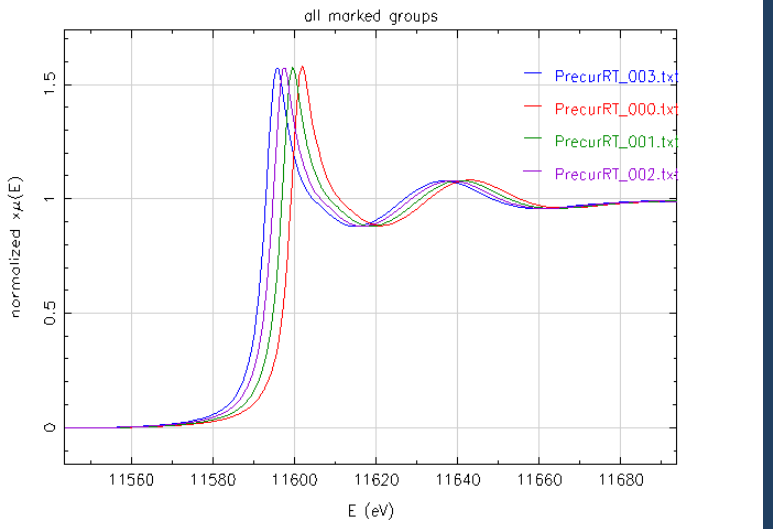
De-glitch

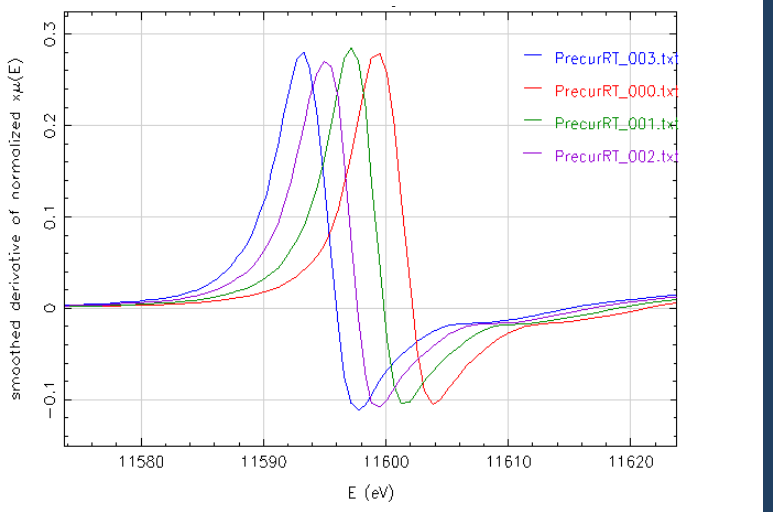


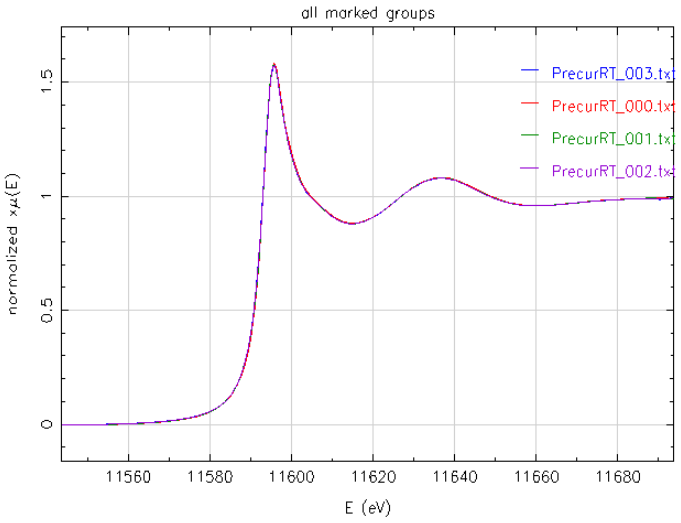


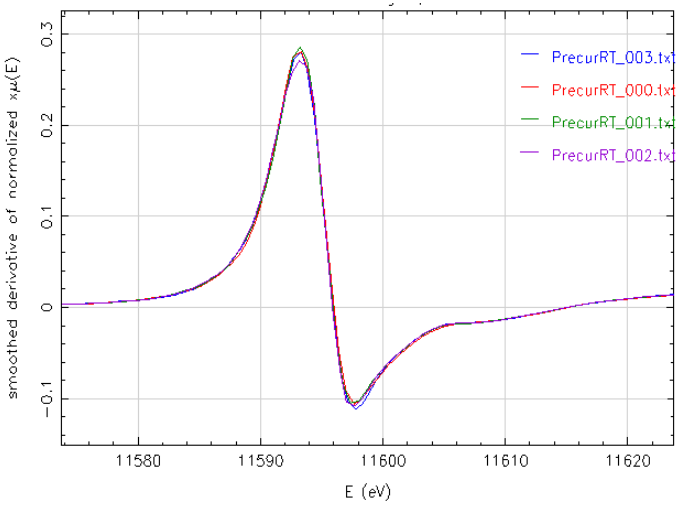
Preliminary data treatment

Align



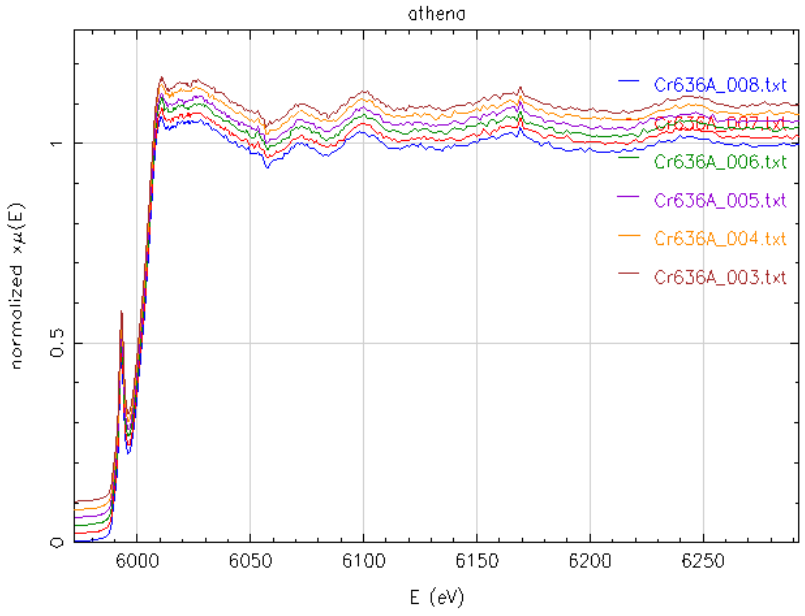


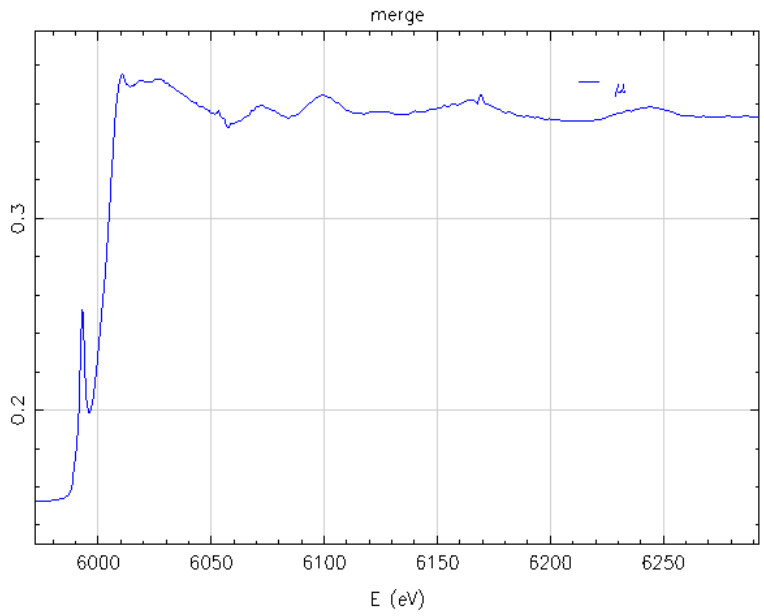




Preliminary data treatment

Average





Preliminary data treatment

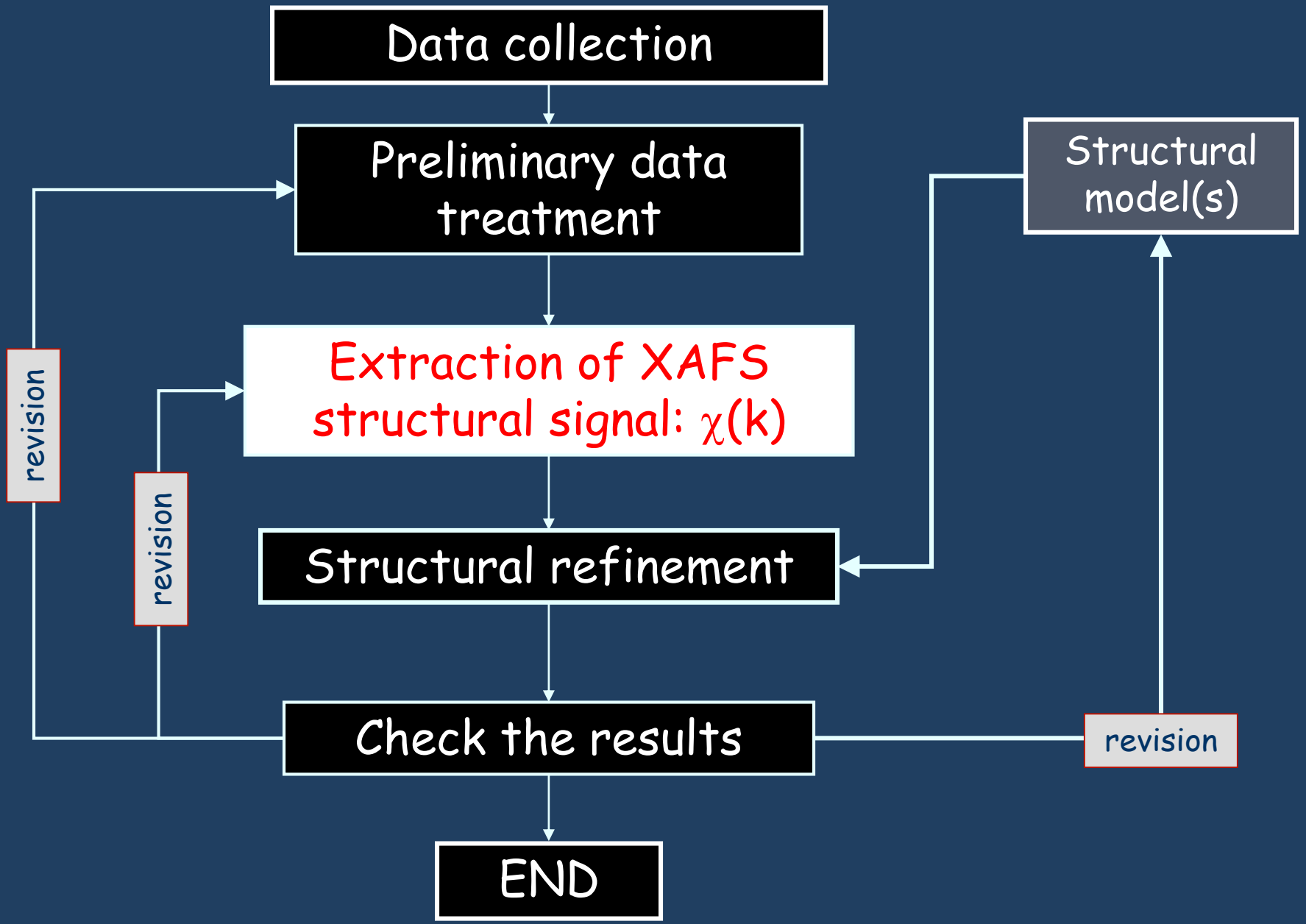
Preliminary data treatment is boring, it may be long…

While you are waiting for your data collection to finish…

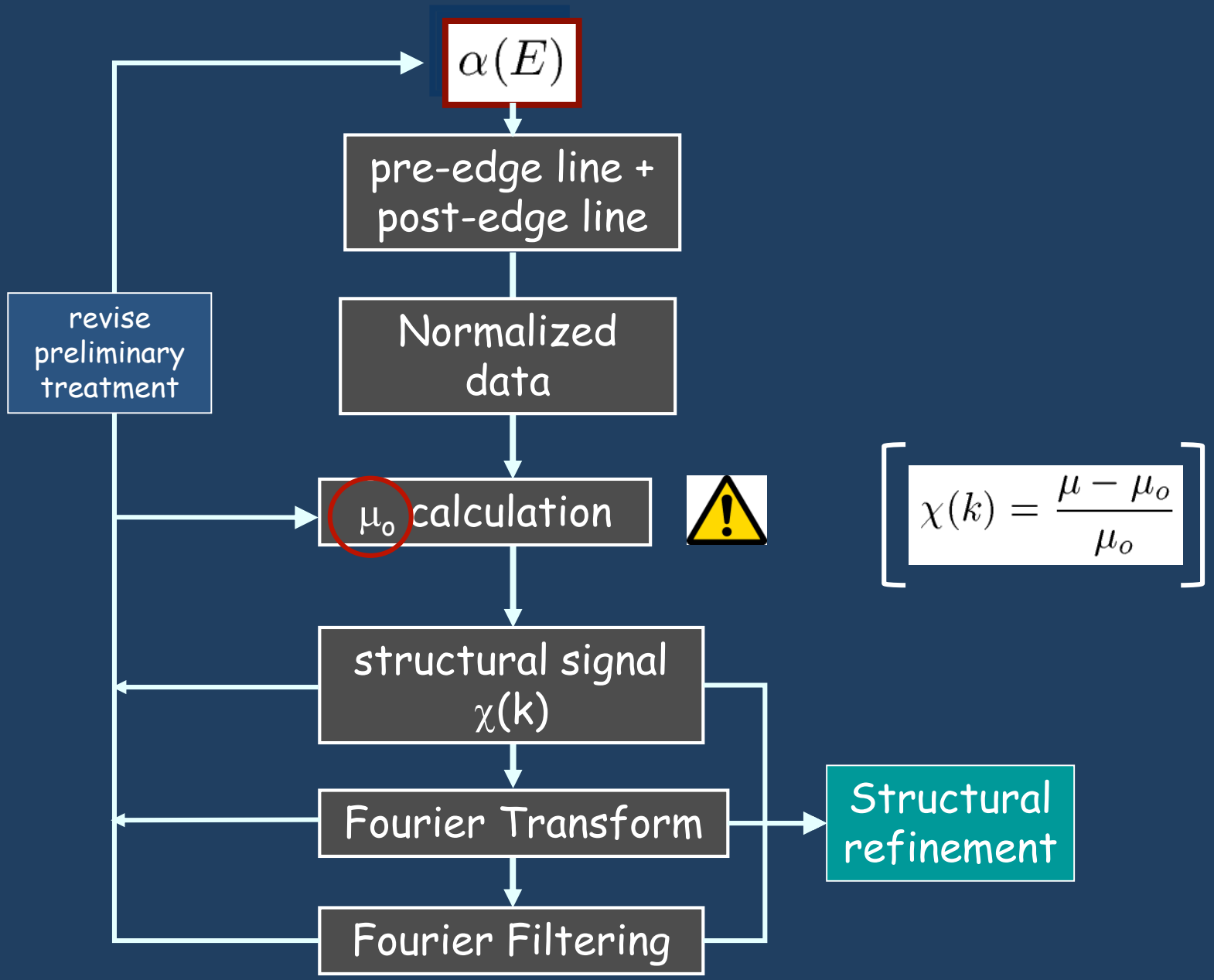
Do it on already collected data!!

You will save your time at home!!

XAFS analysis: from experiment to results



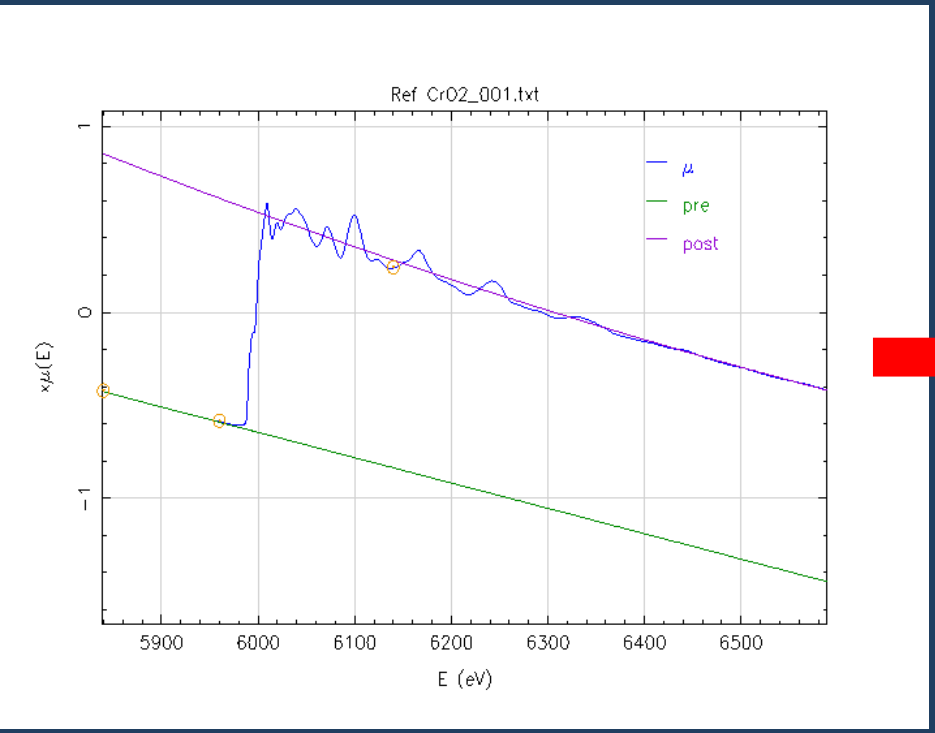
Extraction of the EXAFS signal

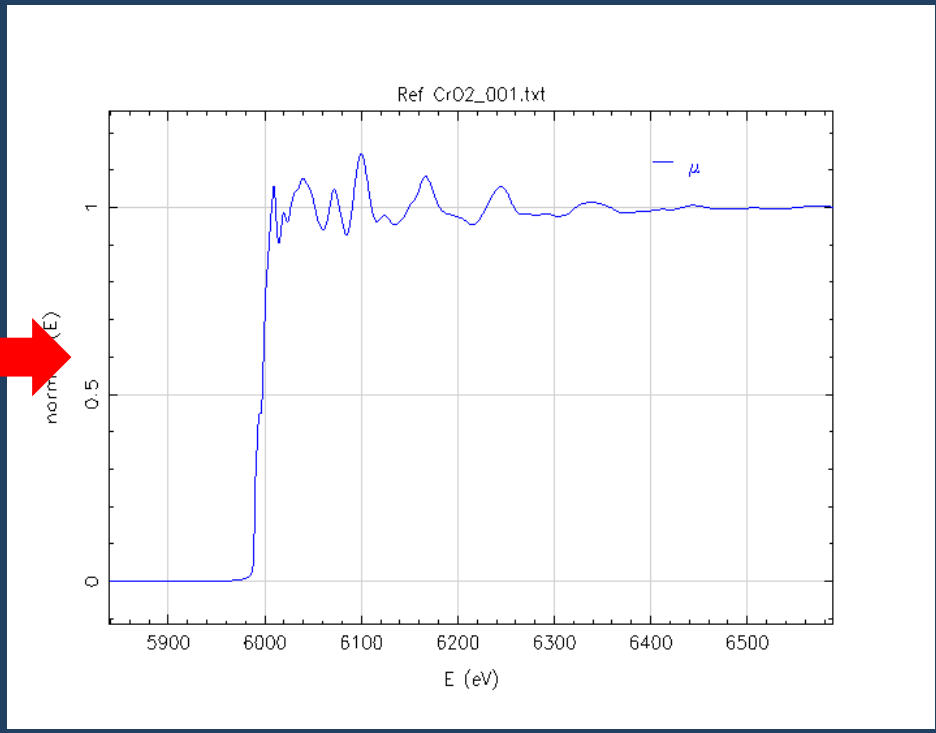


Extraction of the EXAFS signal

pre-edge line + post-edge line

Normalized data

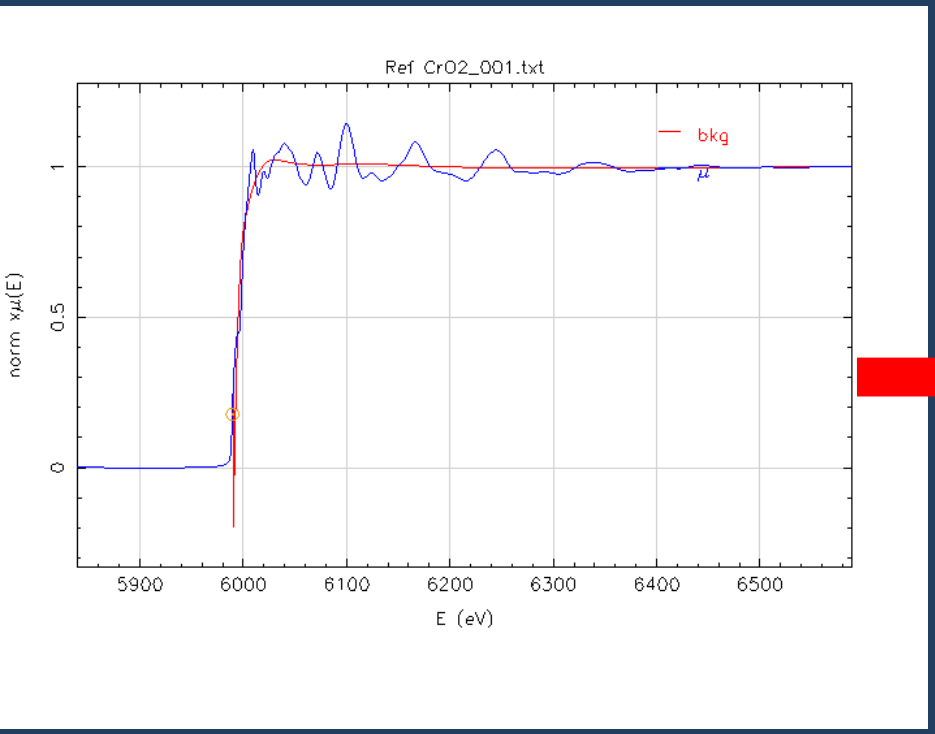


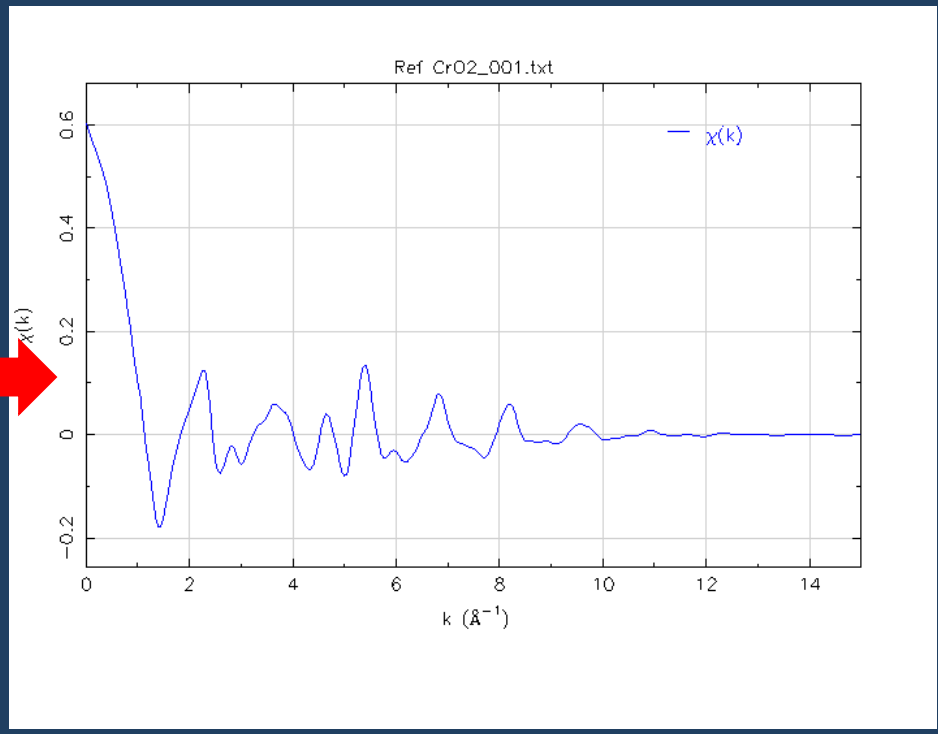


Extraction of the EXAFS signal

μ_o calculation

structural signal $\chi(k)$

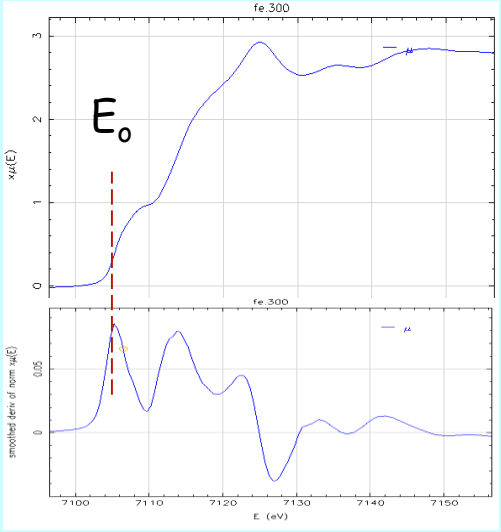




Extraction of the EXAFS signal

μ_0 calculation

1) Define E_0



E_0 will allow to set the starting point of χ(k).

It is generally taken at the maximum of the 1st derivative of the absorption

2) Calculate μ_0

μ_0 is the bare atom atomic background.

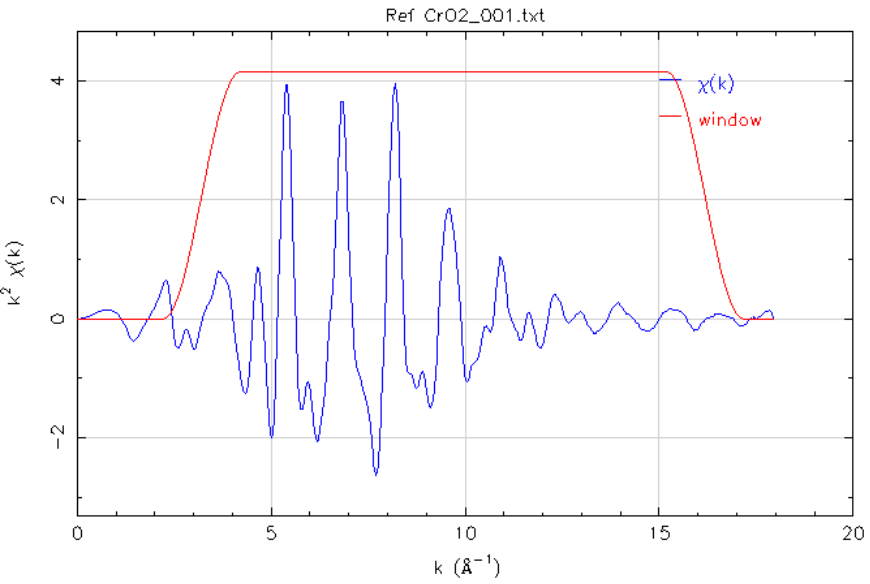
It is calculated **empirically as a smooth curve** across the data.

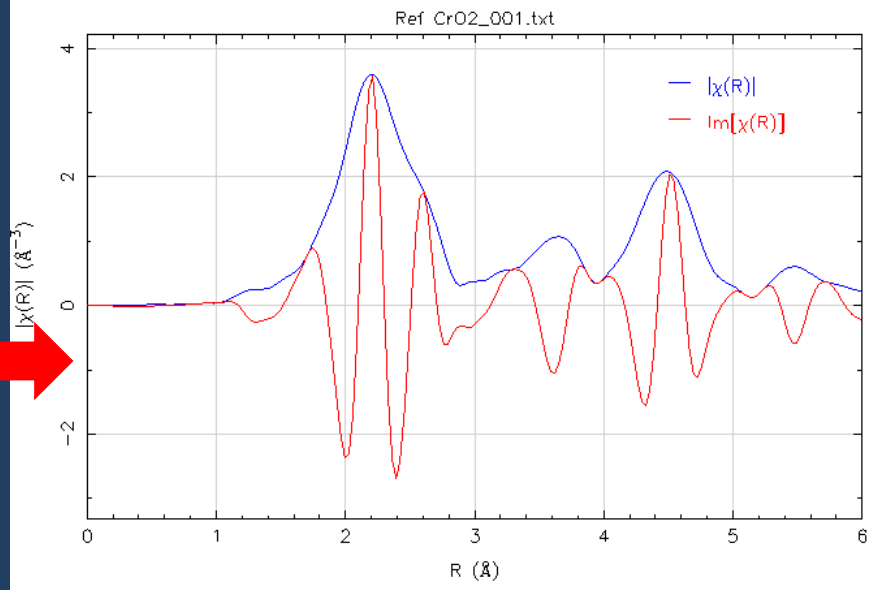
Different XAFS data analysis softwares apply different (equivalent) approaches

3) Subtract μ_0 from μ

Extraction of the EXAFS signal

Fourier Transform



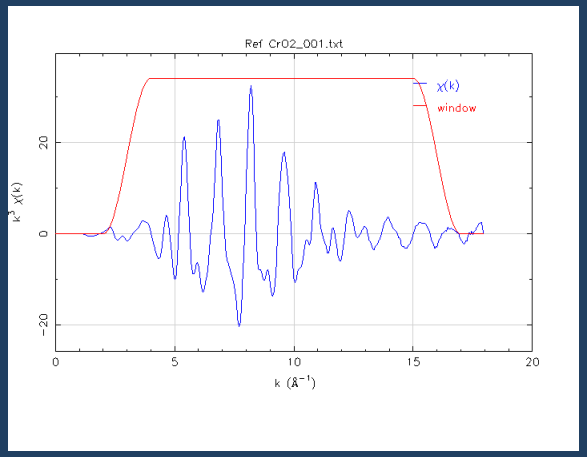


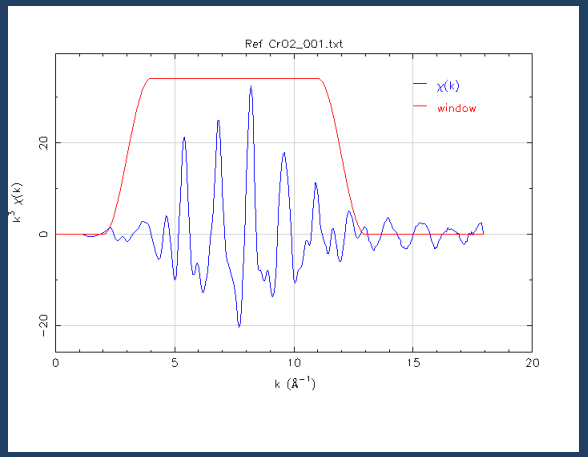
FT shows more intuitively the main structural features in the real space: the FT modulus represent a pseudo-radial distribution function (RDF)

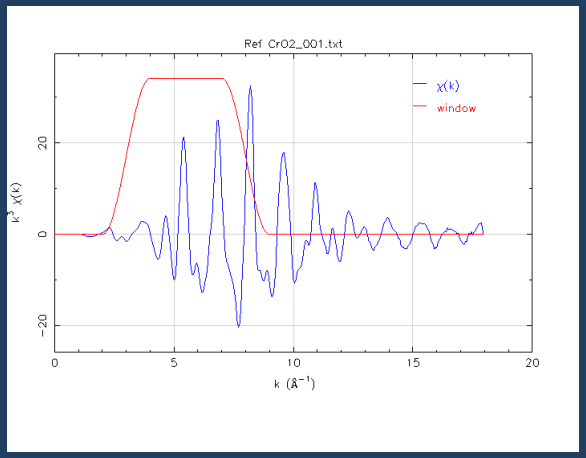
|FT| peaks represent interatomic correlation

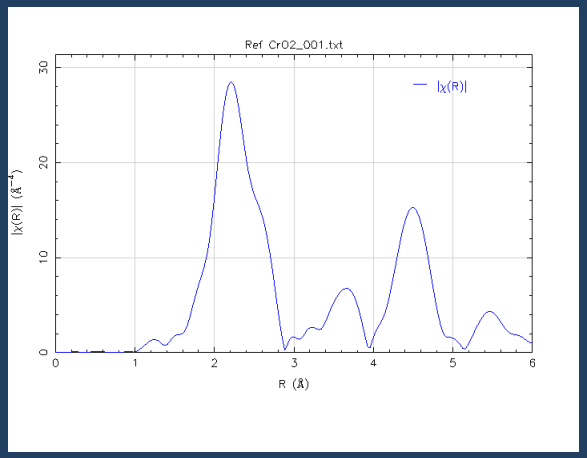
Peak position are not the true correlation distances due to the phase shift effect

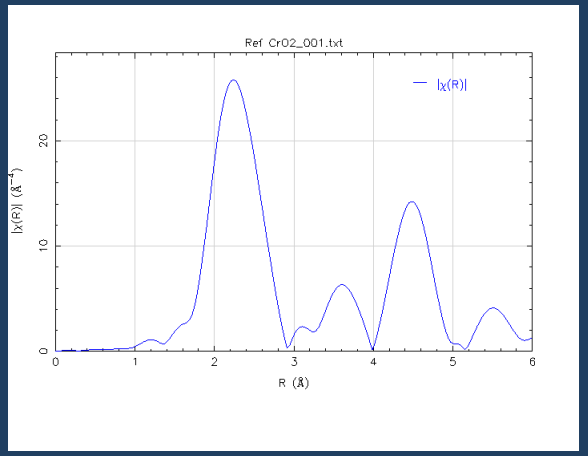
Fourier Transform – window size effect

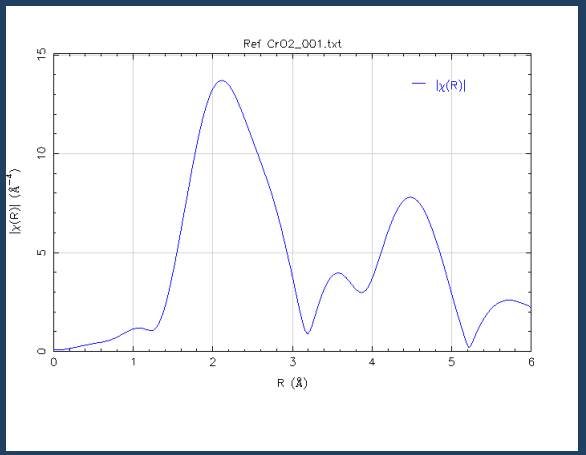








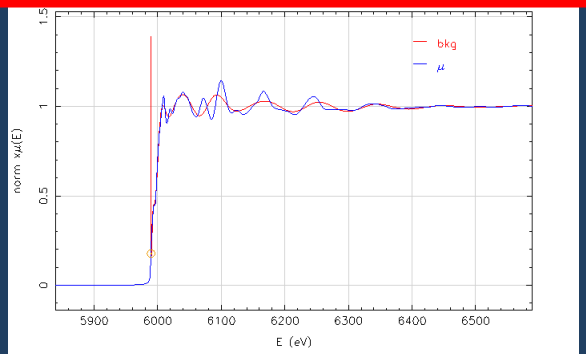


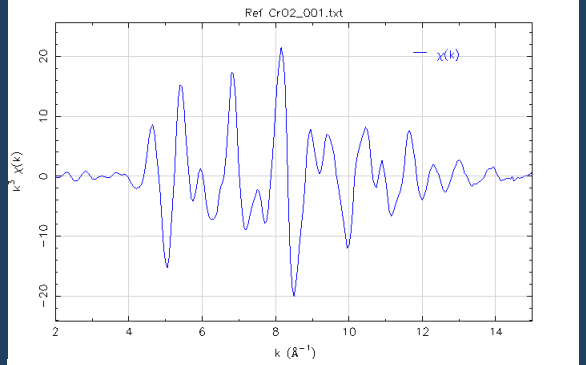


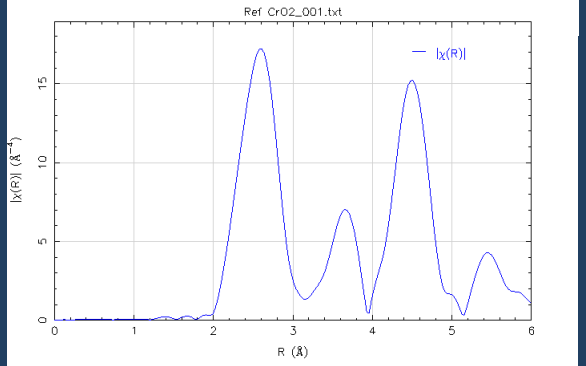
Minor effects are given by type of windows (Hanning, Kaiser-Bessel, Sine) and apodization

Extraction of the EXAFS signal

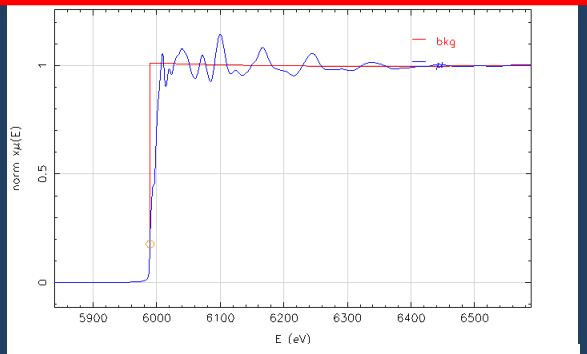
DO NOT REMOVE TRUE STRUCTURAL FEATURES

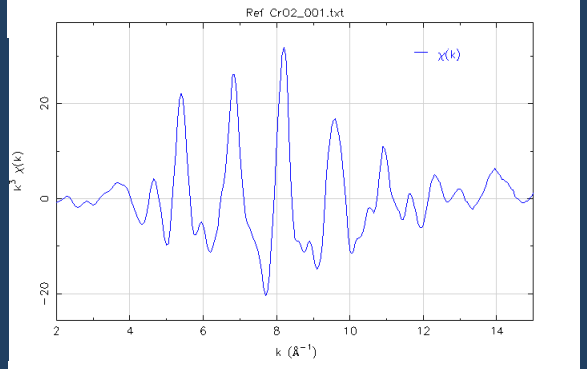


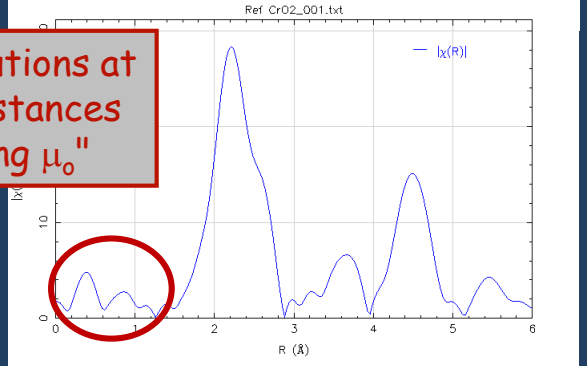




DO NOT DO THE OPPOSITE ERROR





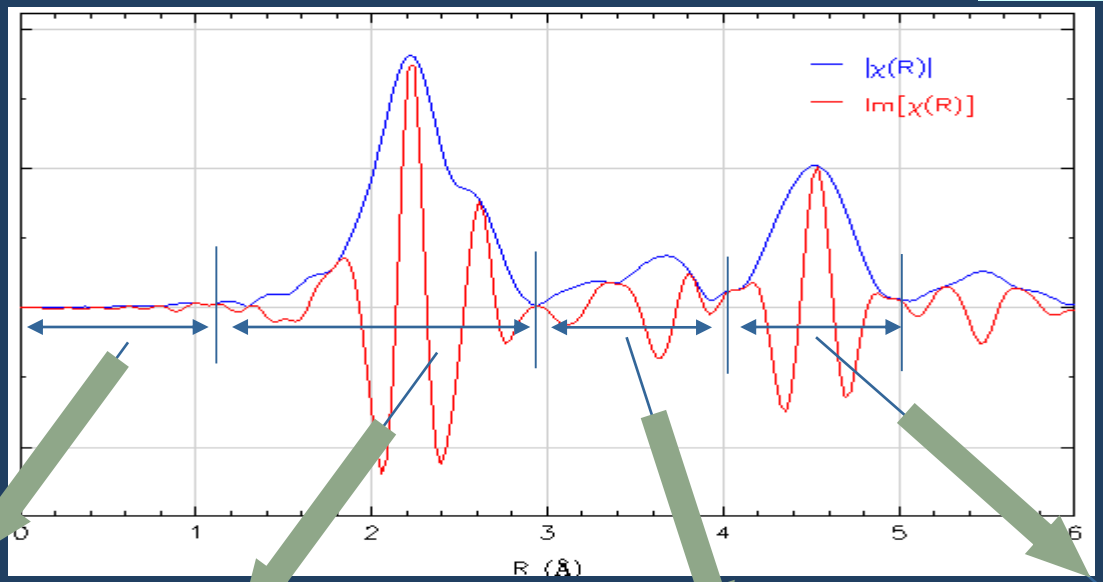


Large |FT| contributions at low (unphysical) distances may signify "wrong μ_0"

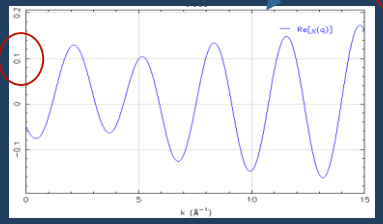
Extraction of the EXAFS signal

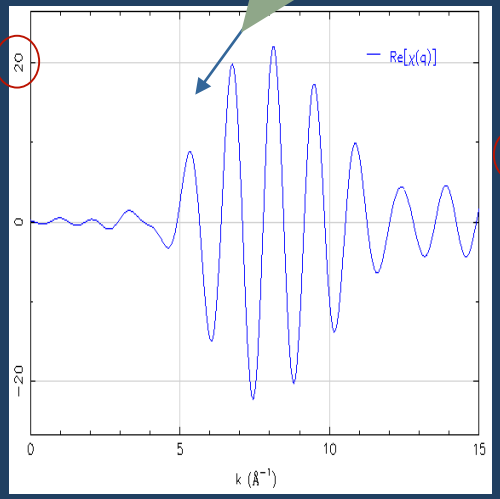
Fourier Filtering

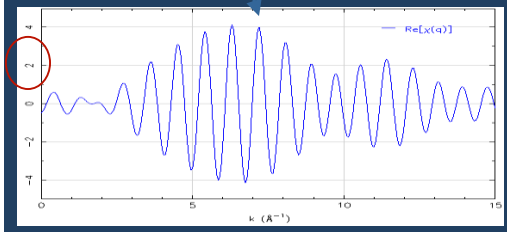
Fourier filtering allows isolating contributions of selected regions of the FT

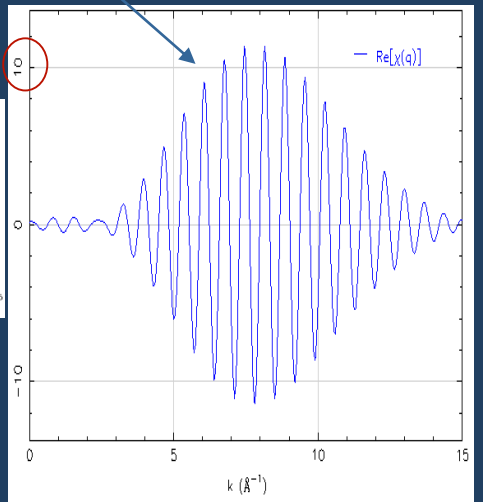


Background contribution

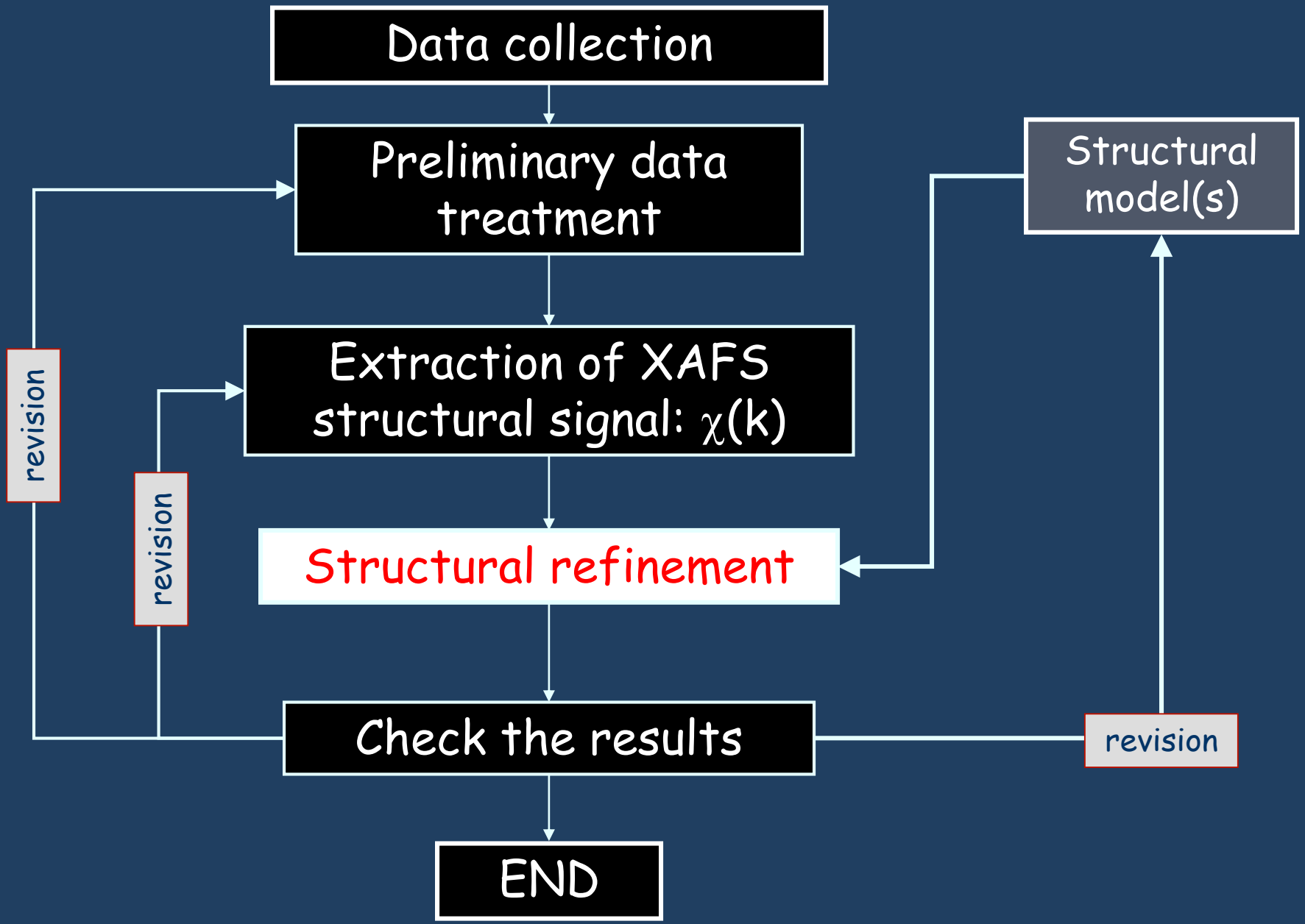








XAFS analysis: from experiment to results

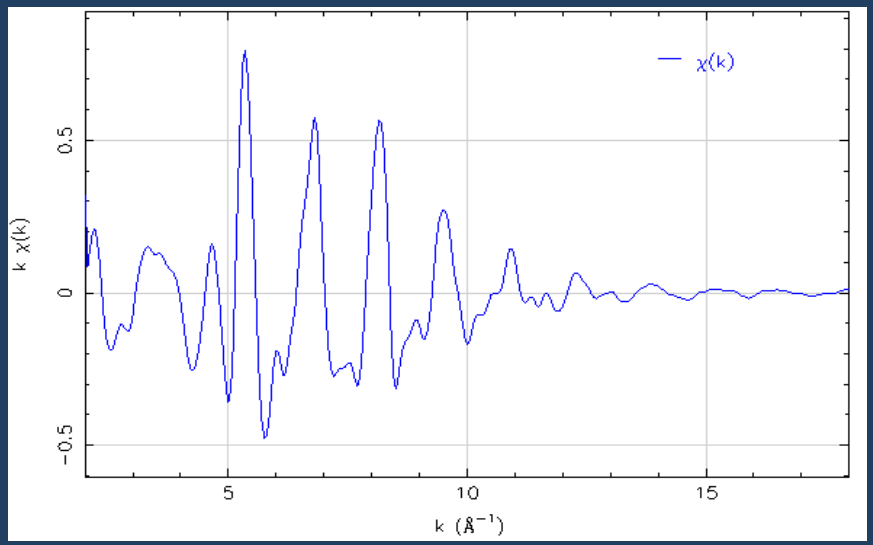


Structural refinement

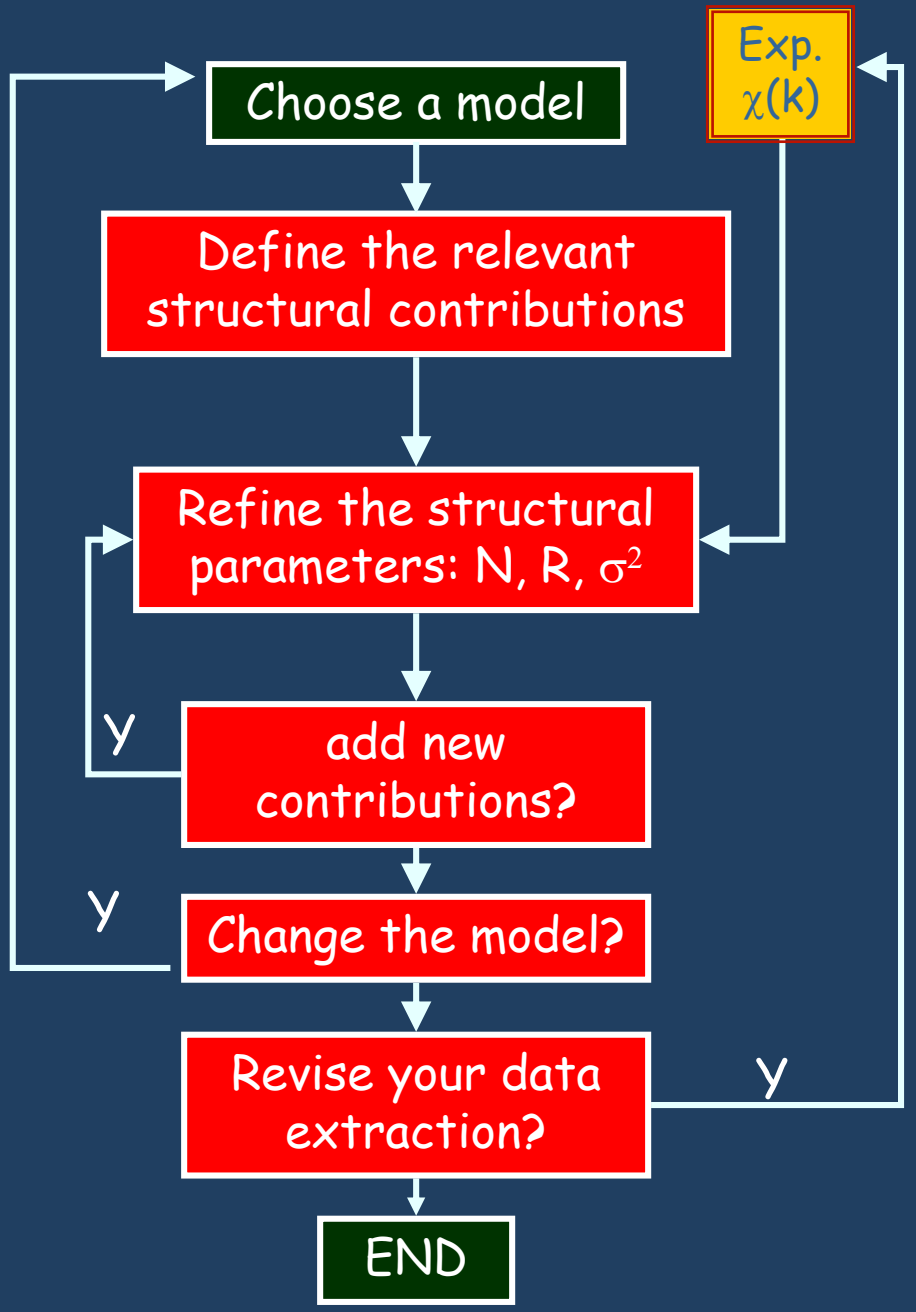
Theoretical $\chi(k)$

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

Experimental $\chi(k)$



Require data analysis programs



Structural refinement

Choose a model

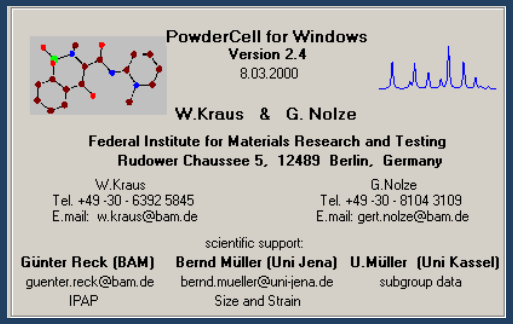
How to find a model structure

How to visualize the structure

How to calculate distances and geometries

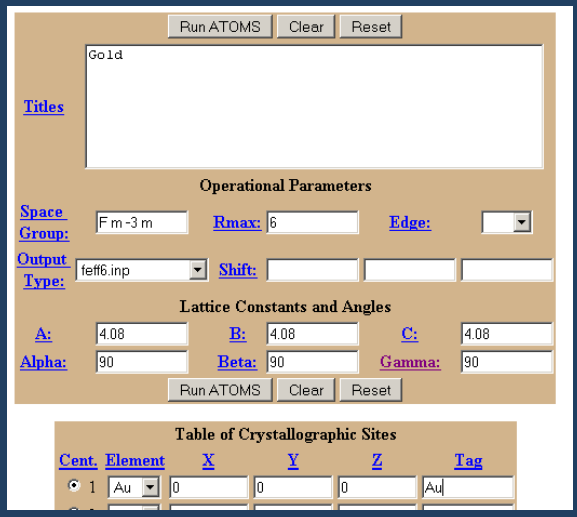
https://icsd.fizkarlsruhe.de

Database for inorganic structures

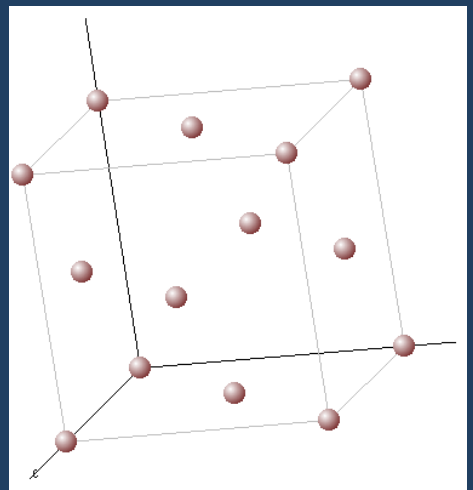


ATOMS on the Web

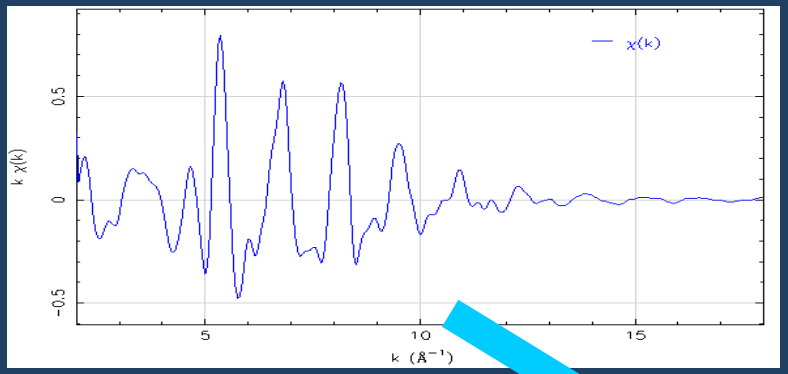
http://millenia.cars.aps.anl.gov/cgi-bin/atoms/atoms.cgi



http://database.iem.ac.ru/mincryst/

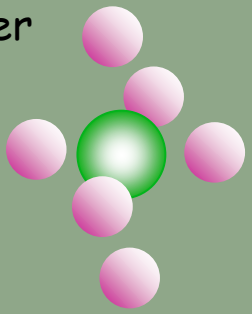


ICSD database

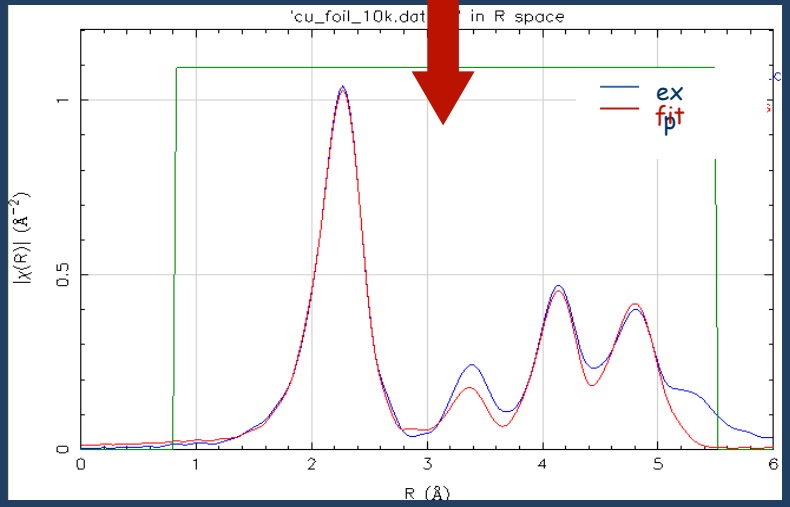


$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

Amplitude and phase functions from atomic cluster models



Data refinement program



XAFS data analysis softwares

http://www.xafs.org/

www.ixasportal.net

http://cars9.uchicago.edu/ifeffit/

Click DOWNLOADS

Click ifeffit-1.2.11.exe

http://bruceravel.github.io/demeter/

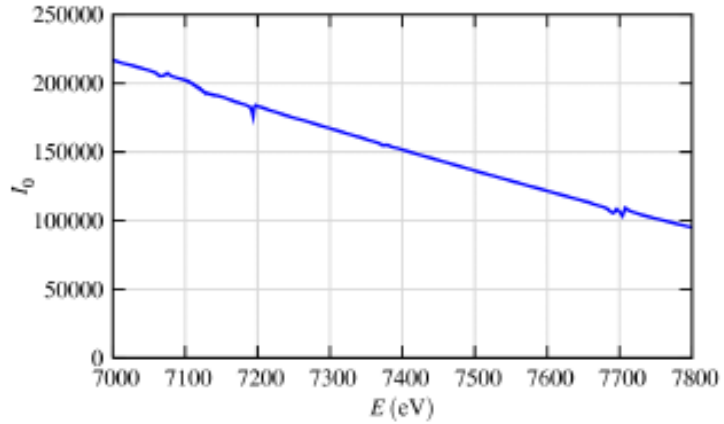
Data treatment: strategy

Step for reducing measured data to μ(E) and then to χ(k):

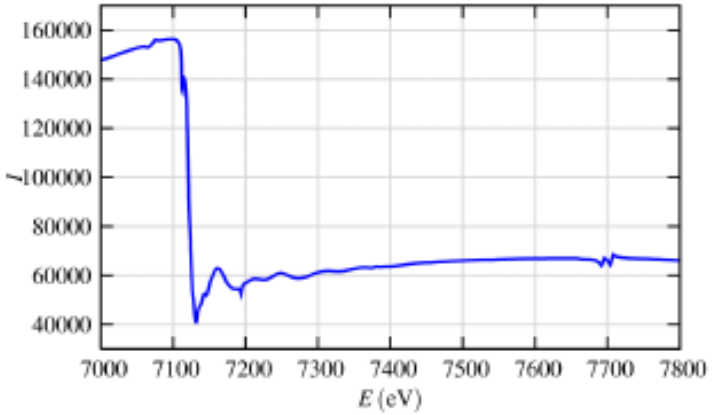
1. convert measured intensities to μ(E)
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize μ(E) to go from 0 to 1, so that it represents 1 absorption event
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS χ.
5. identify the threshold energy E_0, and convert from E to k space: $k = \frac{\sqrt{2m(E - E_0)}}{\hbar^2}$
6. weight the XAFS χ(k) and Fourier transform from k to R space.
7. isolate the χ(k) for an individual "shell" by Fourier filtering.

Converting raw data to μ(E)

I_0



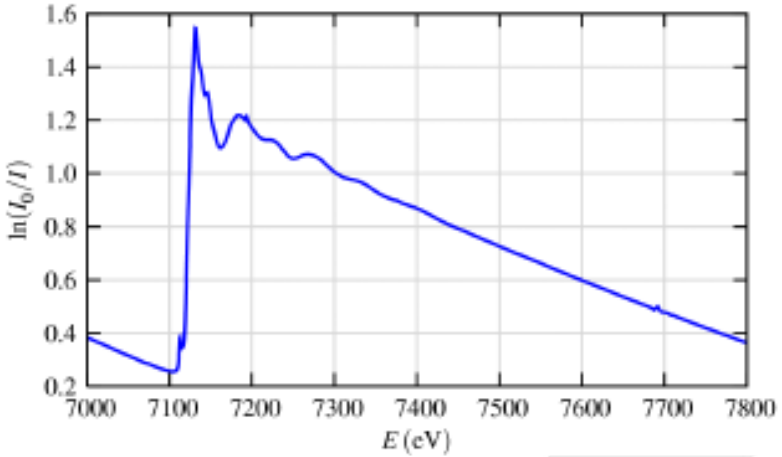
I



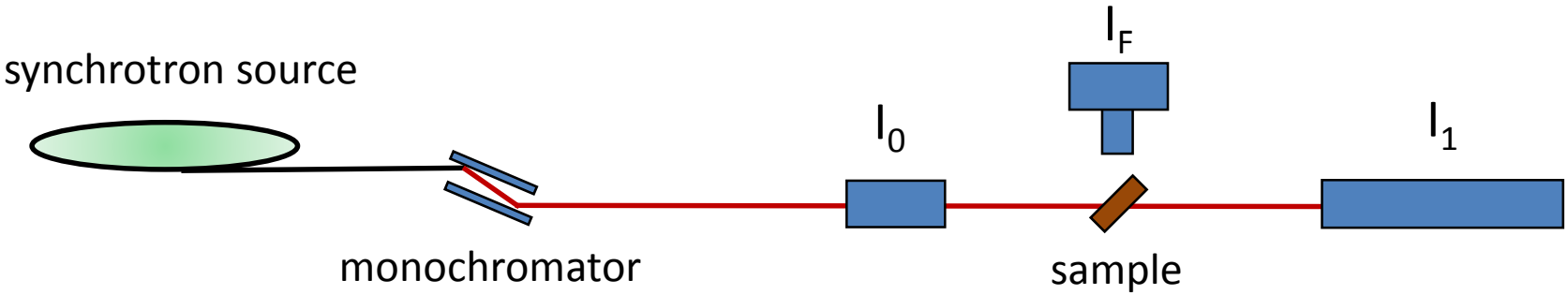
For transmission XAFS:

$I = I_0 \exp[-\mu(E)\, t]$

$\mu(E)\, t = \ln [I_0/I]$



Absorption measurements in real life



Transmission

The absorption is measured directly by measuring what is transmitted through the sample

$$I = I_0 e^{-\mu(E)t}$$

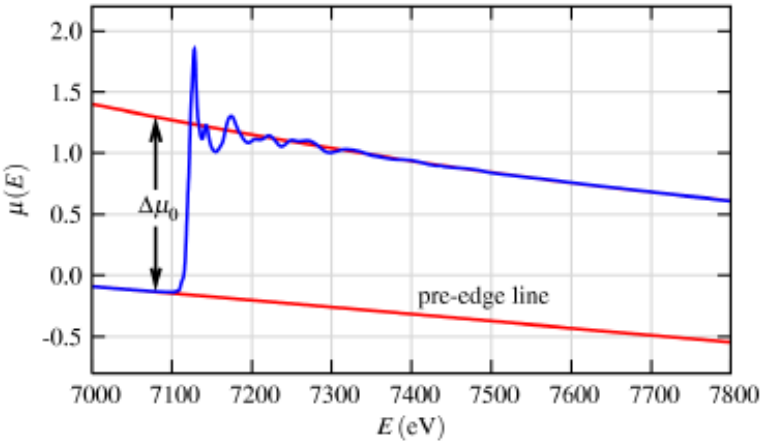
$$\mu(E)t = \alpha = \ln I_0/I_1$$

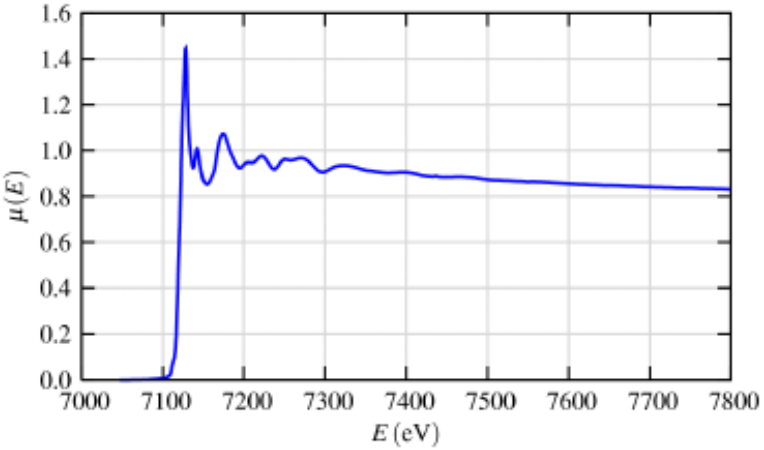
Fluorescence

The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured

$$\alpha \propto I_F/I_0$$

Pre-edge subtraction and normalization





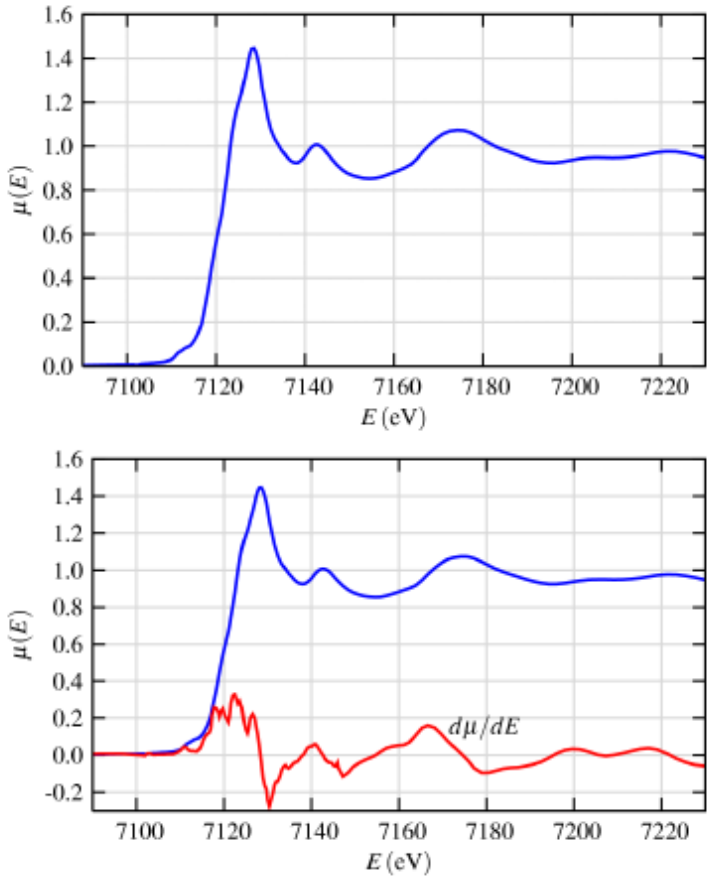
Pre-edge subtraction

We subtract away the background that fits the *pre edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).

Normalization

We estimate the *edge step*, $\mu_0(E_0)$ by extrapolating a simple fit to the above μ(E) to the edge.

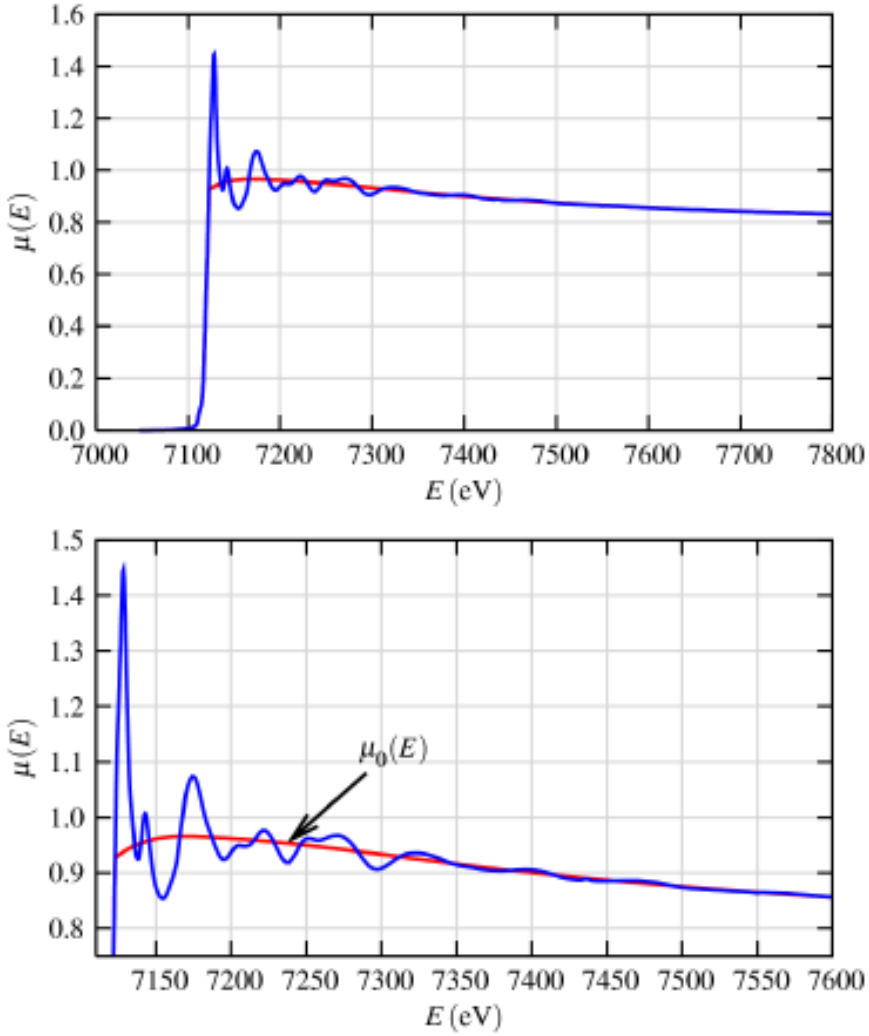
Determination of E_0



Derivative and E_0

We can select E_0 roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we will keep in mind that we may need to refine this value later on.

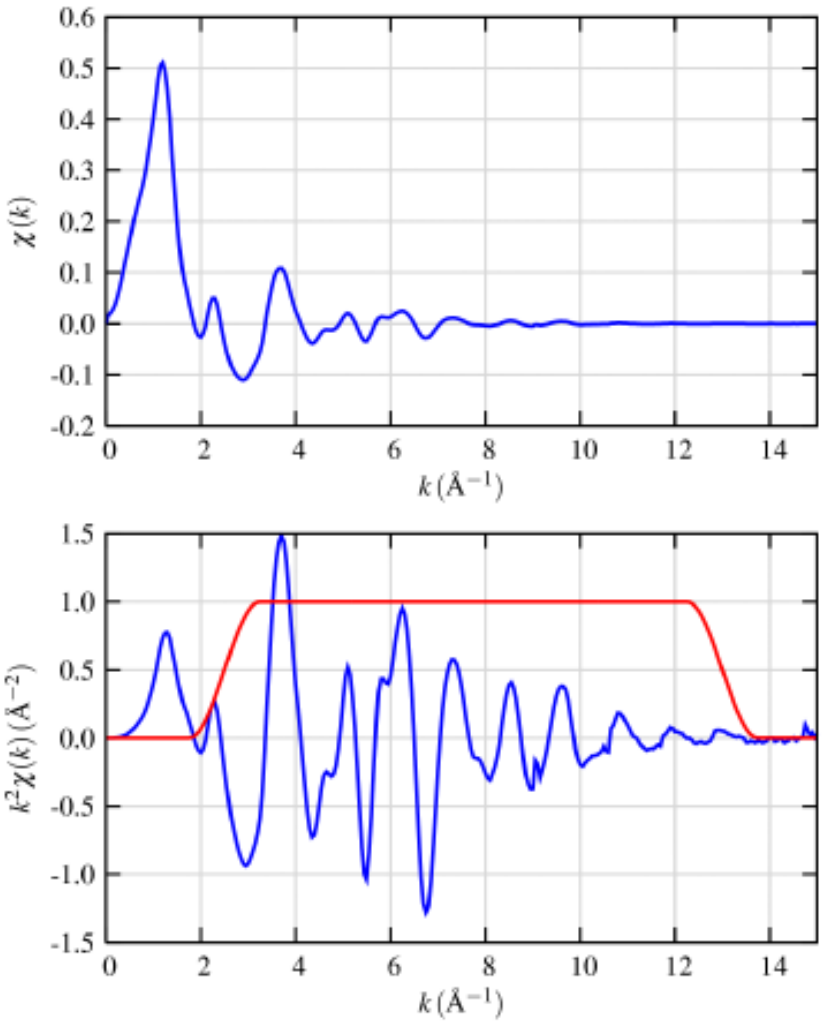
Post-edge background subtraction



Post-edge background

- We do not have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).
- We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.
- A flexible enough spline should not match the μ(E) and remove all the EXAFS. We want a spline that will match the *low frequency* components of $\mu_0(E)$.

X(k), k-weighting



χ(k)

The raw EXAFS χ(k) usually decays quickly with k, and difficult to assess or interpret by itself.

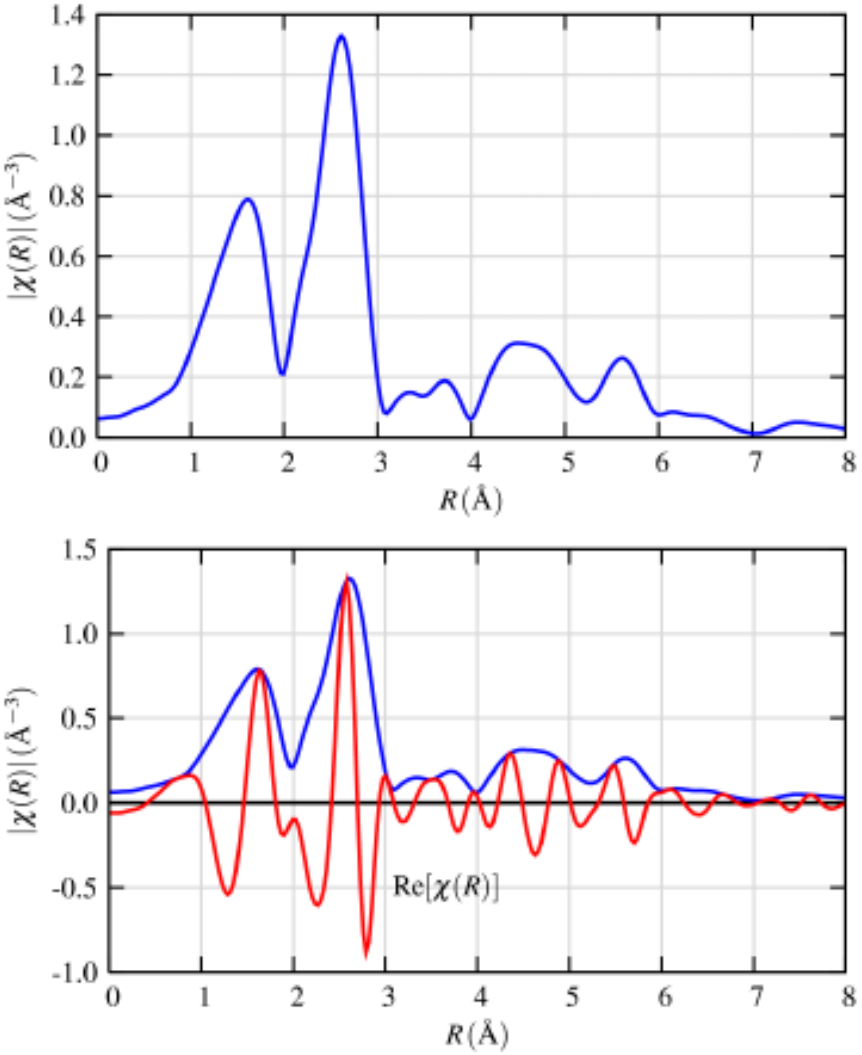
It is customary to weight the higher k portion of the spectra by multiplying by k^2 or k^3.

k-weighted χ(k): $k^2\chi(k)$

χ(k) is composed of sine waves, so we'll Fourier Transform from k to R-space.

To avoid "ringing", we'll multiply by a *window function*.

Fourier Transform: χ(R)



χ(R)

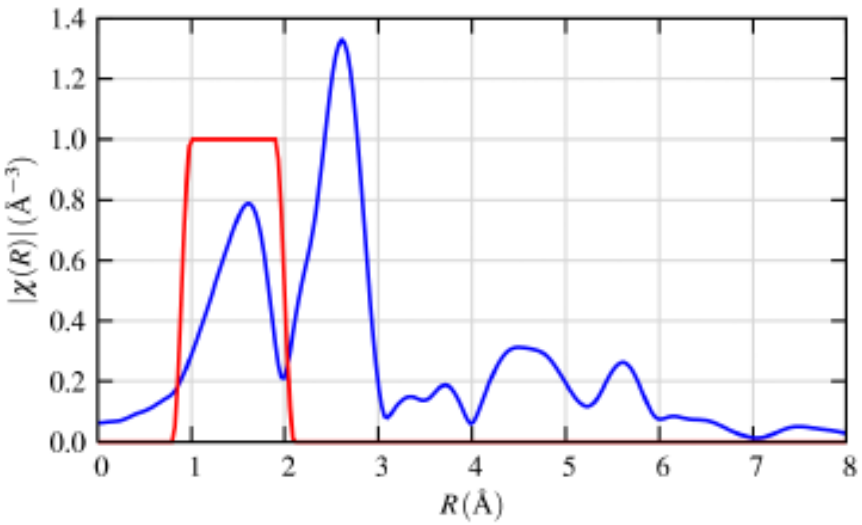
The Fourier Transform of $k^2(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe- Fe.
The Fe-O distance in FeO is 2.14Å , but the first peak is at 1.66Å .
This shift in the first peak is due to the *phase-shift*, δ(k): sin[2kR + δ(k)] .

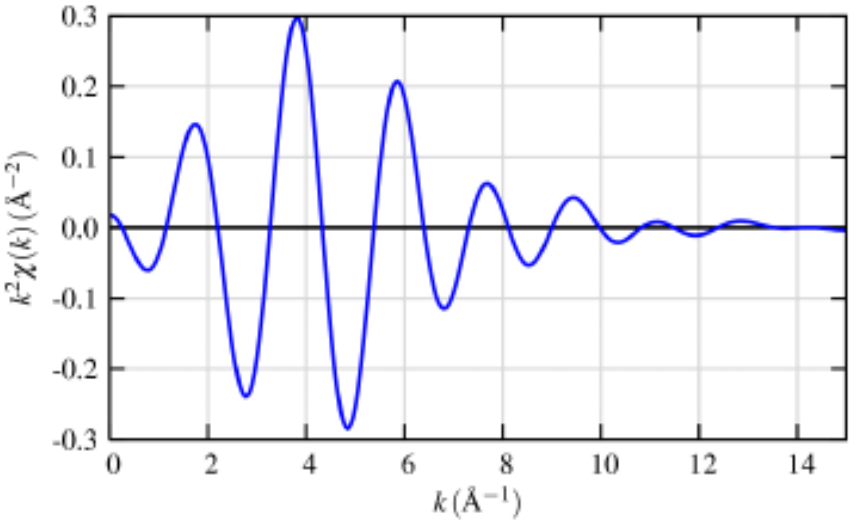
A shift of -0.5 Å is typical.

χ(R) is complex:

The FT makes c(R) complex.
Usually only the amplitude is shown, but there are really oscillations in c(R).
Both real and imaginary components are used in modeling.

Fourier filtering





$\chi(R)$ often has well separated peaks for different “shells”.

This shell can be isolated by a Filtered Back-Fourier Transform, using the window shown for the first shell of FeO.

This results in the filtered $\chi(k)$ for the selected shell. Many analysis programs use such filtering to remove shells at higher R.

Beyond the first shell, isolating a shell in this way can be difficult.

The information content of EXAFS

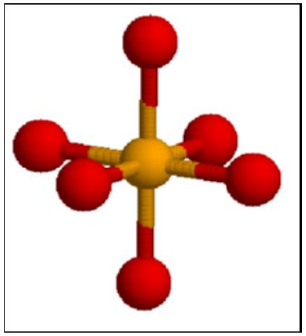
- The number of parameters we can reliably measure from our data is limited:

$$N \approx \frac{2\,\Delta k\,\Delta R}{\pi}$$

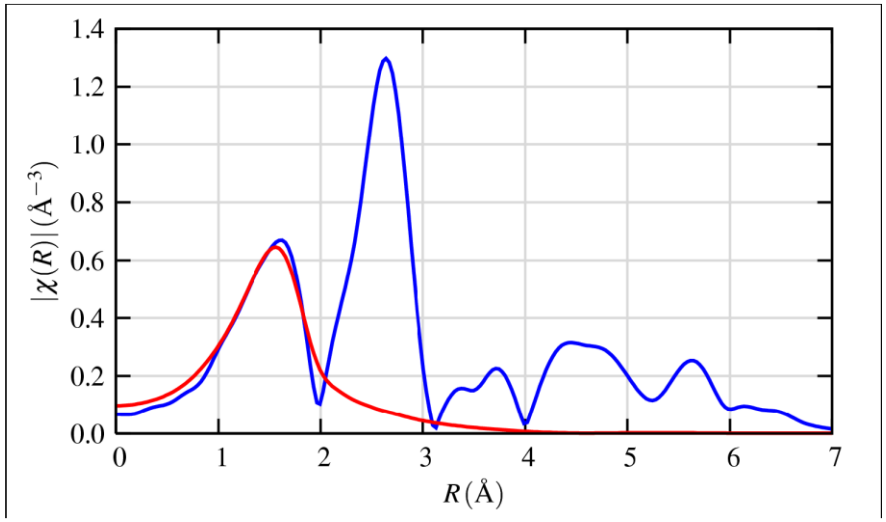
  where Δk and ΔR are the k- and R-ranges of the usable data.
- For the typical ranges like k = [3.0, 12.0] $Å^{-1}$ and R = [1.0, 3.0] Å, there are ~ 11 parameters that can be determined from EXAFS.
- The "Goodness of Fit" statistics, and confidence in the measured parameters need to reflect this limited amount of data.
- It is often important to constrain parameters R, N, σ^2 for different paths or even different data sets (different edge elements, temperatures, etc)
- Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).
- Use as much other information about the system as possible!

Modeling the first shell of FeO - 1

FeO has a rock-salt structure.



To model the FeO EXAFS, we calculate the scattering amplitude f(k) and phase-shift $\delta(k)$, based on a guess of the structure, with Fe-O distance R = 2.14 Å (a regular octahedral coordination). We will use these functions to *refine* the values R, N, σ^2, and E_0 so our model EXAFS function matches our data.



$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).

Fit results

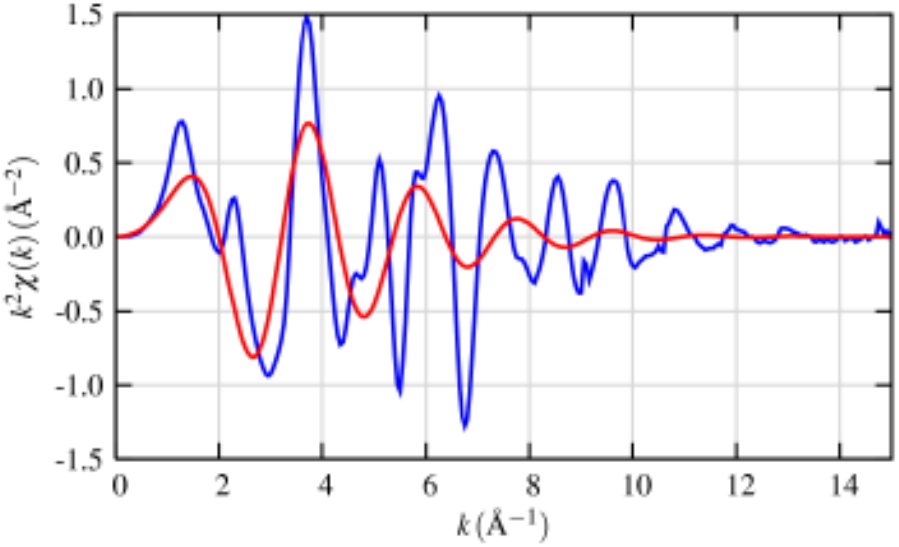
N = 5.8 ± 1.8

R = 2.10 ± 0.02 Å

E_0 = -3.1 ± 2.5 eV

σ^2 = 0.015 ± 0.005 Å ^{2}.

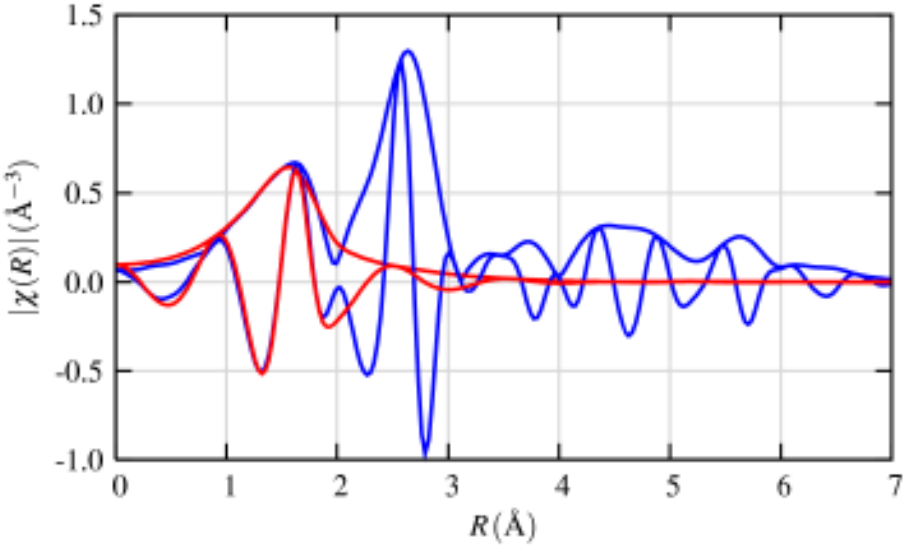
Modeling the first shell of FeO - 2



1st shell fit in k space

The 1st shell fit to FeO in k space.

There is clearly another component in the XAFS



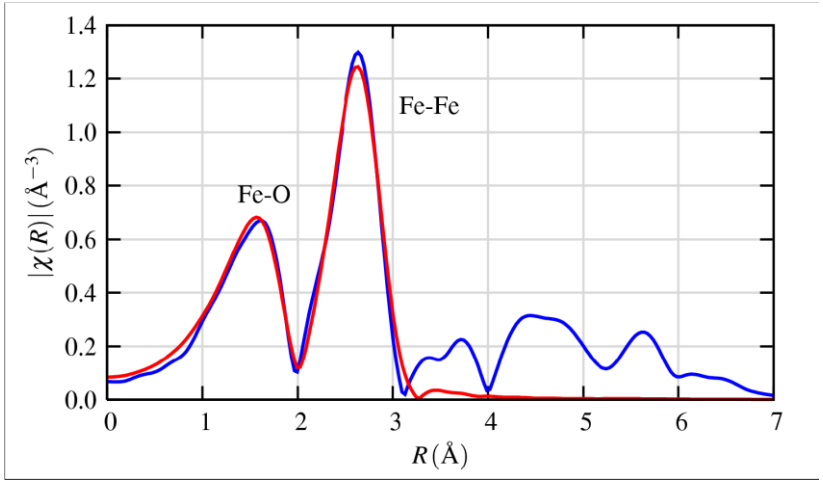
1st shell fit in R space

|χ(R)| and Re[χ(R)] for FeO (blue), and a 1st shell fit (red).

Modeling the second shell of FeO - 1

To add the second shell Fe to the model, we use calculation for f(k) and δ(k) based on a guess of the Fe-Fe distance, and refine the values R,N, σ^2.

Such a fit gives a result like this:



|χ(R)| data for FeO (blue), and fit of 1st and 2nd shells (red).

The results are fairly consistent with the known values for crystalline FeO:

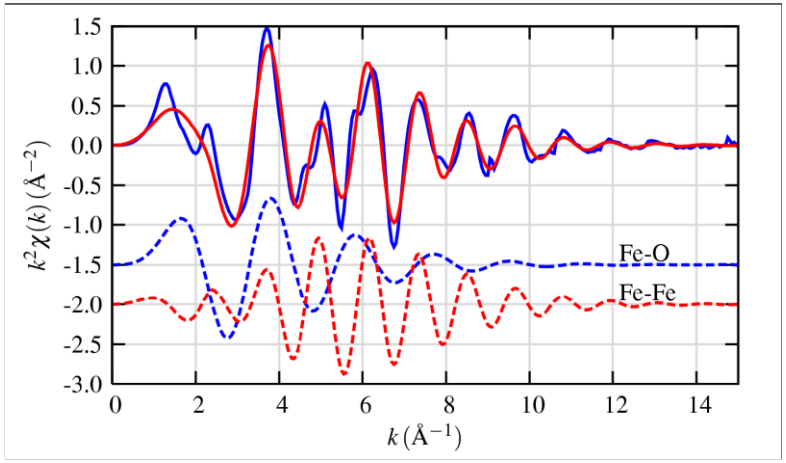
6 O at 2.13Å, 12 Fe at 3.02Å .

Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

Modeling the second shell of FeO - 2

Other views of the data and two-shell fit:



The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.
Even in this simple system, there is some *overlap* of shells in R-space.
The agreement in Re[χ(R)] look especially good – this is how the fits are done.
The modeling can get more complicated than this