

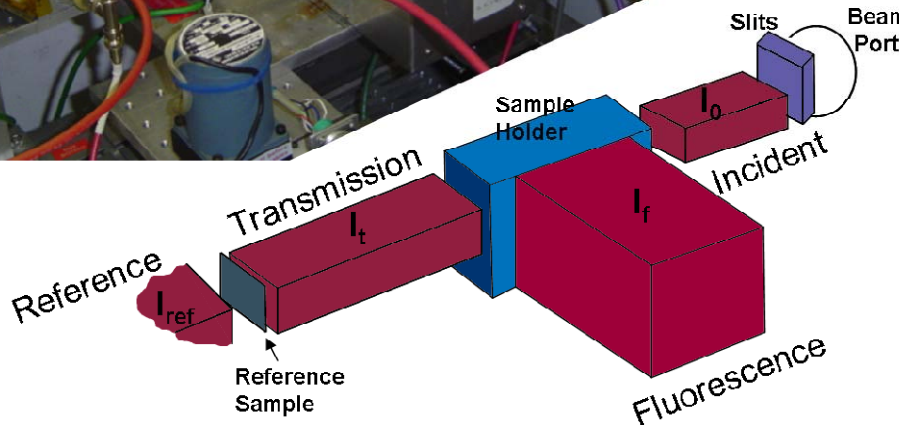
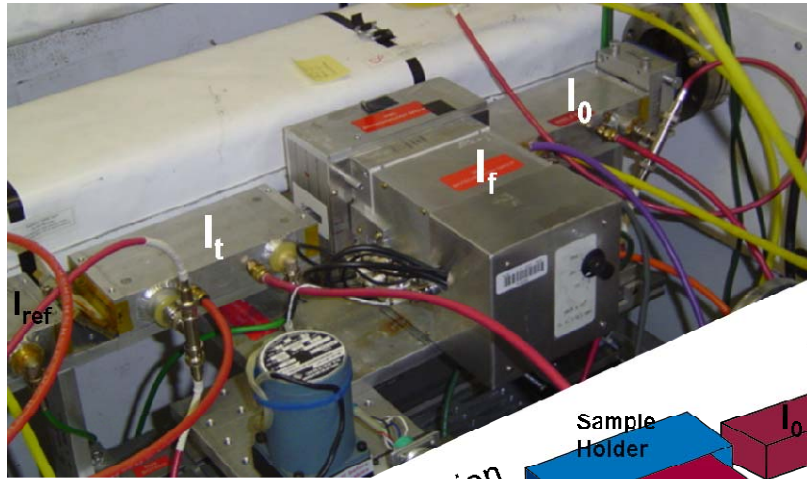
Basics of EXAFS Processing

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Honeywell

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X-ray-Absorption Fine Structure

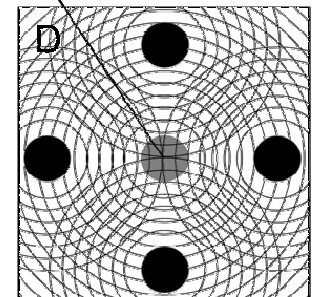
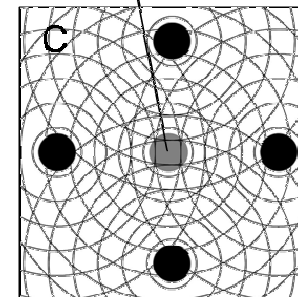
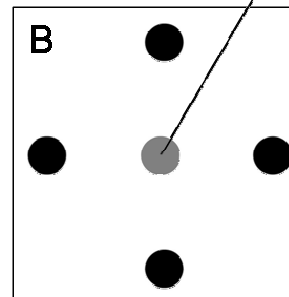
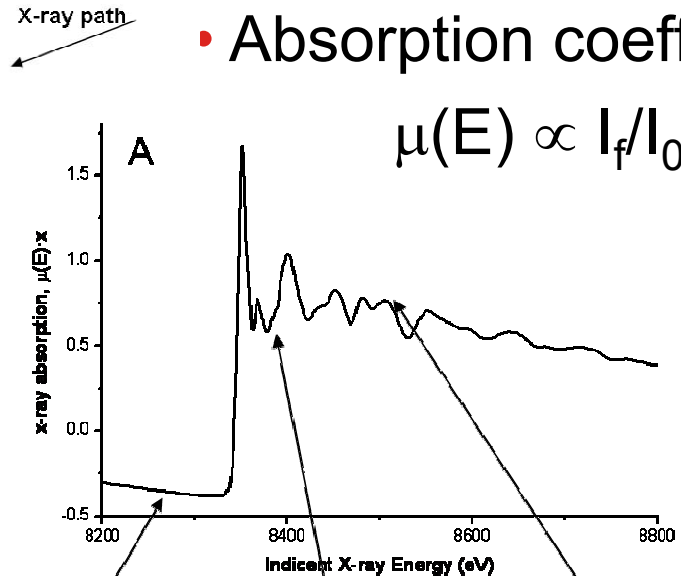


- Attenuation of x-rays

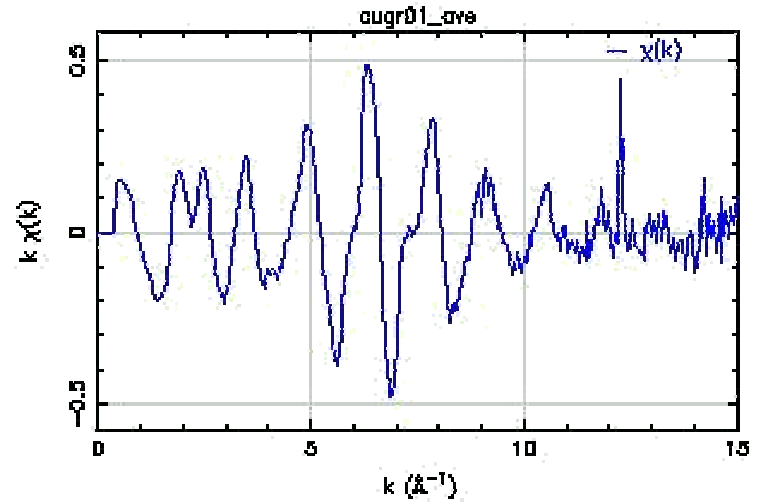
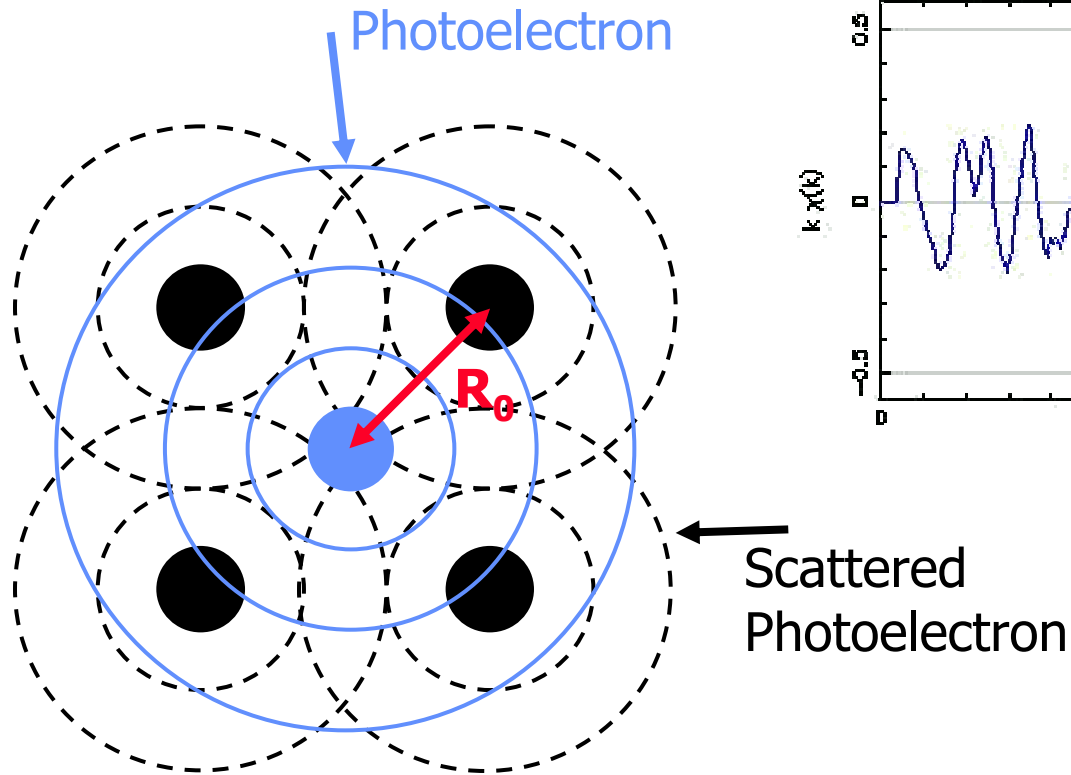
$$I_t = I_0 e^{-\mu(E) \cdot x}$$

- Absorption coefficient

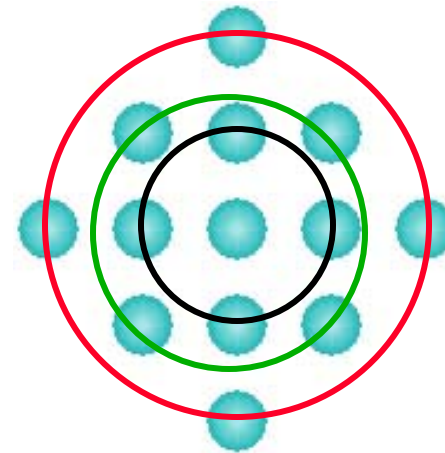
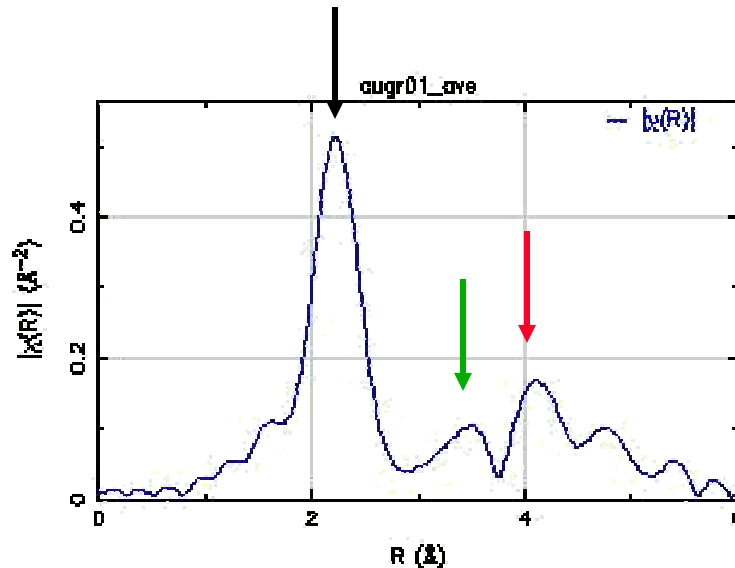
$$\mu(E) \propto I_f / I_0$$



X-ray-Absorption Fine Structure



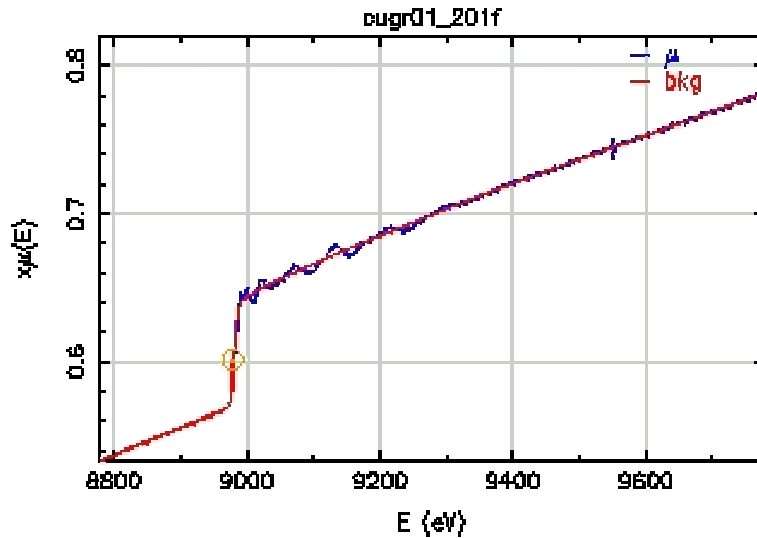
Fourier Transform of $\chi(k)$



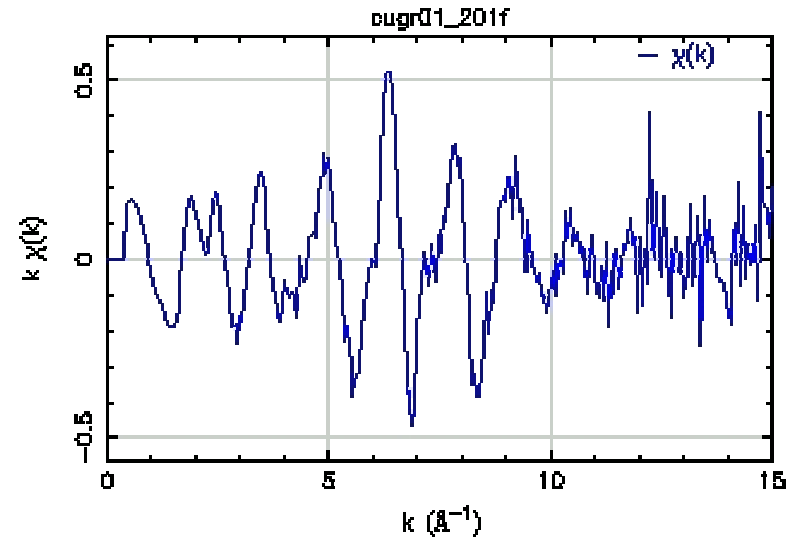
- Similar to an atomic radial distribution function
 - Distance
 - Number
 - Type
 - Structural disorder
- Fourier transform is not a radial distribution function
 - See http://www.xafs.org/Common_Mistakes

- Definition of EXAFS
 - Edge Step
 - Energy to wave number
- Fourier Transform (FT) of $\chi(k)$
 - FT is a frequency filter
 - Different parts of a FT and backward FT
 - FT windows and sills
 - Determining Kmin and Kmax of FT
- IFEFFIT method for constructing the background function
 - FT and background (bkg) function
 - Wavelength of bkg
- EXAFS Equation

Definition of EXAFS



=>



Normalized
oscillatory part
of absorption
coefficient

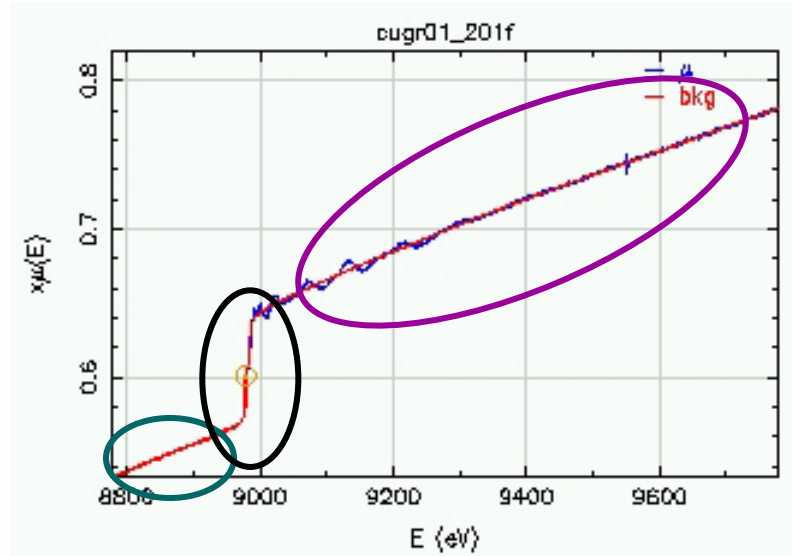
Measured Absorption
coefficient

Bkg: Absorption coefficient without
contribution from neighboring atoms
(Calculated)

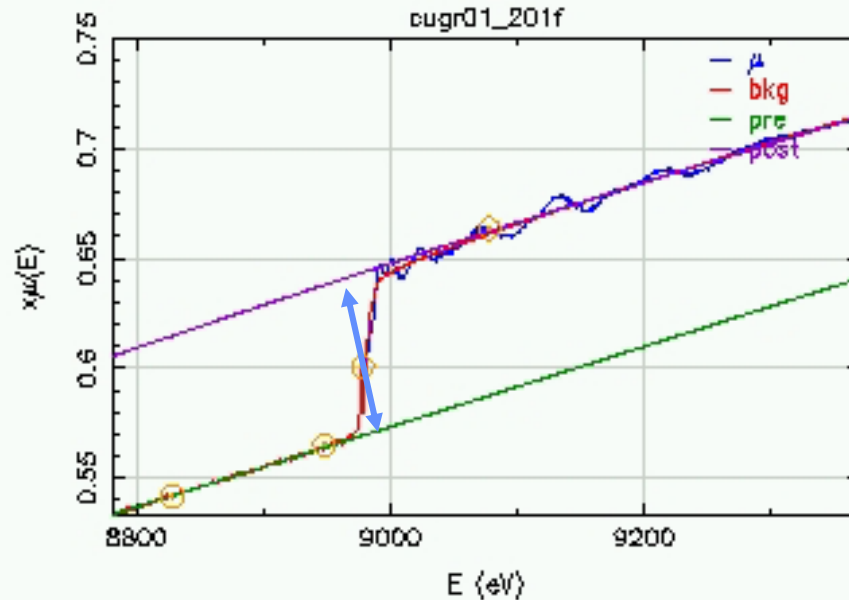
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)} \sim \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$

Evaluated at the Edge step (E_0)

Absorption coefficient



- **Pre-edge region** 300 to 50 eV before the edge
- **Edge region** the rise in the absorption coefficient
- **Post-edge region** 50 to 1000 eV after the edge



- **Pre-edge line** 200 to 50 eV before the edge
- **Post-edge line** 100 to 1000 eV after the edge
- **Edge step** the change in the absorption coefficient at the edge
 - Evaluated by taking the difference of the pre-edge and post-edge lines at E_0

Athena normalization parameters

Athena

File Edit Group Values Plot Mark Data Merge Analysis Settings Help

Project ocuments/Current Projects/foils/raw_data/Cufoil_10ID.prj

Current group cufoil_003

File: /home/skelly/Xafs/Cu/Cu-Stds-Jan02/stds.prj

Z: Cu Edge: K E shift: 0 Importance: 1

Background removal Show additional parameters

E0: 8977.068 Rbkg: 1

k-weight: 1 Edge step: 1.58688 ☒ fix step

Pre-edge range: -150 to -30

Normalization range: 100 to 919.55

Spline range: k: 0.5 to 16.359

E: 0.952 to 1019.55

Forward Fourier transform

k-range: 2 to 16.359

dk: 2 window type: kaiser-bessel

Phase correction: ☒ off arbitrary k-weight: 0.5

Backward Fourier transform

R-range: 1 to 3

dr: 0.5 window type: kaiser-bessel

Plotting parameters

plot multiplier: 1 y-axis offset: 0

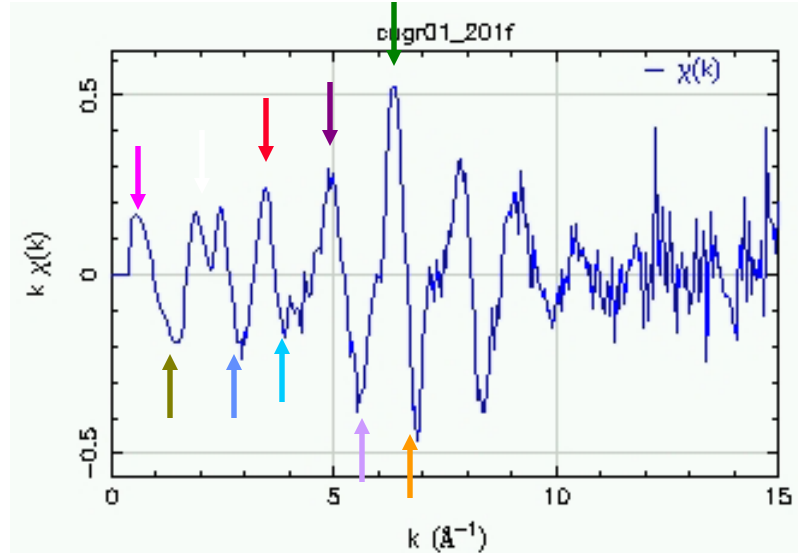
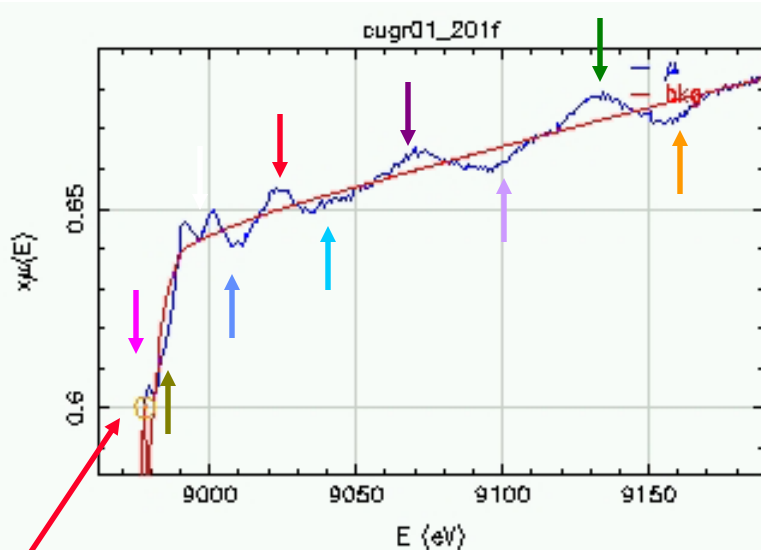
Plotting options

☒ mu(E) ☐ background ☐ pre-edge line ☐ post-edge line ☐ Normalized ☐ Derivative

Emin: -500 Emax: 1000

plotting in energy from group 'cufoil_003' ... done!

Energy to wave number



E_0 Must be somewhere on the edge

$$k^2 = \frac{2 m_e (E - E_0)}{\hbar^2} \sim \frac{\Delta E}{3.81}$$

Mass of the electron
Edge Energy

\hbar
Plank's constant

Athena edge energy E0

The screenshot shows the Athena software interface with the following sections:

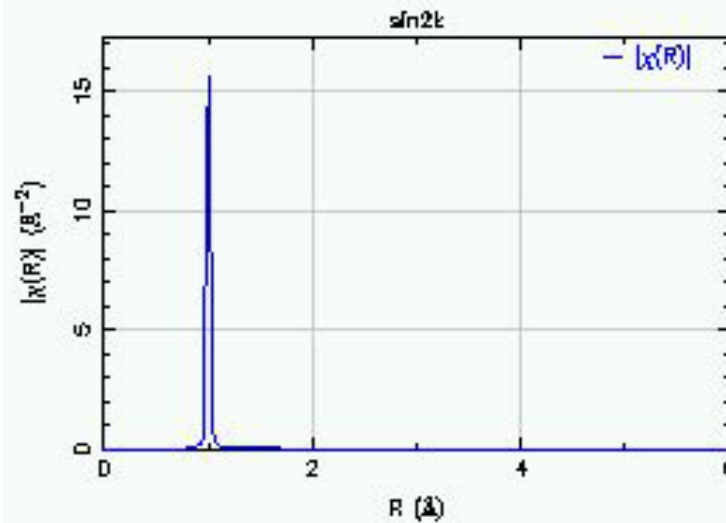
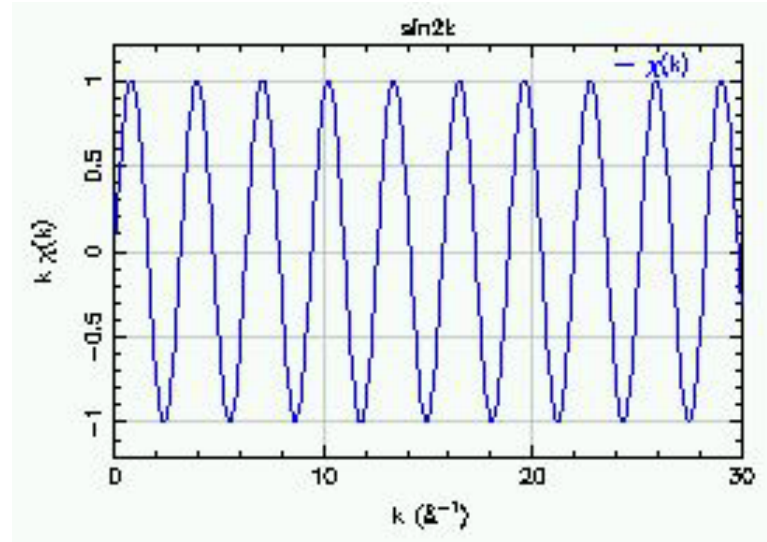
- Project:** ocuments/Current Projects/foils/raw_data/Cufoil_10ID.prj
- Current group:** cufoil_003
- File:** /home/skelly/Xafs/Cu/Cu-Stds-Jan02/stds.prj
- Z:** Cu **Edge:** K **E shift:** 0 **Importance:** 1
- Background removal:** (highlighted with a red circle and arrow)
 - E0:** 8977.068 ☒
 - Rbkg:** 1 ☒
 - k-weight:** 1 **Edge step:** 1.58688 ☒ fix step
 - Pre-edge range:** -150 ☒ to -30 ☒
 - Normalization range:** 100 ☒ to 919.55 ☒
 - Spline range:** k: 0.5 ☒ to 16.359 ☒ E: 0.952 ☒ to 1019.55 ☒
- Forward Fourier transform:**
 - k-range:** 2 ☒ to 16.359 ☒
 - dk:** 2 **window type:** kaiser-bessel
 - Phase correction:** ☒ off **arbitrary k-weight:** 0.5
- Backward Fourier transform:**
 - R-range:** 1 ☒ to 3 ☒
 - dr:** 0.5 **window type:** kaiser-bessel
- Plotting parameters:**
 - plot multiplier:** 1 **y-axis offset:** 0

On the right side, there is a list of files and a plotting options panel:

- Files:** cufoil_003, cufoil_004, cufoil_005, cufoil_merge, cufoil_10k.001, cu_amp1nleg6td_1k.fit
- Plotting options:**
 - E k R q kq**
 - E k R q**
 - 0 1 2 3 kw**
 - Plotting options:** E k R q Stack Ind PF
 - ☒ mu(E)
 - ☒ background
 - ☒ pre-edge line
 - ☒ post-edge line
 - ☒ Normalized
 - ☒ Derivative
 - Emin:** -500 **Emax:** 1000

At the bottom, a status bar reads: plotting in energy from group 'cufoil_003' ... done!

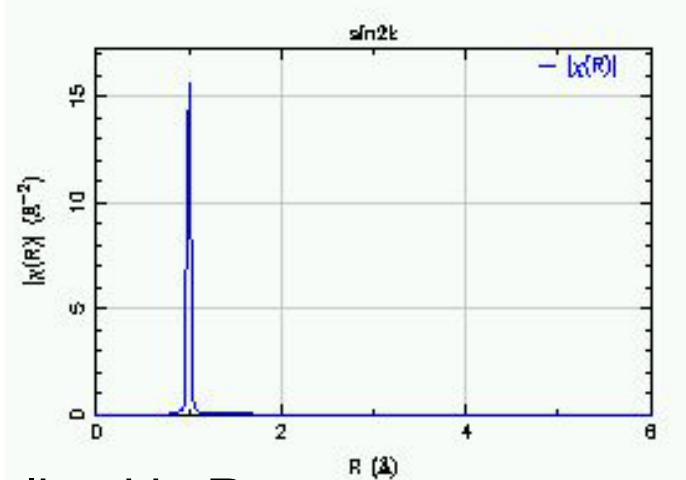
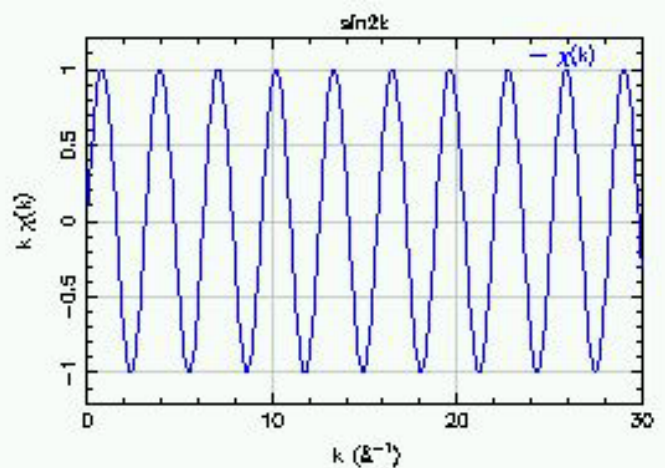
Fourier Transform is a frequency filter



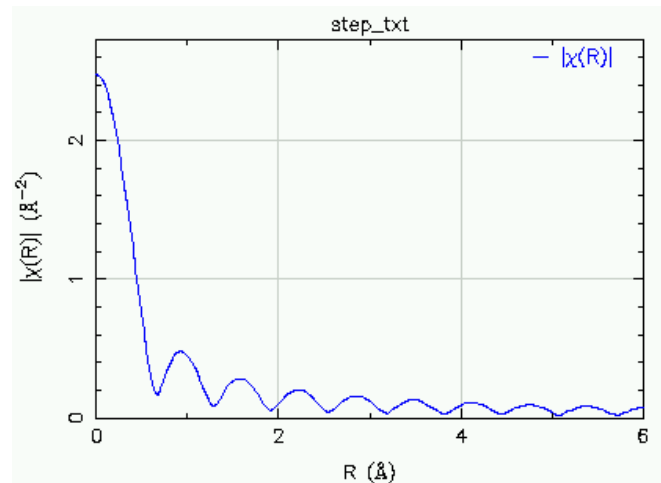
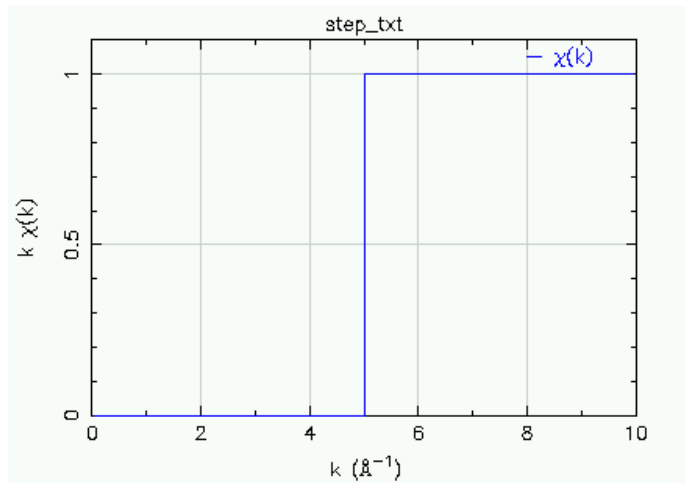
- FT of $\sin(2Rk)$ is a peak at $R=1$
- FT of infinite sine wave is a delta function
- Signal that is de-localized in k -space is localized in R -space
- FT is a frequency filter

Fourier Transform of a function that is:

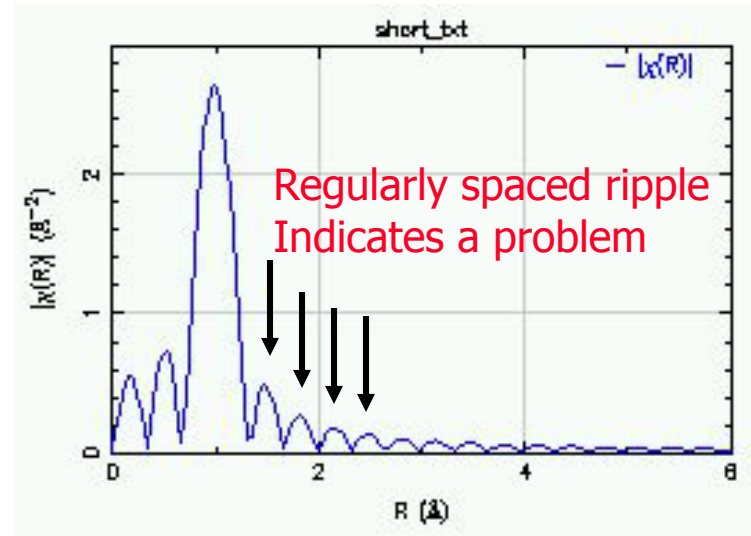
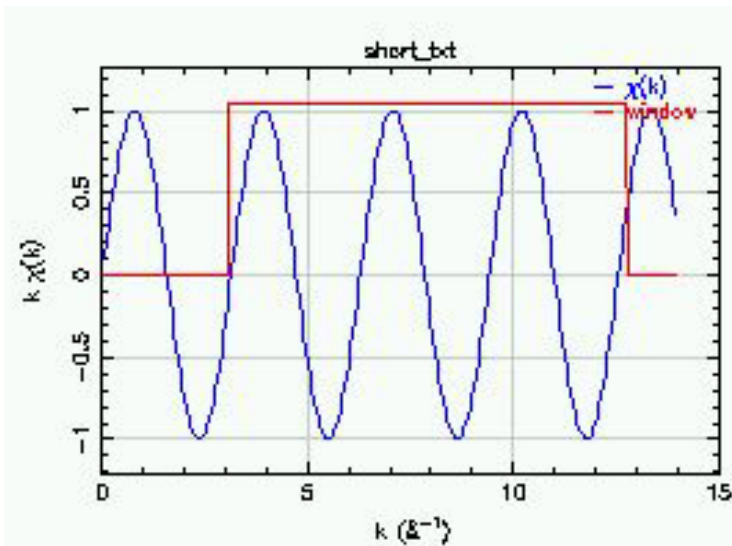
De-localized in k-space \Rightarrow localized in R-space



Localized in k-space \Rightarrow de-localized in R-space

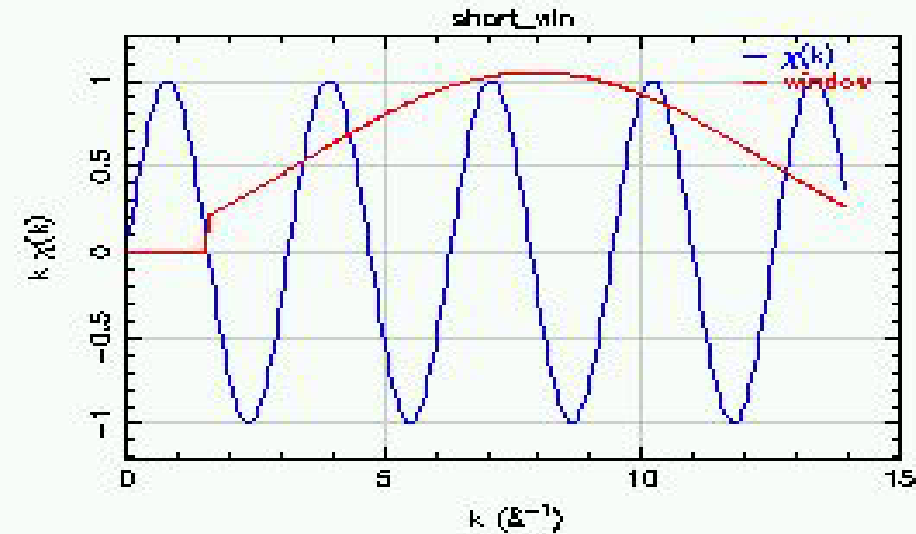


Fourier Transform is a frequency filter



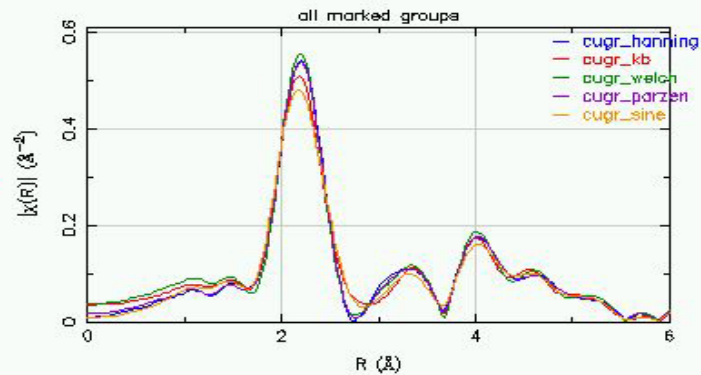
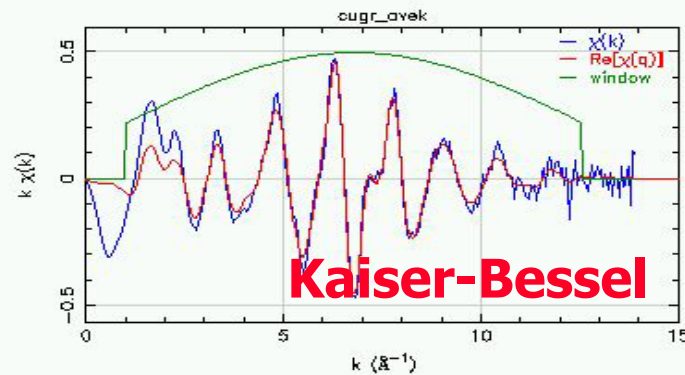
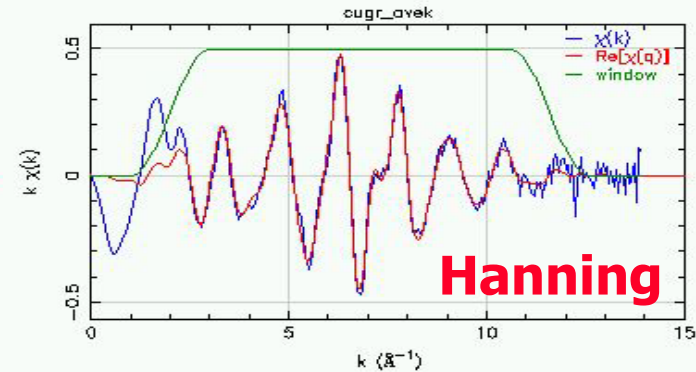
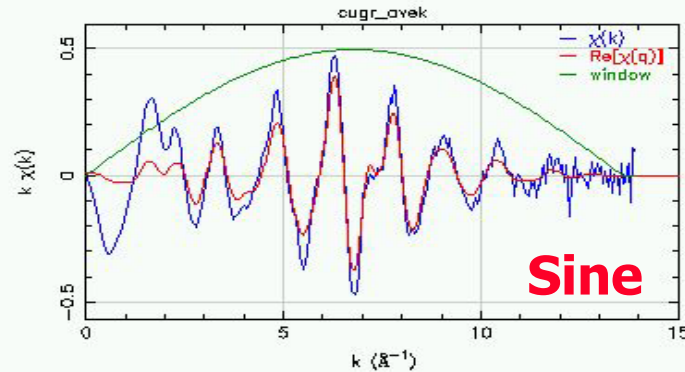
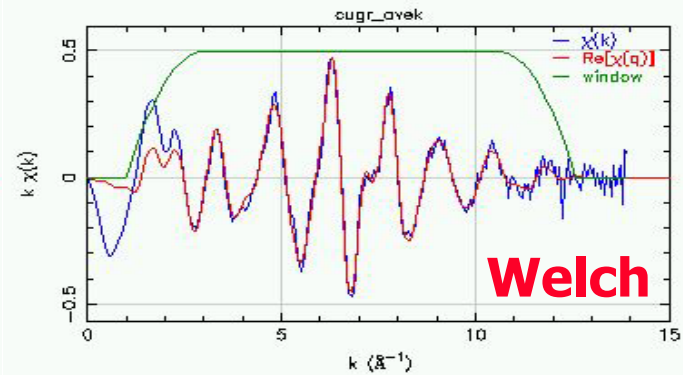
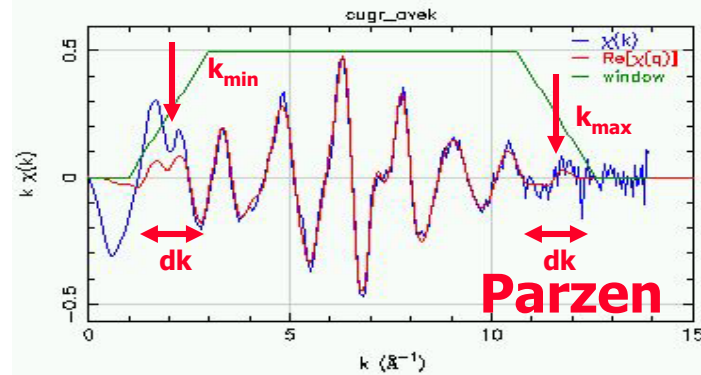
- The signal of a discrete sine wave is the sum of an infinite sine wave and a step function.
- FT of a discrete sine wave is a distorted peak.
- EXAFS data is a sum of discrete sine waves.
- Solution for finite data set is to multiply the data with a window.

Fourier Transform



- Multiplying the discrete sine wave by a window that gradually increases the amplitude of the data smoothes the FT of the data.

Fourier Transform Windows



Athena plotting in R-space

The screenshot shows the Athena software interface with the following sections:

- Project:** ocuments/Current Projects/foils/raw_data/Cufoil_10ID.prj
- Current group:** cufoil_003
- File:** /home/skelly/Xafs/Cu/Cu-Stds-Jan02/stds.prj
- Z:** Cu **Edge:** K **E shift:** 0 **Importance:** 1
- Background removal:** E0: 8977.068 ☒ Rbkg: 1 ☒ k-weight: 1 Edge step: 1.58688 ☒ fix step Pre-edge range: -150 ☒ to -30 ☒ Normalization range: 100 ☒ to 919.55 ☒ Spline range: k: 0.5 ☒ to 16.359 ☒ E: 0.952 ☒ to 1019.55 ☒
- Forward Fourier transform:** k-range: 2 ☒ to 16.359 ☒ dk: 2 window type: kaiser-bessel Phase correction: ☒ off arbitrary k-weight: 0.5
- Backward Fourier transform:** R-range: 1 ☒ to 3 ☒ dr: 0.5 window type: kaiser-bessel
- Plotting parameters:** plot multiplier: 1 y-axis offset: 0

On the right side, the **Plotting options** panel is visible, showing a list of groups and a set of checkboxes for plotting options. The **Plotting options** panel includes a list of groups (cufoil_003, cufoil_004, cufoil_005, cufoil_merge, cufoil_10k.001, cu_amp1nleg6td_1k.fit) and a set of checkboxes for plotting options. The **Plotting options** panel is circled in red, and the **Plotting options** panel is also circled in red.

The **Plotting options** panel includes the following options:

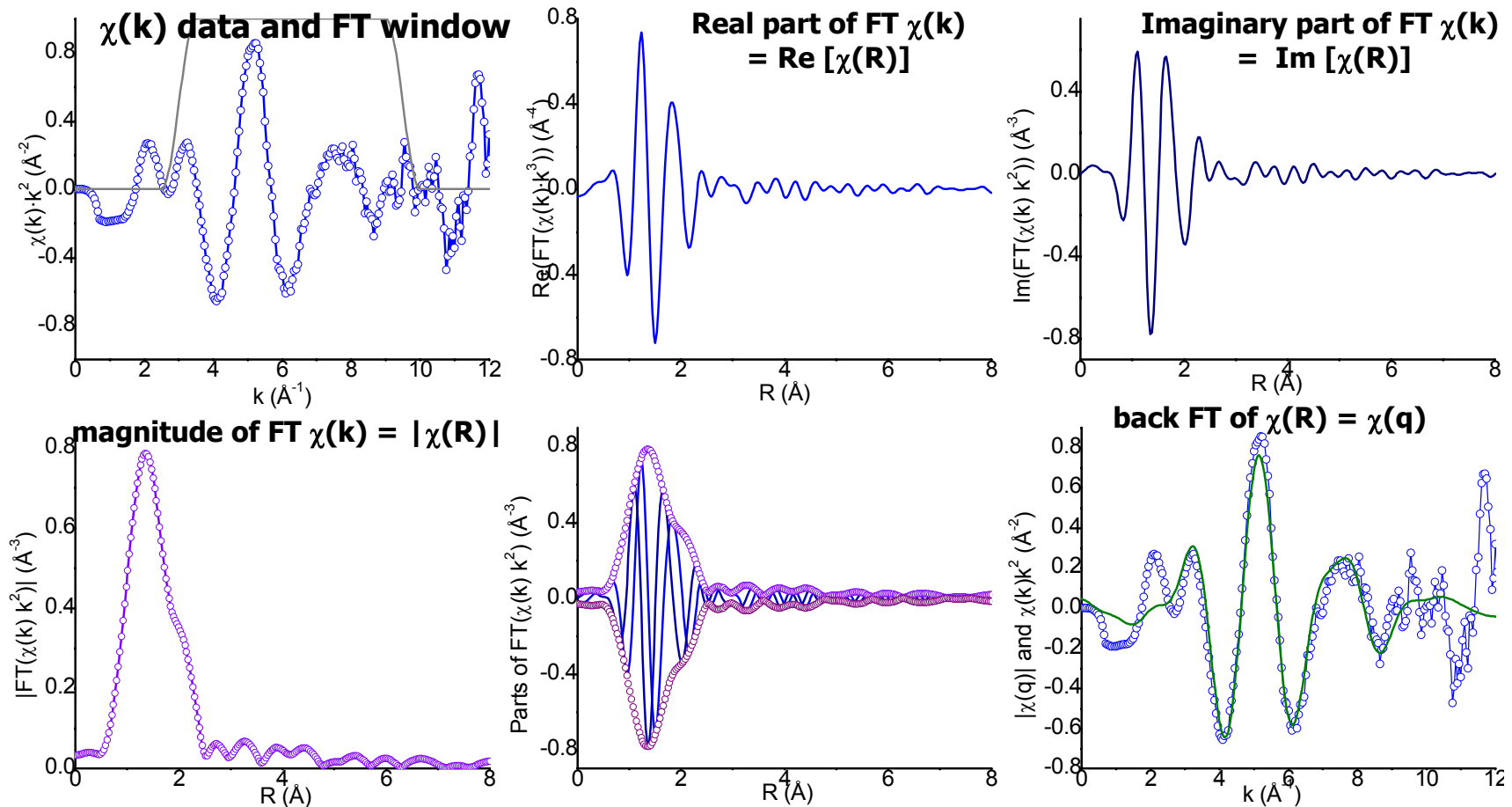
- ☒ mu(E)
- ☒ background
- ☒ pre-edge line
- ☒ post-edge line
- ☒ Normalized
- ☒ Derivative

The **Plotting options** panel also includes a section for **Plotting options** with the following options:

- ☒ E
- ☒ k
- ☒ R
- ☒ q
- ☒ kw

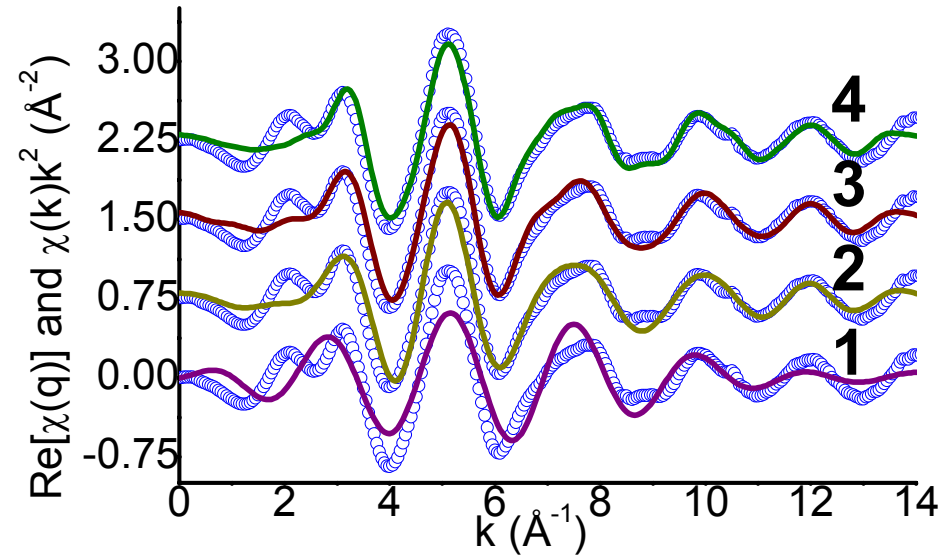
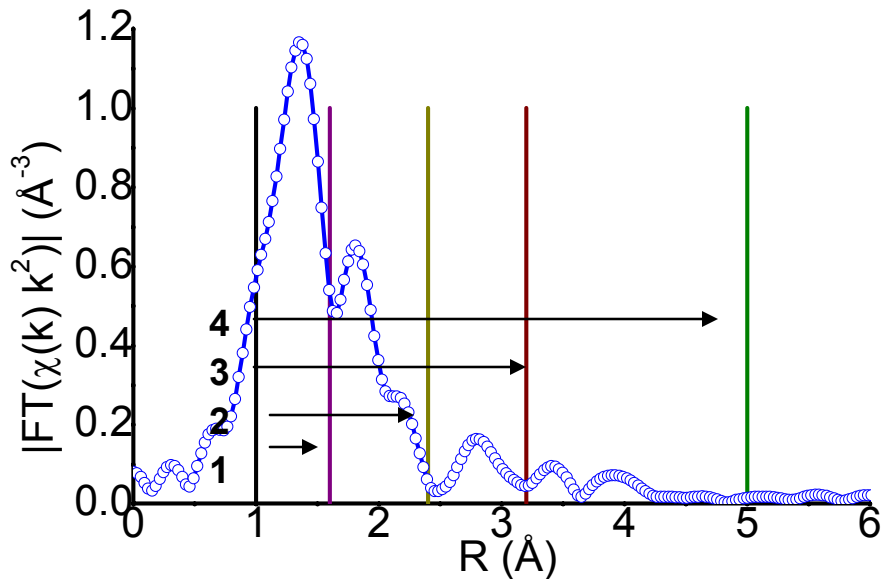
The status bar at the bottom indicates: plotting in energy from group 'cufoil_003' ... done!

Parts of the Fourier transform



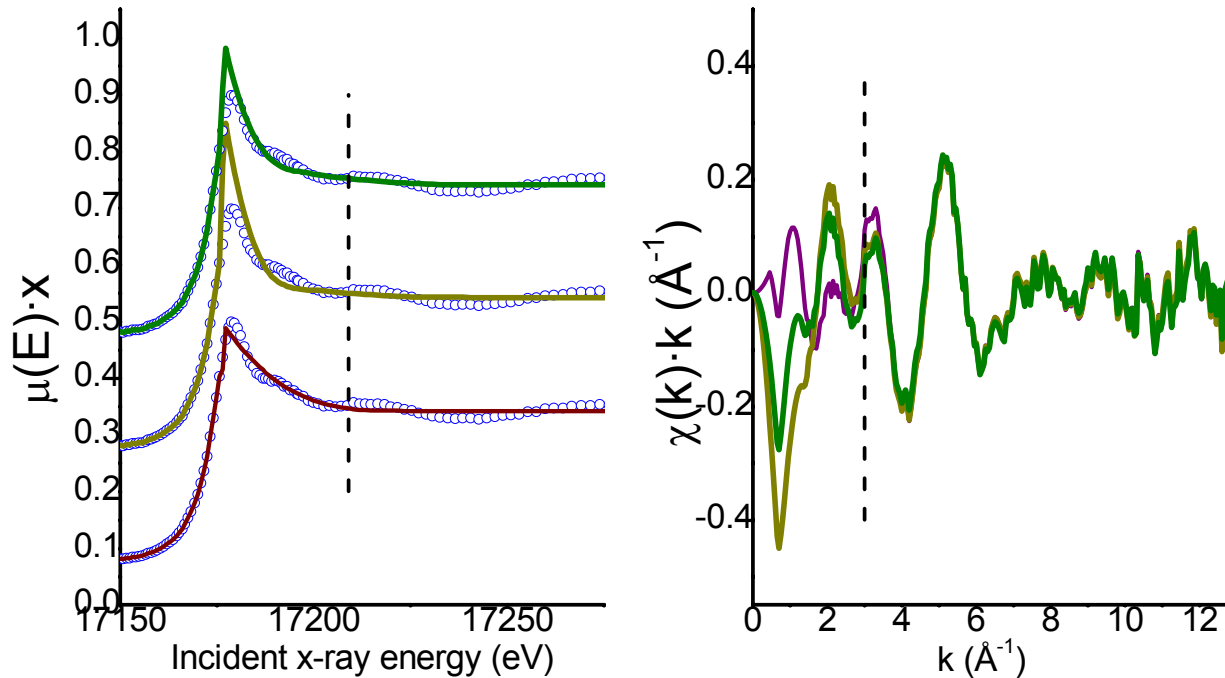
- The Magnitude of the Fourier transform does not contain as much information as the Real or Imaginary parts of the FT.

Backward Fourier transform



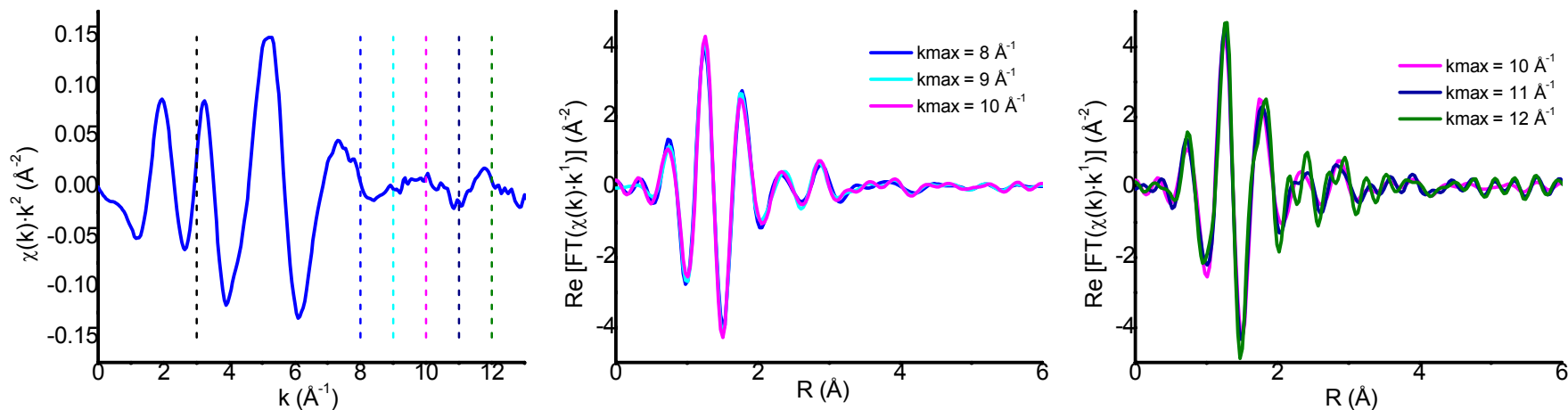
- Only the wavelengths that are contained in the back Fourier transform R range are present in the $\text{Re}[\chi(q)]$ spectra
- As a larger R range is included the back FT looks more like the original spectra (blue symbols)

How to Choose Minimum K of FT



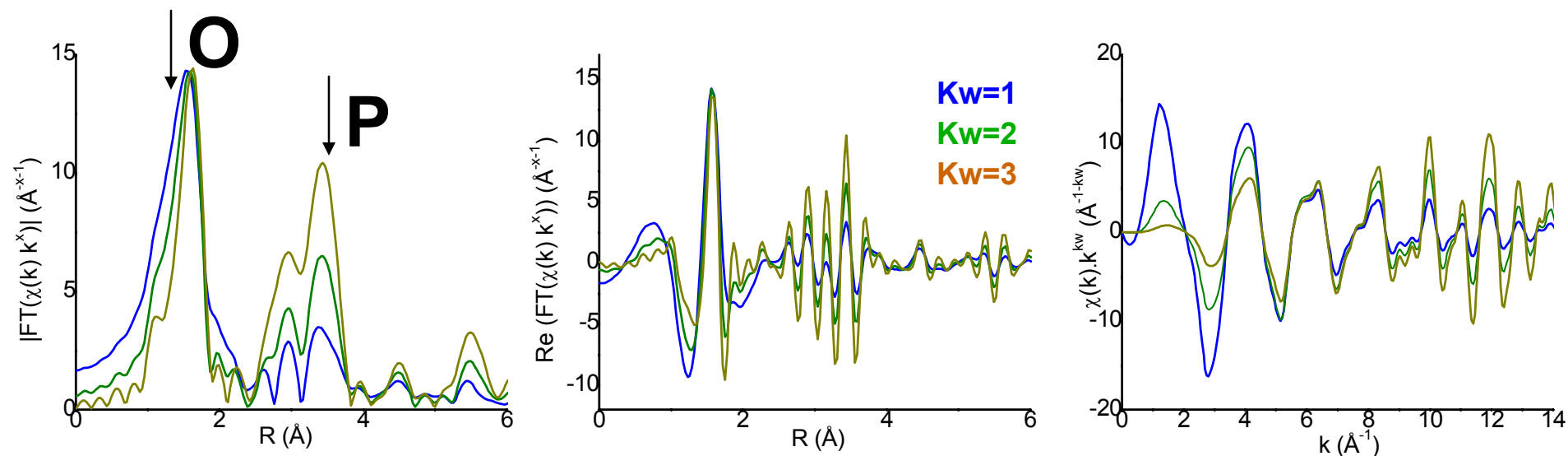
- **Choose Kmin in the region where the background doesn't change rapidly.**
 - Often around 2 to 4 Å⁻¹
 - Vary E_0 and plot the resulting χ spectra with low k-weight to determine the best value.

Choosing Maximum K-range



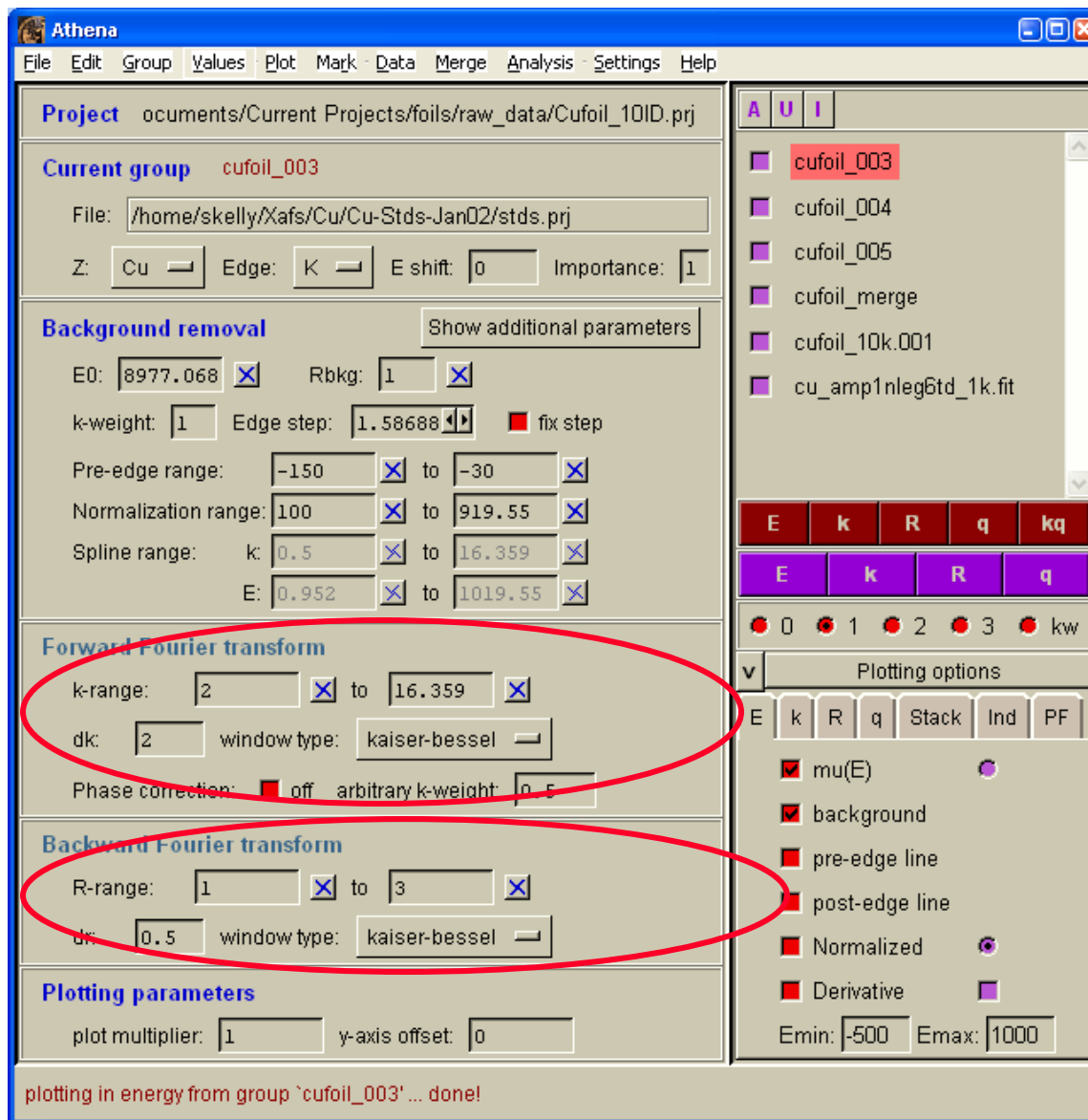
- The FT should be smooth and free of ringing
- To choose K_{max} make vary the k_{max} value and plot the data using the largest k -weight that will be used in modeling
- Look for ringing in the real or imaginary part of FT
- In the example above k_{max} of 10 or 11 \AA^{-1} best

Effect of K-weight on FT

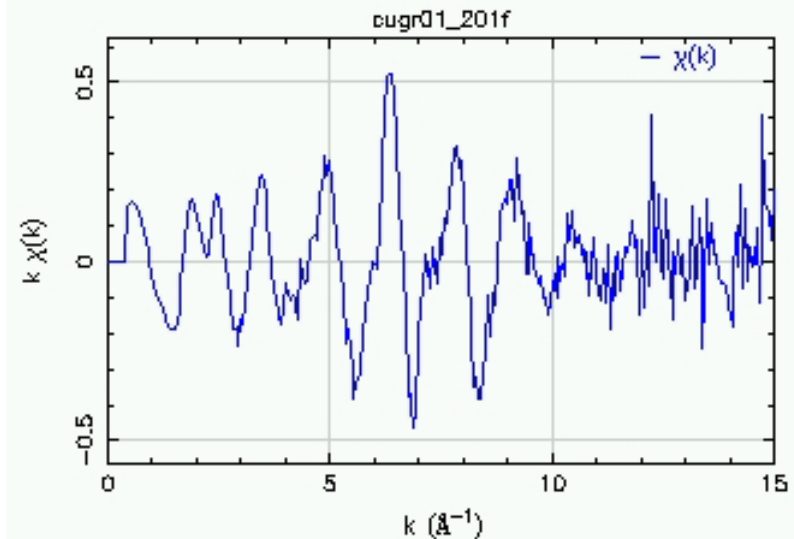
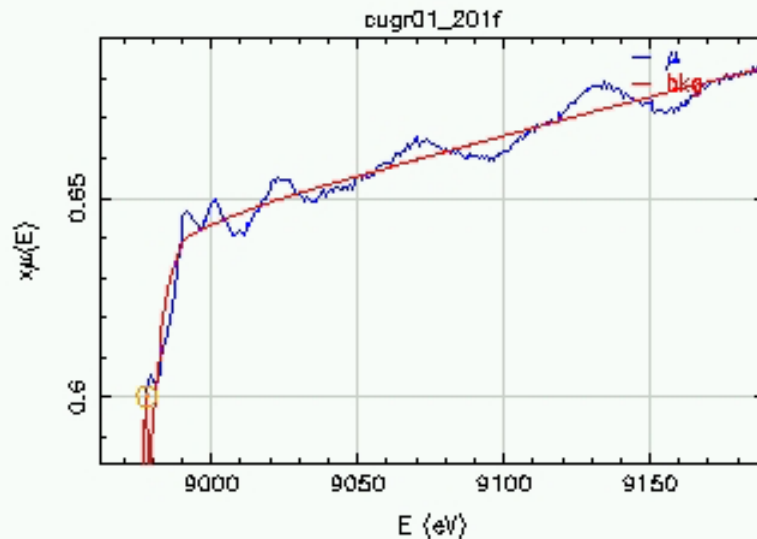


- These spectra have been k-weighted by 1, 2, and 3 and then rescaled so that the first peak in the FT are the same height
- The higher k-weight values give more importance to the data above 6\AA^{-1} , this emphasizes the signal due to the P neighbor relative to the O in the first shell

Fourier transform parameters in Athena

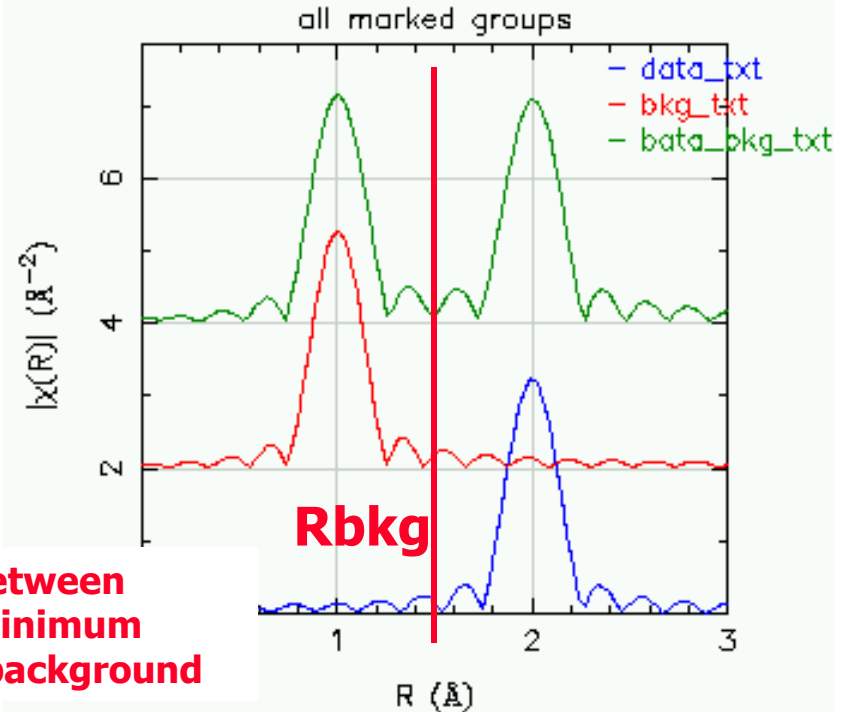
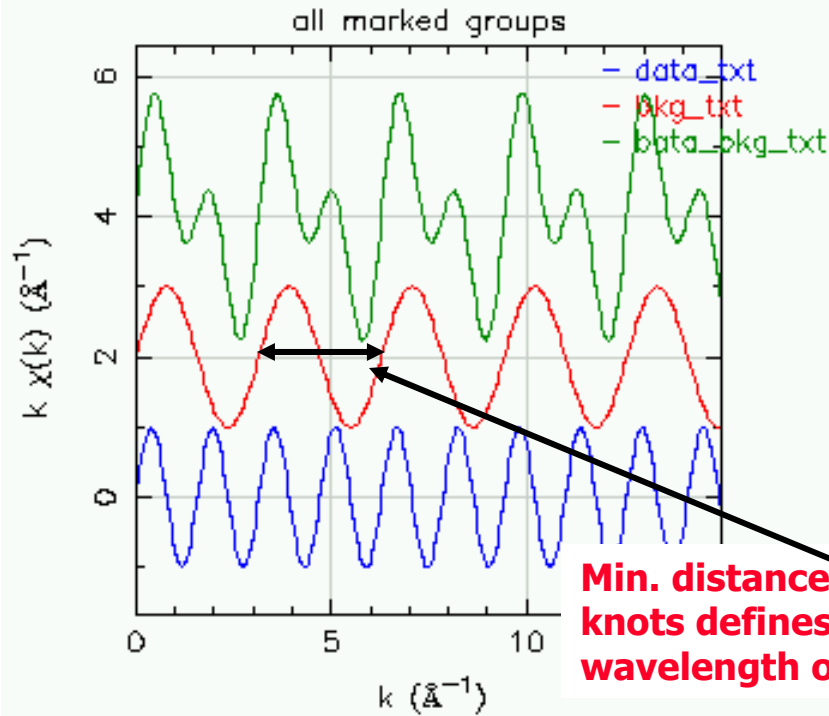


Background function overview



- A good background function removes long wavelength oscillations from $\chi(k)$.
- Constrain background so that it cannot contain oscillations that are part of the data.
- Long wavelength oscillations in $\chi(k)$ will appear as peaks in FT at low R-values
- FT is a frequency filter – use it to separate the data from the background!

Separating the background function from the data using Fourier transform



- Background function is made up of knots connected by 3rd order splines.
- Distance between knots is limited restricting background from containing wavelengths that are part of the data.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.

Rbkg value in Athena

The screenshot shows the Athena software interface with the following sections:

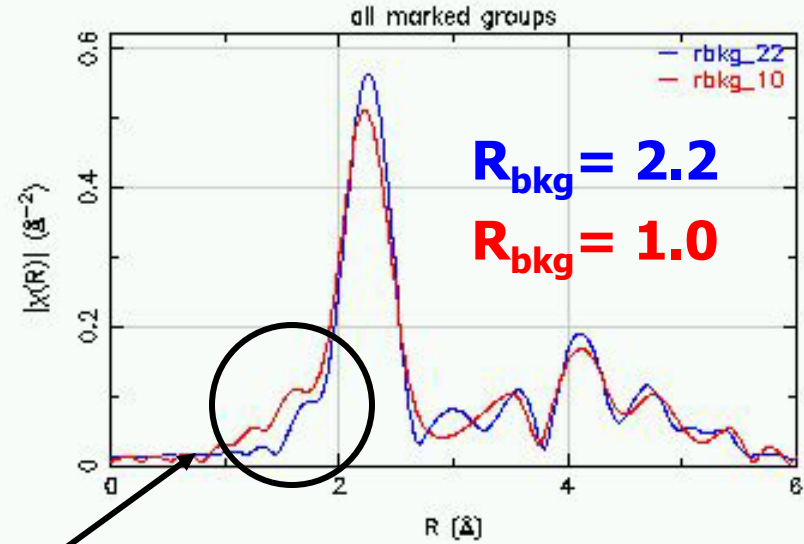
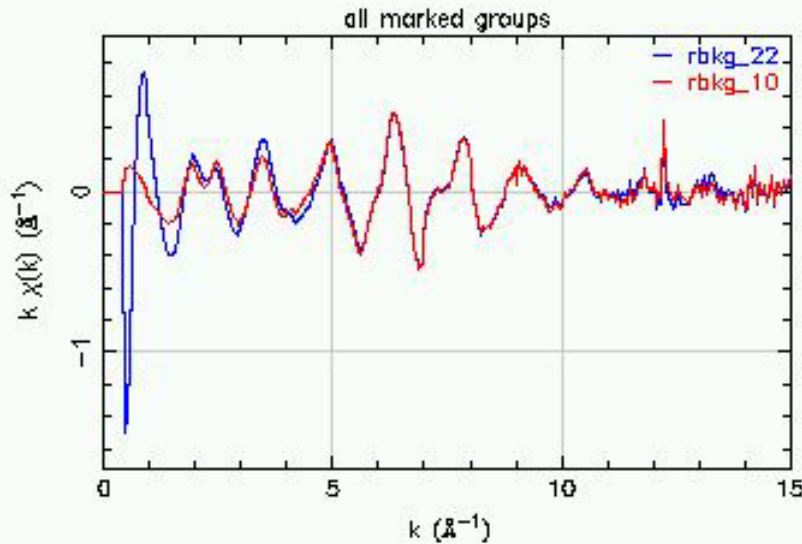
- Project:** ocuments/Current Projects/foils/raw_data/Cufoil_10ID.prj
- Current group:** cufoil_003
- File:** /home/skelly/Xafs/Cu/Cu-Stds-Jan02/stds.prj
- Z:** Cu **Edge:** K **E shift:** 0 **Importance:** 1
- Background removal:**
 - E0:** 8977.068 ☒
 - Rbkg:** 1 ☒ (highlighted with a red circle)
 - k-weight:** 1 **Edge step:** 1.58888 ☒ **fix step**
 - Pre-edge range:** -150 ☒ to -30 ☒
 - Normalization range:** 100 ☒ to 919.55 ☒
 - Spline range:** k: 0.5 ☒ to 16.359 ☒ E: 0.952 ☒ to 1019.55 ☒
- Forward Fourier transform:**
 - k-range:** 2 ☒ to 16.359 ☒
 - dk:** 2 **window type:** kaiser-bessel
 - Phase correction:** ☒ off **arbitrary k-weight:** 0.5
- Backward Fourier transform:**
 - R-range:** 1 ☒ to 3 ☒
 - dr:** 0.5 **window type:** kaiser-bessel
- Plotting parameters:**
 - plot multiplier:** 1 **y-axis offset:** 0

Plotting options:

- ☒ mu(E)
- ☒ background
- ☒ pre-edge line
- ☒ post-edge line
- ☒ Normalized
- ☒ Derivative
- Emin:** -500 **Emax:** 1000

plotting in energy from group 'cufoil_003' ... done!

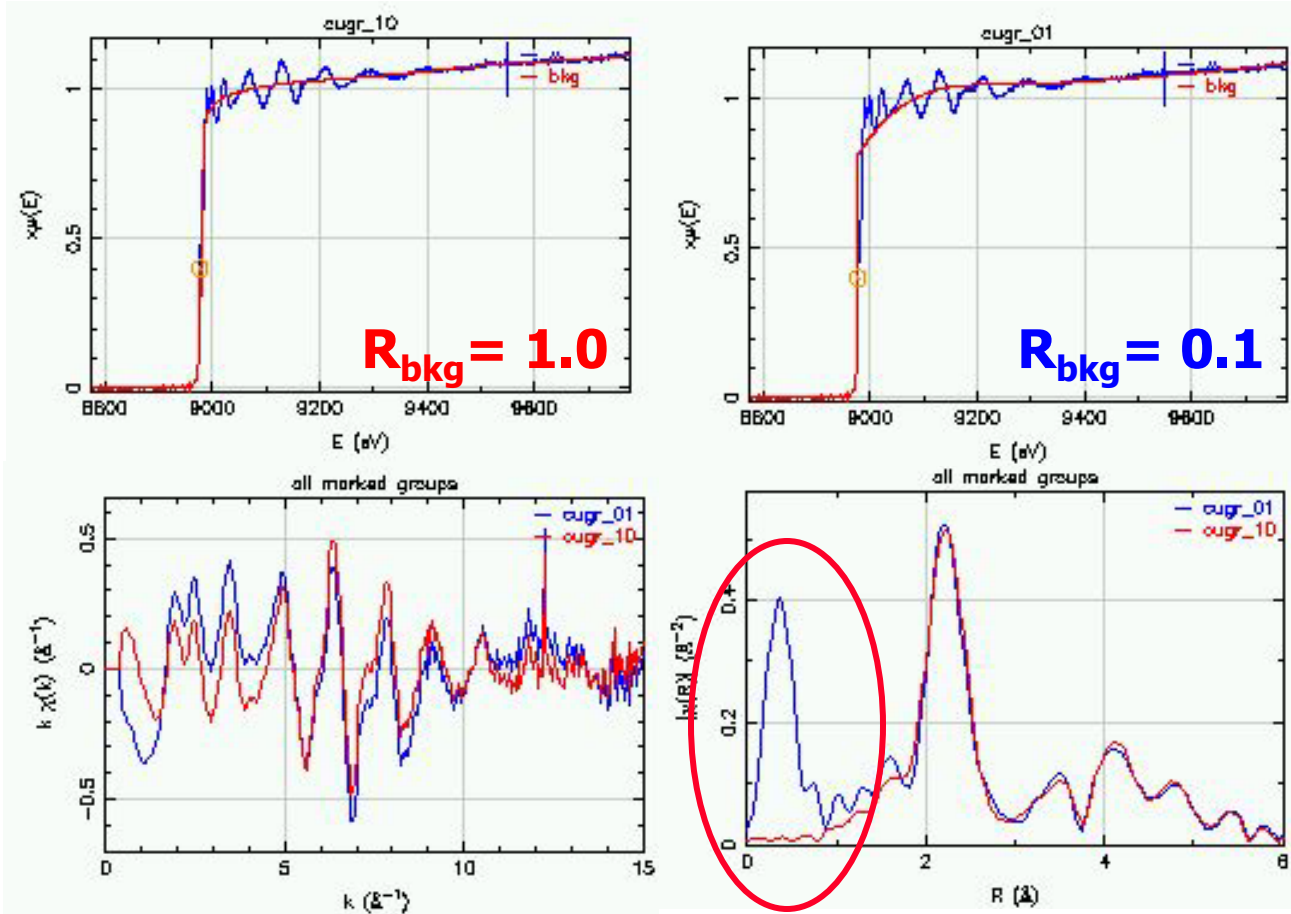
How to choose R_{bkg} value



A Hint that R_{bkg} may be too large.
Data should be smooth, not pinched!

- An example where background distorts the first shell peak.
- R_{bkg} should be about half the R value for the first peak.

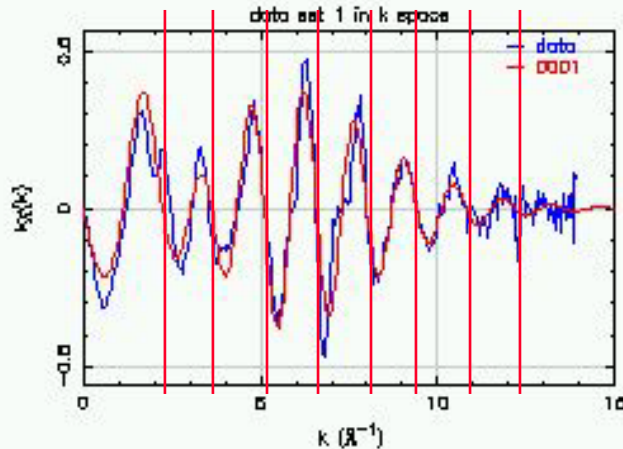
FT and Background function



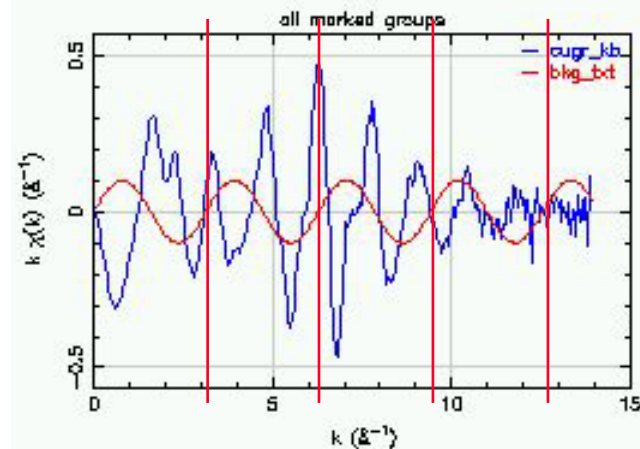
- An example where long wavelength oscillations appear as (false) peak in the FT

Frequency of Background function

Data contains this and shorter wavelengths



Bkg contains this and longer wavelengths

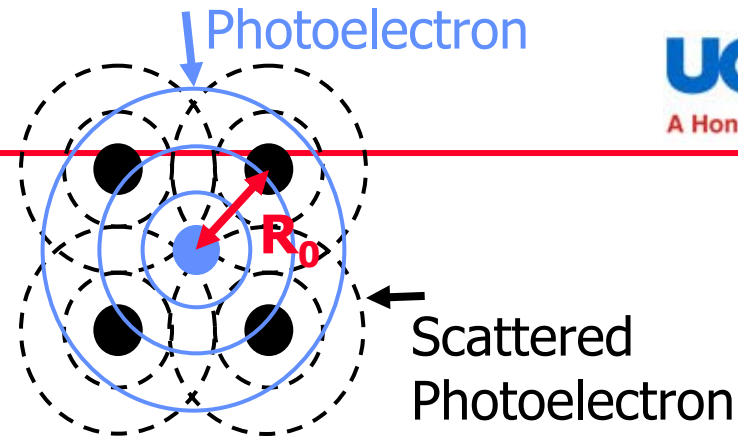


- Constrain background so that it cannot contain wavelengths that are part of the data.
 - Use information theory, number of knots = $2 R_{\text{bkg}} \Delta k / \pi$
 - 8 knots in bkg using $R_{\text{bkg}}=1.0$ and $\Delta k = 14.0$
- Background may contain only longer wavelengths. Therefore knots are not constrained.

The EXAFS Equation

$$\chi(k) = \sum_i \chi_i(k)$$

with



$$\chi_i(k) = \text{Im} \left(\frac{(N_i S_0^2) F_i(k)}{k R_i^2} \exp(i(2kR_i + \phi_i(k))) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 m_e (E - E_0) / \hbar$$

Theoretically calculated values

$F_i(k)$ effective scattering amplitude
 $\phi_i(k)$ effective scattering phase shift
 $\lambda(k)$ mean free path

Starting values

R_0 initial path length

Parameters often determined from a fit to data

N_i degeneracy of path
 S_0^2 passive electron reduction factor
 σ_i^2 mean squared displacement of half-path length
 E_0 energy shift
 ΔR change in half-path length

- www.xafs.org
- Kelly, S D, Hesterberg, D and Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In *Methods of soil analysis, Part 5 -Mineralogical methods*; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, USA, 2008; pp 367.