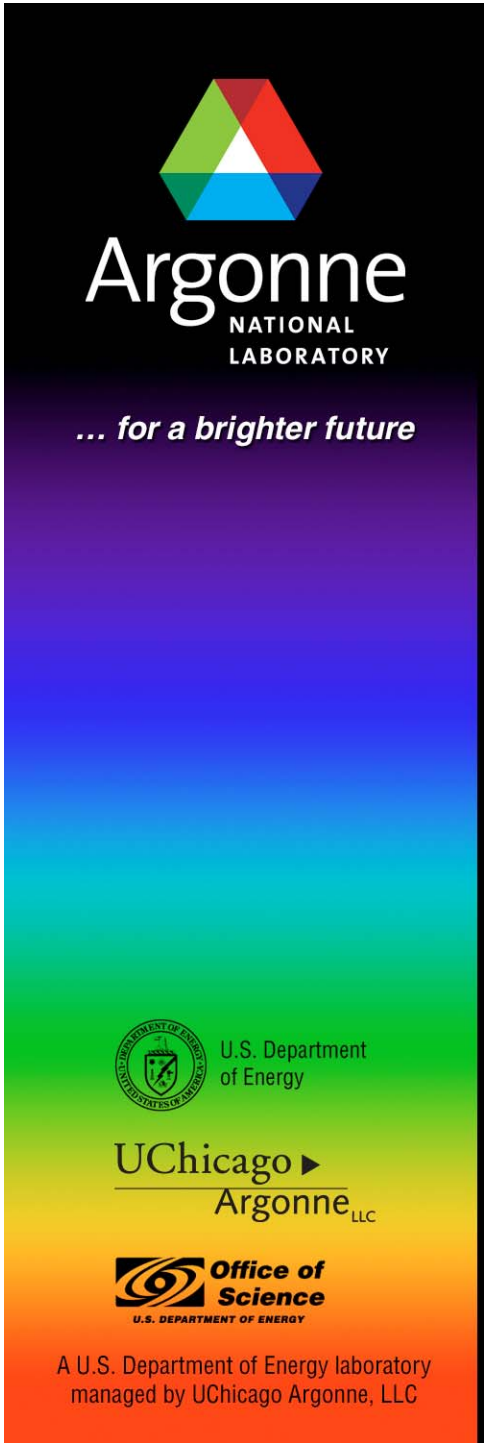


XAS Data Processing

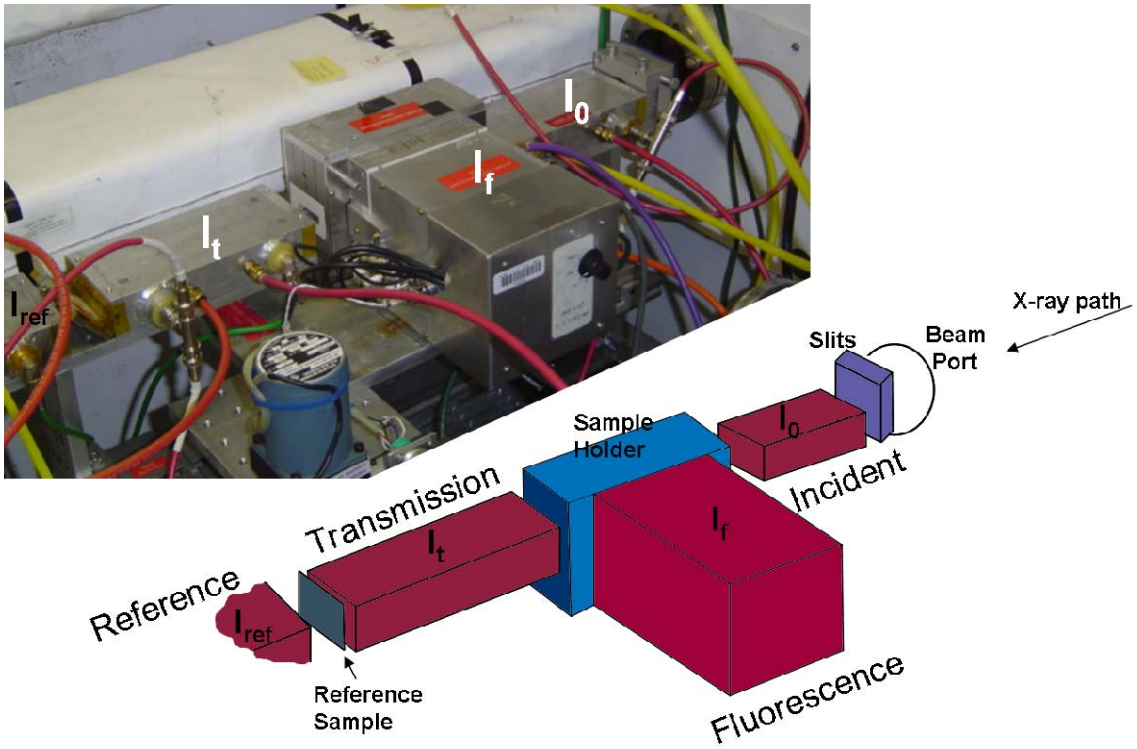
Shelly Kelly

Argonne National Laboratory

Outline

- X-ray absorption signal
- Reference spectra
- Aligning and merging EXAFS signals
- Normalizing EXAFS spectra
- Conversion from energy to wavenumber
- Basics of Fourier transforms
- Background functions
- Fourier transform k-weights
- EXAFS Equation

X-ray Absorption Measurement

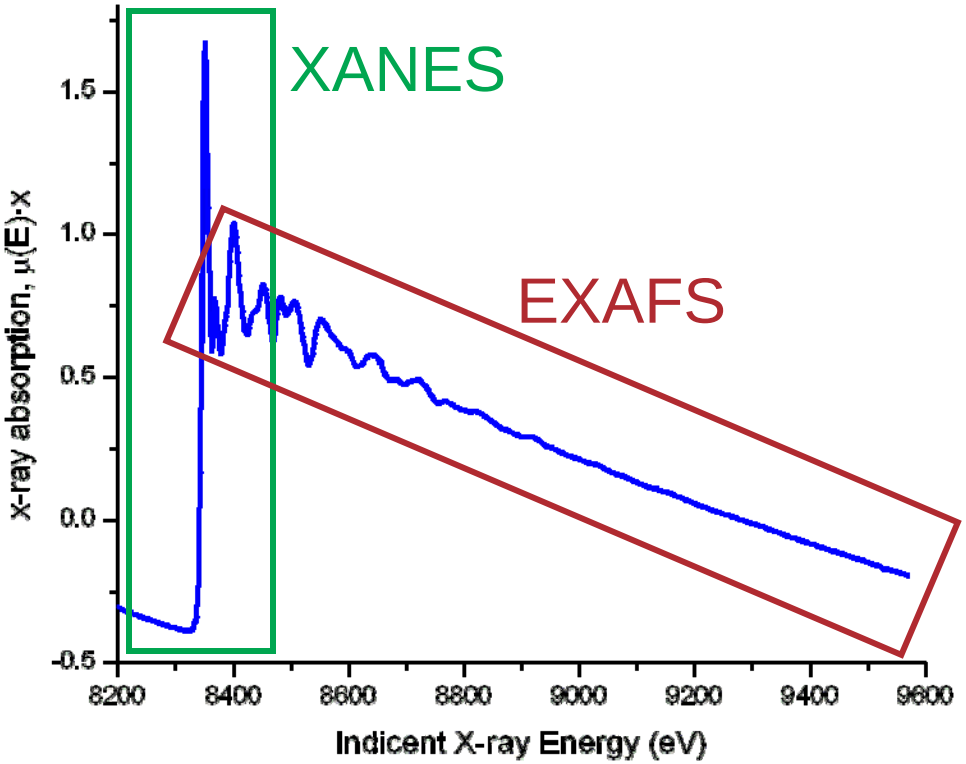


$$I_t = I_0 e^{-\mu \cdot x}$$

$$\mu \cdot x \propto \frac{I_f}{I_O}$$

The number of X-rays transmitted (I_t) through a sample is given the intensity of X-rays impinging on the sample (I_0) decreased exponentially by the thickness of the sample (x) and the absorption coefficient of the sample (μ)

X-ray Absorption Cross Section



Transmission Signal

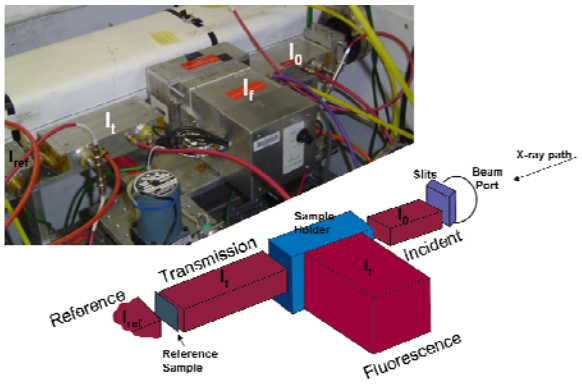
$$\mu \cdot x = \ln\left(\frac{I_0}{I_t}\right)$$

Fluorescence Signal

$$\mu \cdot x \propto \frac{I_f}{I_O}$$

- XAS: X-ray Absorption Spectroscopy
  - XANES: X-ray Absorption Near Edge Structure
  - EXAFS: Extended X-ray Absorption Fine Structure

Reference Spectra



Reference Placed in beam behind sample

$$\mu \cdot x = \ln\left(\frac{I_t}{I_{ref}}\right)$$

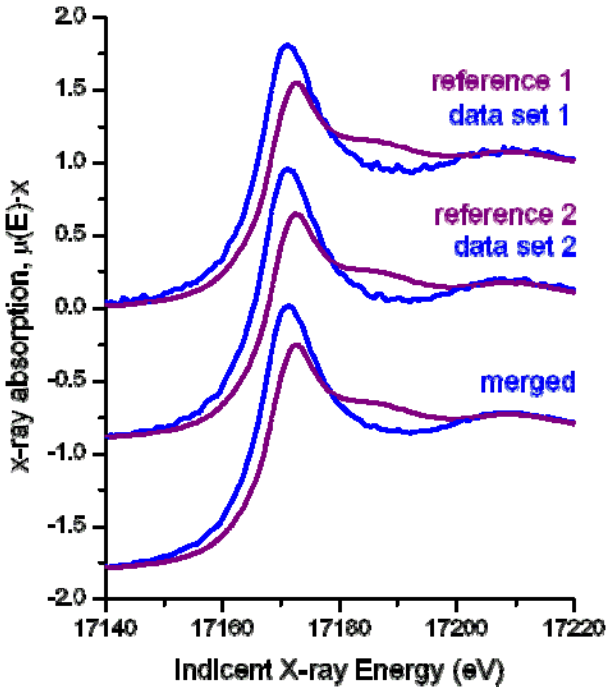
Reference placed beside beam[1]

$$\mu \cdot x = \ln\left(\frac{I_0}{I_{ref}}\right)$$

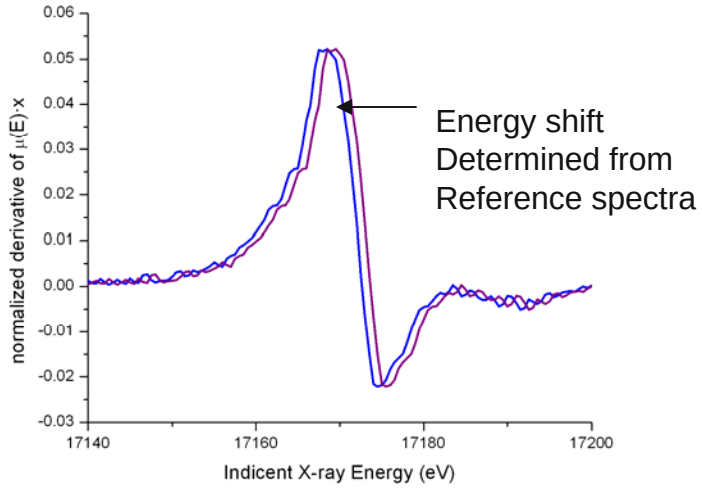
- X-ray absorption spectra should be checked for alignment before the spectra are averaged.
- A reference spectra can be collected with each sample spectra for this purpose.
  - Reference place behind transmission ionization chamber
  - Reference placed beside x-ray beam with a pin diode detector (for samples that do not transmit x-rays)
- The reference spectra are then shifted in energy so that their absorption edges are aligned and the shift is applied to the corresponding sample spectrum

[1]Cross J. O. and Frenkel A. I. (1998) Use of scattered radiation for absolute energy calibration. *Rev. Sci. Instrum.* **70**, 38-40.

Aligning and Averaging Spectra

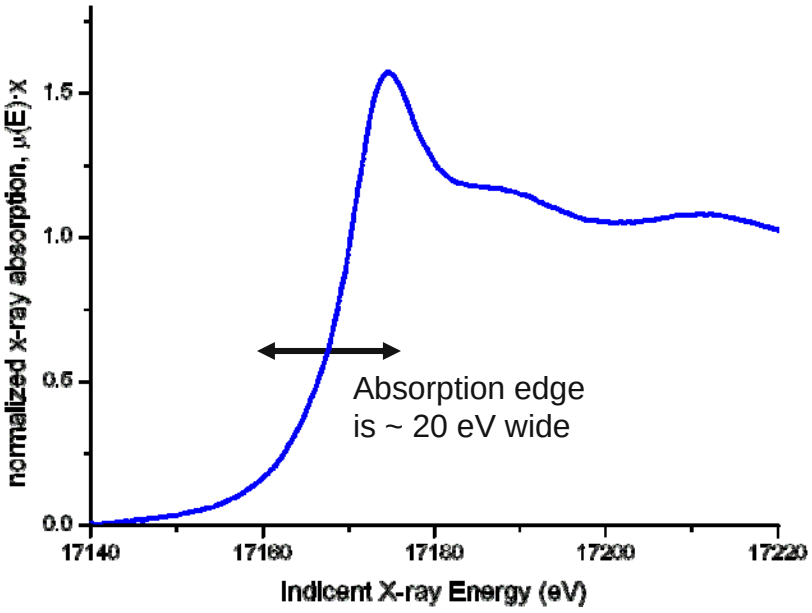


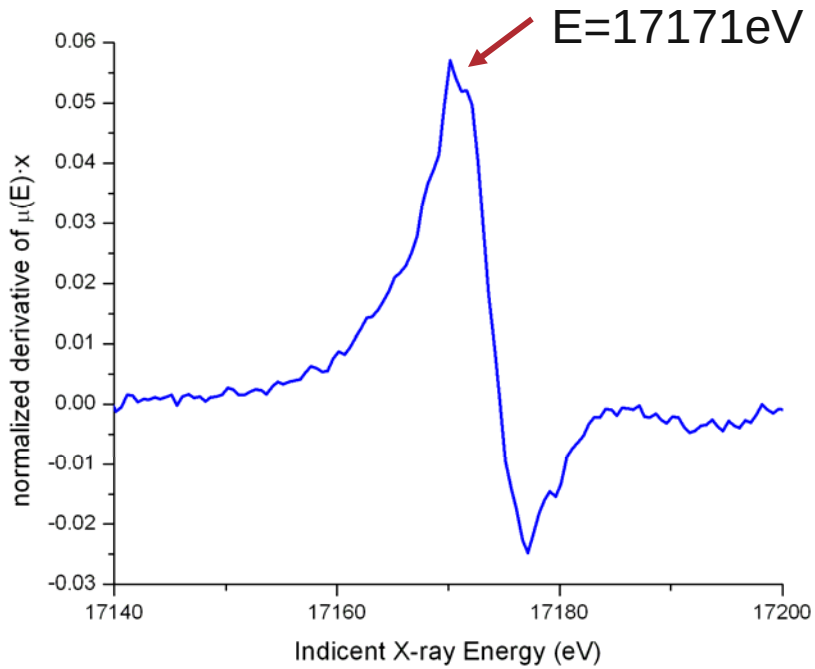
Derivative of Reference Spectra Edge



- Procedure
  - Reference spectrum 2 is aligned to reference spectrum 1 using derivative of edge
  - Data set 2 and reference 2 are shifted by the amount determined.
  - Data sets 1 and 2 are merged.
- It is good practice to align all the spectra to the same reference spectra for a given project.
- Data are often averaged as absorption spectra

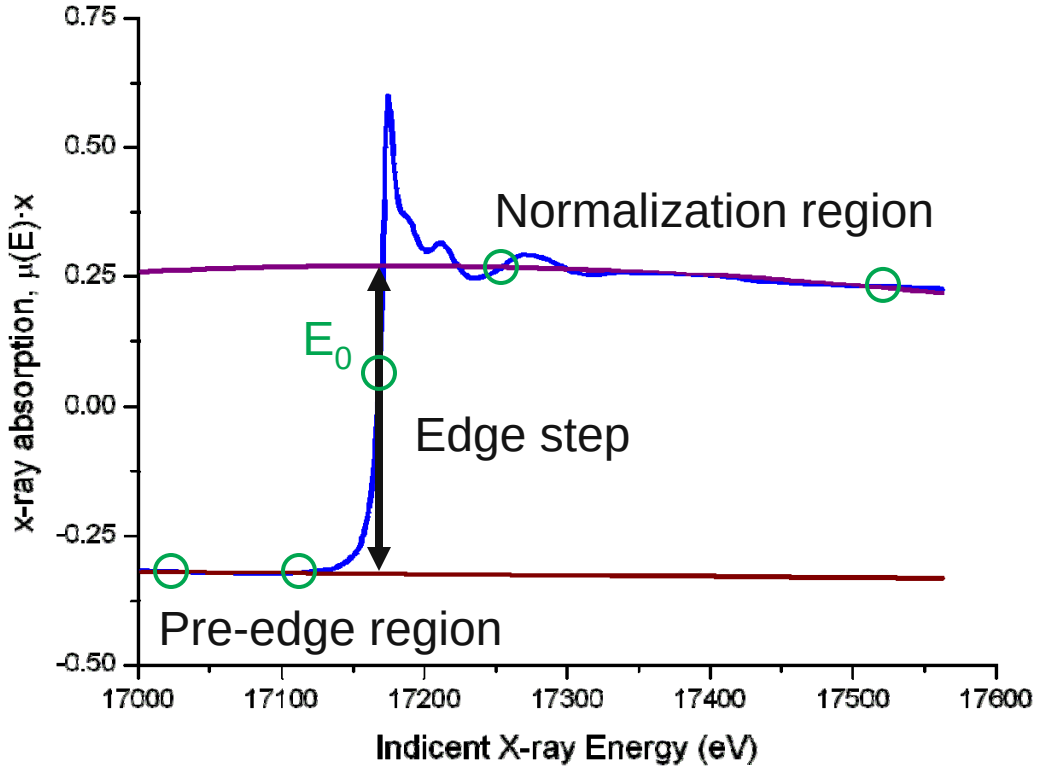
Edge Energy





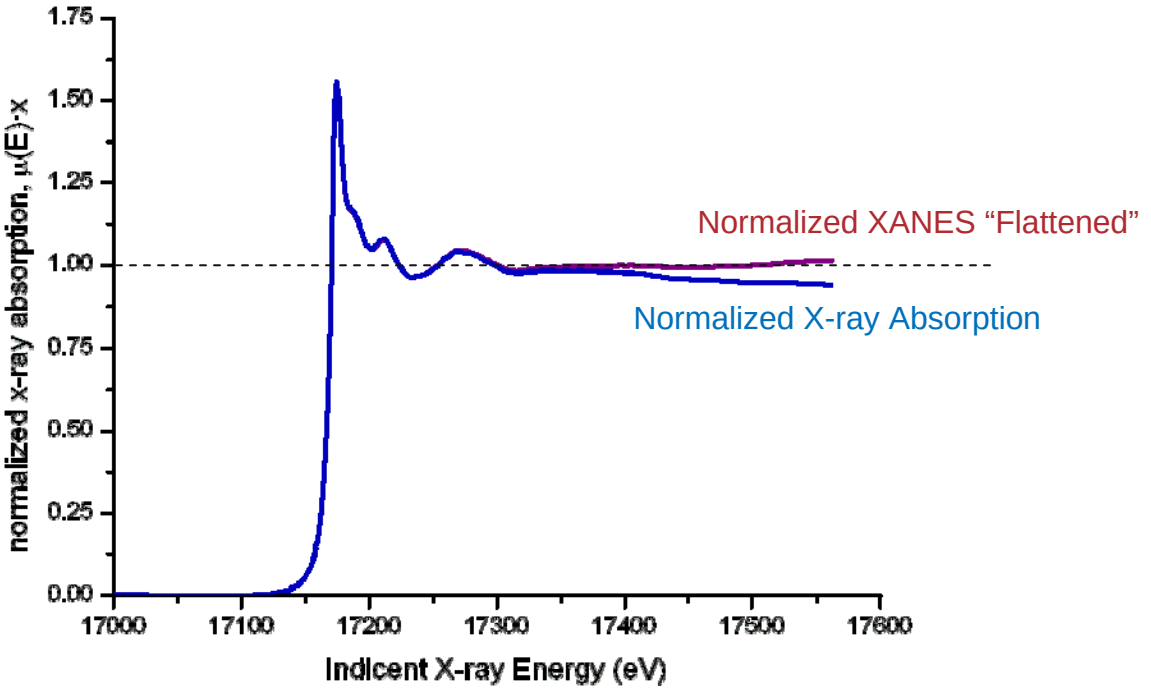
- The U L_{III}-edge absorption energy for U is defined as 17166 eV.
- The measured absorption edge is broad covering many eV.
- The first derivative of the edge for U(VI) is by convention set to 17171 eV and is useful for XANES comparisons.
- For EXAFS analysis E_0 (the edge energy) is used to defined k = 0 $Å^{-1}$and is used to align the measured spectra to theoretical calculations.

Normalized X-ray Absorption Spectra



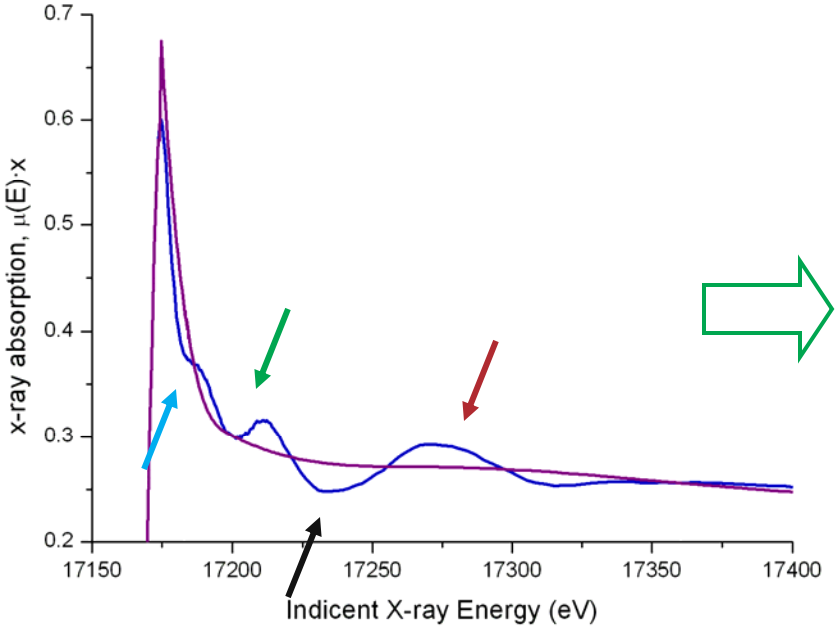
- Pre-edge line 200 to 50 eV before the edge
- Normalization line 100 to ~400 eV after the edge
- Edge step the change in the absorption coefficient at the edge
  - Evaluated by taking the difference of the pre-edge and normalization lines at E_0

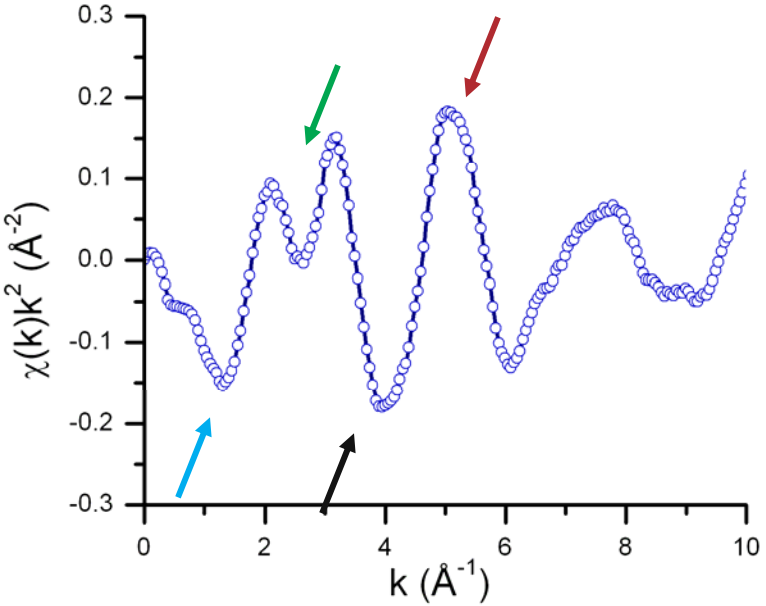
Normalized X-ray Absorption Spectra



- Normalized X-ray Absorption Spectra is calculated by subtracting the pre-edge line from the entire spectra and dividing the entire spectra by the absorption edge step
- Athena has an extra feature used to flatten the absorption spectra above the edge, which can be helpful for comparing XANES spectra from different detectors.

Conversion from Energy to Wavenumber





$$k^2 = \frac{2m_e\left(E - E_0 + \Delta E_0\right)}{\hbar}$$

Mass of electron

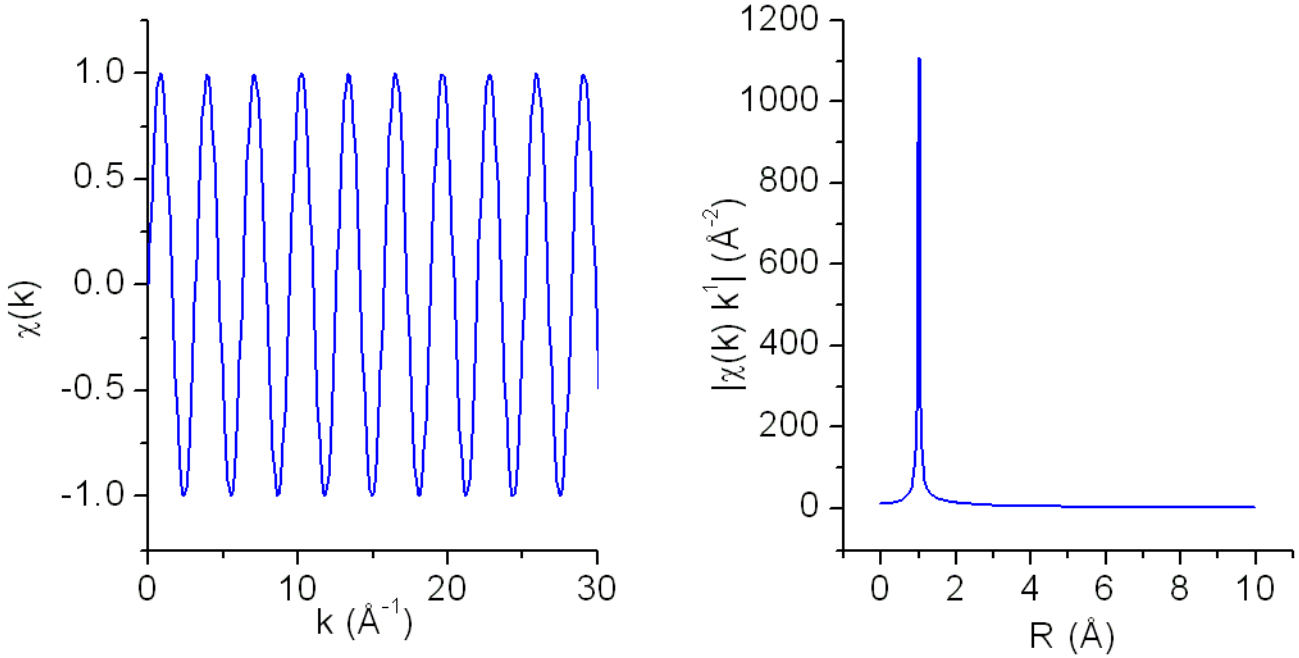
Energy above edge

Energy shift to align data to theory

wavenumber

Plank's constant

Fourier Transforms

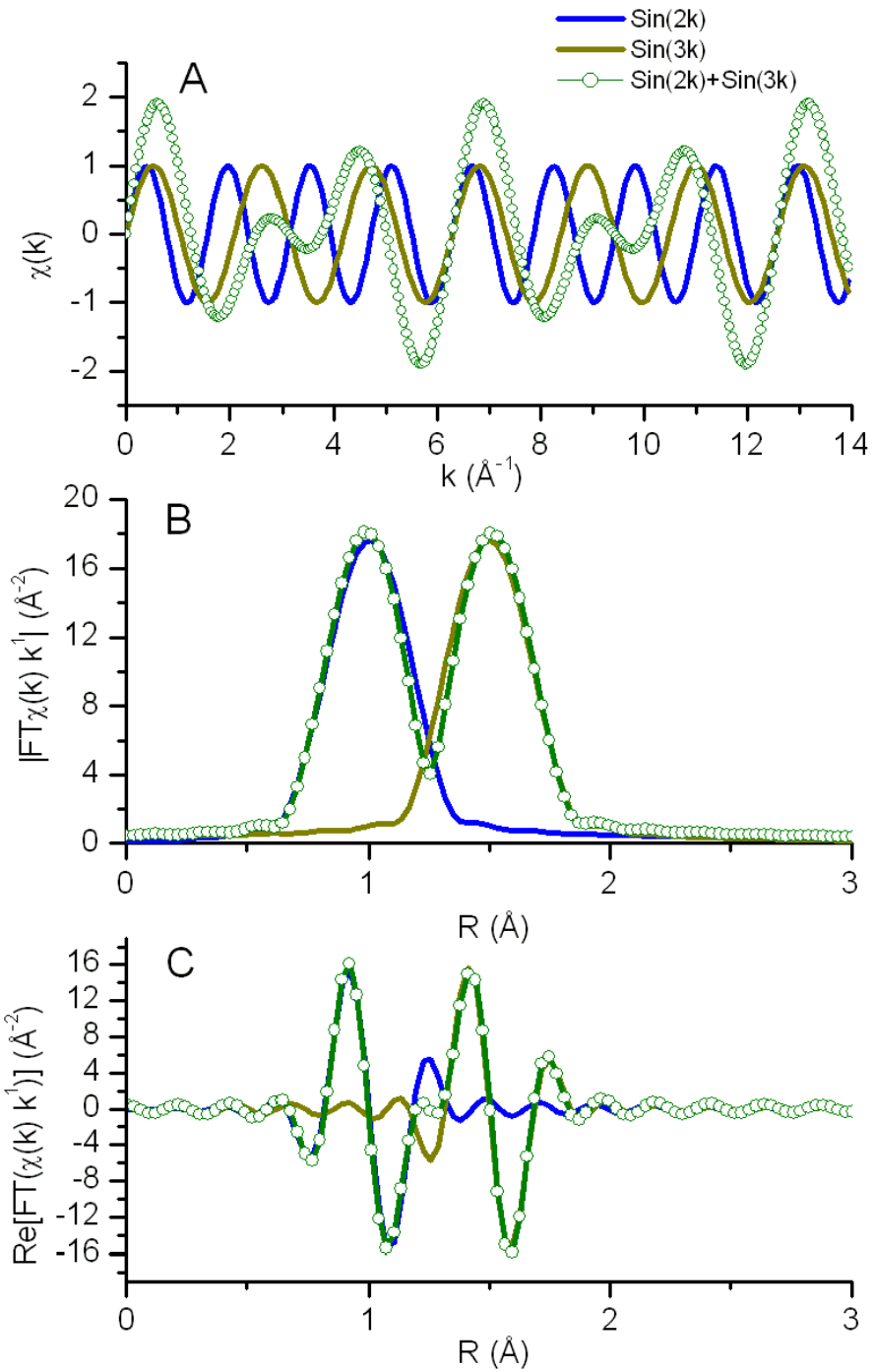


- Fourier transform of an infinite sign wave with a single phase of 2k is a delta function at R = 1 Å.
- Signal that is de-localized in k-space is localized in R-space
- FT is a frequency filter

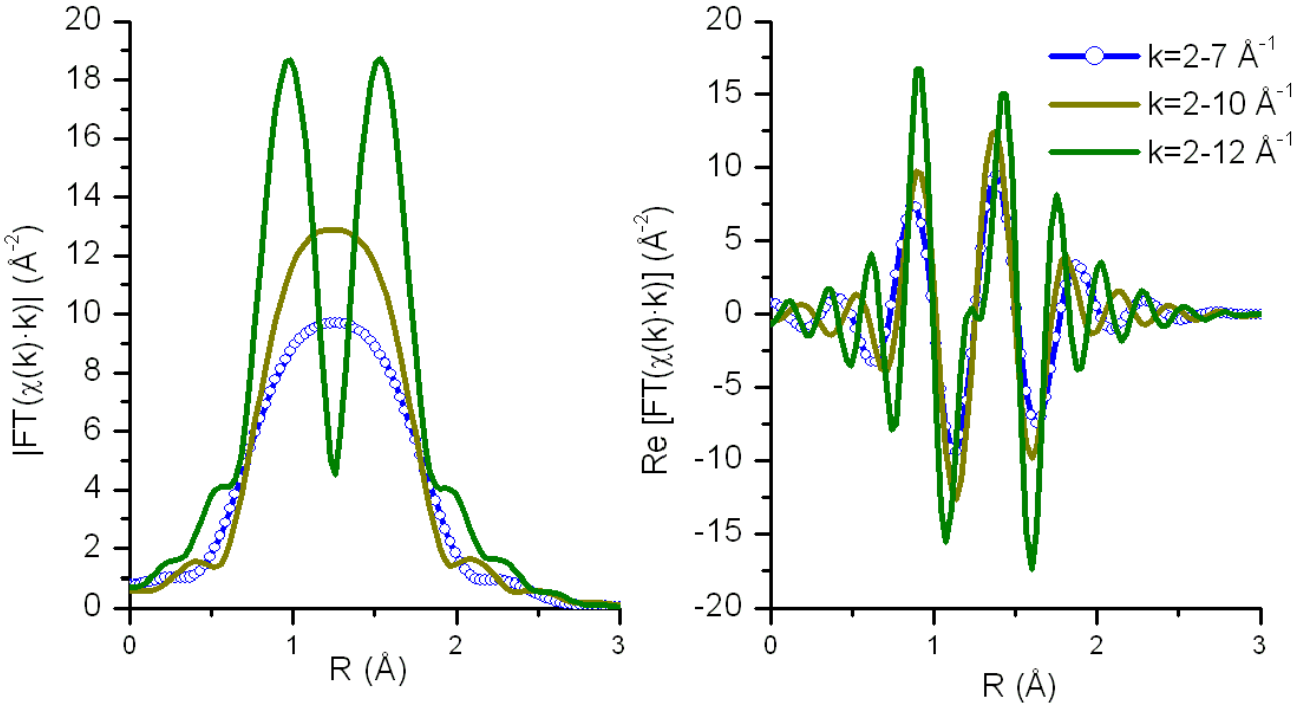
FT of two phase sine wave

- The Fourier transform of finite data range is a broad peak rather than a delta function
- The real part of the FT is a sum of the components of the FT of each sine wave
- The information content of a FT signal is given by Nyquist theorem

$$N_{IP} = \frac{2}{\pi} \cdot \Delta k \cdot \Delta R + 1$$



Information Content in the Fourier Transform

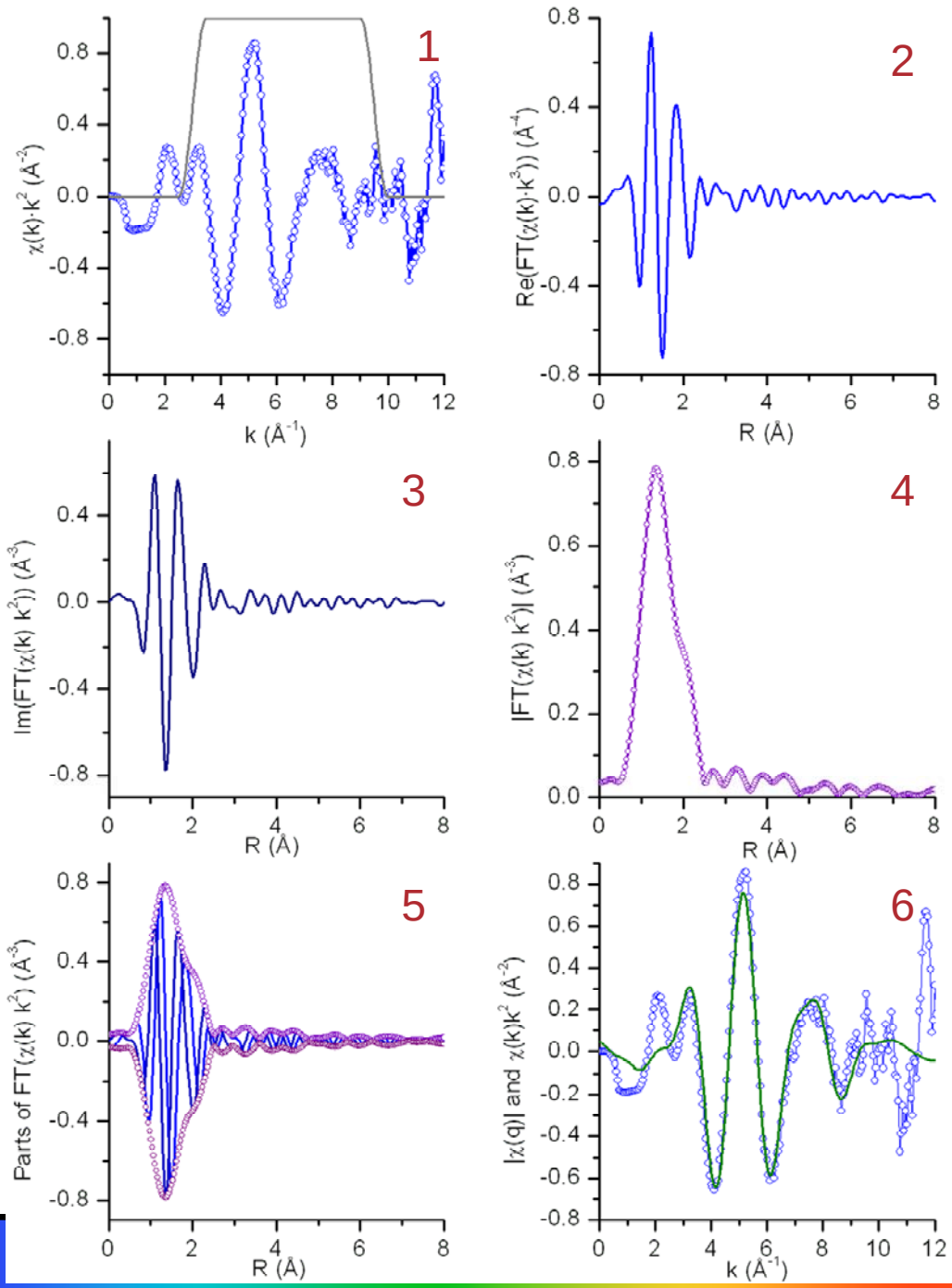


- Increasing the k-range included in the Fourier transform increases the information contained in the Fourier transformed signal
- All signals are included in the FT from k=0 and there content is carried to the FT signal
- The resolution given in these signals is R = 0.3 Å 0.2 Å and 0.15 Å, hence the signal separated by 1 Å can be resolved even with the lowest k-range

Parts of Fourier Transform

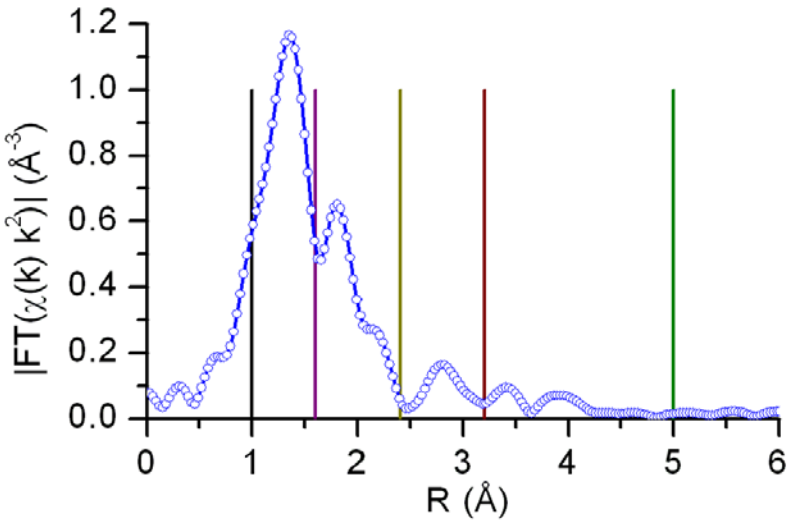
- 1: EXAFS spectra and window function
- 2: Real part of FT
- 3: Imaginary part of FT
- 4: Magnitude of FT
- 5: Real, imaginary, magnitude and inverse of magnitude of FT
- 6: EXAFS spectra and back Fourier transformed spectra

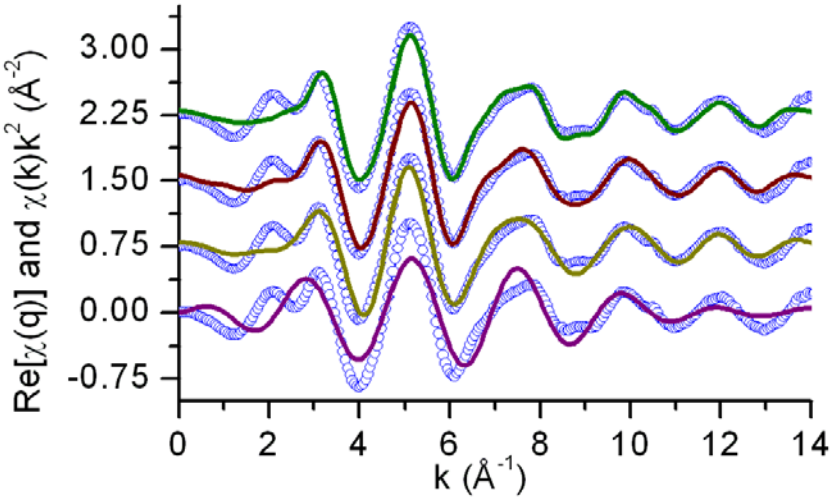
- The real and imaginary parts of the Fourier transform contain more information than the magnitude of the FT.



Back Fourier Transform

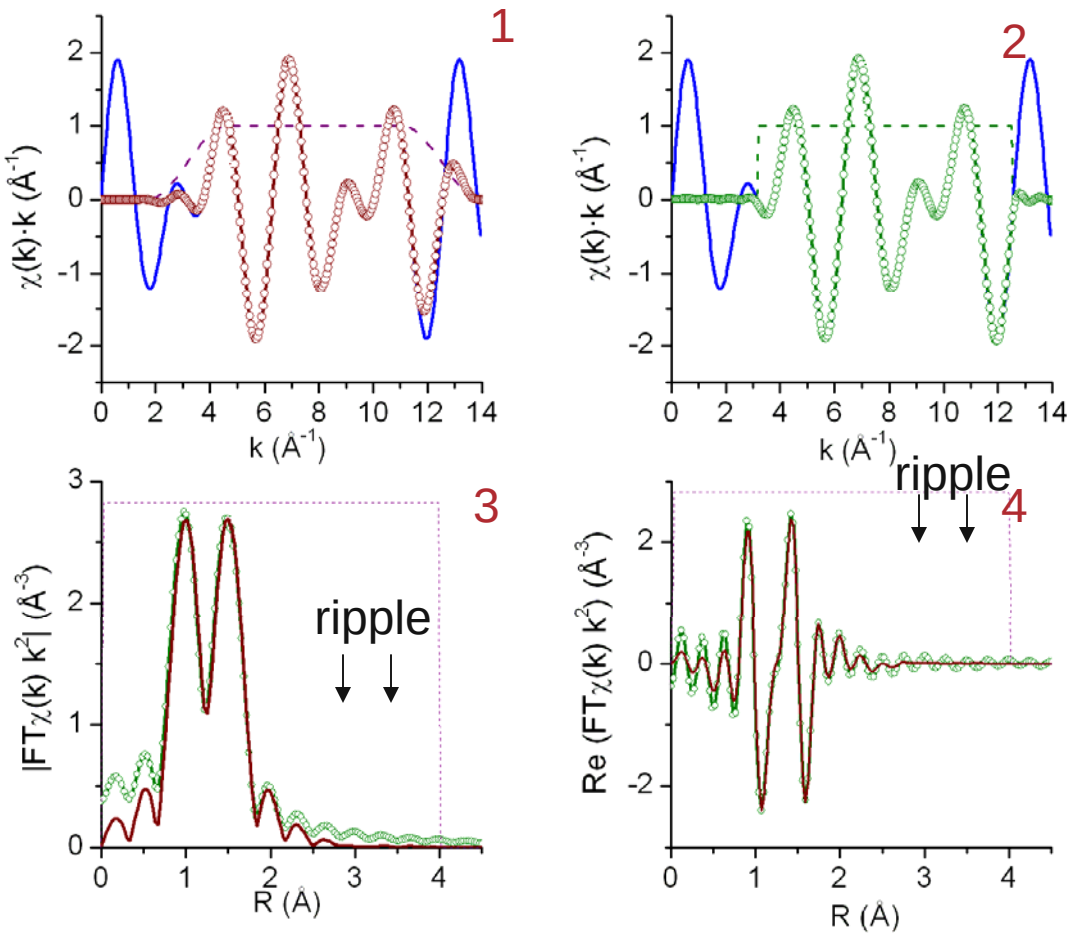
- The Back Fourier transform contains the information within the R-range.
- Used to compare the signal content within an R-range to the original EXAFS signal
- Longer phase signals are Fourier transformed to peaks at lower R values





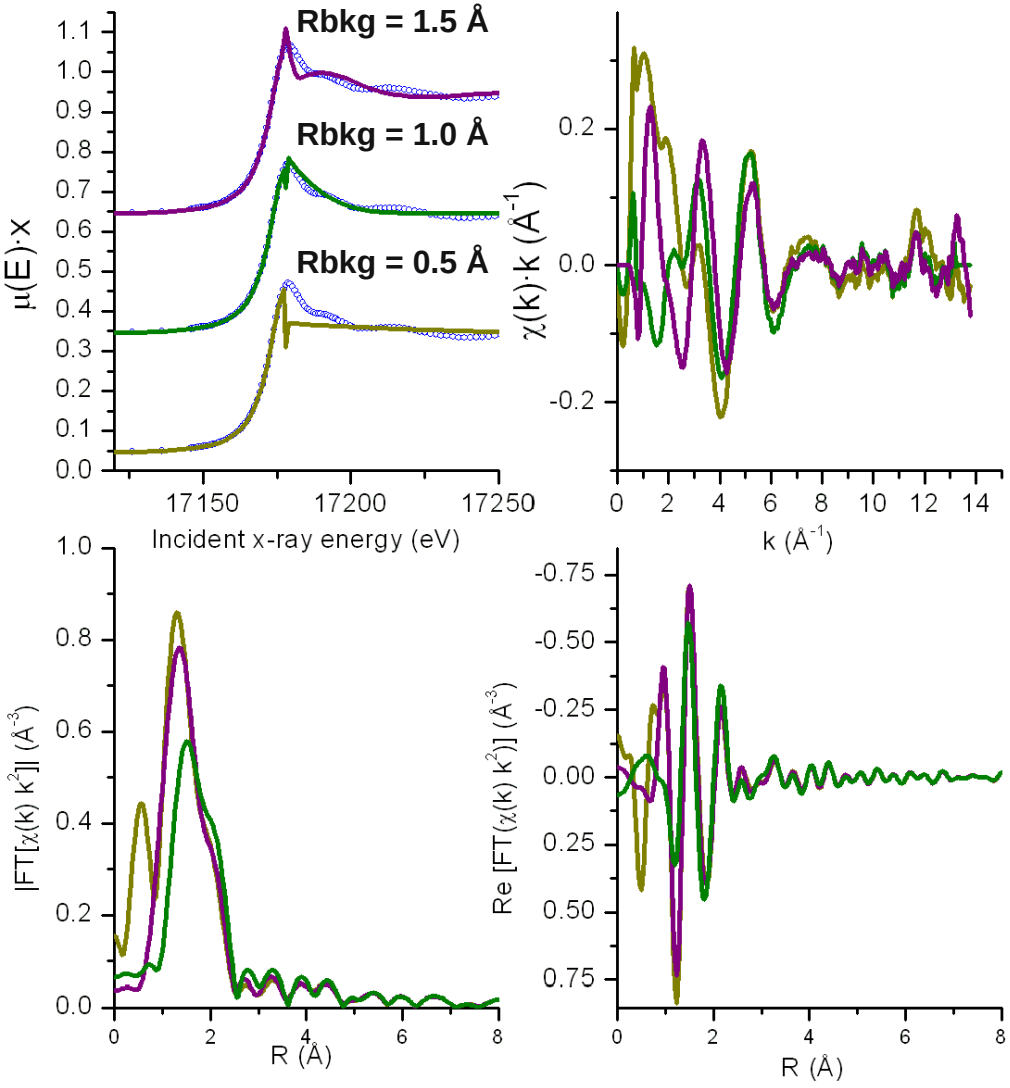
Fourier Transform Ripple

- Same data in blue is shown in 1 and 2.
- FT window is broad in 1 and sharp in 2
- Magnitude and real part of FT is shown in 3 and 4.
- Sharp window results in a FT ripple
- Back Fourier transformed spectra are shown in 1 and 2 illustrating the abrupt change in the green spectrum

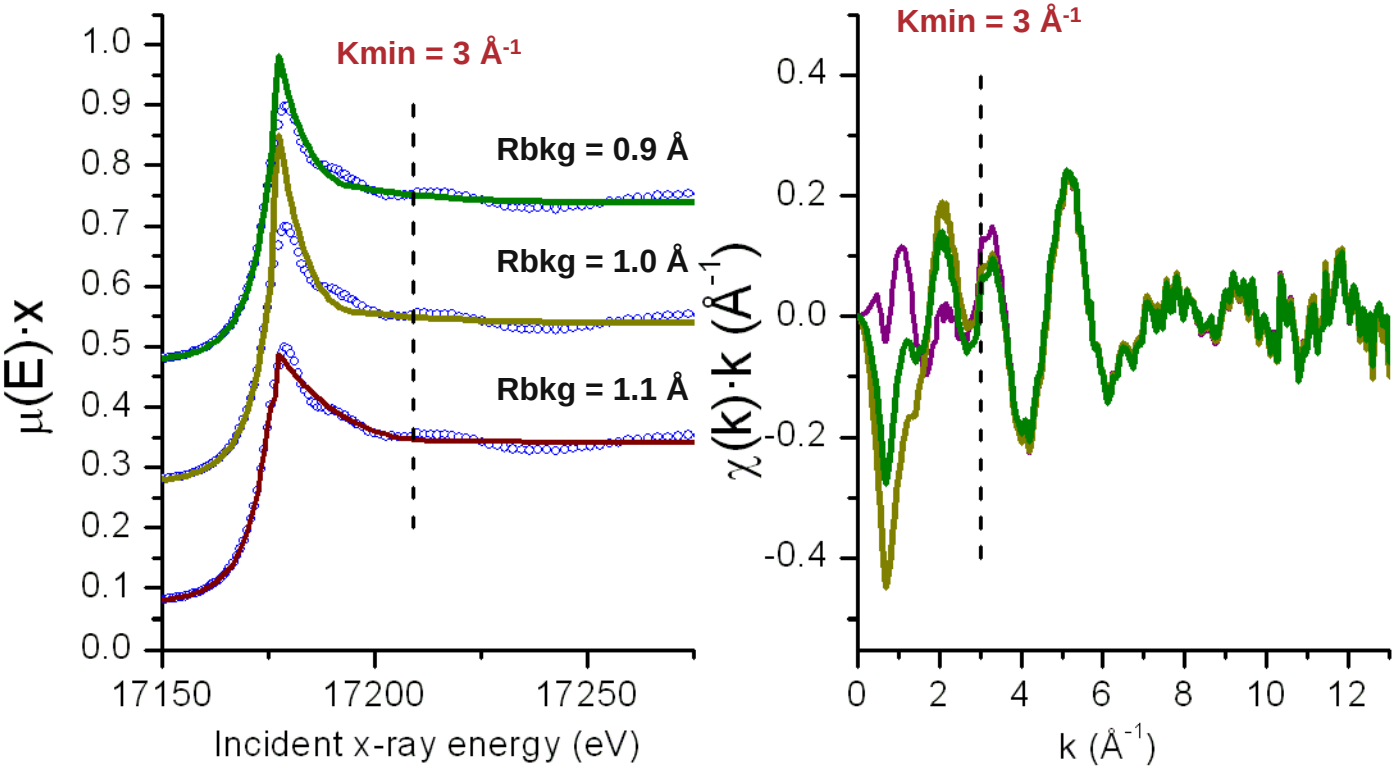


Effect of a large change in Rbkg

- Rbkg: Controls the curvature of the background and is usually set to about half the first nearest neighbor distance.
- Small values for Rbkg (0.5 Å) result in significant signal at low R values, where no neighboring atoms are present.
- Large values for Rbkg (1.5 Å) result in the removal of signal from the first shell signal.



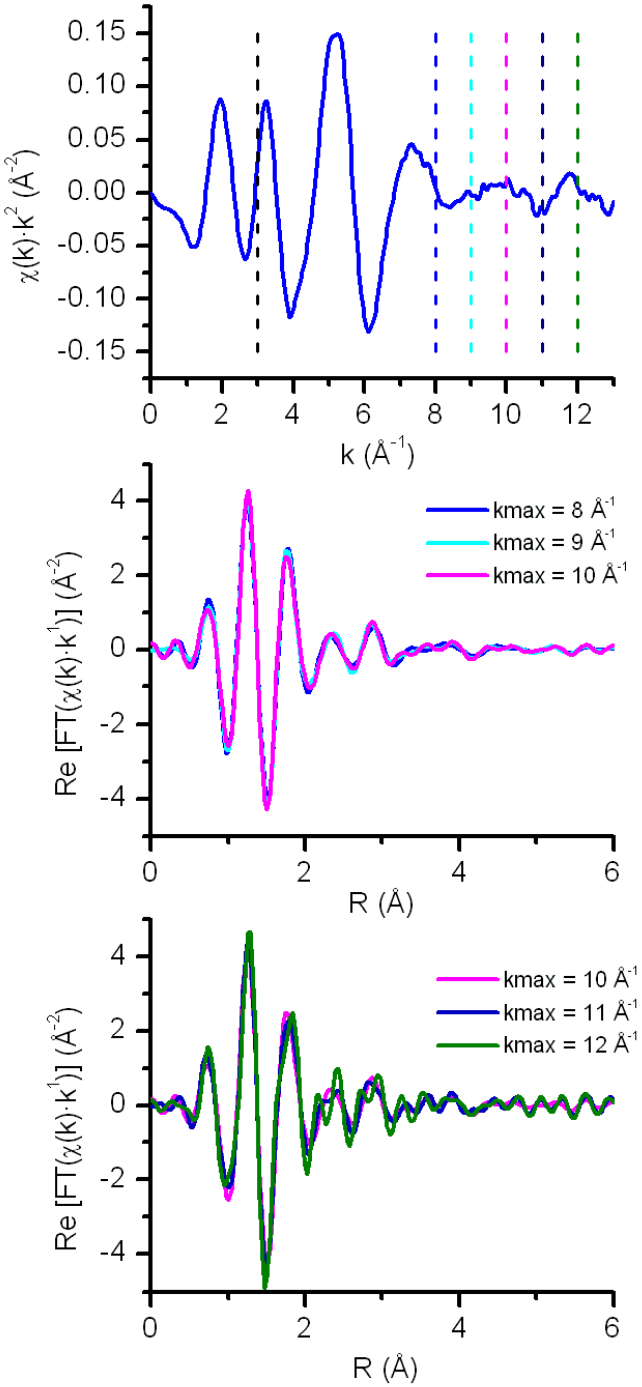
Effect of a small change in Rbkg



- Small changes in Rbkg can be used to determine the minimum k-range to use in the Fourier transform.
- EXAFS signal should not depend on Rbkg.
- Kmin of 3 Å^{-1} uses the part of the spectra that does not depend on Rbkg.

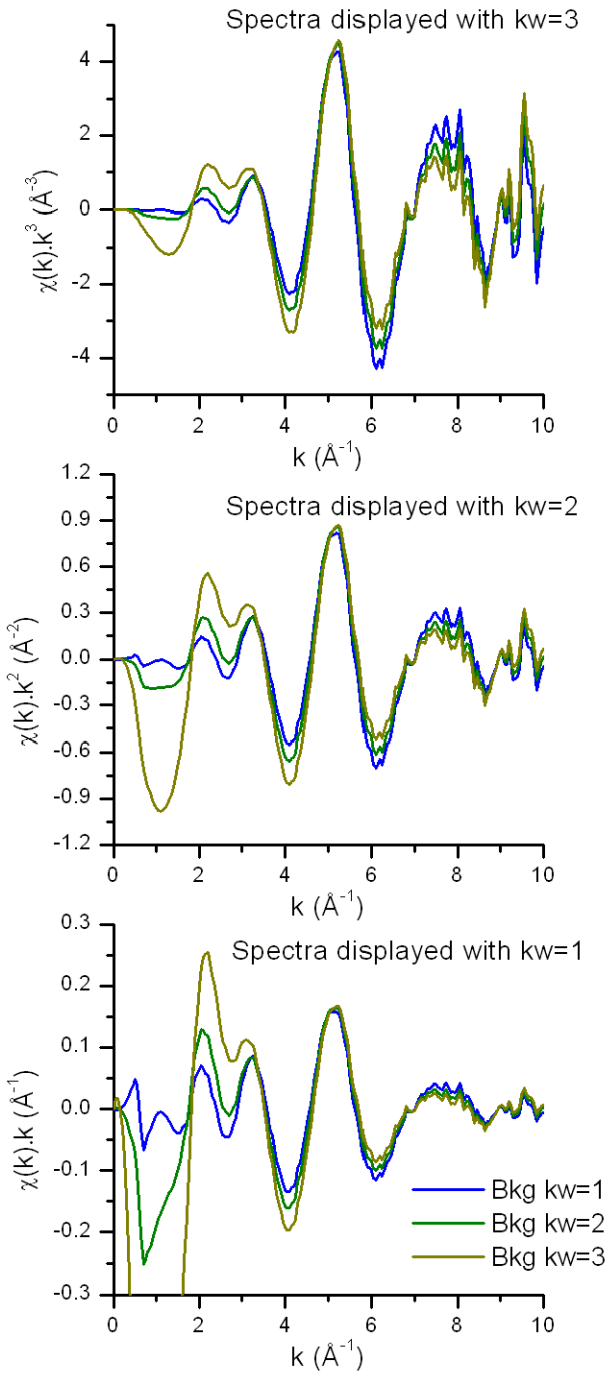
Choosing Kmax in the Fourier Transform

- Comparison of the Real part of the Fourier transform using incremental values for the maximum k-value (Kmax) can be used to determine Kmax.
- The Real part of the Fourier transform will be smooth and similar for the different kmax values as long as significant noise is not included in the Fourier transform.
- Kmax values of 11 $Å^{-1}$ and 12 $Å^{-1}$ include some noise in the FT



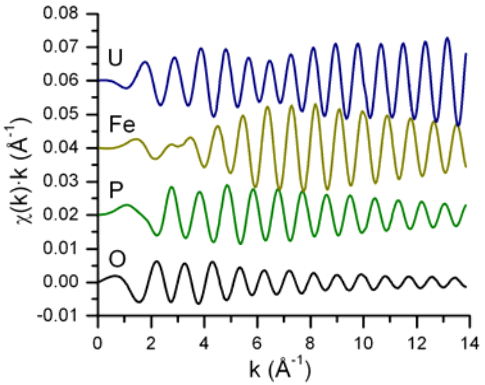
Effect of k-weight in the background removal process

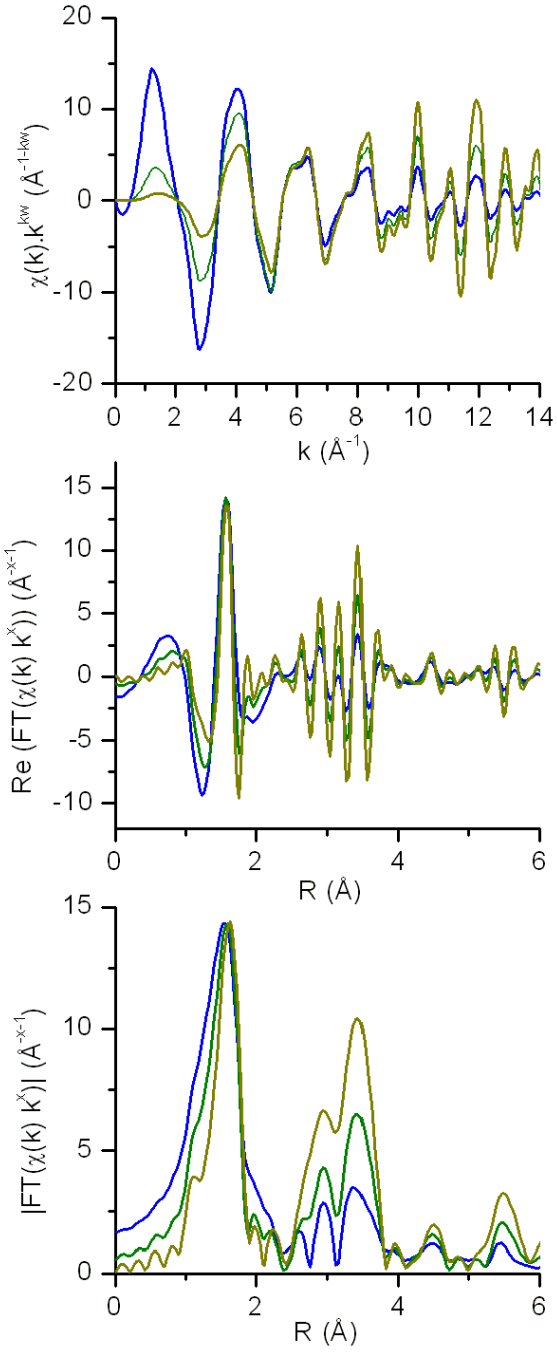
- Background is removed by using a k-weight of 1, 2, or 3.
- Resulting EXAFS signal is displayed using a k-weight of 1, 2, or 3
- Use the background k-weight that results in an evenly weighted EXAFS signal at low k, independent of the k-weight used to display the spectrum



K-weight used in Fourier Transform

EXAFS signal for U-X neighbor
at 4 Angstroms

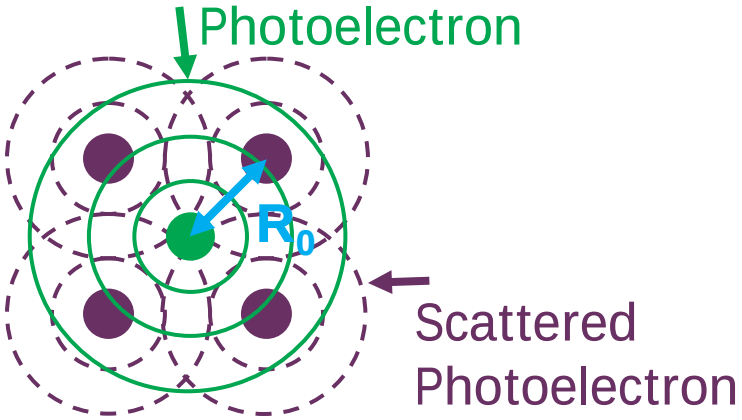




- EXAFS signal is processed with k-weight of 1, 2, and 3 and then rescaled so that the signal is the same height for the first shell in the Fourier transform.
- The signal from 3 to 4 A increases with k-weight indicating that there is a atom with stronger signal at higher k-values in this shell
- K-dependence of the EXAFS signal can be used to differentiate neighboring atom types and reduce correlations between EXAFS parameters

EXAFS Equation

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



$$\chi_i(k) \equiv \frac{(N_i S_0^2) F_{eff_i}(k)}{kR_i^2} \sin(2kR_i + \varphi_i(k)) e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}}$$

$$R_i = R_{0i} + \Delta R_i$$

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

Theoretically calculated values

$F_i(k)$ effective scattering amplitude

$\varphi_i(k)$ 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

ΔE_0 energy shift

ΔR change in half-path length