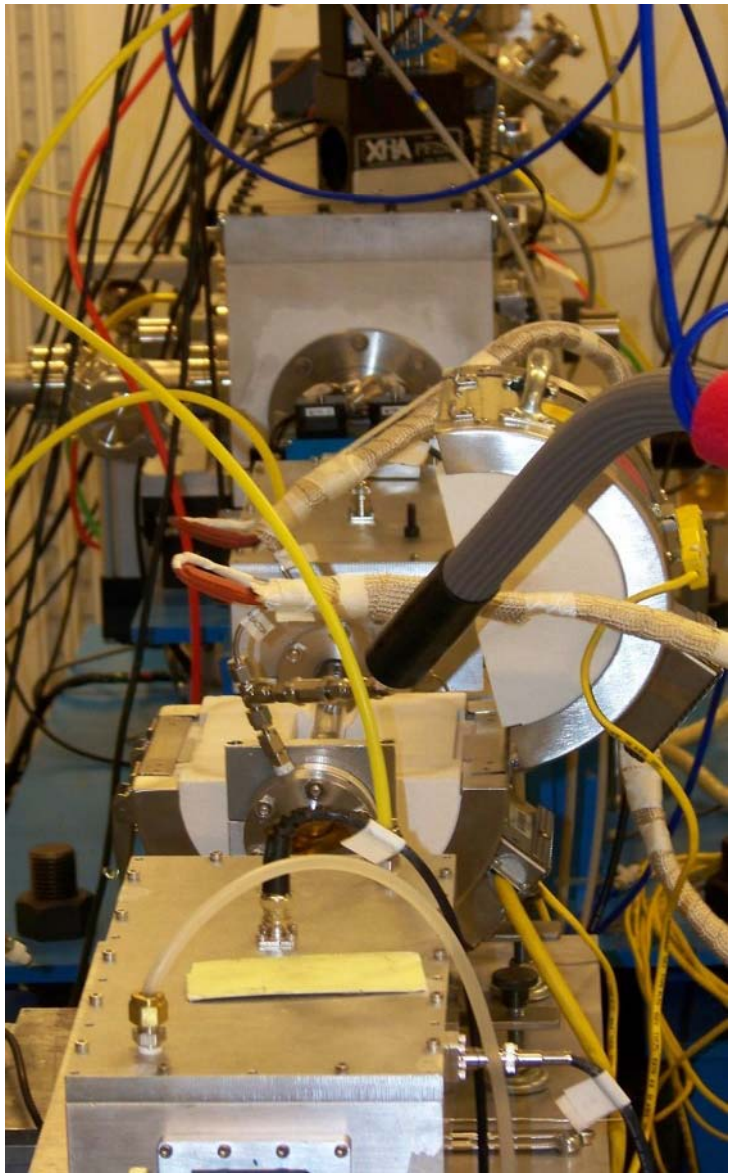
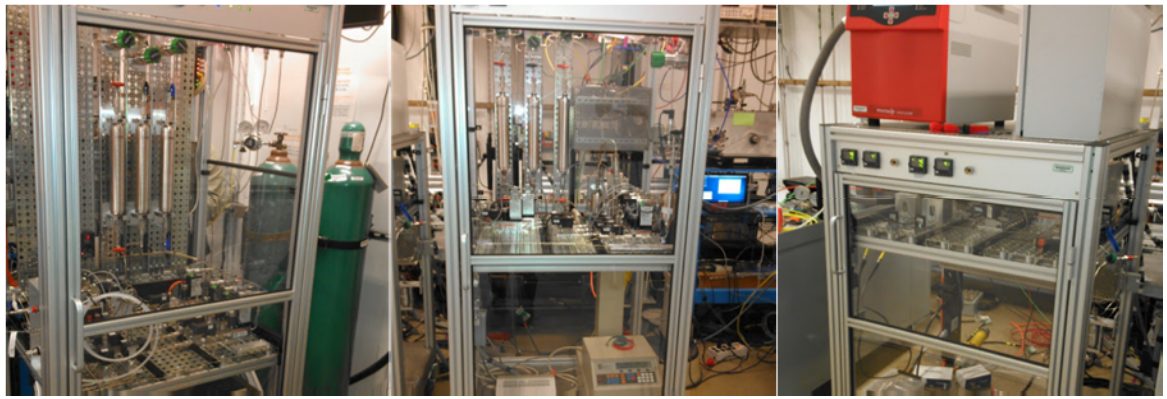
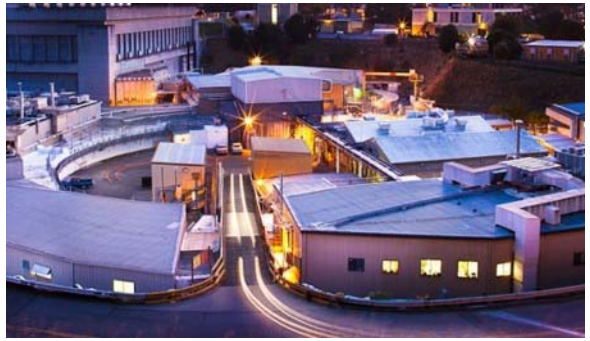






Shelly D. Kelly

Nov. 1, 2016

OVERVIEW OF DATA ANALYSIS

NSLSII EXAFS Workshop

Honeywell UOP

© 2016 UOP LLC. A Honeywell Company All rights reserved.

Outline

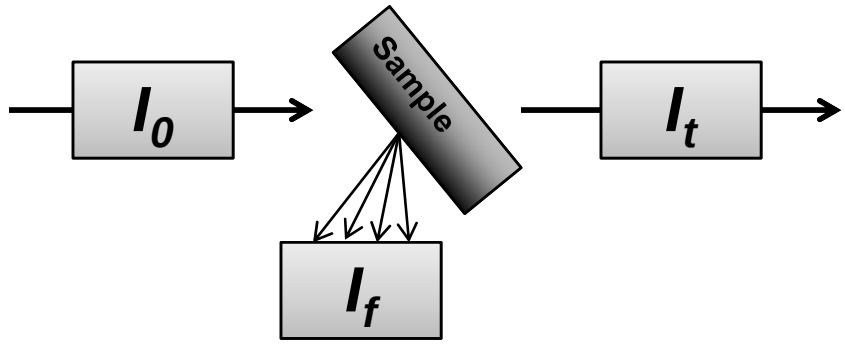
- Extracting the EXAFS signal
  - Aligning spectra
  - Merging spectra
  - Removing background
  - Fourier transforms
- Theoretical Calculations
  - Atoms
  - FEFF
- Data Modeling
  - Building an EXAFS Model
  - Number of variables
  - Comparison of models

© 2016 by Honeywell International Inc. All rights reserved.

Measurement of X-ray Absorption Coefficient

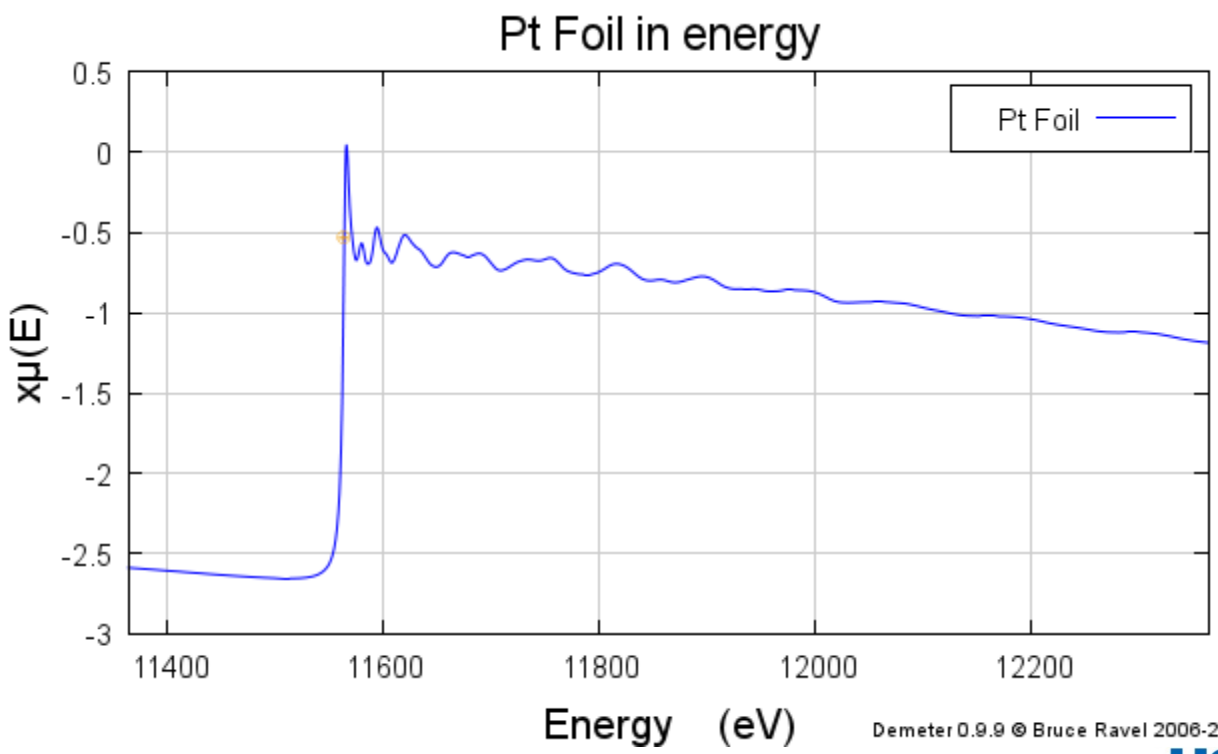
Transmission

$$\mu = \log \frac{I_0}{I_t}$$



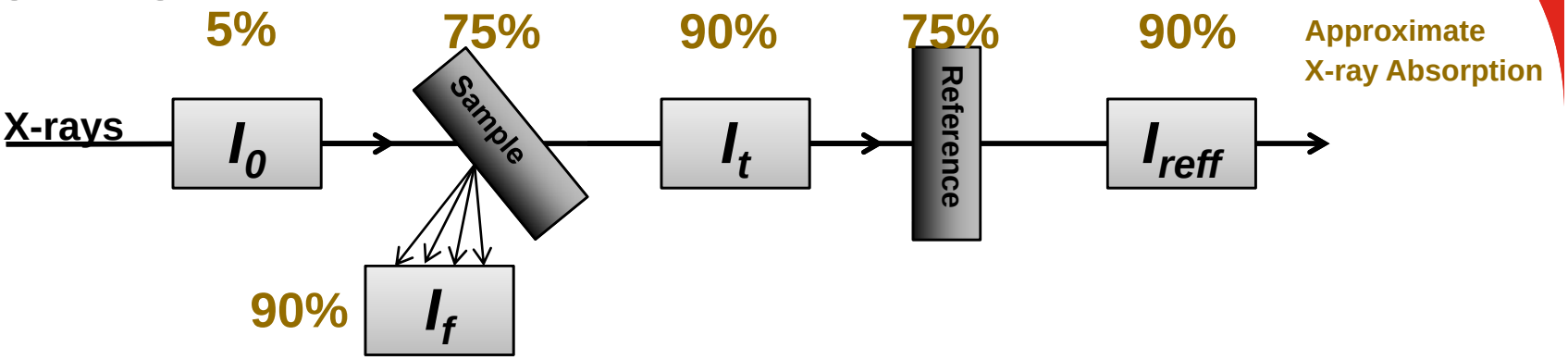
Fluorescence

$$\mu \propto \frac{I_f}{I_0}$$



© 2016 by Honeywell International Inc. All rights reserved.

Aligning Spectra

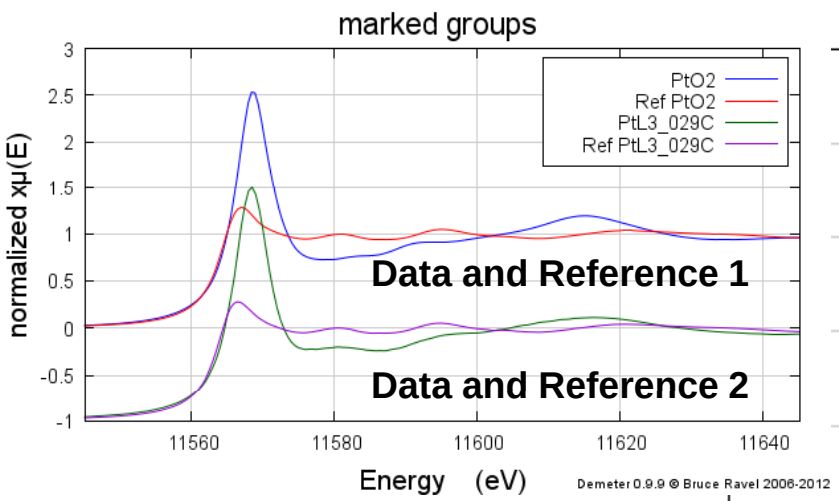


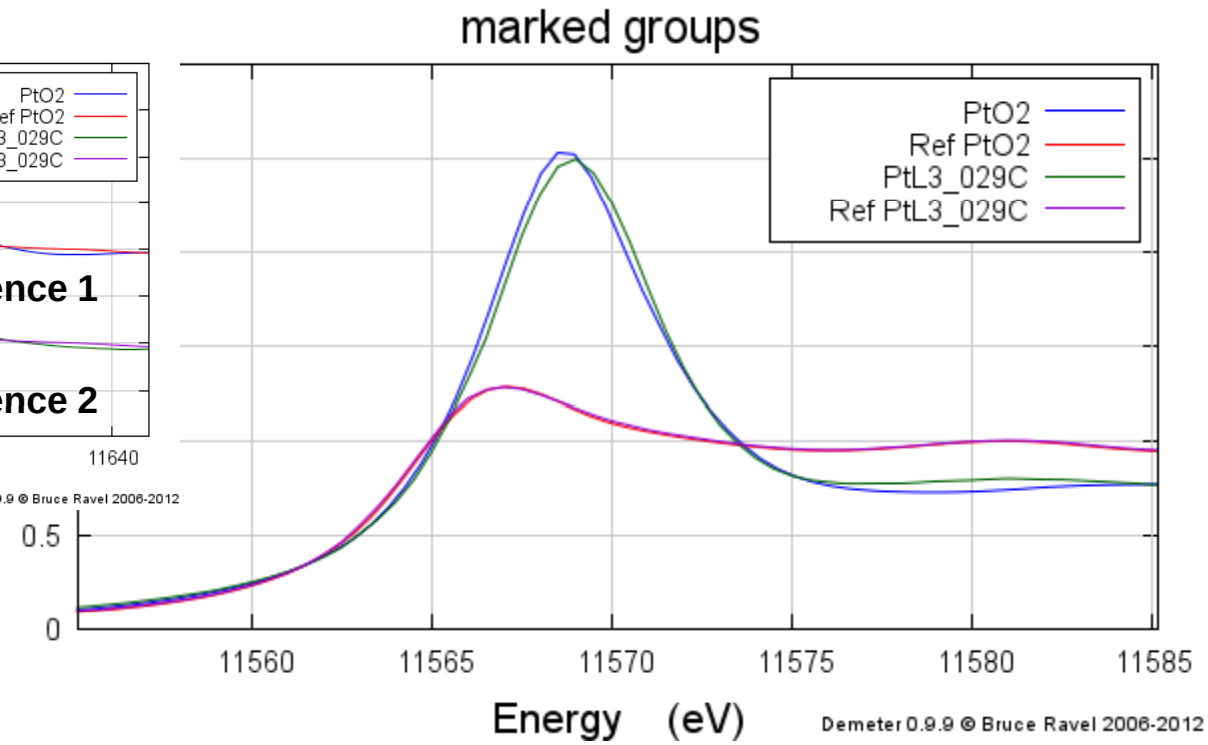
$$\mu = \log \frac{I_t}{I_{reff}}$$

- Need to measure a reference spectrum simultaneously with the unknown sample or it can be measured before and after the sample.

© 2016 by Honeywell International Inc. All rights reserved.

Alignment of Spectra

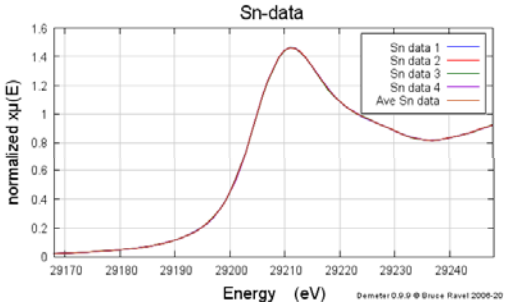


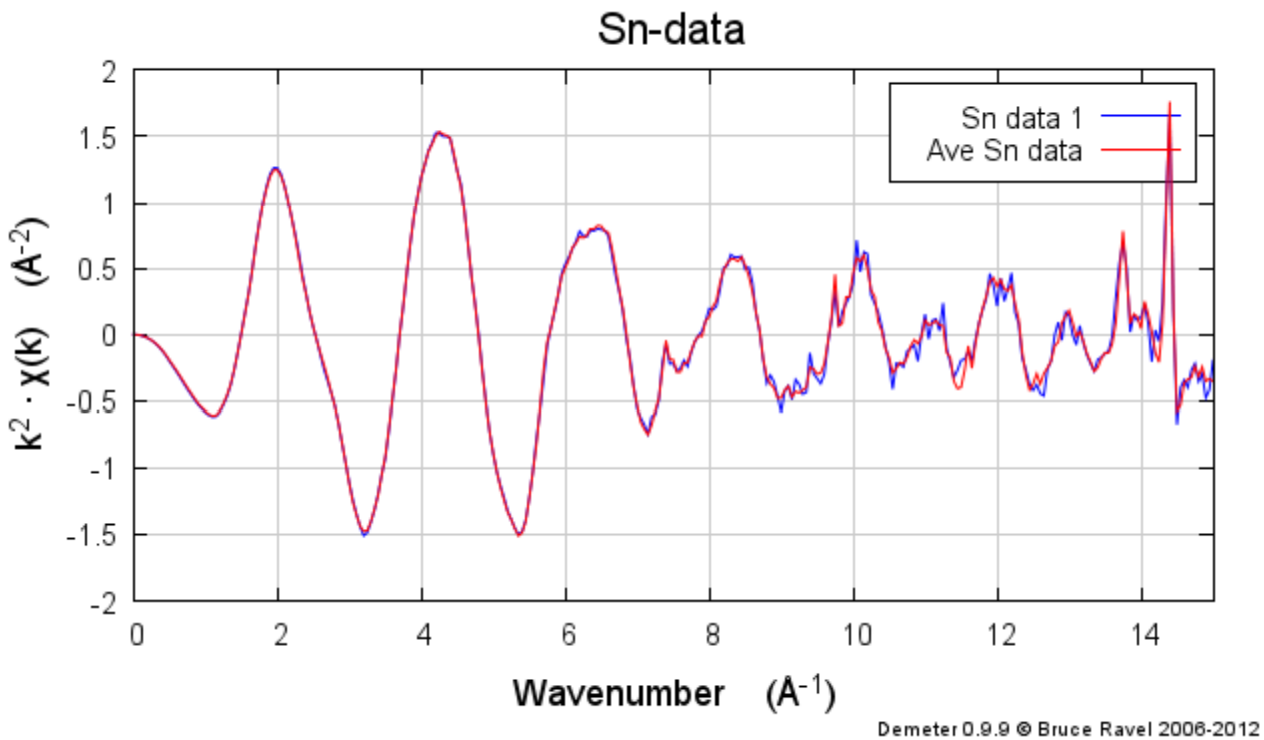


- Align Reference 2 to Reference 1 and determine offset in energy.
- Apply this offset to Data 2.

© 2016 by Honeywell International Inc. All rights reserved.

Merging Data

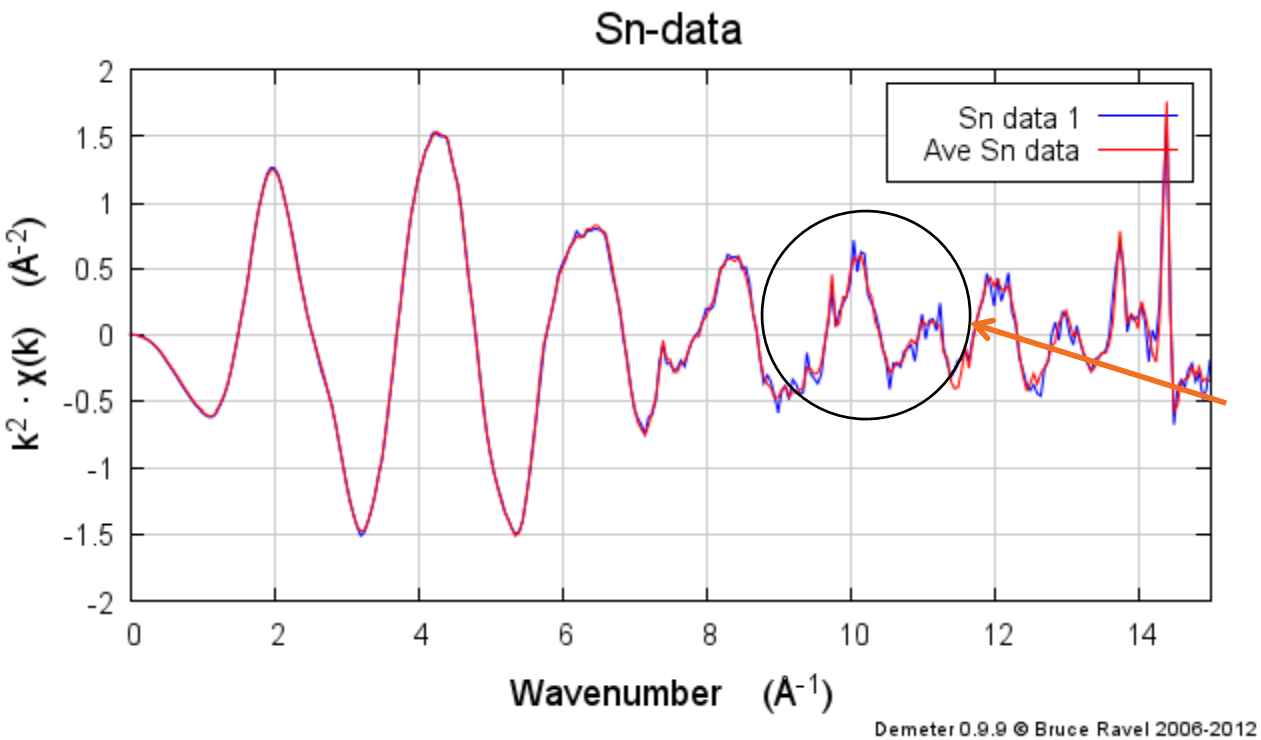




- Inspect data in E-space and then merge in E-space (non normalized)
- Inspect data in k-space to determine noise level.

© 2016 by Honeywell International Inc. All rights reserved.

Random Noise in EXAFS Spectra



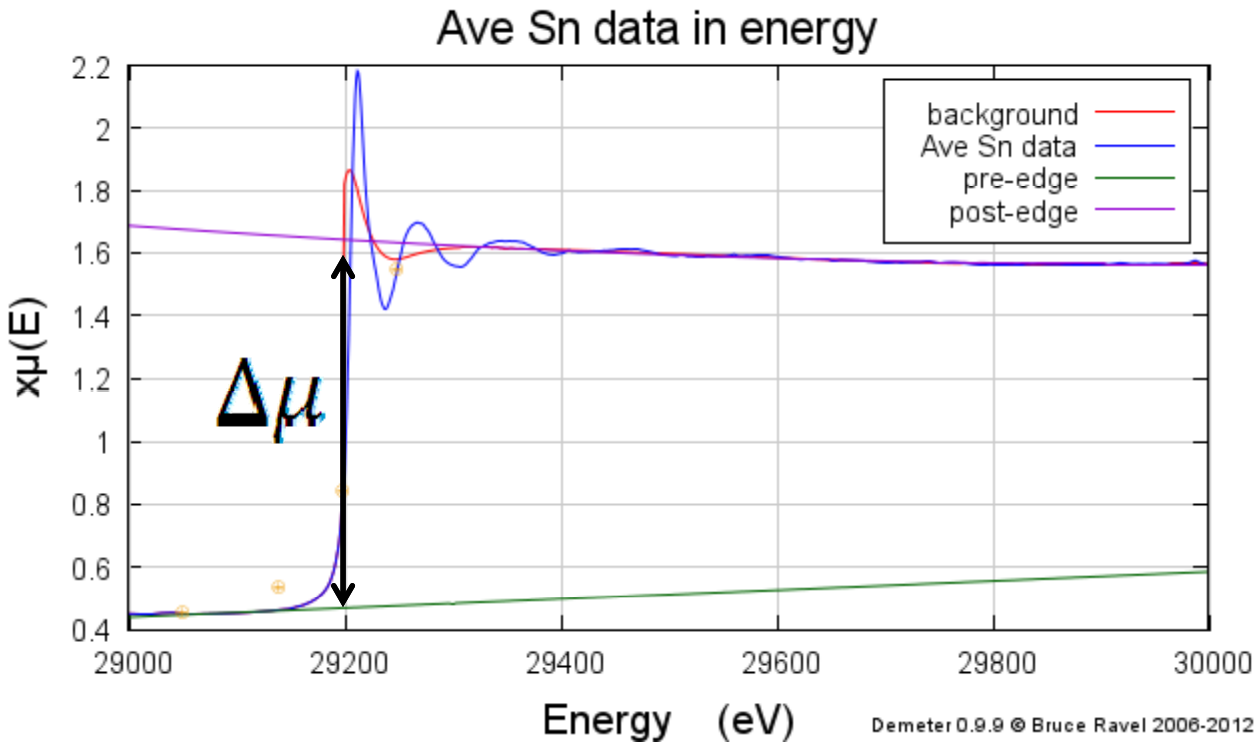
$$SN = \frac{1}{\sqrt{N_{Xrays}}}$$

Random Fluctuations Less than 0.1%

- Noise level of <0.1% is desired. This means that we need at least 10^6 x-rays on the sample.
- Noise can be easily measured in the EXAFS signal at 10 Å^{-1} with k-weight =2 (data has already been multiplied by 100%)
- To reduce noise by 2, 4 scans need to be collected.

© 2016 by Honeywell International Inc. All rights reserved.

Remove Background



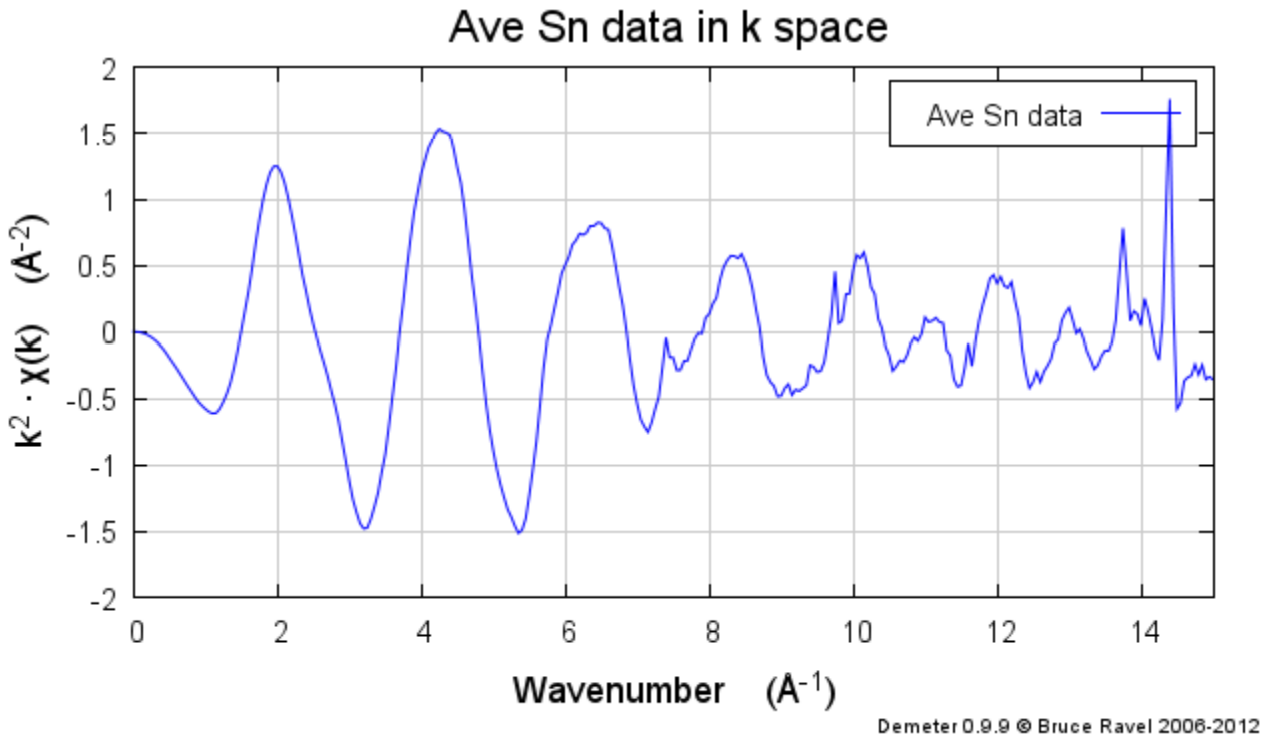
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

Background

Edge Step

© 2016 by Honeywell International Inc. All rights reserved.

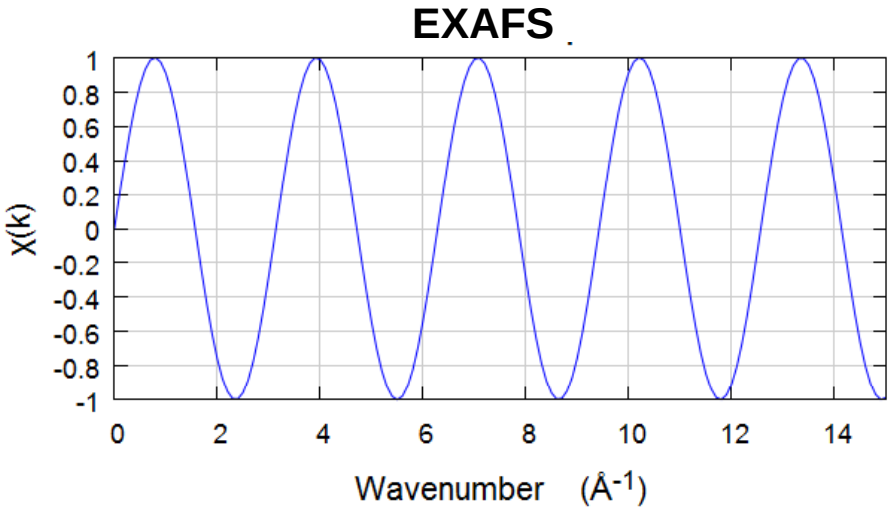
Sn EXAFS Signal



- EXAFS signal is a sum of sine waves

© 2016 by Honeywell International Inc. All rights reserved.

Fourier Transform is a frequency filter



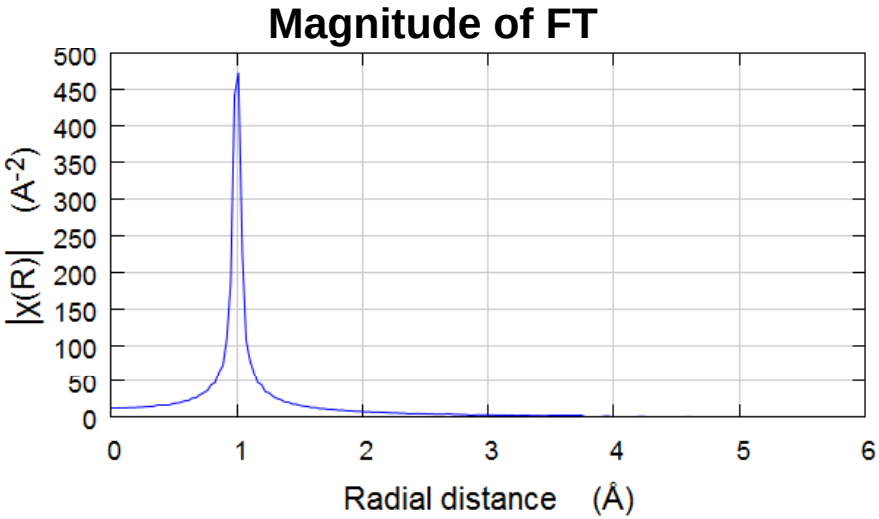


Fig.20

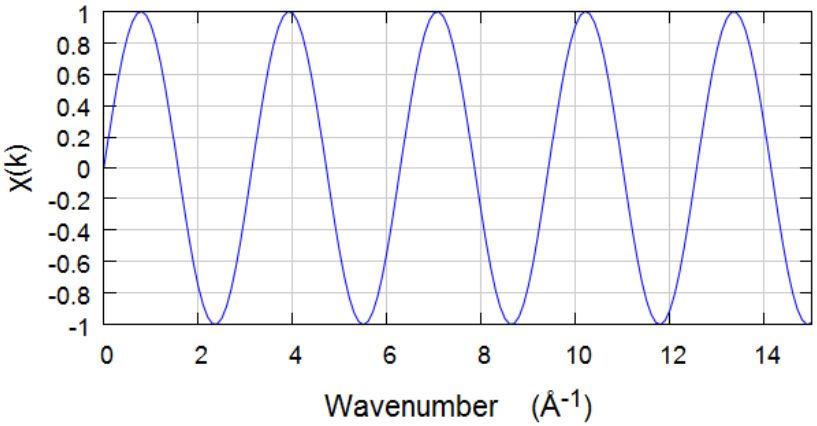
- FT of Sin(2Rk) is a peak at R=1
- FT of infinite sine wave is a delta function
- Signal that is de-localized in k-space is localized in R-space
- FT is a frequency filter

© 2016 by Honeywell International Inc. All rights reserved.

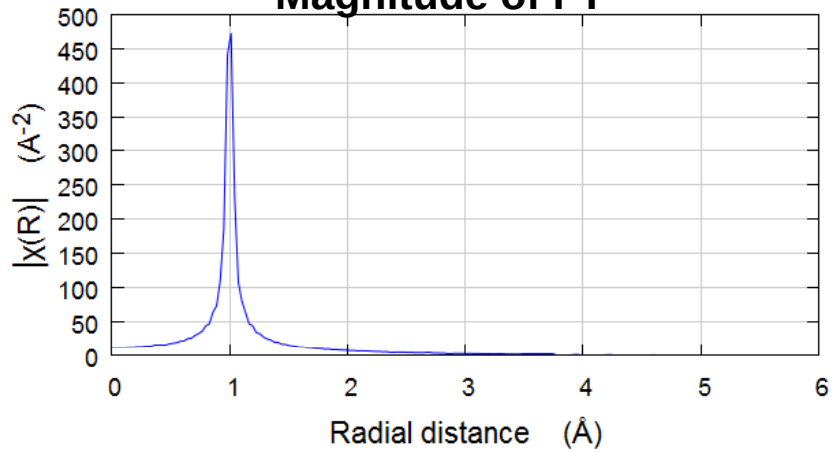
Fourier Transform of a function that is:

De-localized in k-space ⇒ localized in R-space

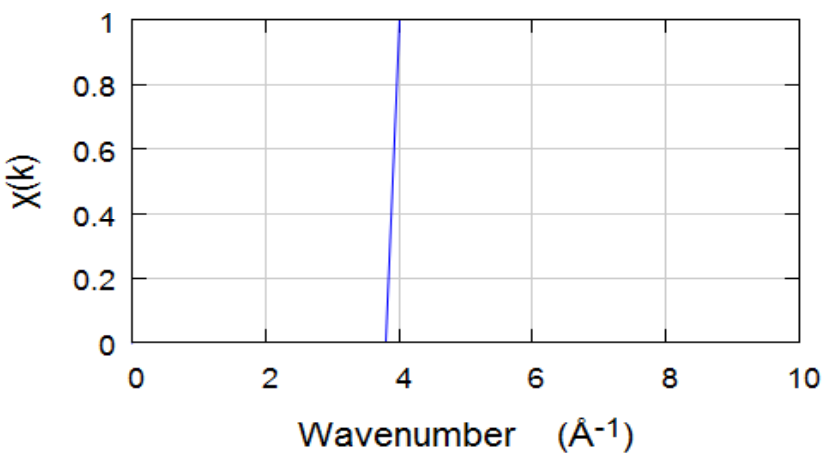
EXAFS

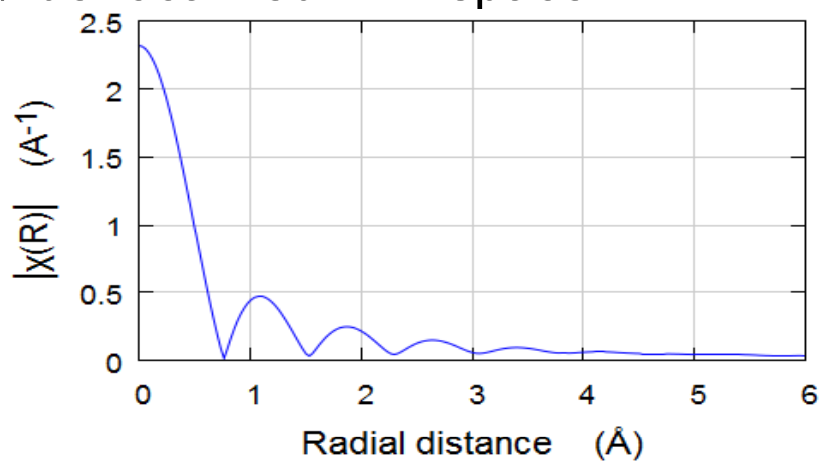


Magnitude of FT



Localized in k-space ⇒ de-localized in R-space

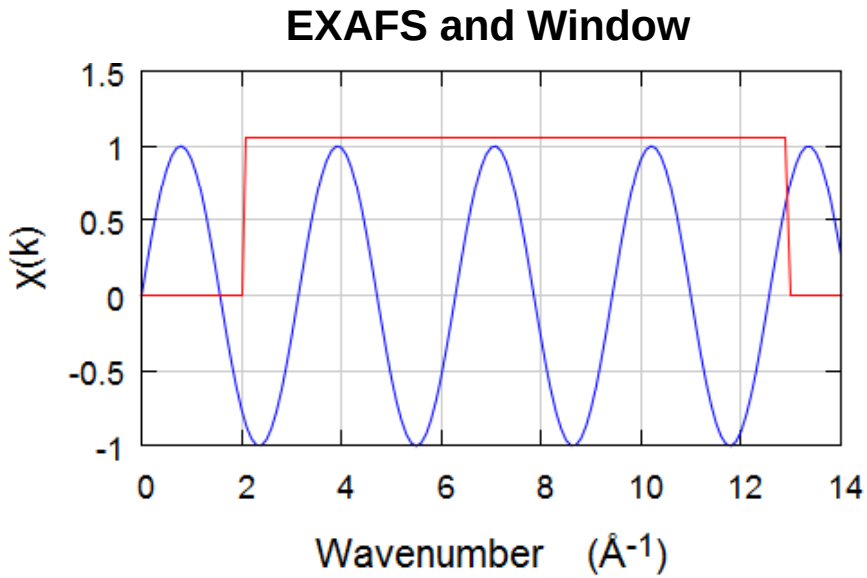




Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.

Fourier Transform is a frequency filter



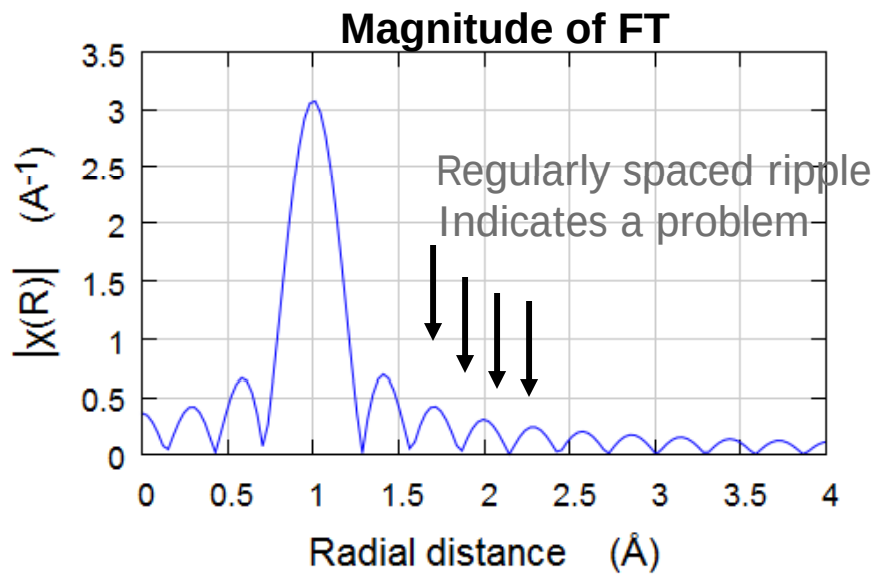
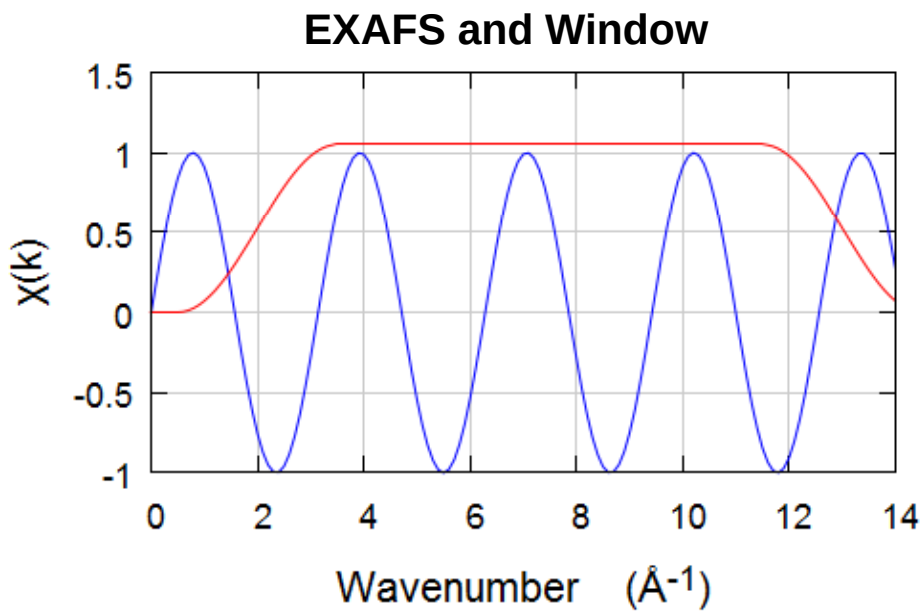


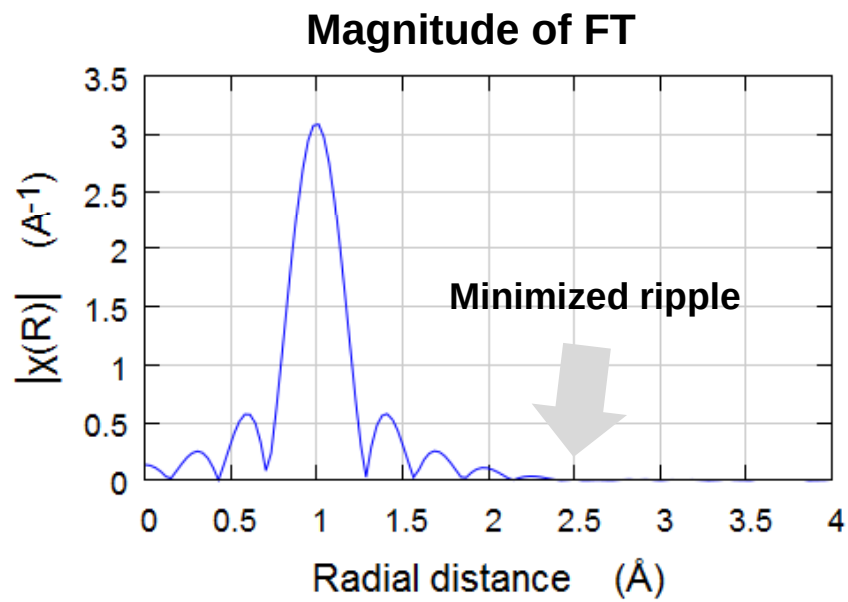
Fig.24

- 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.

© 2016 by Honeywell International Inc. All rights reserved.

Fourier Transform

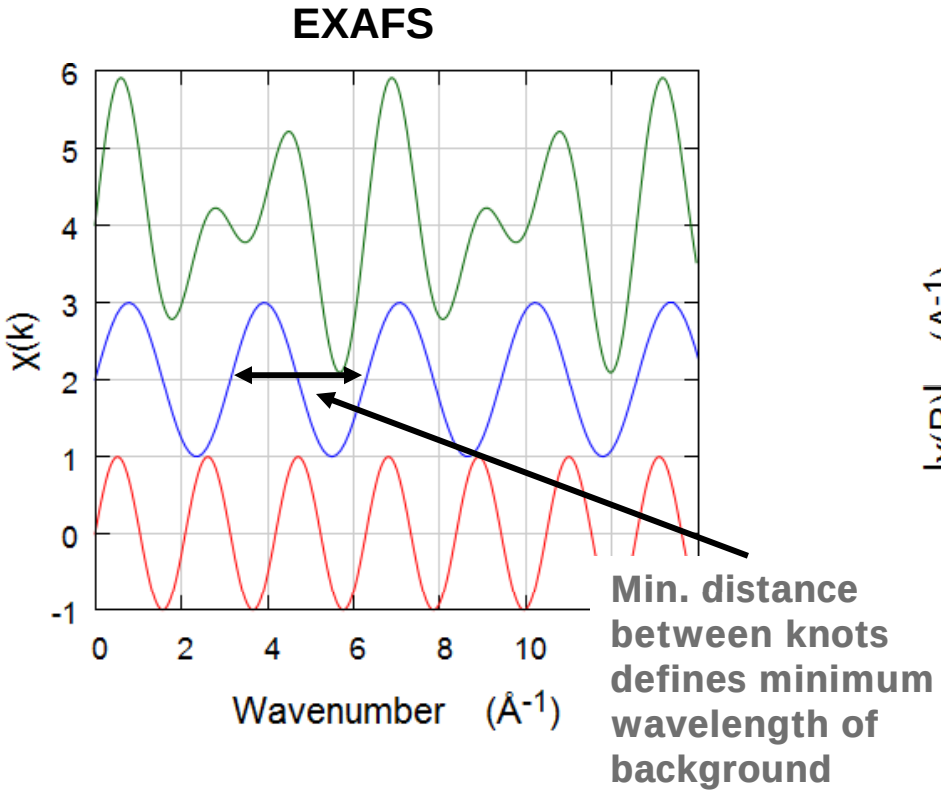


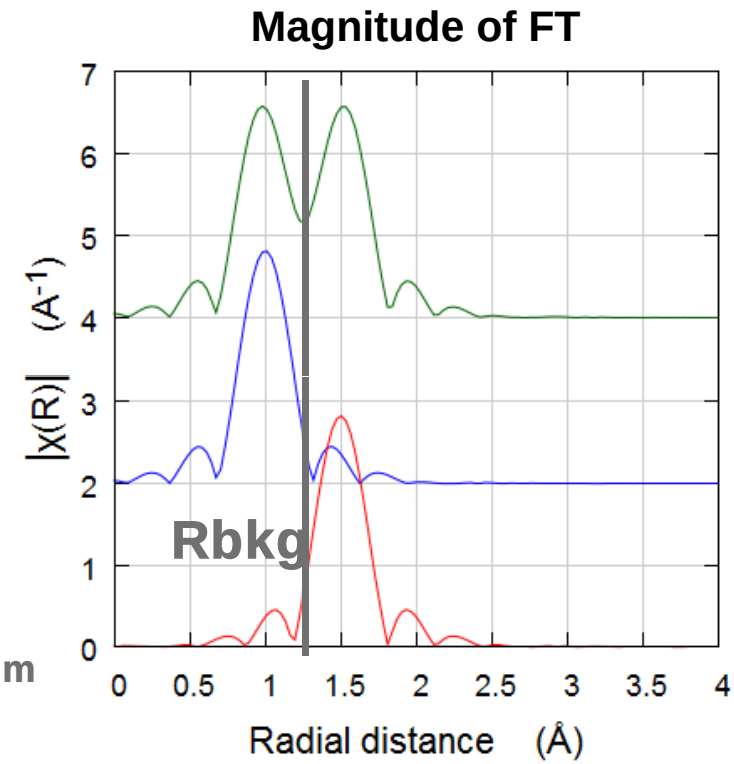


- Applying a window that gradually increases the amplitude of the data minimizes the ripple in FT.

© 2016 by Honeywell International Inc. All rights reserved.

Separating the background function from the data using Fourier transform



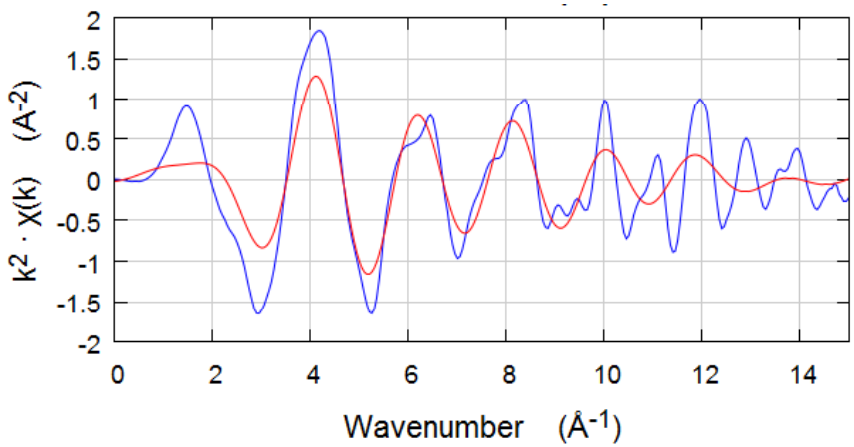


- Background function is made up of knots connected by 3rd order splines.
- Distance between knots is limited, restricting background from containing wavelengths that are part of the data.
- The number of knots are calculated from the value for Rbkg and the data range in k-space.

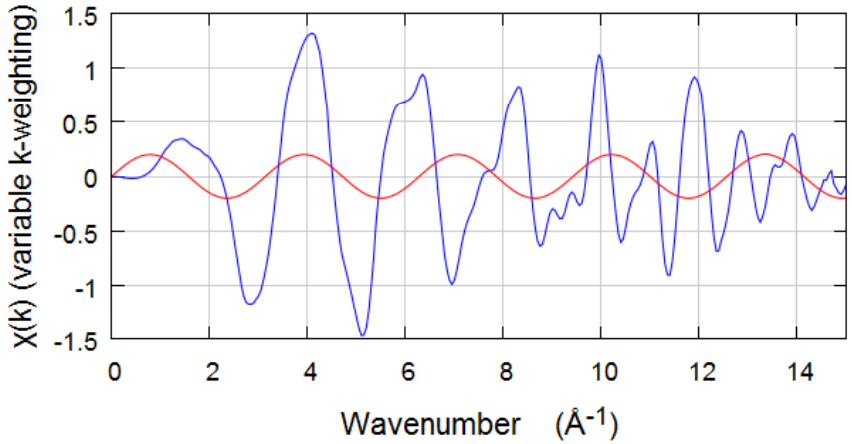
© 2016 by Honeywell International Inc. All rights reserved.

Background function

Data contains wavelengths shown in red and shorter



Bkg contains wavelengths shown in red and longer



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

© 2016 by Honeywell International Inc. All rights reserved.

Parts of the Fourier transform

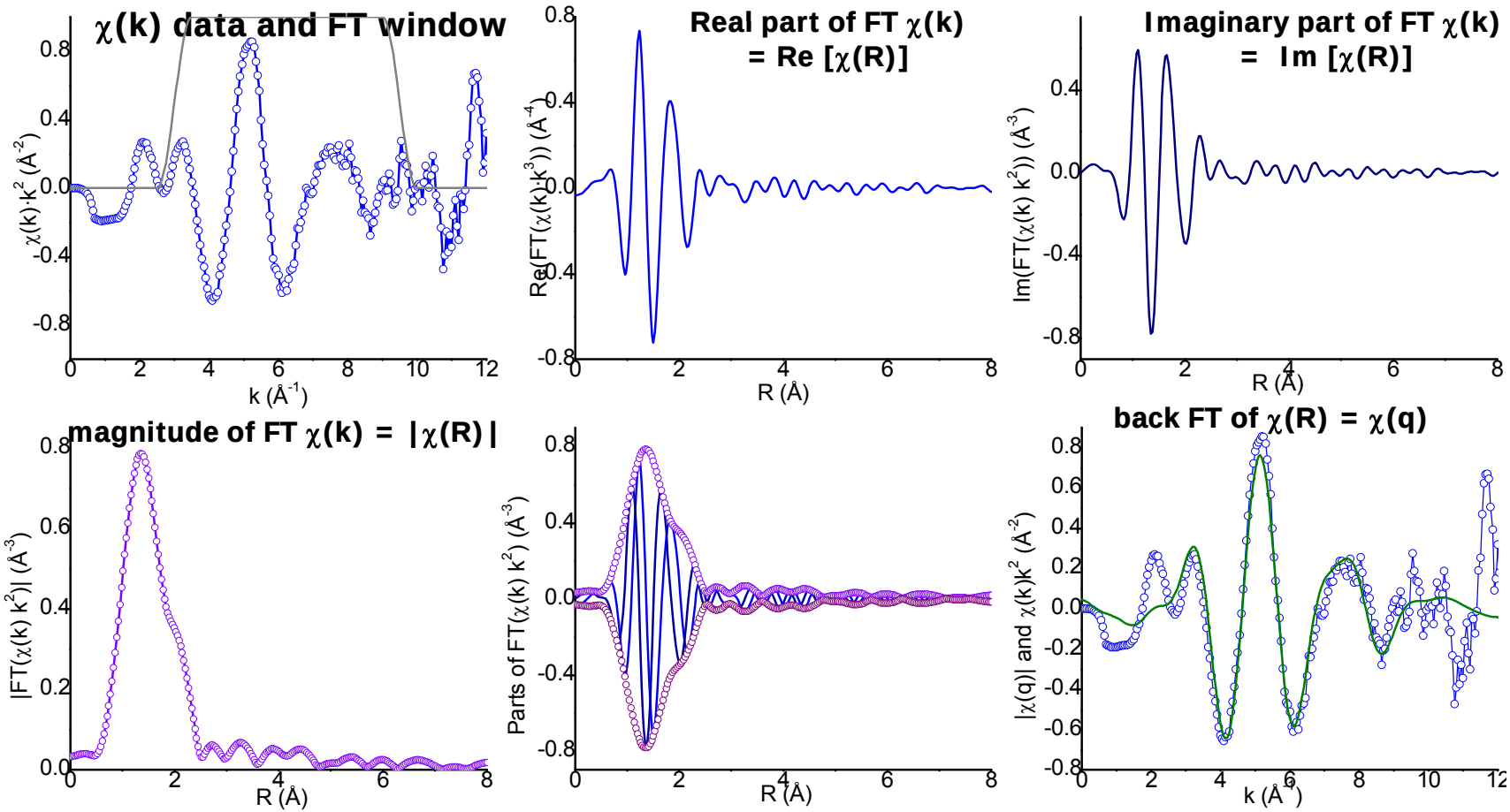
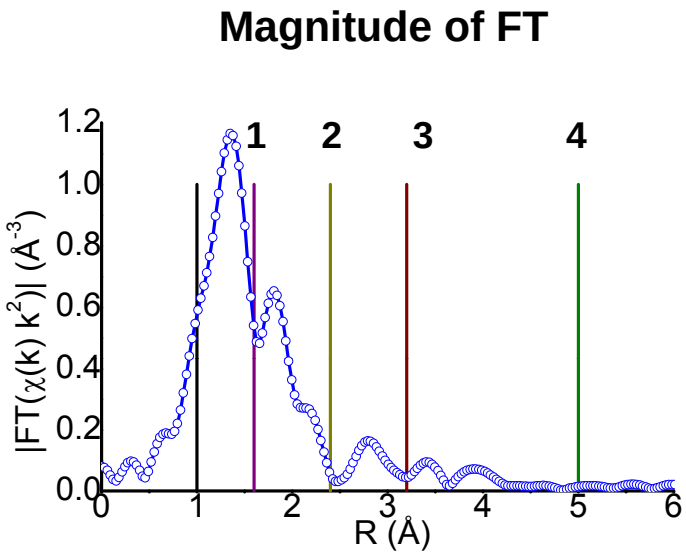


Fig.22

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

© 2016 by Honeywell International Inc. All rights reserved.

Backward Fourier transform



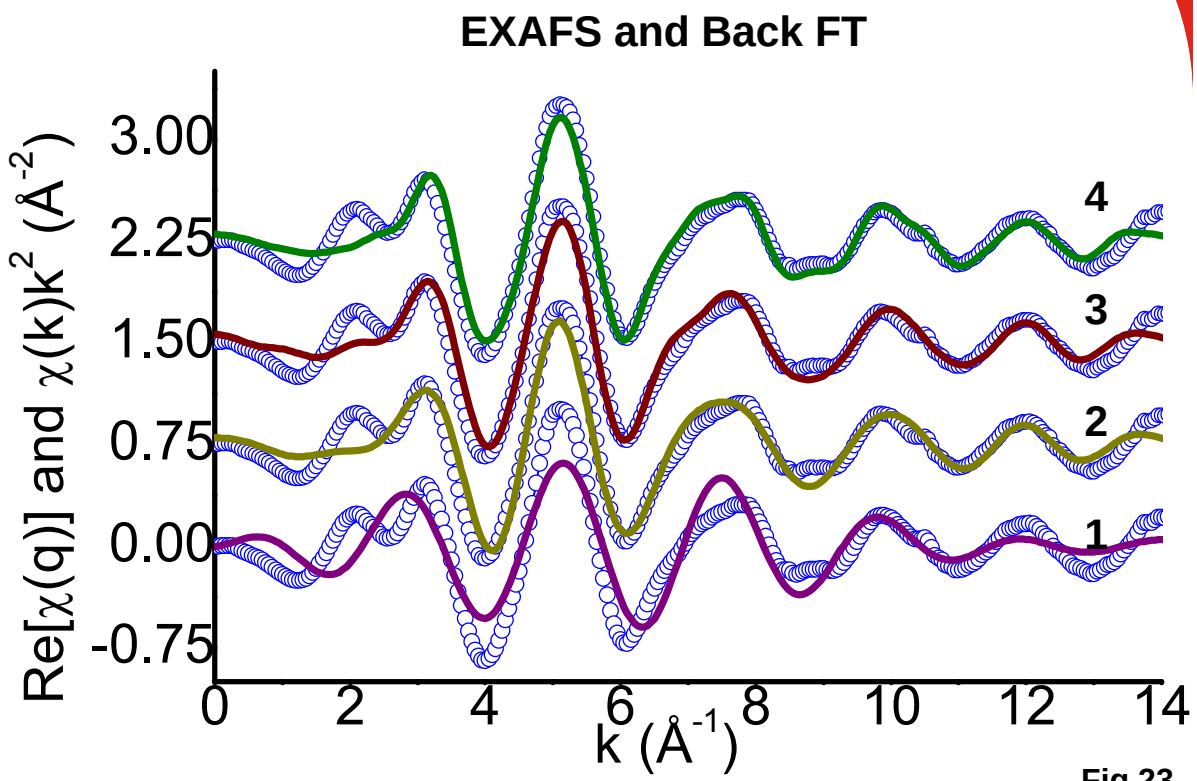


Fig.23

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

© 2016 by Honeywell International Inc. All rights reserved.

How to Choose Minimum K of FT

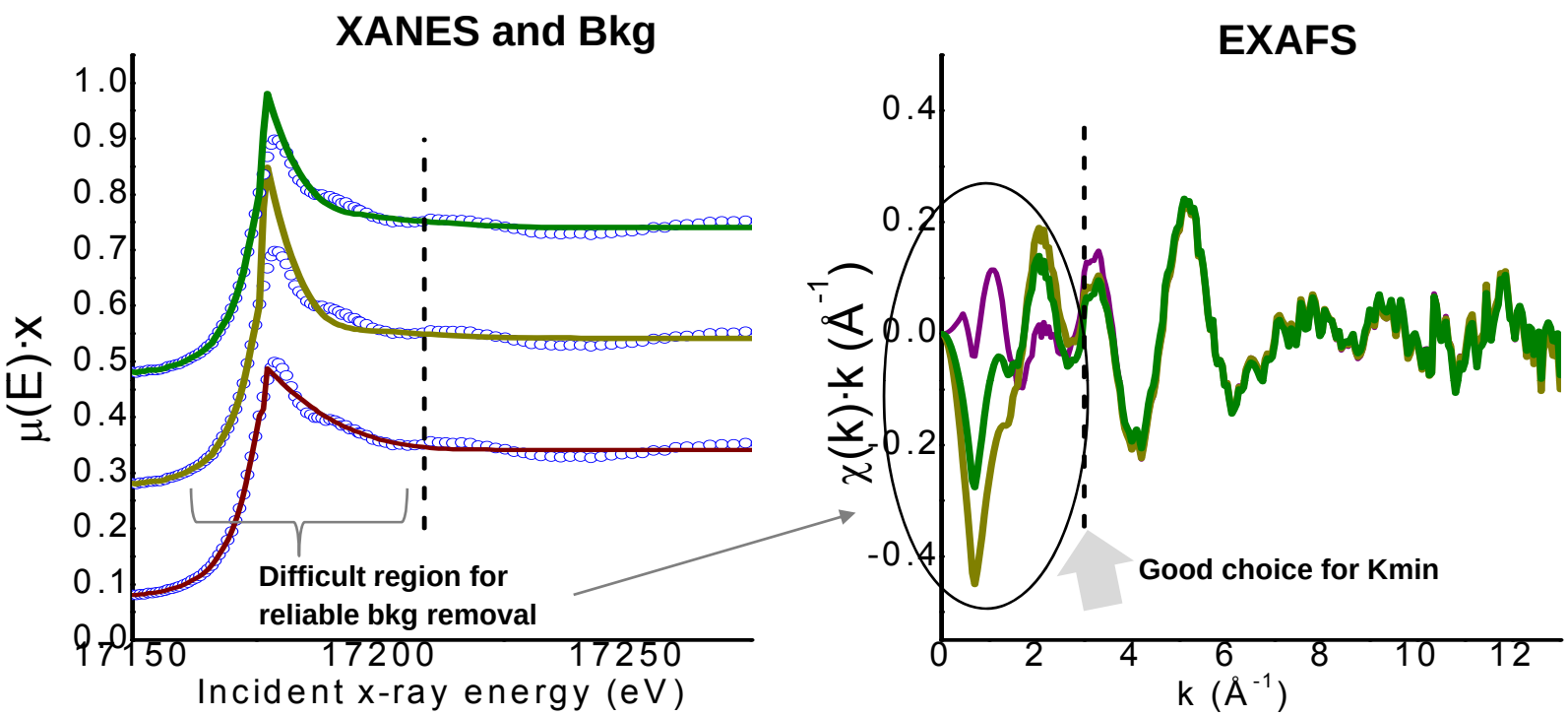


Fig.30

- Choose Kmin in the region where the background doesn't change.
  - 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.

© 2016 by Honeywell International Inc. All rights reserved.

Choosing Maximum K-range

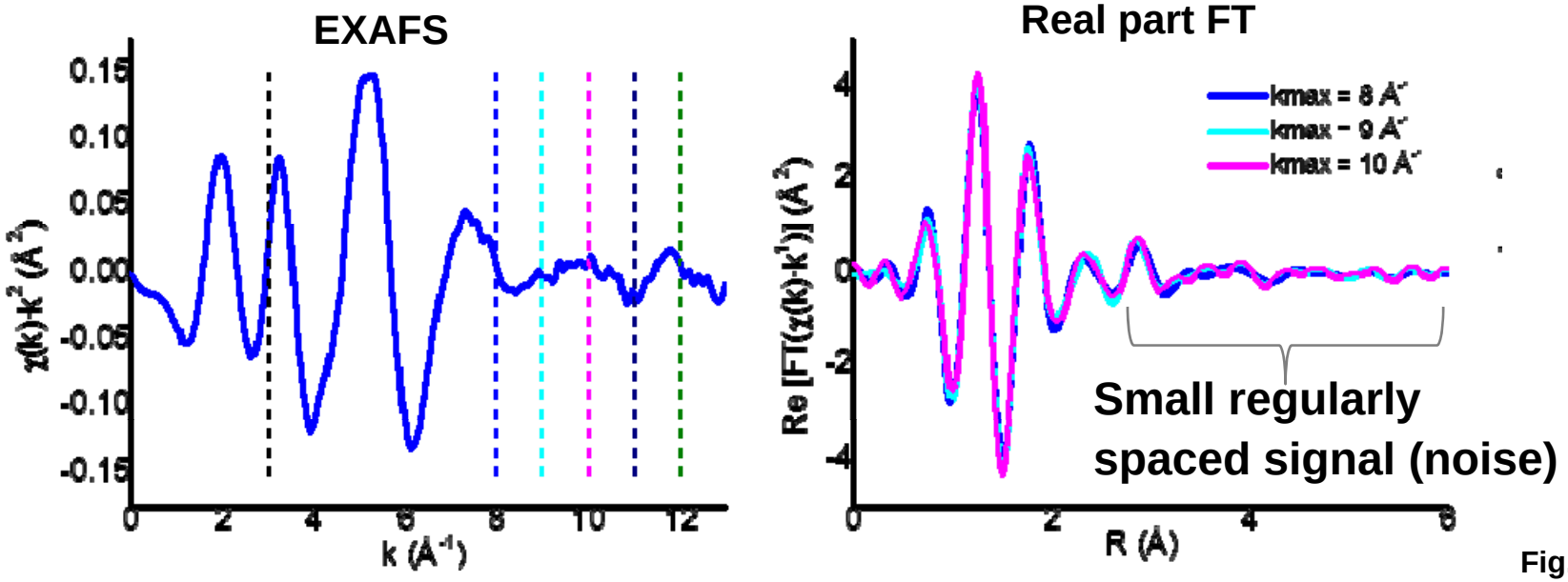


Fig.26

- The FT should be smooth and free of ringing
- To choose Kmax:
  - vary the kmax 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 kmax of 10 or 11 $Å^{-1}$ best

Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.

Choosing Maximum K-range

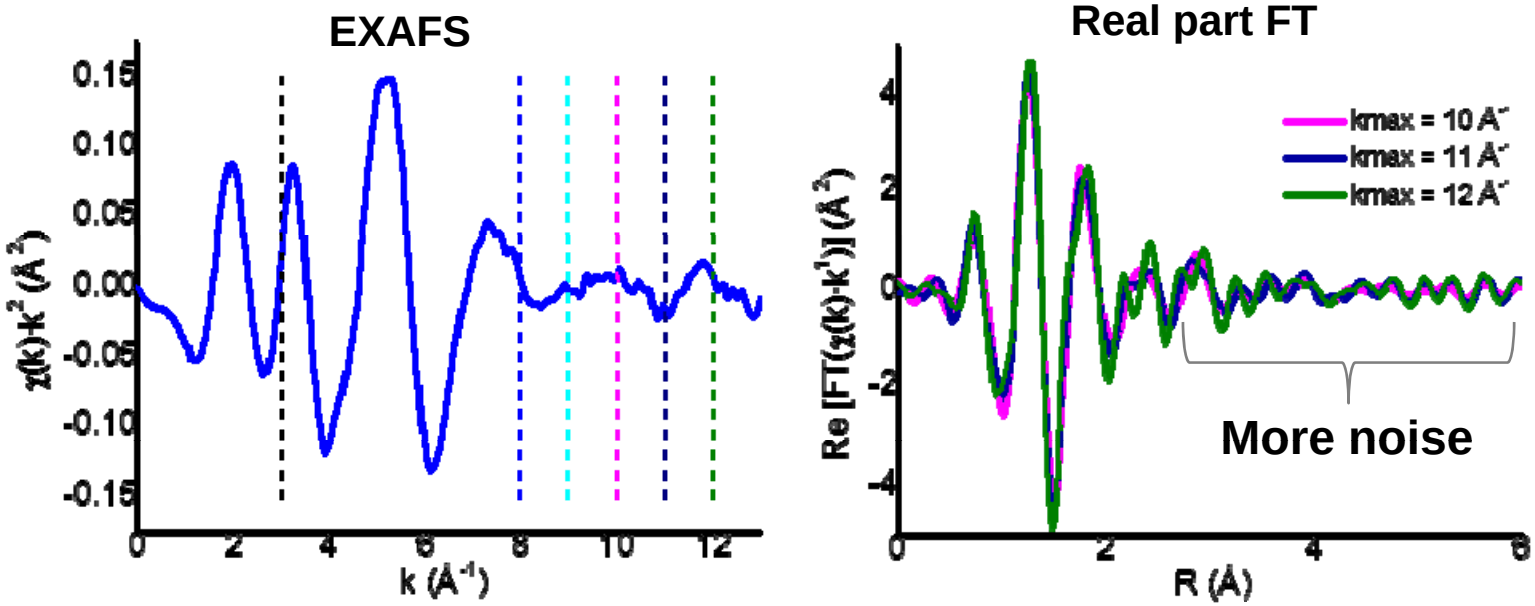


Fig.26

- The FT should be smooth and free of ringing
- To choose Kmax:
  - vary the kmax 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 kmax of 10 $Å^{-1}$ best

Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.

Effect of K-weight on FT

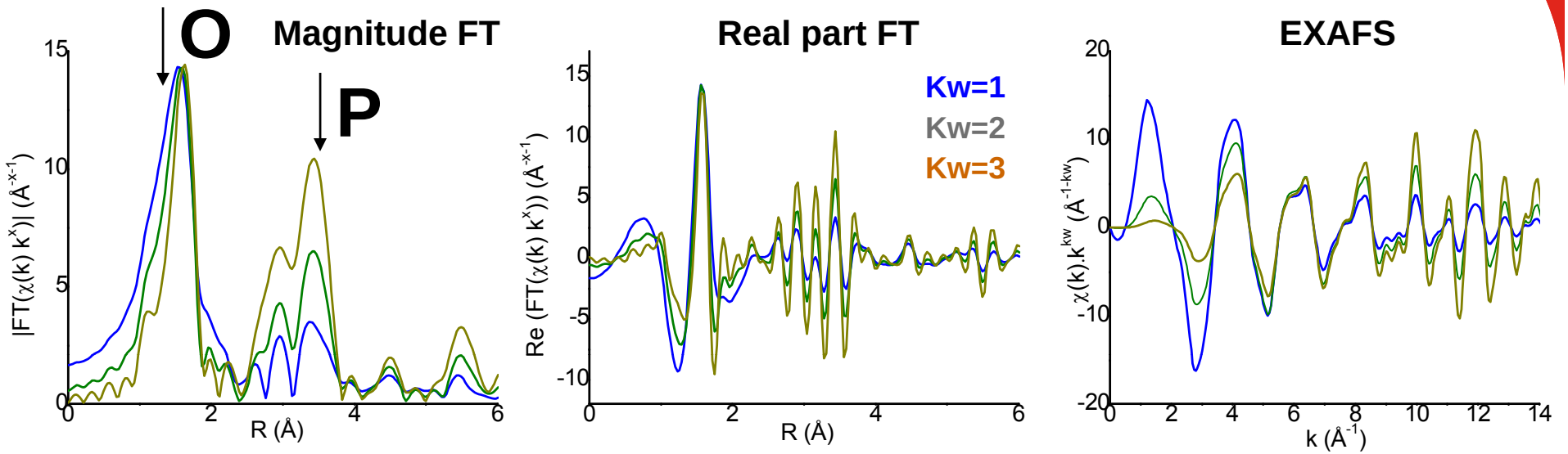


Fig.25

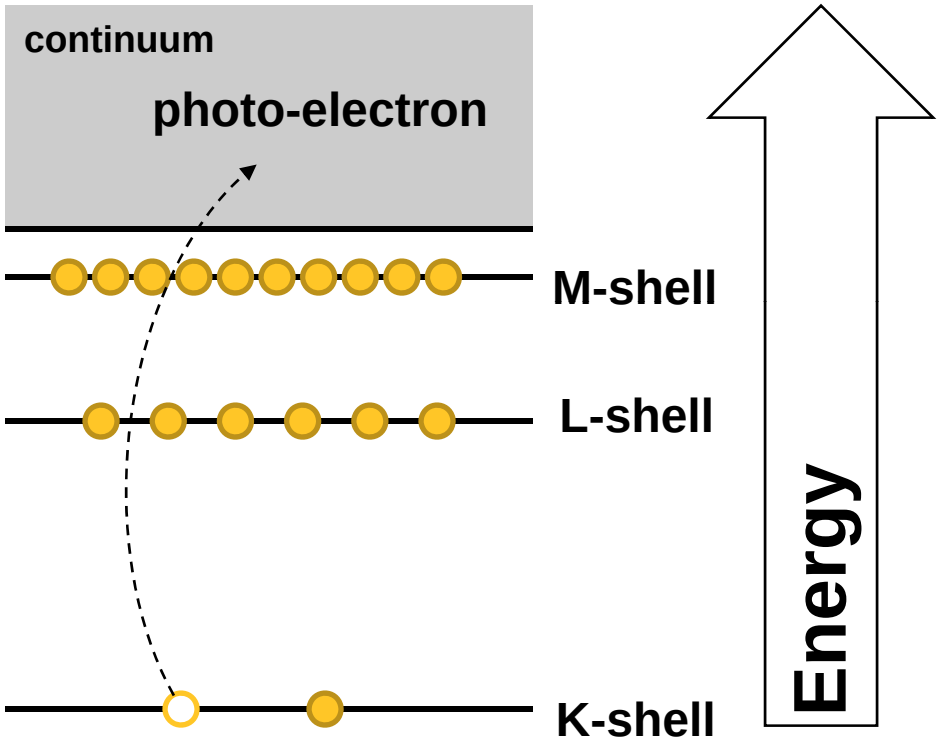
- These spectra have been k-weighted by 1, 2, and 3 and then rescaled so that the first peak in the FT are the same height
- The higher k-weight values give more importance to the data above 6 $Å^{-1}$, this emphasizes the signal due to the P neighbor relative to the O in the first shell

© 2016 by Honeywell International Inc. All rights reserved.

Theoretical Calculations using FEFF

© 2016 by Honeywell International Inc. All rights reserved.

Photoelectric Effect



Muffin Tin Approximation

- Need a distribution of atoms and central atom for theoretical scattering amplitudes *F(k)* and phases *δ(k)*

Honeywell UOP

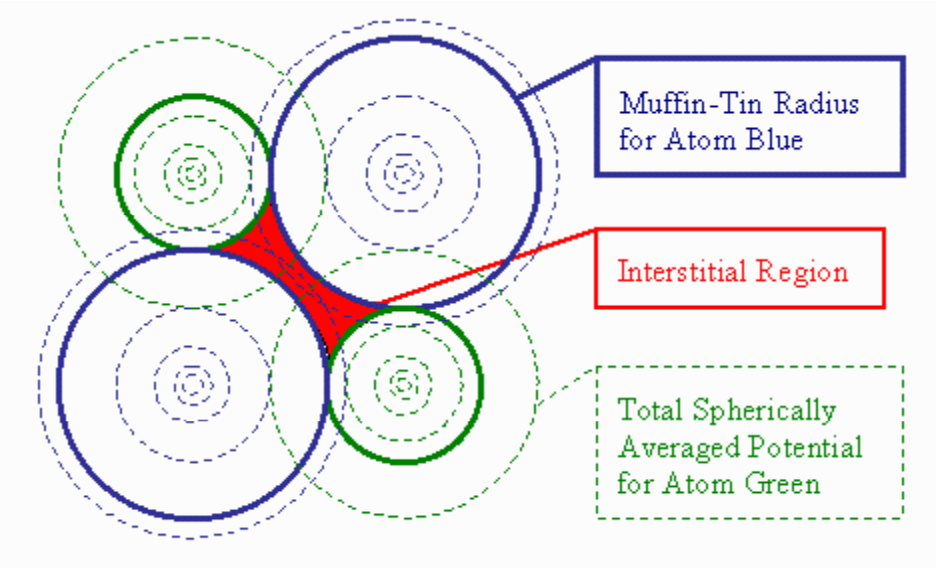
© 2016 by Honeywell International Inc. All rights reserved.

FEFF

- FEFF requires a cluster of atoms and the central absorbing atom
- FEFF outputs feff000n.dat files containing the f(k), δ(k), λ(k) for a scattering path.

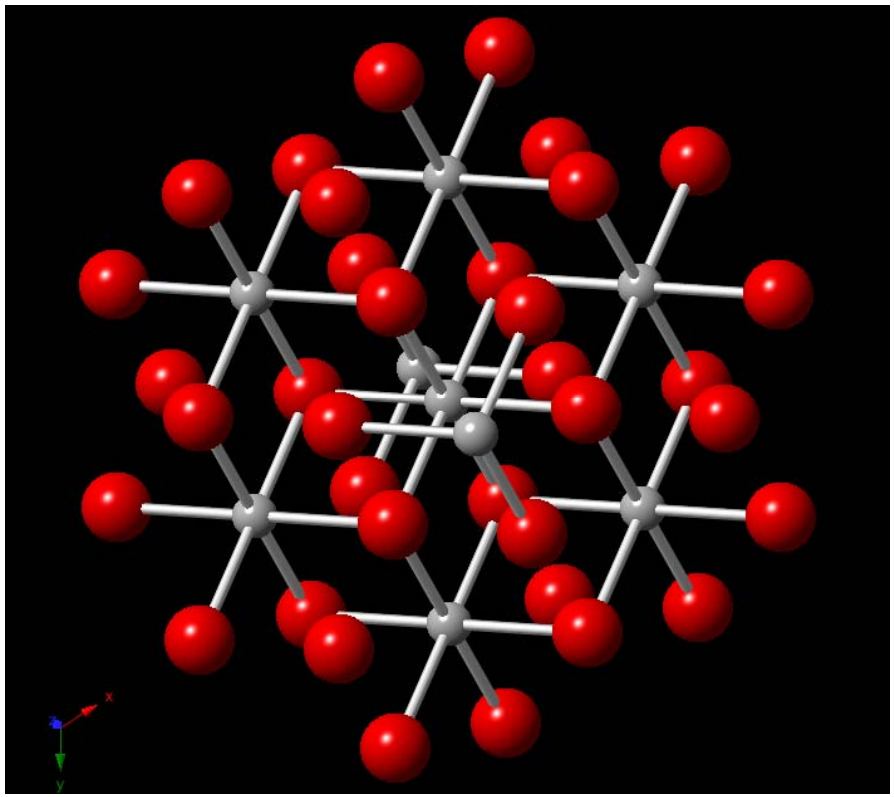
Threshold Fermi energy given by Electron gas theory at the mean interstitial density

Isolated Atoms calculated from Dirac-Fock Desclaux atom code

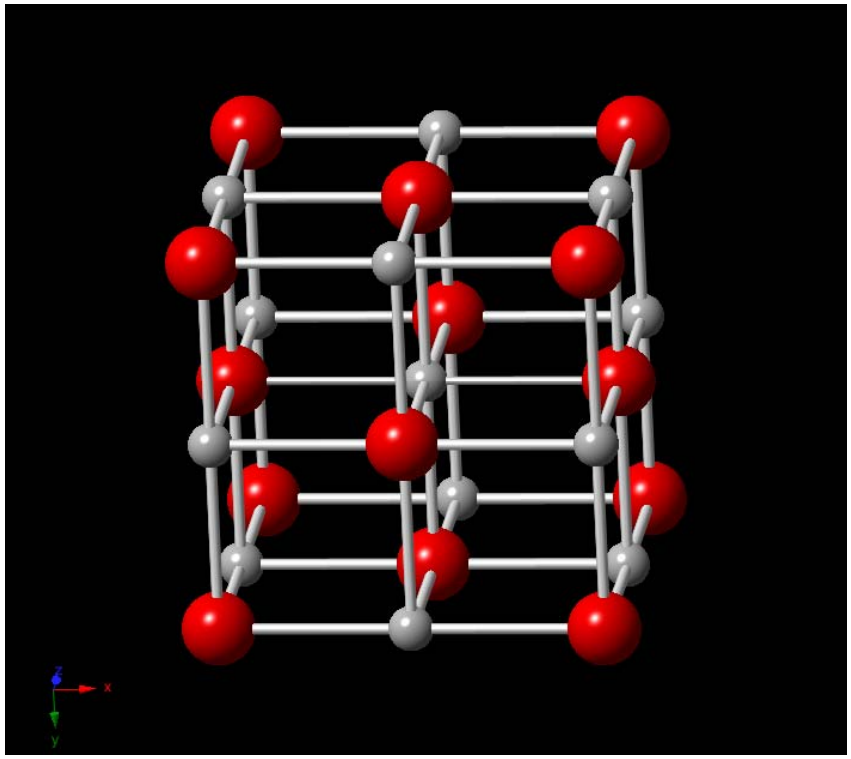


© 2016 by Honeywell International Inc. All rights reserved.

Theoretical Calculations



PtO_2 based on ICSD 164289



PtO based on ICSD 105543

- Often based on clusters of atoms from crystal structures -ATOMS

© 2016 by Honeywell International Inc. All rights reserved.

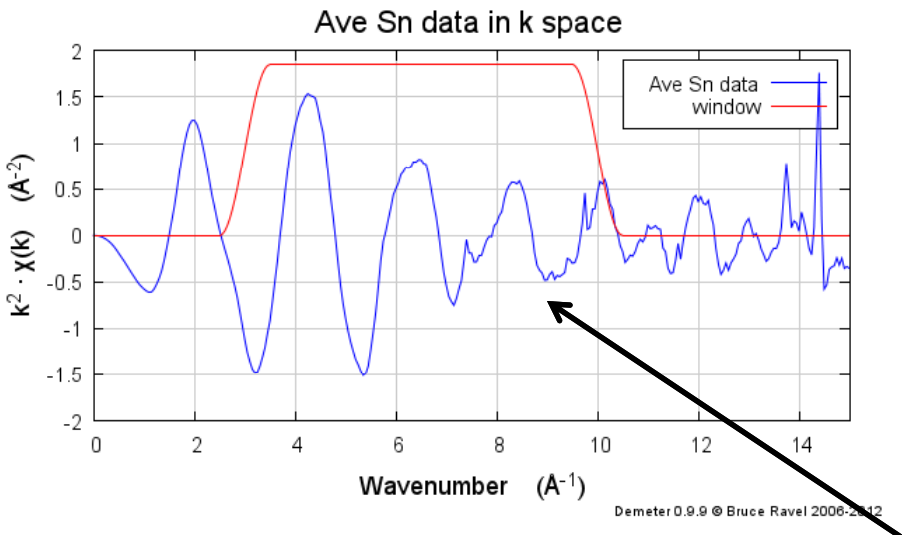
Models to consider:

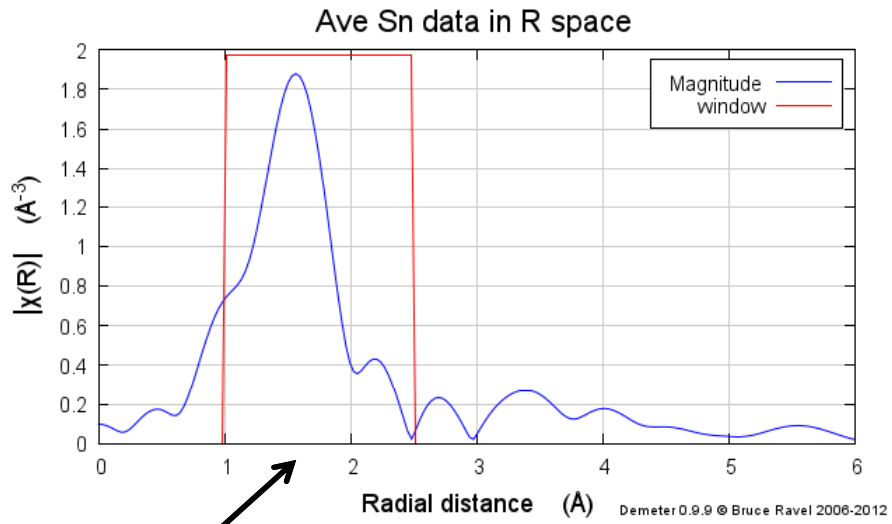
- Δr:
  - Symmetric expansion term: Alpha * reff.
  - Grouped depending on distance and atom types
  - Related to unit cell dimensions
- ΔE:
  - Energy shifts that depend on atom type
  - One energy shift for all paths
  - Two energy shifts, one for first shell and another for all other shells
- σ^2:
  - Grouped depending on distance and atom types.
  - Use a Debye or Einstien model, with one or more characteristic temperatures.
  - Each shell with independent value.
  - Separate structural disorder from thermal disorder components.
- S02:
  - One S02 for all paths.
  - Approximate S02 from standards.
- N:
  - Determined by the crystal structure.
  - Fit a data series were N is expected to change.

Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.

Information Content in Data Set





Nyquist cirterion:

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

- Number of independent points is proportional to the data range used in FT and the fitting range.
- Cannot have more variables determined in a fit than the number of independent points

© 2016 by Honeywell International Inc. All rights reserved.

Comparison of Models

χ^2 : sum of the difference between the data and the theory

$$\chi^2 = \frac{N_{idp}}{\epsilon N_{data}} \sum_{i=min}^{max} [Re(\chi_d(r_i) - \chi_t(r_i))^2] + Im(\chi_d(r_i) - \chi_t(r_i))^2]$$

$$\epsilon = measurement\ uncertainty$$

$$\chi_\nu^2 = \frac{\chi^2}{\nu}$$

Reduced χ^2 : sum of the difference between the data and the theory, scaled by degrees of freedom. $\nu = N_{idp} - N_{var}$

Useful for comparing models with different number of variables

R-factor: fractional misfit

$$\mathcal{R} = \frac{\sum_{i=min}^{max} [\, Re(\chi_d(r_i) - \chi_t(r_i))^2 + Im(\chi_d(r_i) - \chi_t(r_i))^2 \,]}{\sum_{i=min}^{max} [\, Re(\chi_d(r_i))^2 + Im(\chi_d(r_i))^2 \,]}$$

- FEFFIT uses Levenberg-Marquardt non-linear least-squares minimization

Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.

Statistical Measures of Model

- χ_ν^2 are used to compare between two different models. Values are poorly scaled and often 100 – 1000. χ_ν^2 need to change by more than a factor of 2 to be significant.
- Error bars are scaled by $\sqrt{\chi_\nu^2}$, assuming that the model is good.

Honeywell
UOP

© 2016 by Honeywell International Inc. All rights reserved.

Q & A

Honeywell UOP

© 2016 by Honeywell International Inc. All rights reserved.