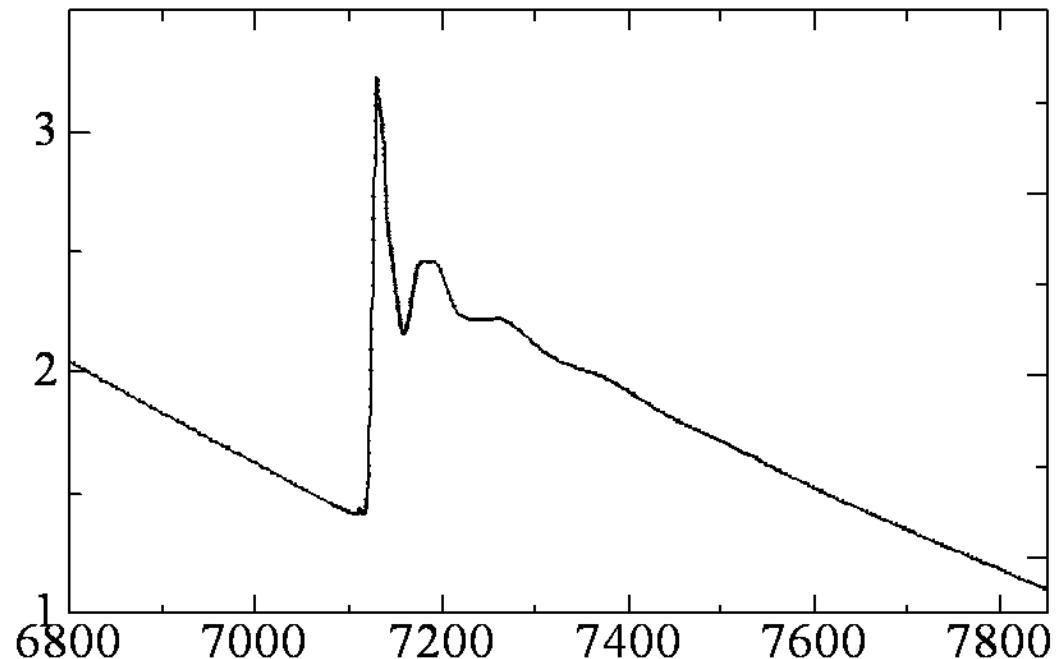


EXAFS

Extended X-ray Absorption Fine Structure

Iwao Watanabe

Ritsumeikan University



EXAFS

Theory

Quantum Mechanics
Models
Approximations

Experiment

Light Source
Monochromator
Higher Harmonics Rejection
Sample Preparation
Detection Methods
Polarization XAFS

Data Analysis

Limited Usable Range in Experimental Data

Estimation of Background Curves

Fourier Transform

Multi-Scattering

Curve Fitting Procedure

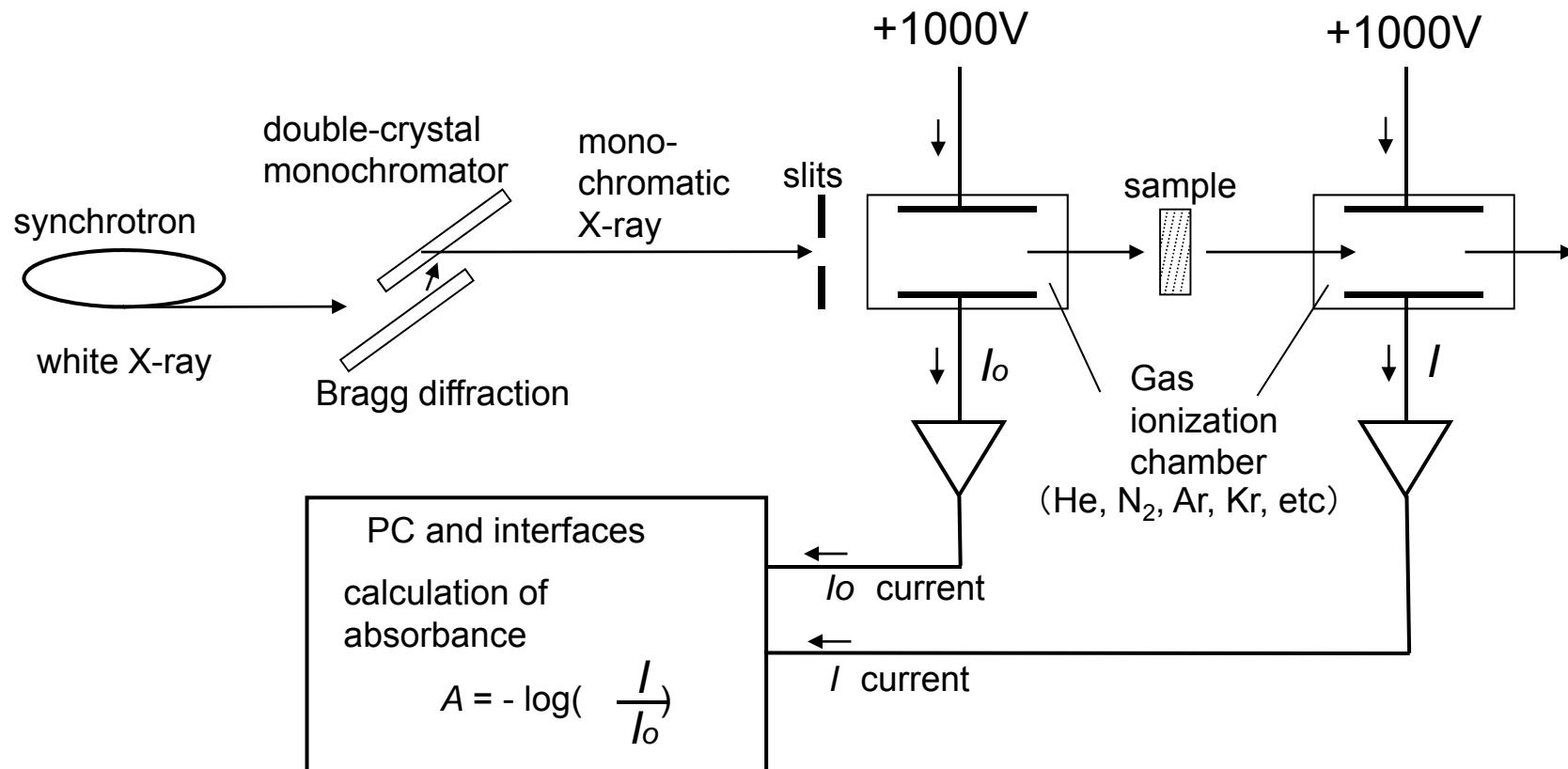
Phase Problems

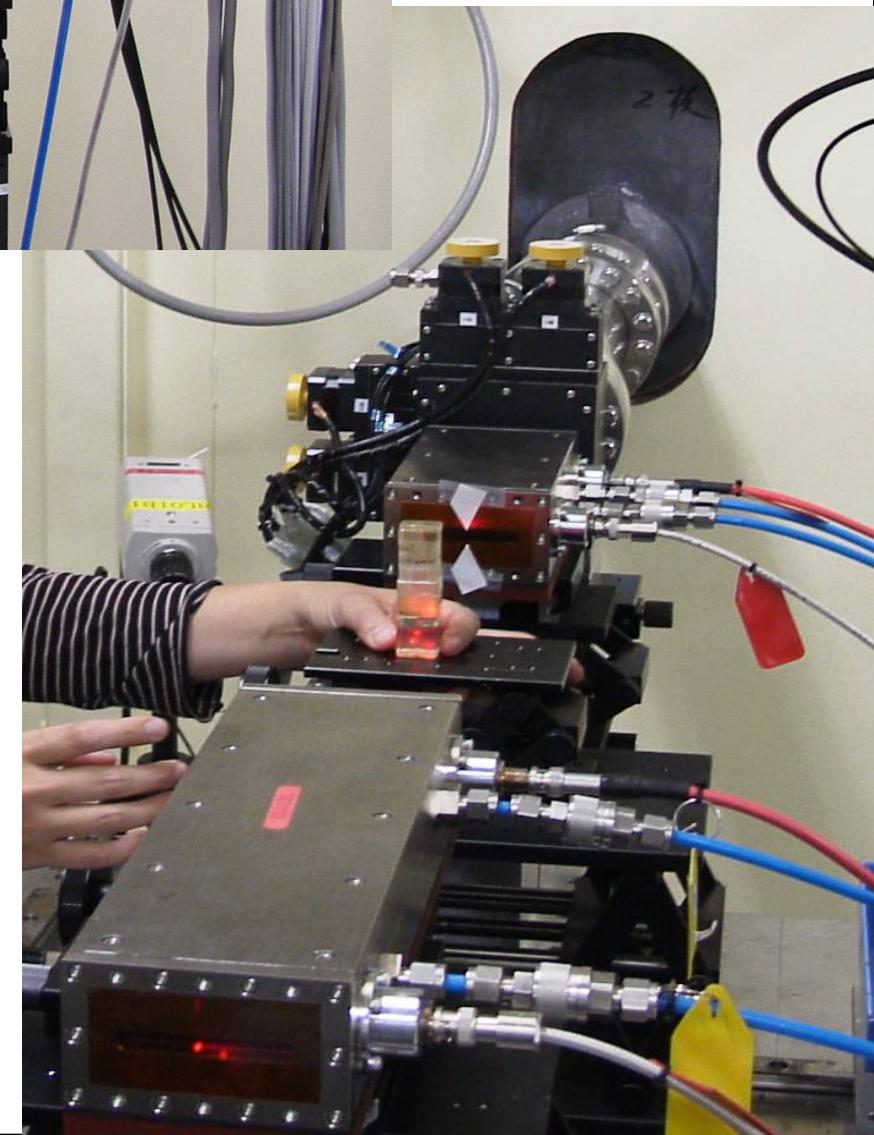
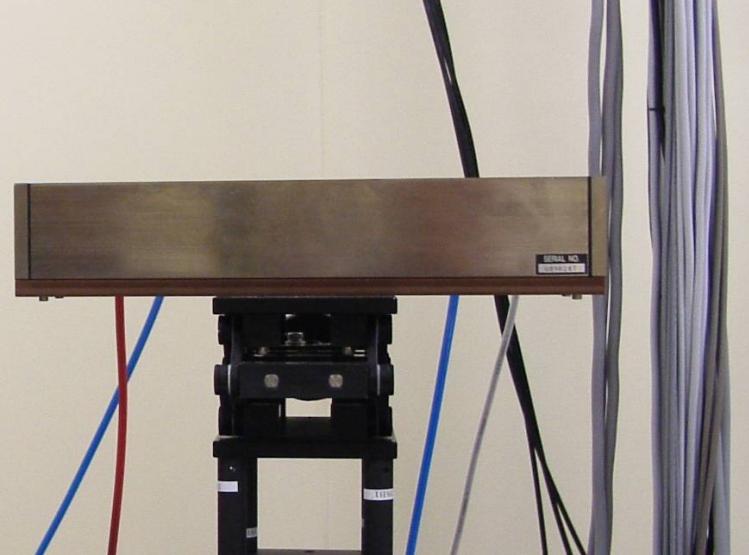
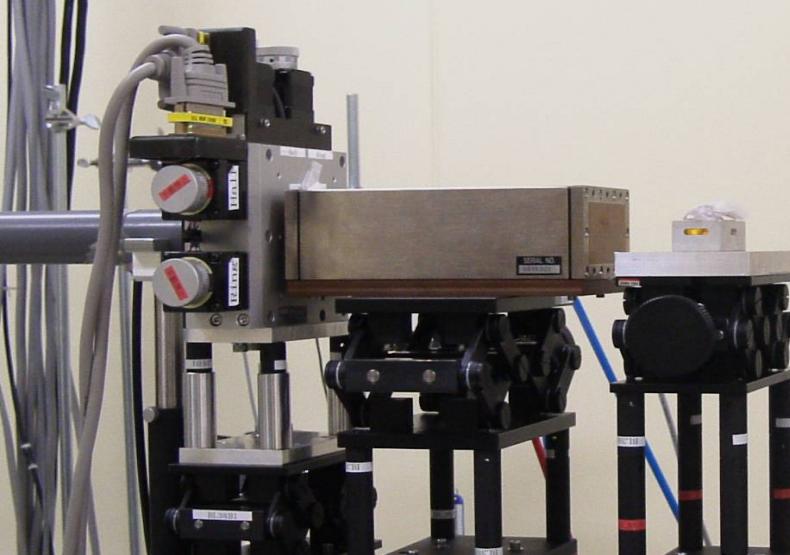
Debye-Waller-Like Parameter

Anharmonicity in Potential

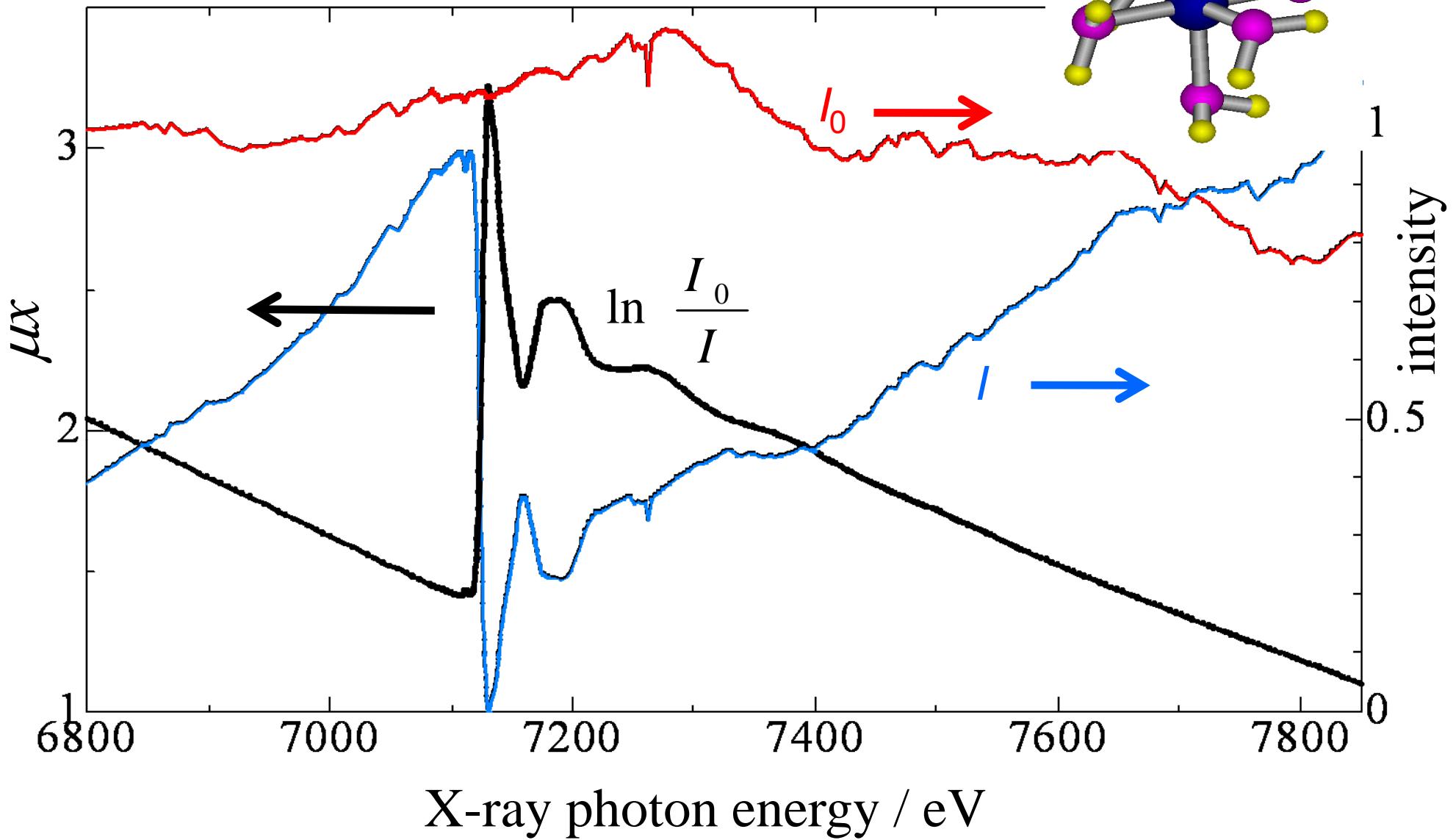
X-ray absorption measurement by transmission method

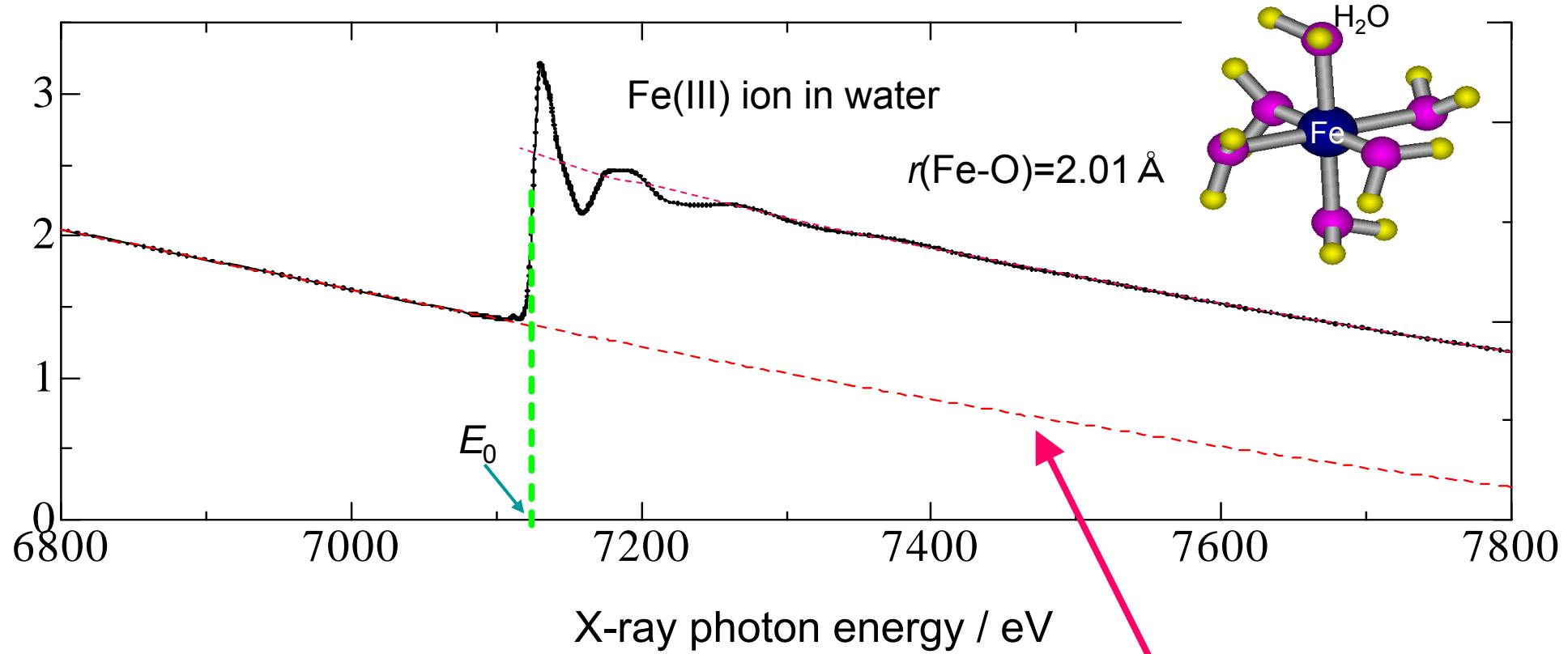
The most reliable and basic method





XAS of Fe(III) aqueous solution





Focusing on K shell (1s electron) excitation

Background absorption due to other atoms and other shell electrons

Fermi's Golden Rule

In XAS we measure the dipole mediated transition of an electron in a deep core state $|i\rangle$ into an unoccupied state $|f\rangle$:

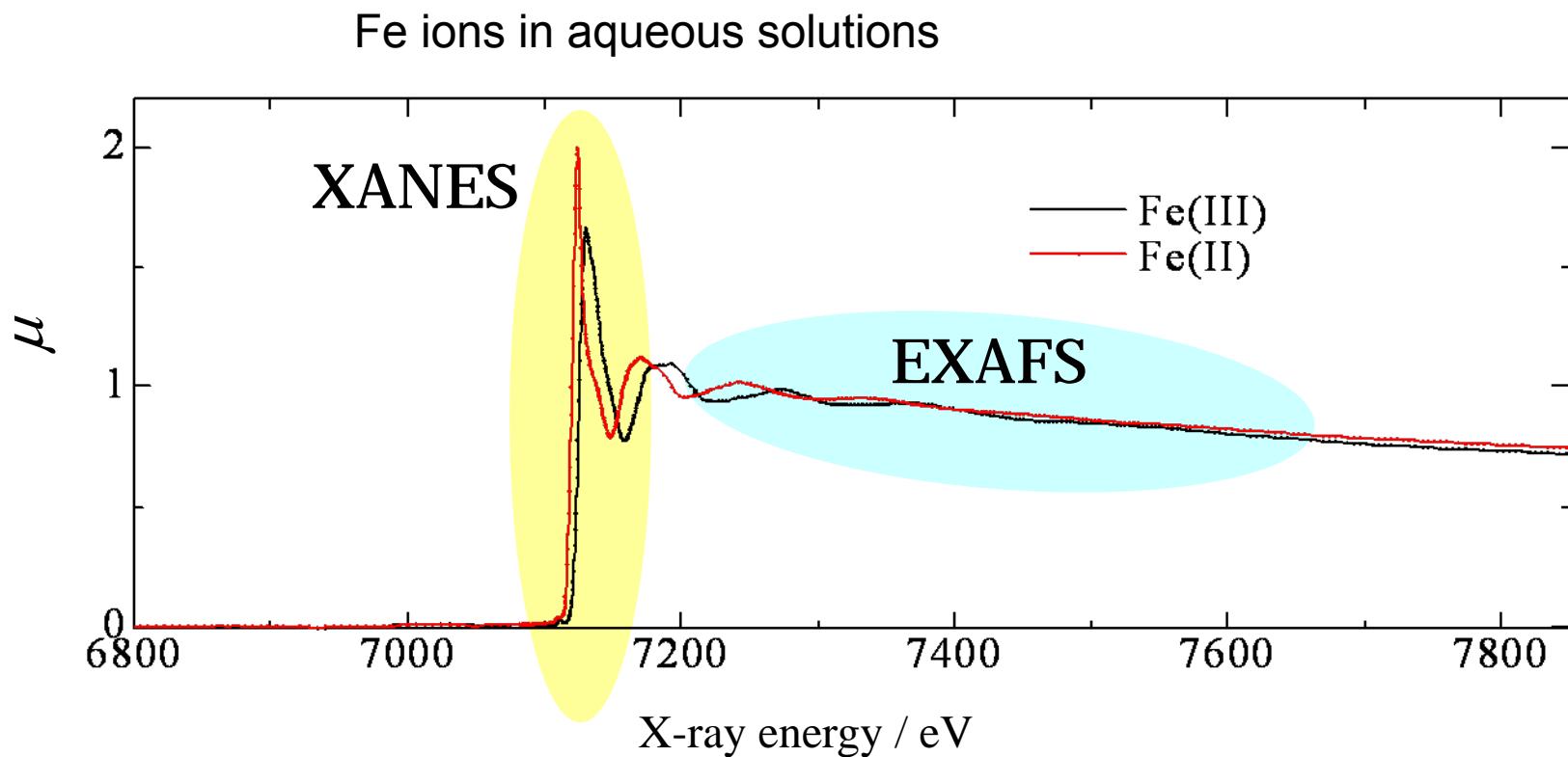
$$\mu(E) \propto \sum_f \begin{matrix} E_f > E_F \\ | \langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle |^2 \delta(E_f) \end{matrix}$$

There are two ways to solve this equation:

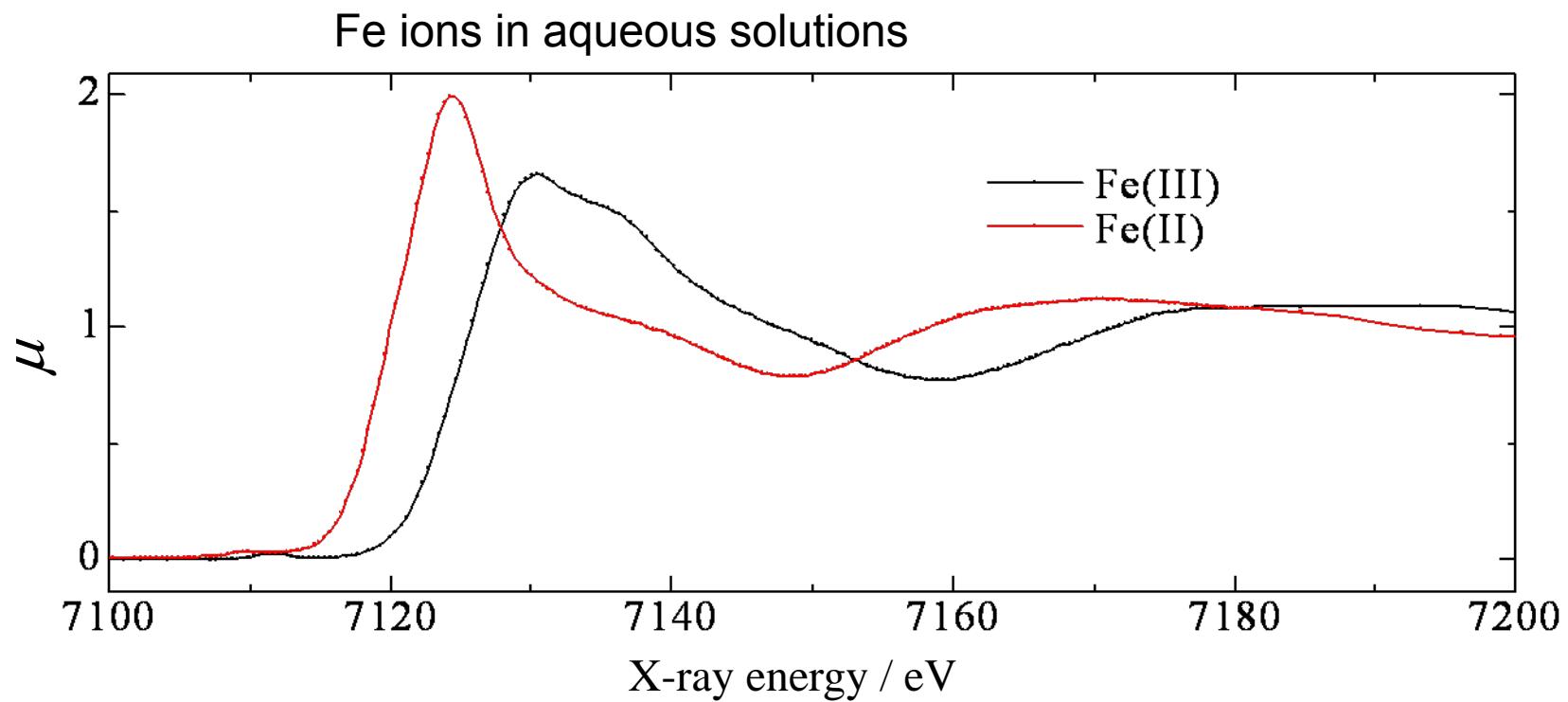
1. Accurately represent $|i\rangle$ and $|f\rangle$, then evaluate the integral directly. This is the approach taken, for example, by molecular orbital theory.
2. Use **multiple scattering theory**:

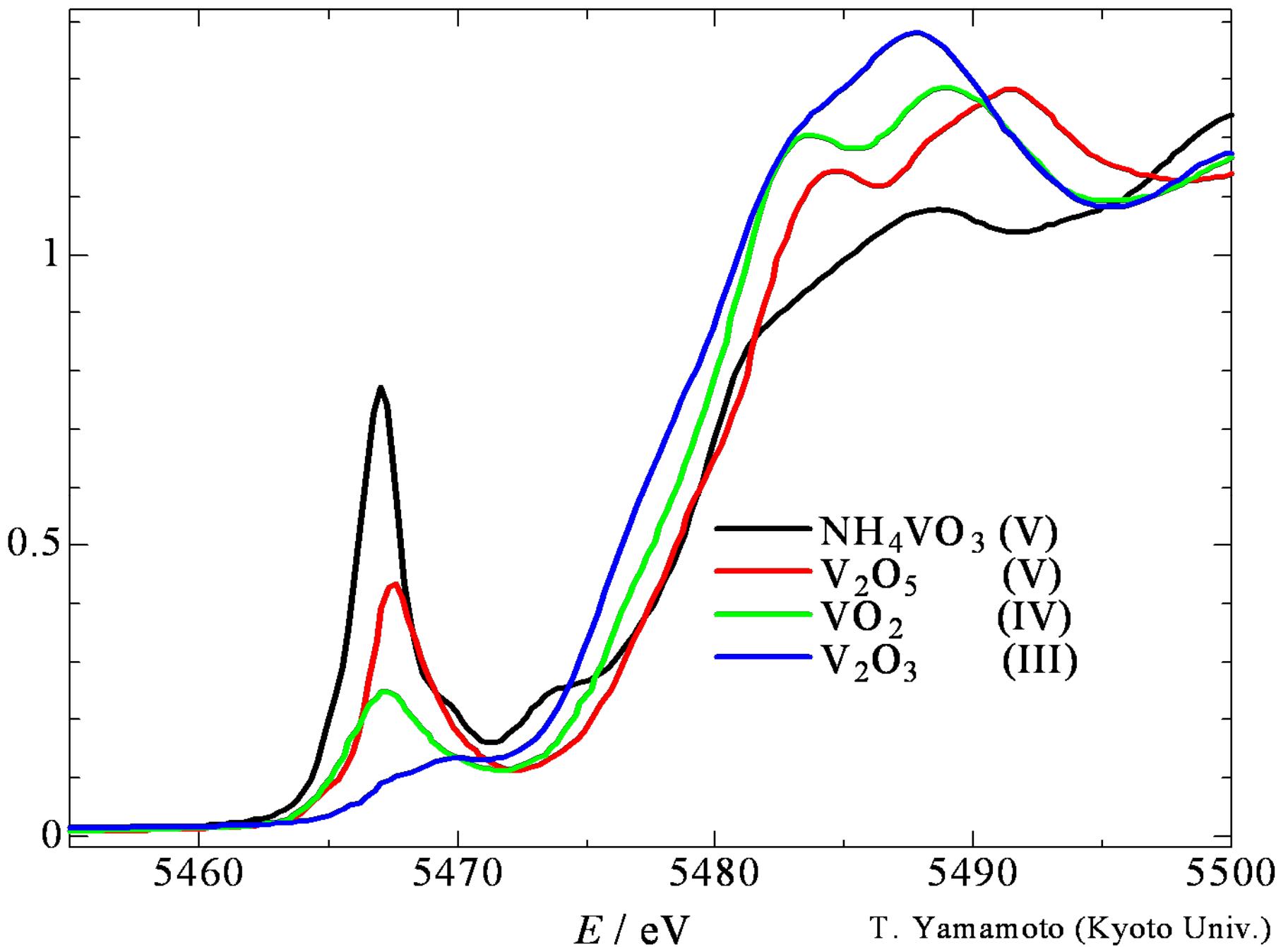
This is the approach taken by **FEFF** and, by extension, by analysis programs which use **FEFF**.

XAFS: X-ray Absorption Fine Structure



XANES: X-ray Absorption Near Edge Structure





E / eV

T. Yamamoto (Kyoto Univ.)

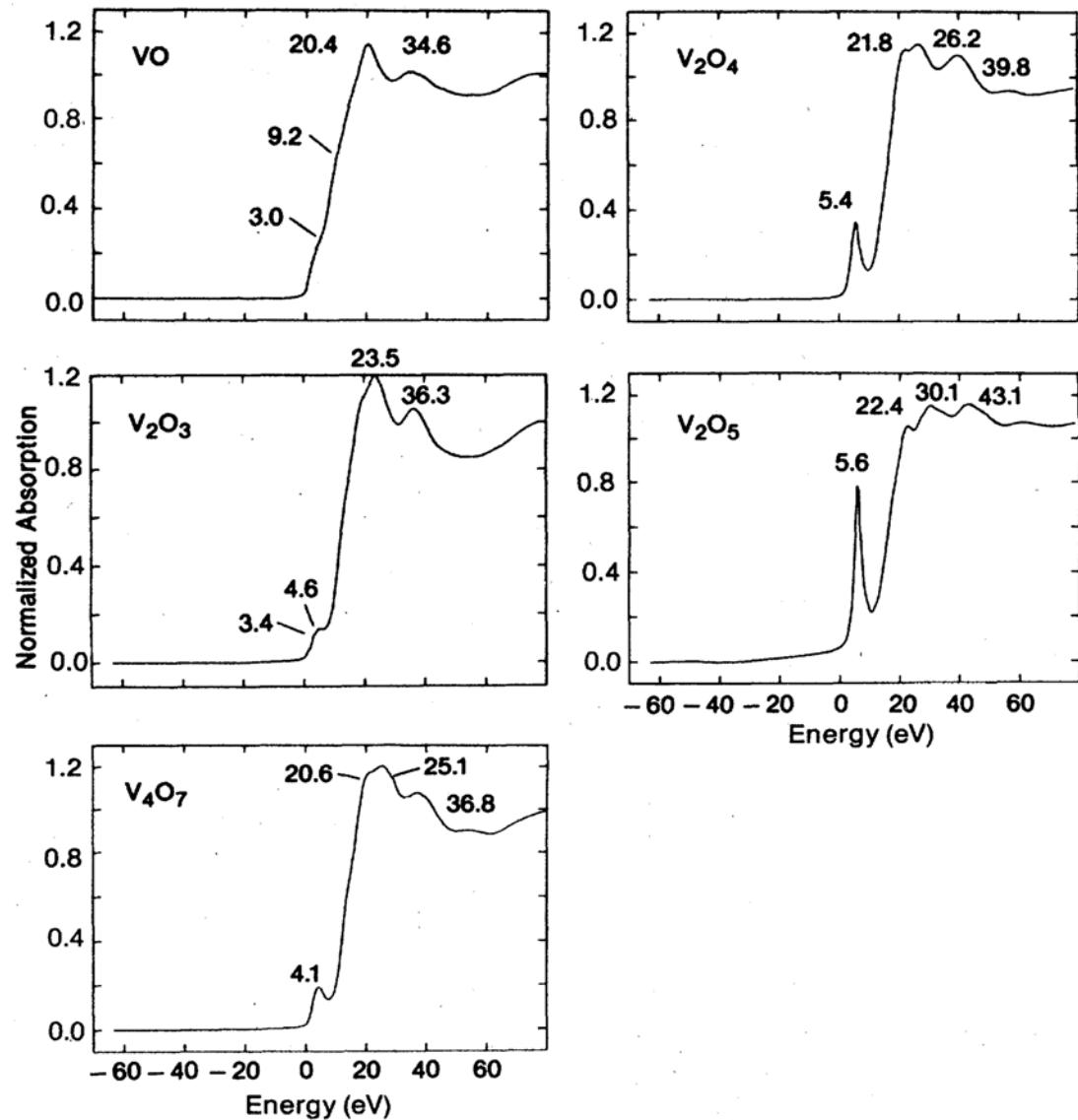
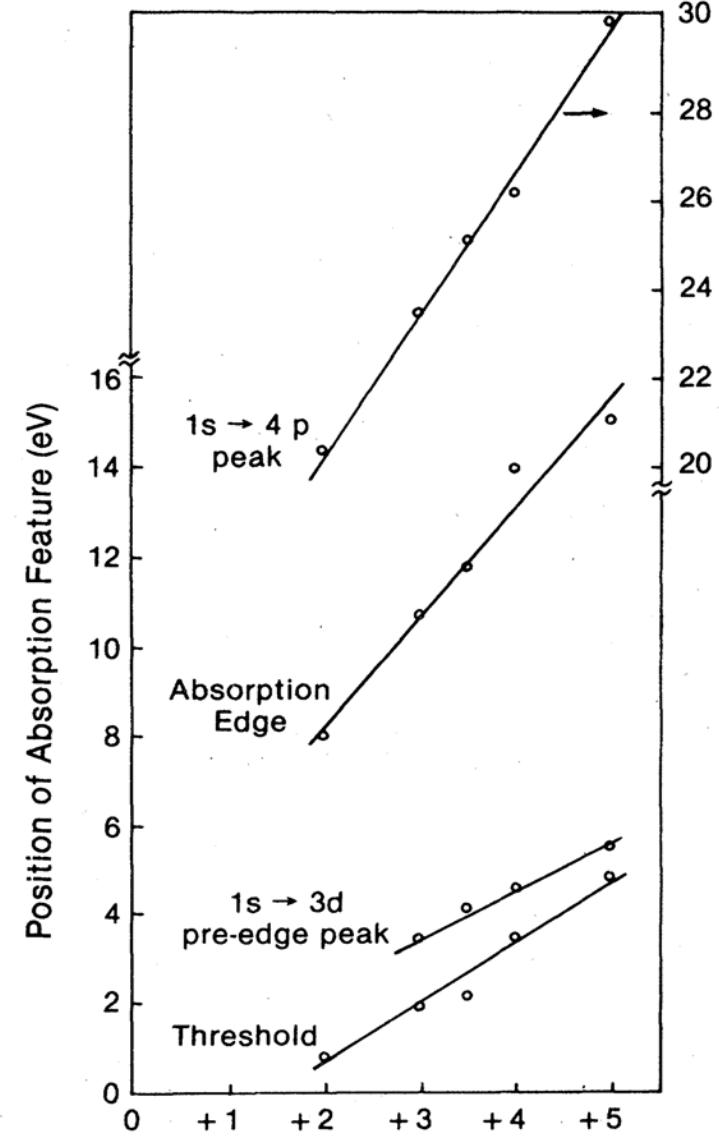
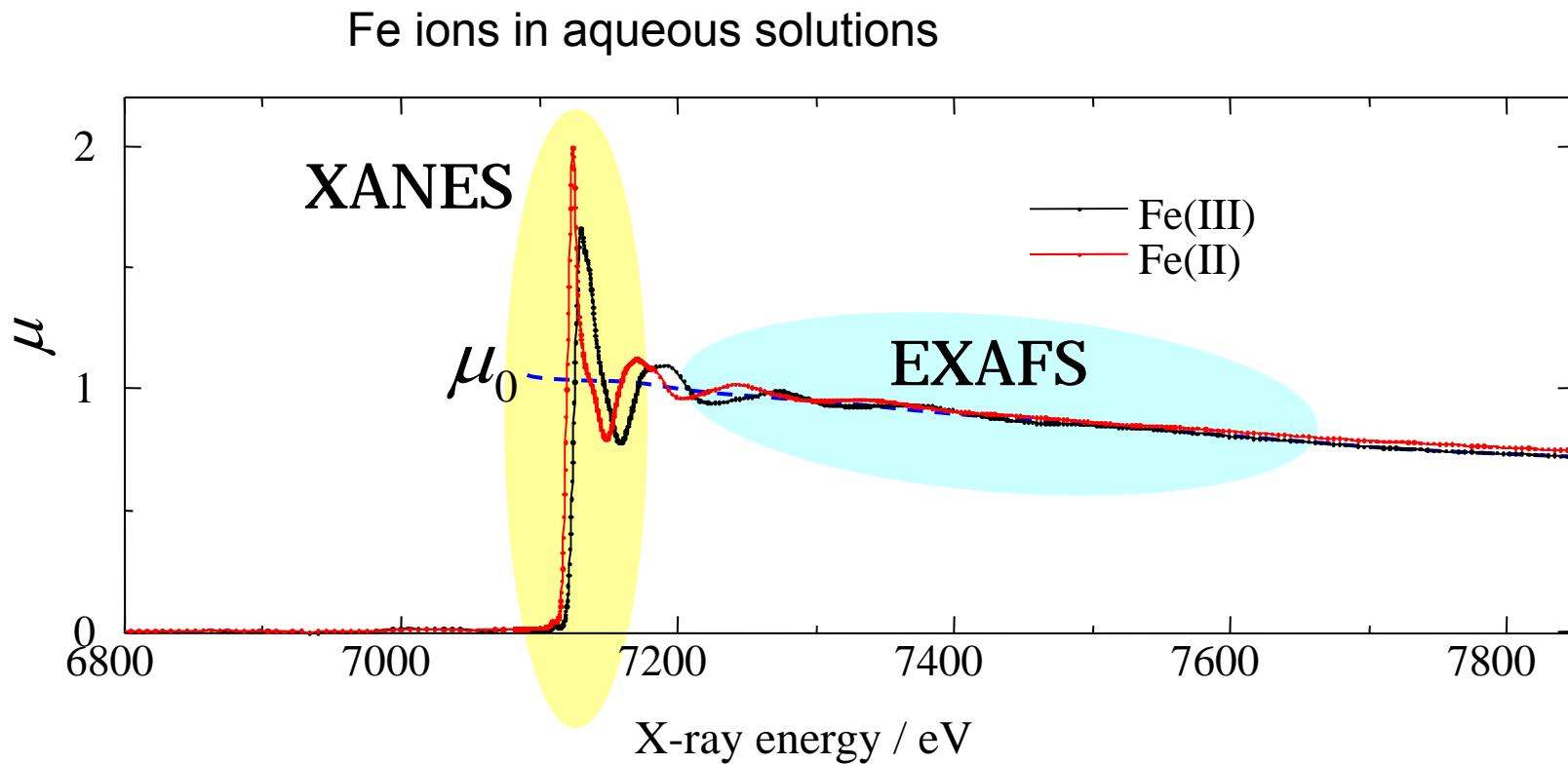


FIG. 3. Normalized K -edge XANES spectra of vanadium oxides, the zero of energy taken at 5465 eV.



Wong et al. Phys.Rev.B 30
(1984) 5596

EXAFS: Extended X-ray Absorption Fine Structure

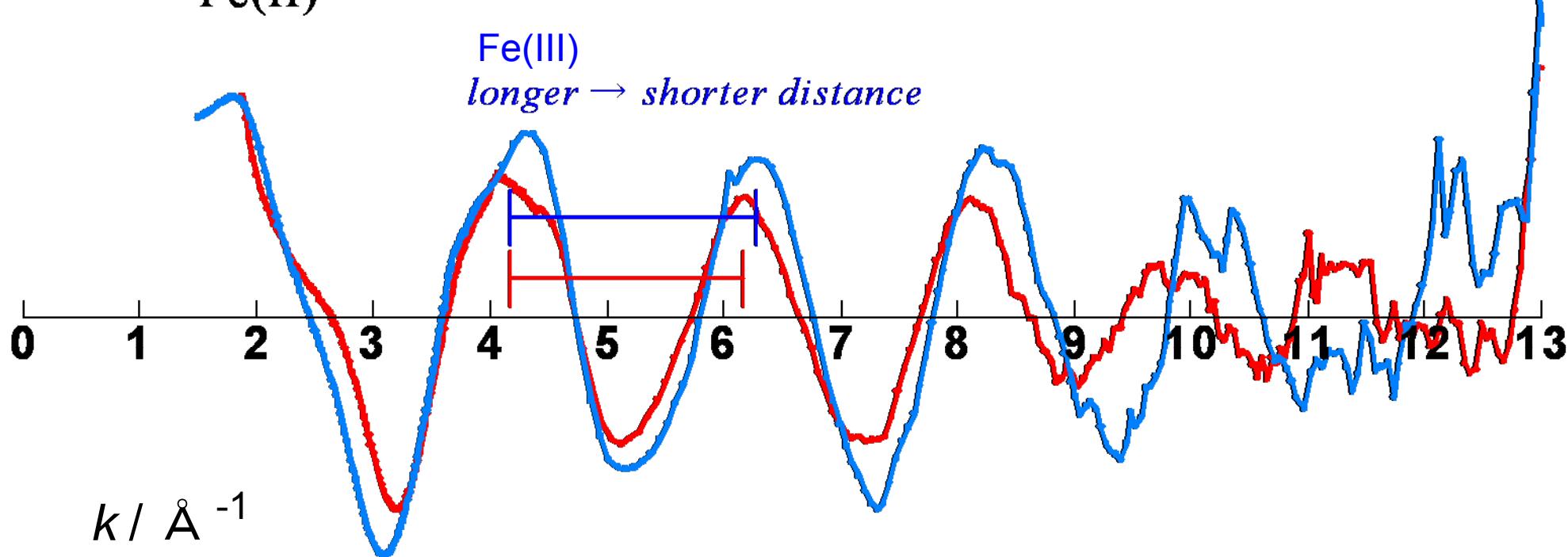


$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

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

— Fe(III)
— Fe(II)

EXAFS: $\chi(k)$ spectra



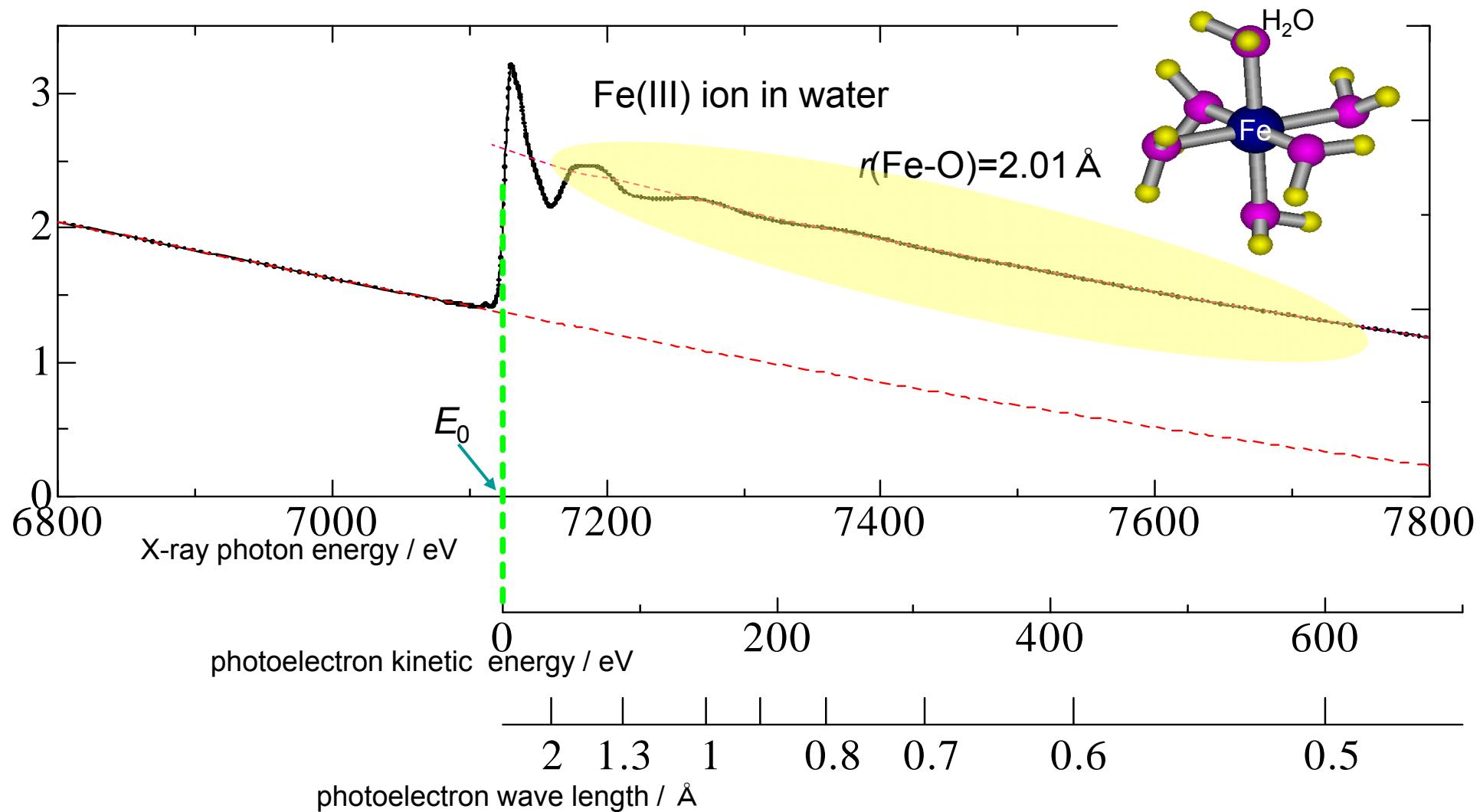
k : wave number, wave vector

$$k = \frac{2\pi}{\lambda}$$

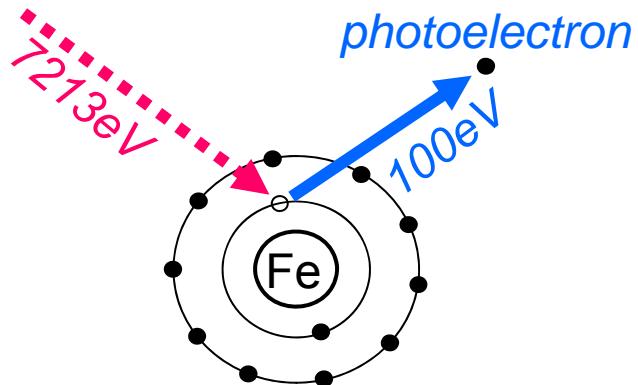
$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

$(E - E_0)$
kinetic energy of
photoelectron

Simplest model to explain how the EXAFS oscillation occurs



X-ray photon



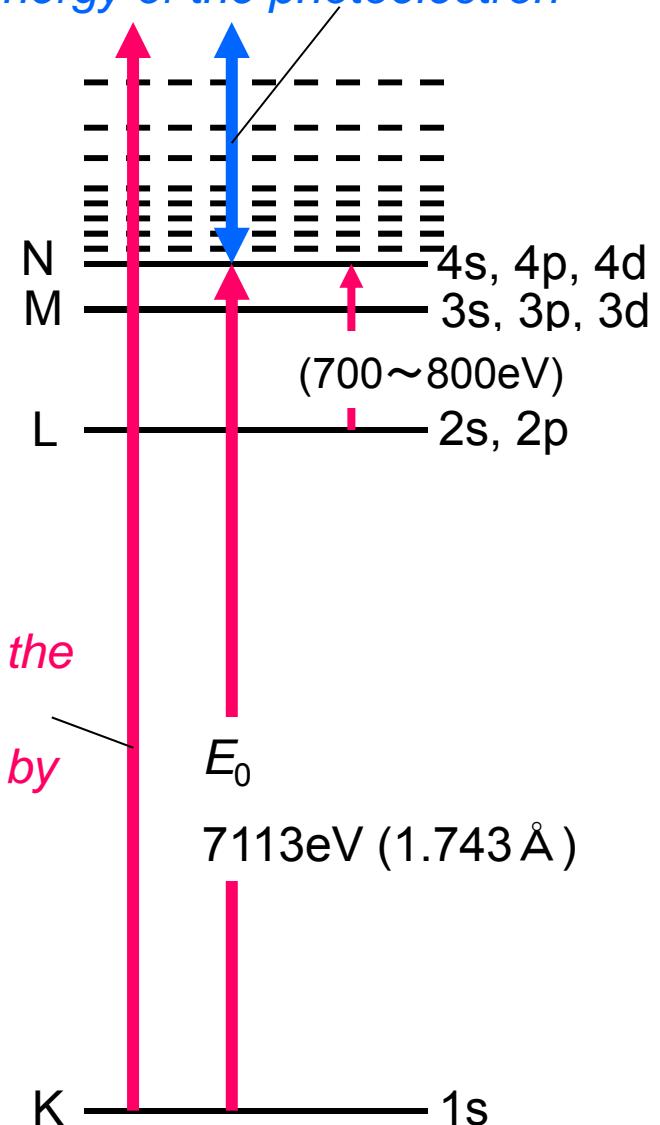
an electron with $E_k=100\text{eV}$ behaves as a wave with $\lambda=1.2\text{\AA}$

$$\lambda = \frac{h}{p} : \text{de Broglie}$$

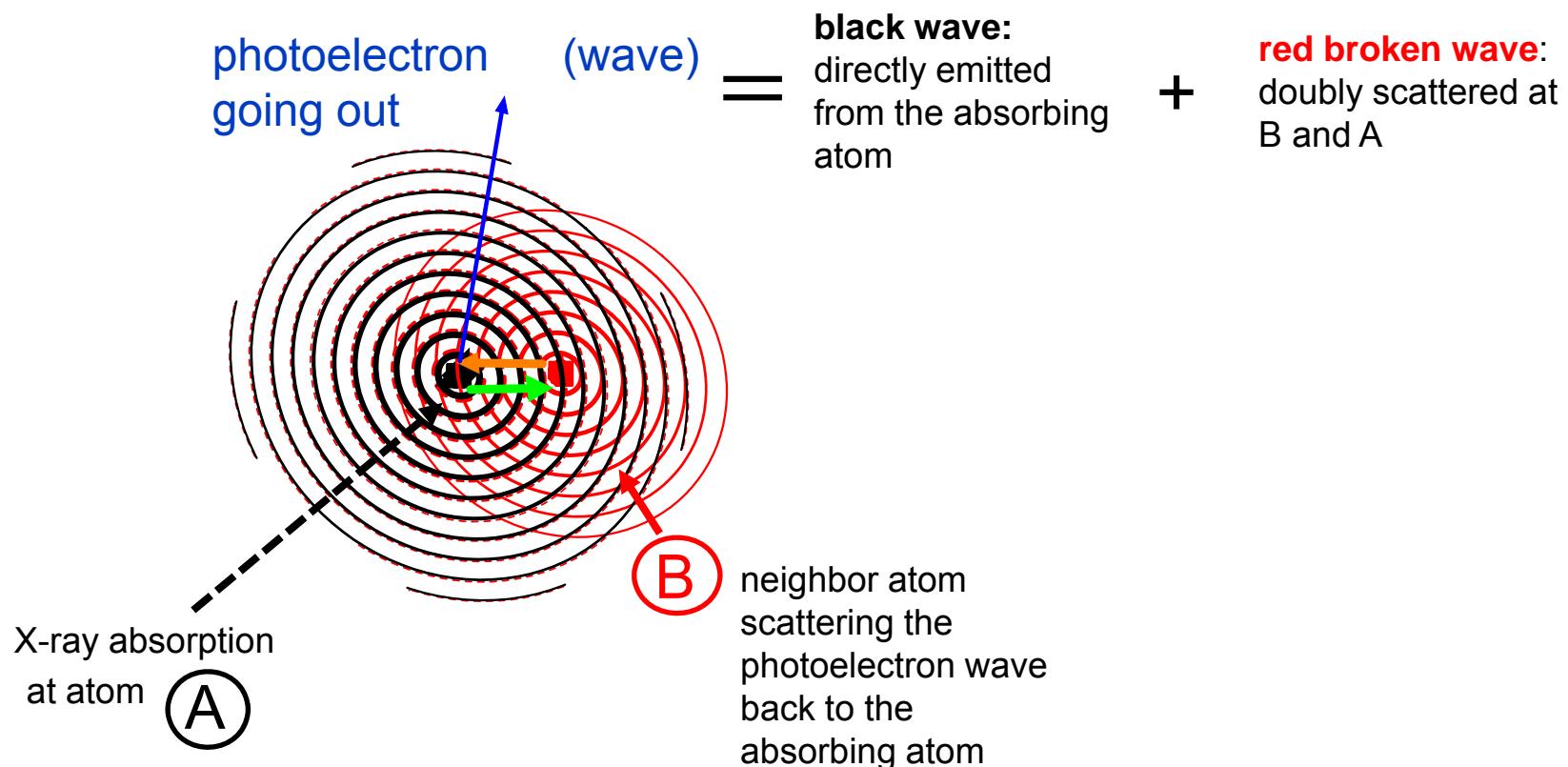
This wave length is just the order of normal atom-atom bond distance !!!

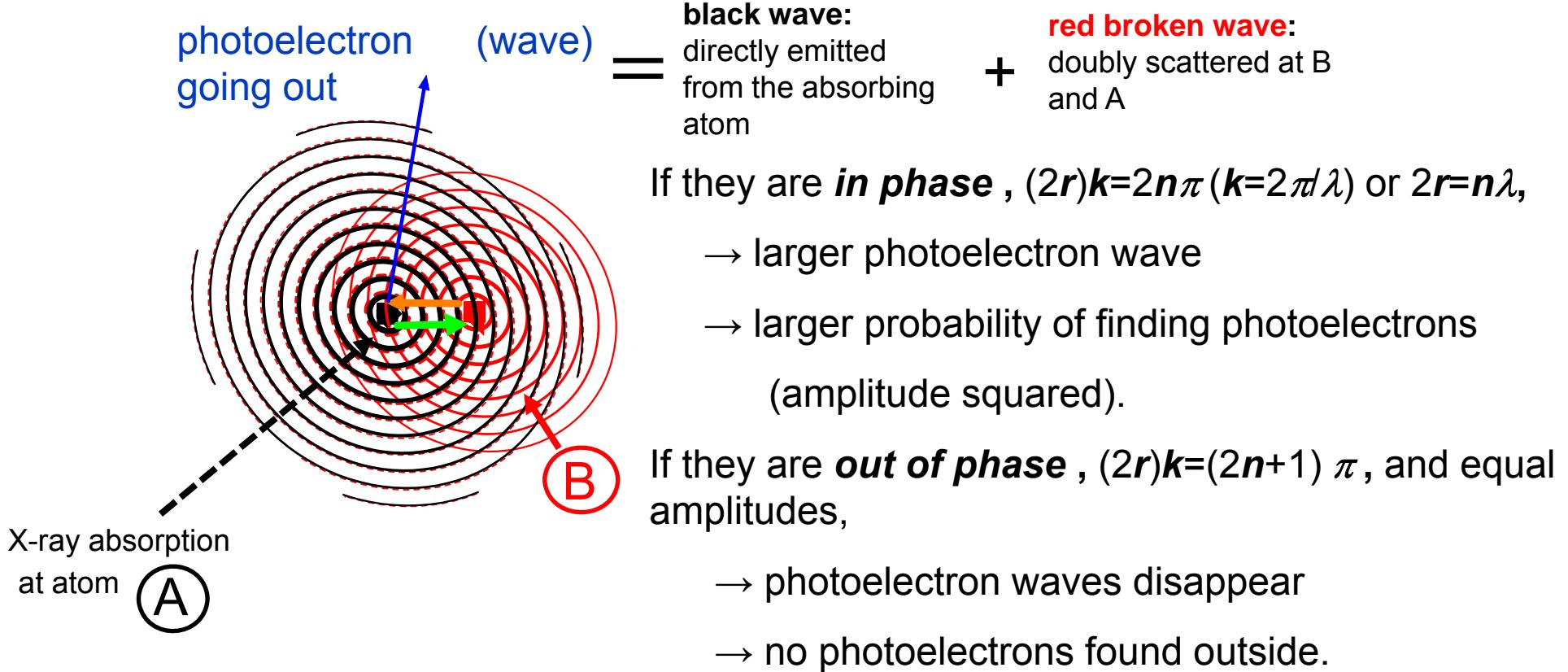
The cause for EXAFS appearance !!!

kinetic energy of the photoelectron



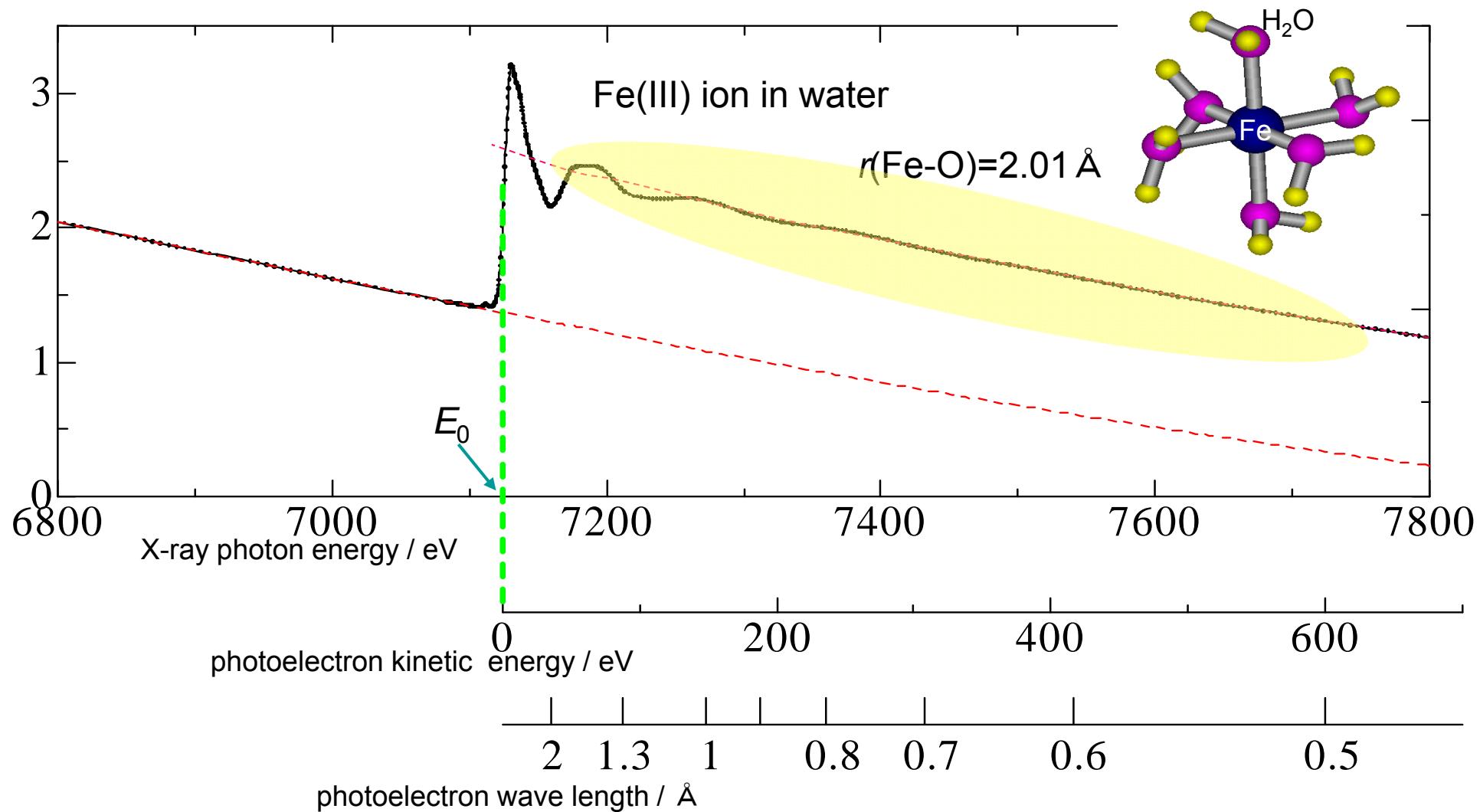
energy of the photon absorbed by Fe atom





The law of conservation of energy tells that
 when no photoelectrons are emitted, no photons should be absorbed !!!
 if the X-ray photons are absorbed, the photoelectrons must be emitted !!!

Larger probability of finding photoelectrons → STRONG X-ray absorption
Smaller probability of finding photoelectrons → WEAK X-ray absorption



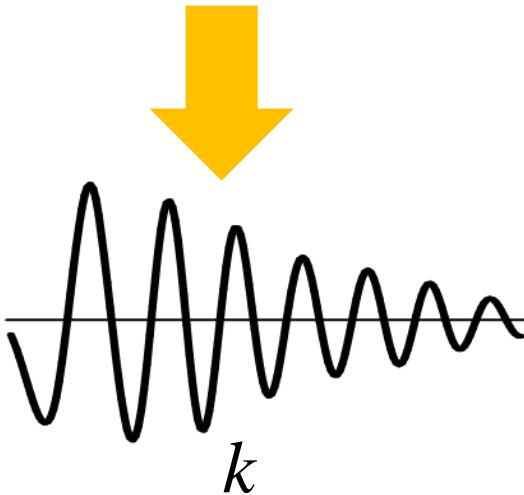
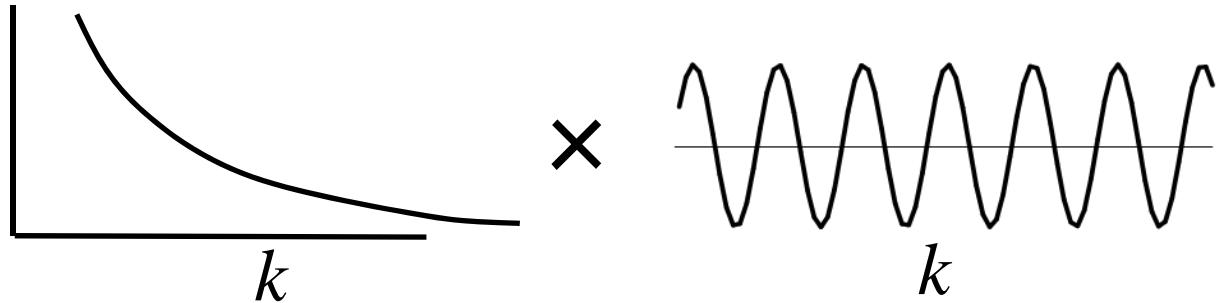
BASIC EXAFS equation

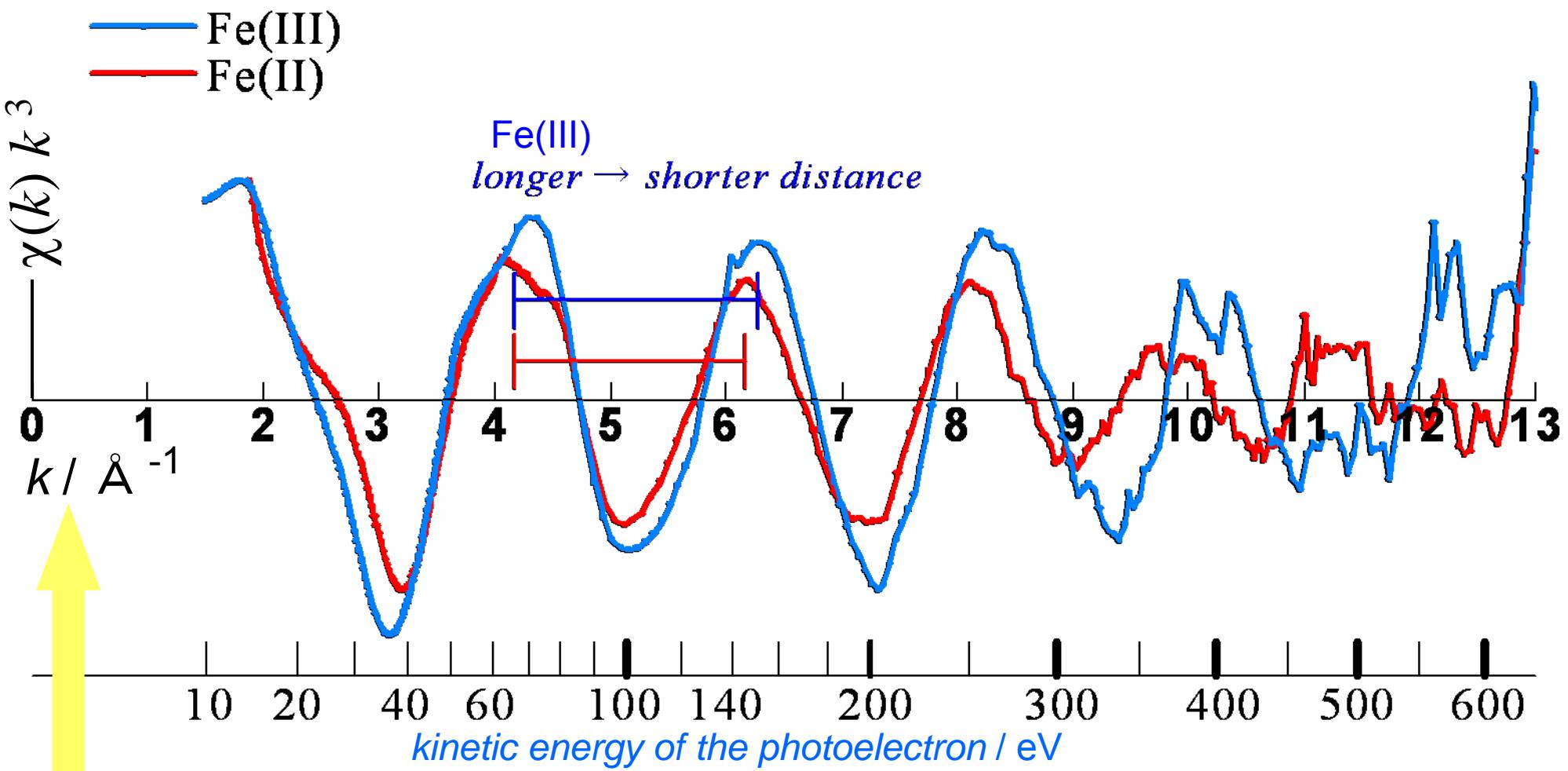
$$\chi(k) = -\sum_i \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

BASIC EXAFS equation

$$\chi(k) = -\sum_i \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

amplitude part oscillation part



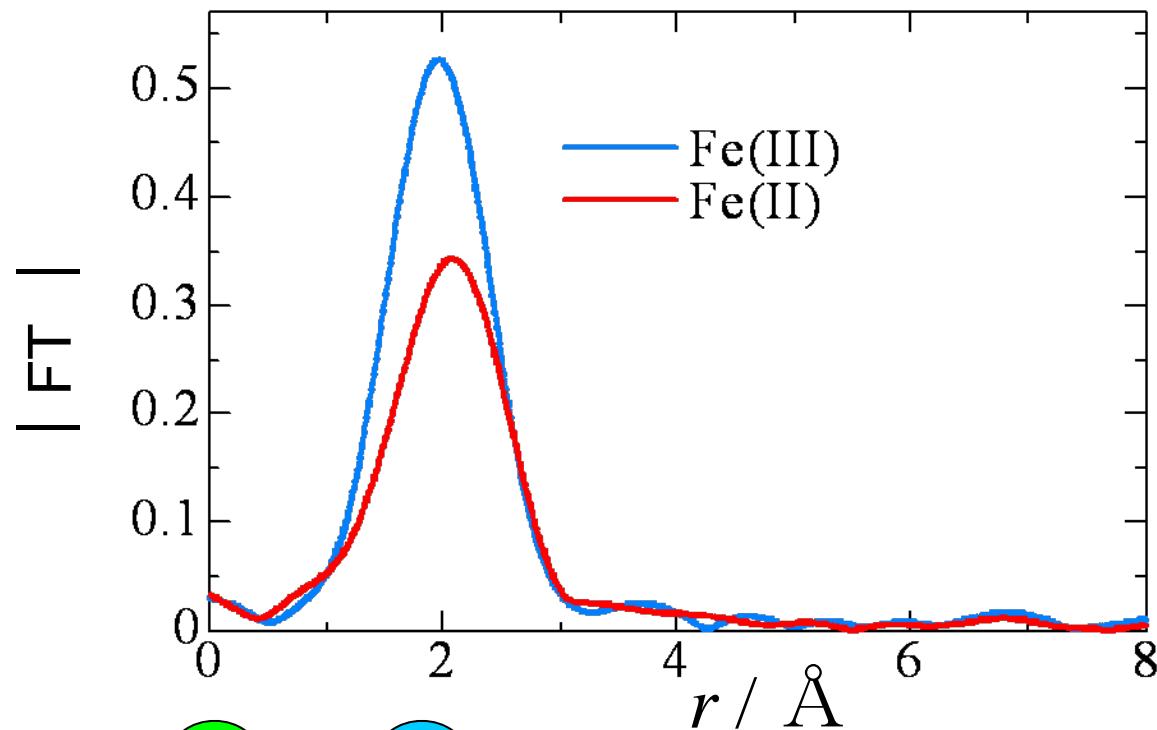


photoelectron wave number (vector)

$$k = \frac{2\pi}{\lambda}$$

*Fourier Transform:
Simplest way to analyze the EXAFS
oscillation*

The simplest way of knowing the wave number (corresponding to the distance) is Fourier Transformation of wave on k

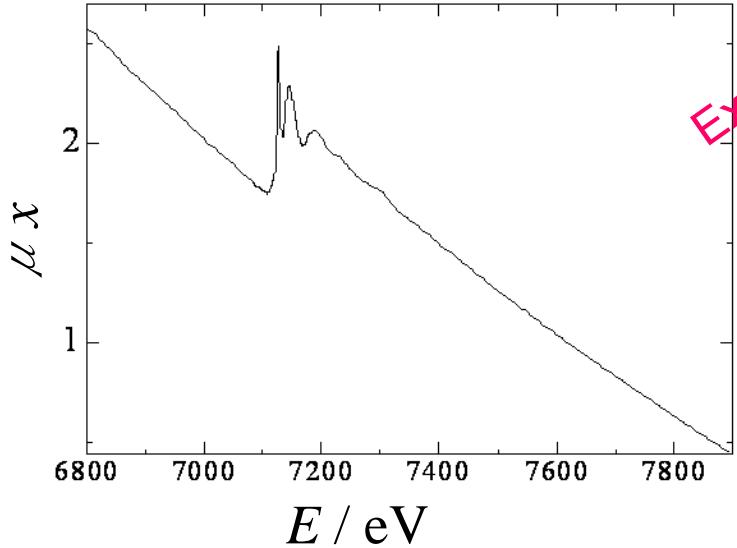
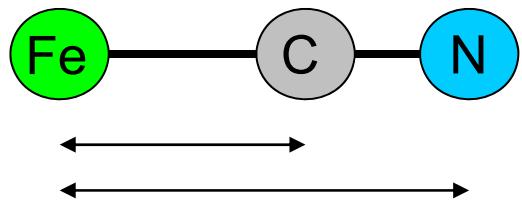


Fe(III) shorter

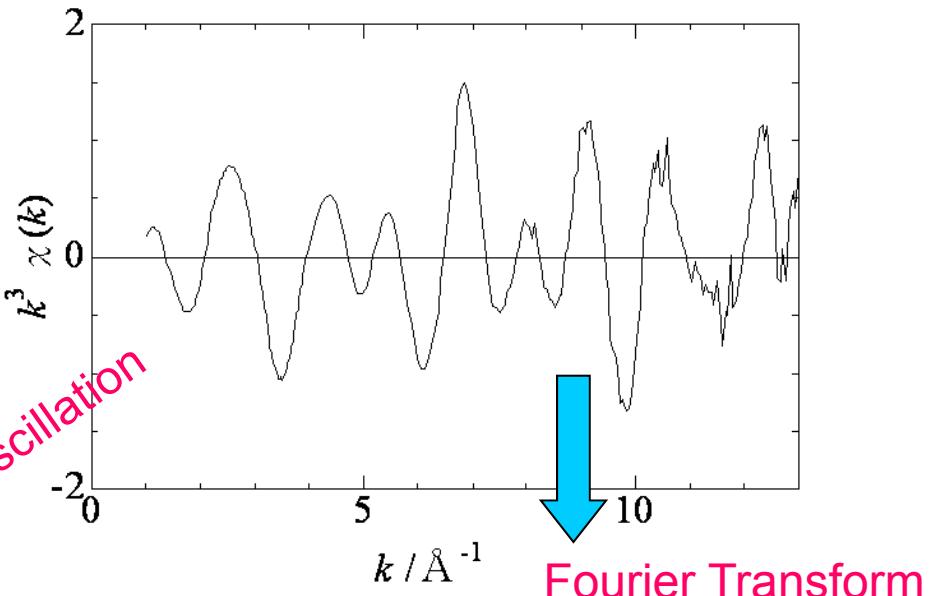


Fe(II) longer

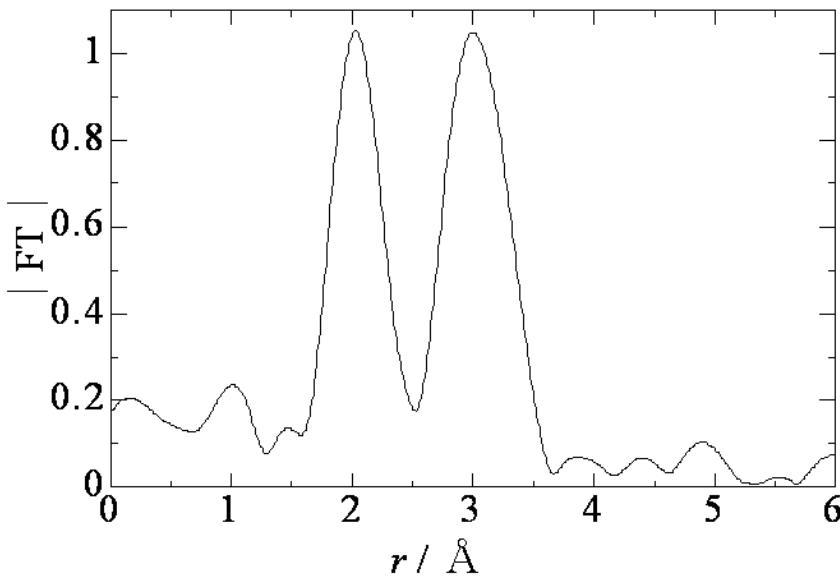




Extract $\chi(k)$ oscillation

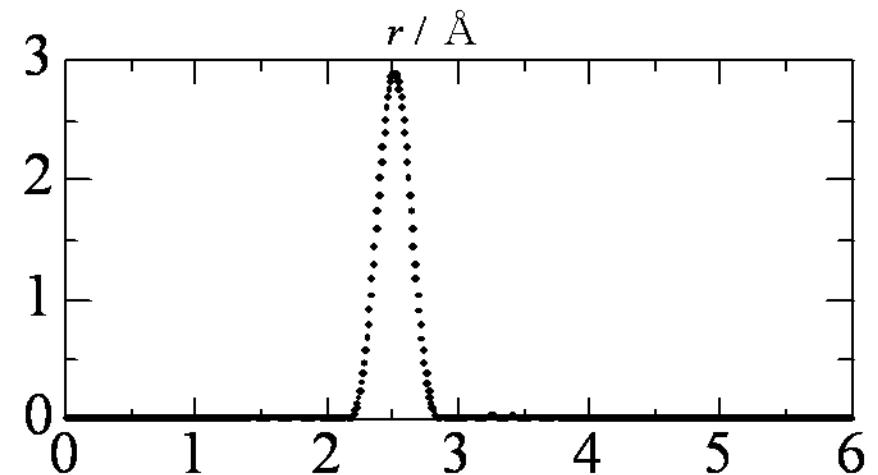
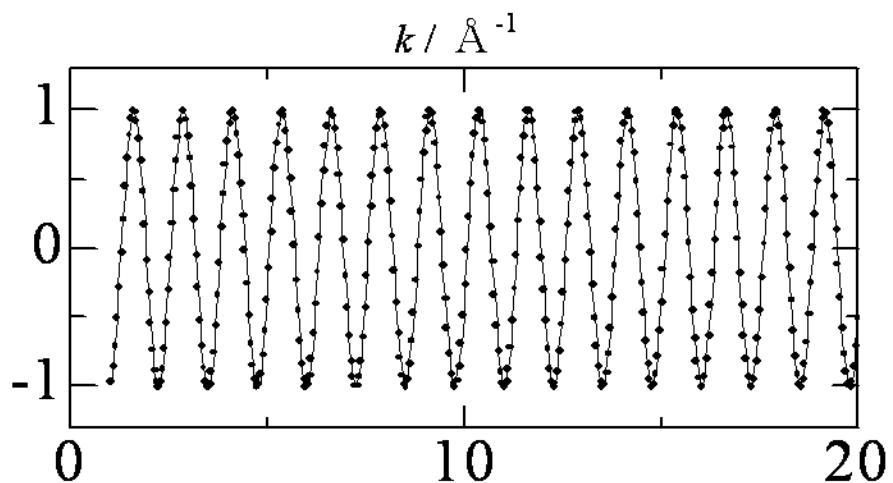


Fourier Transform

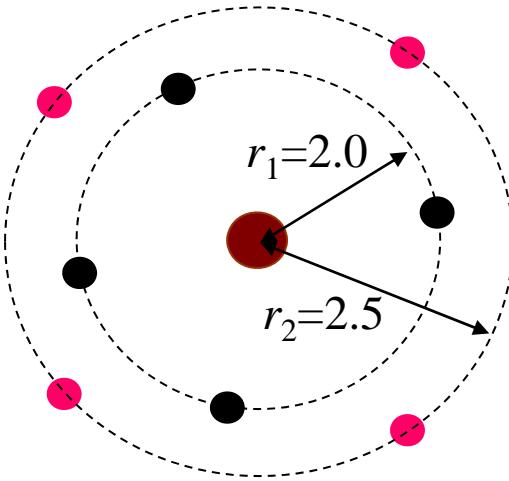
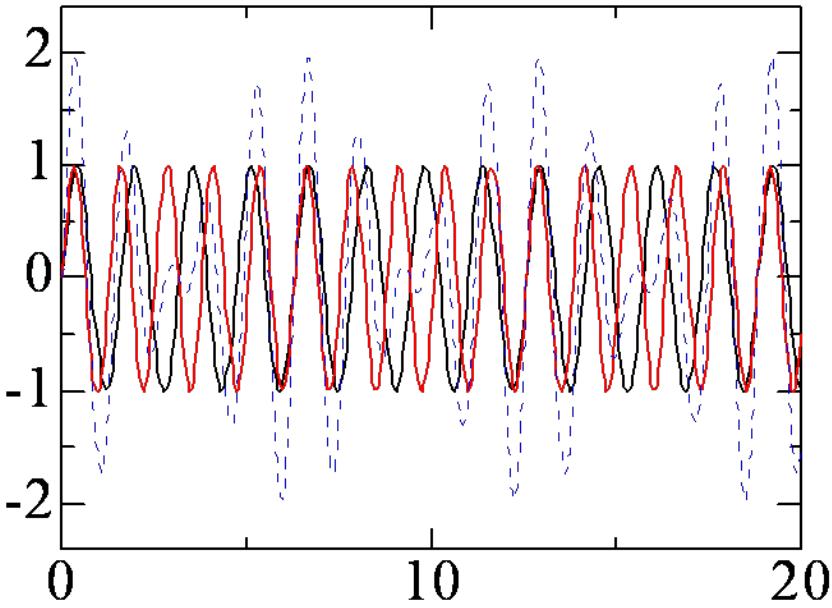


Fourier Transform (Frequency Filter)

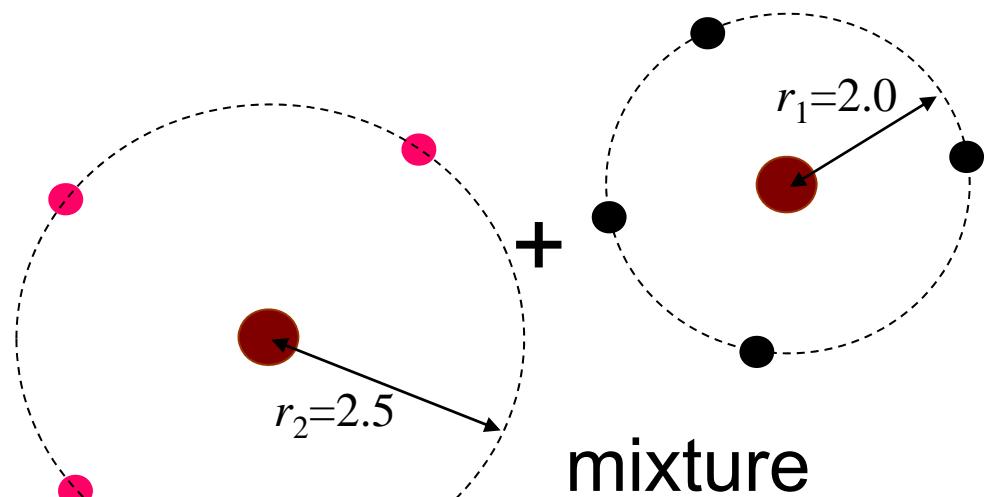
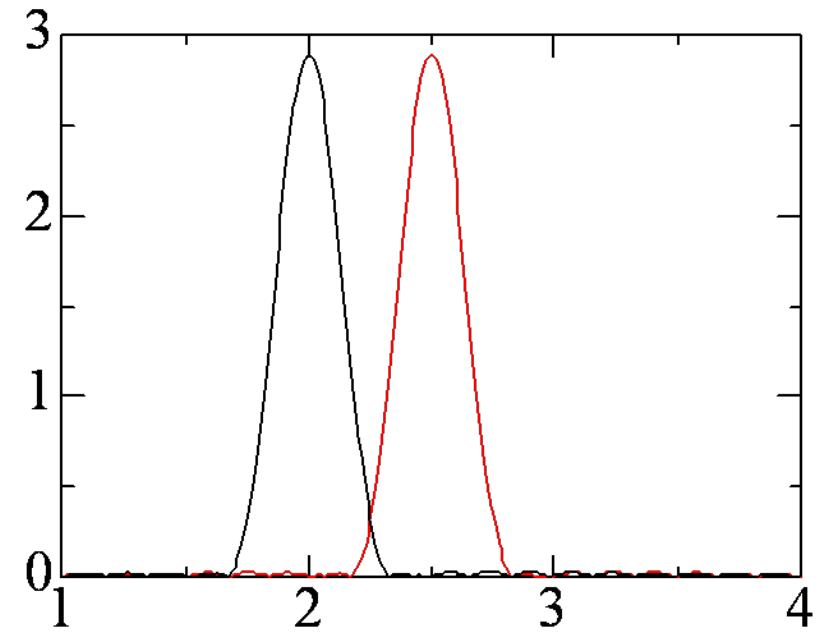
*will let you know the frequencies
of the waves*



$$\sin(kr)$$

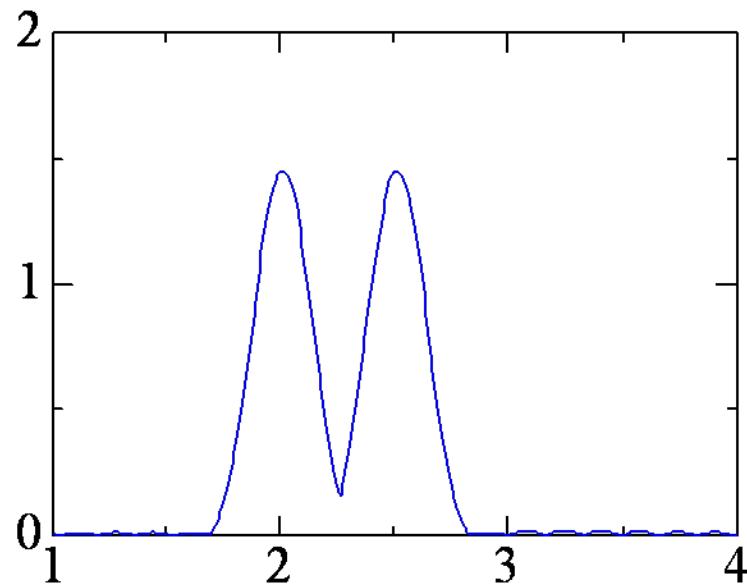
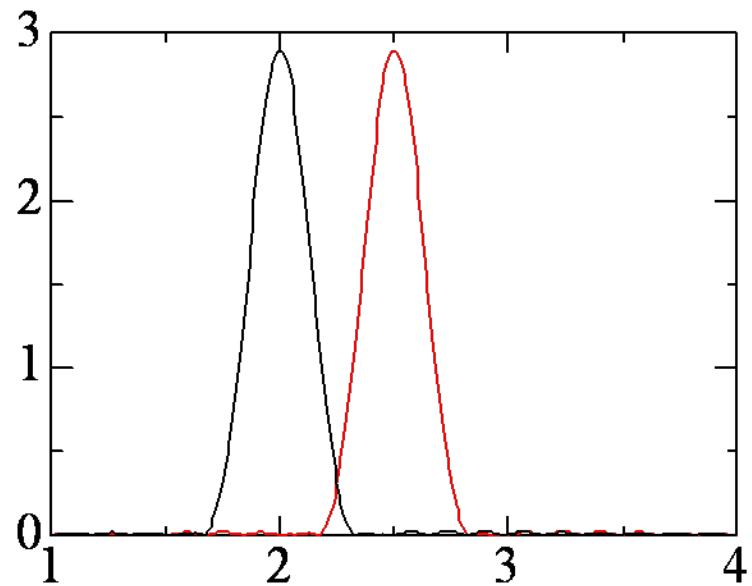
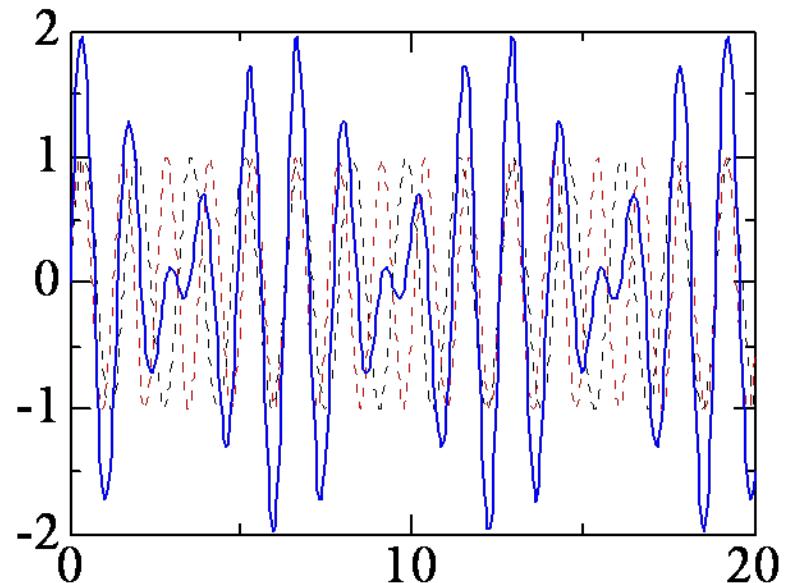
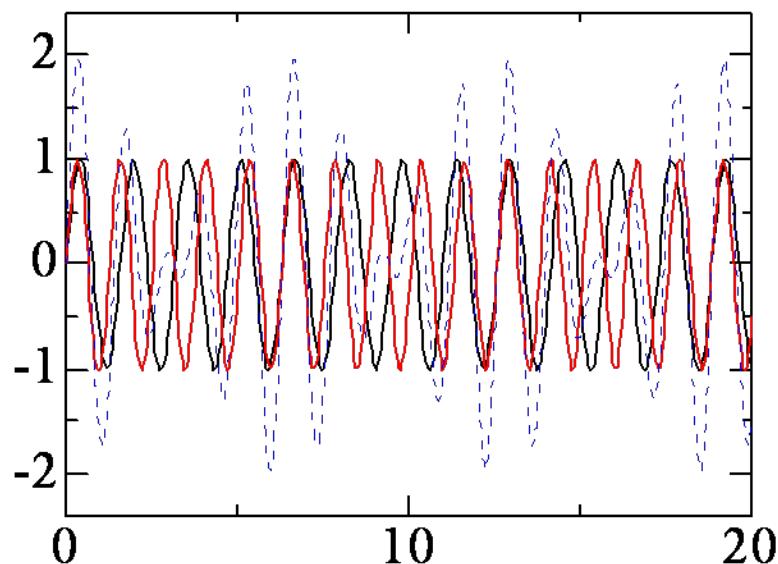


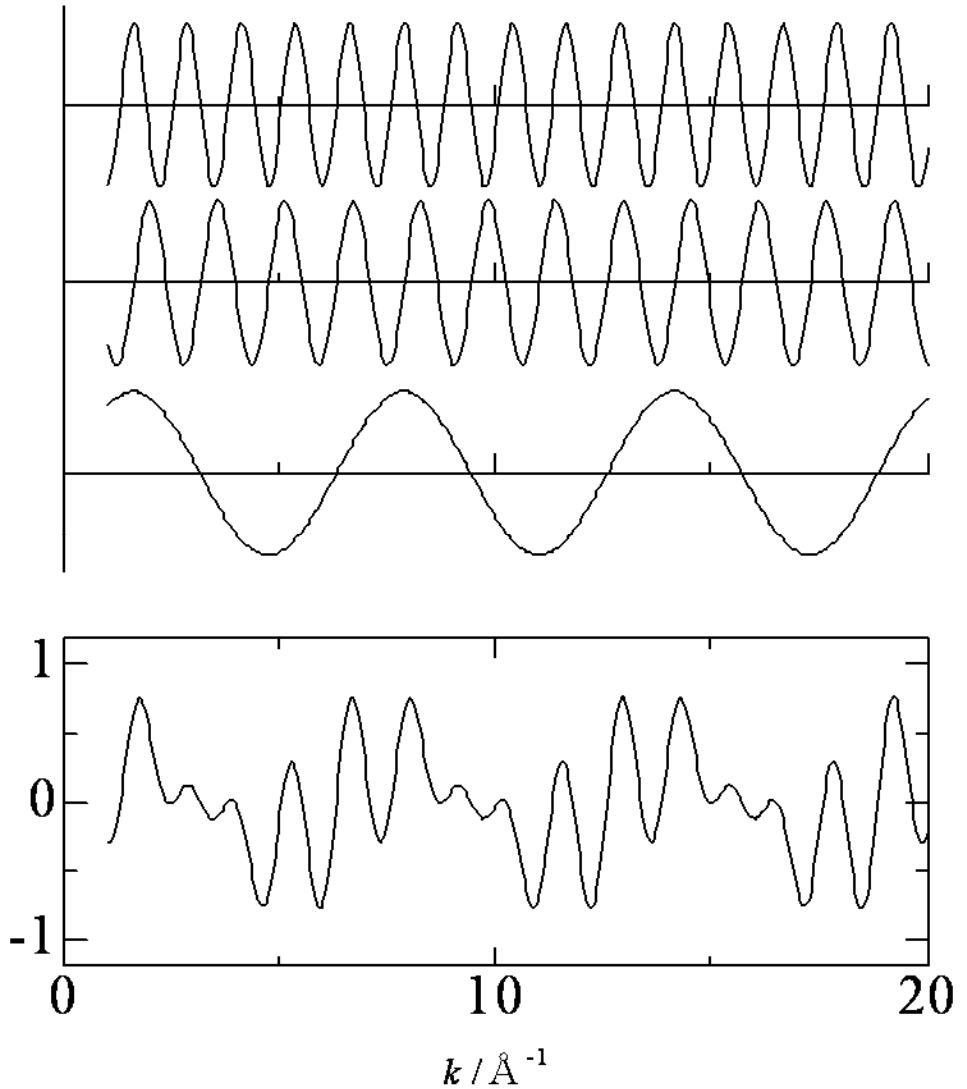
or



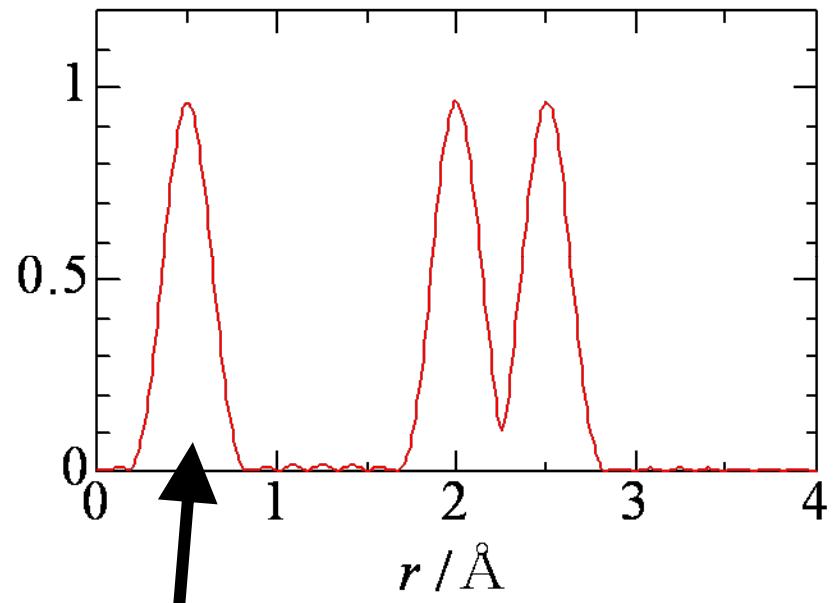
mixture

Fourier Transform for two-shell model

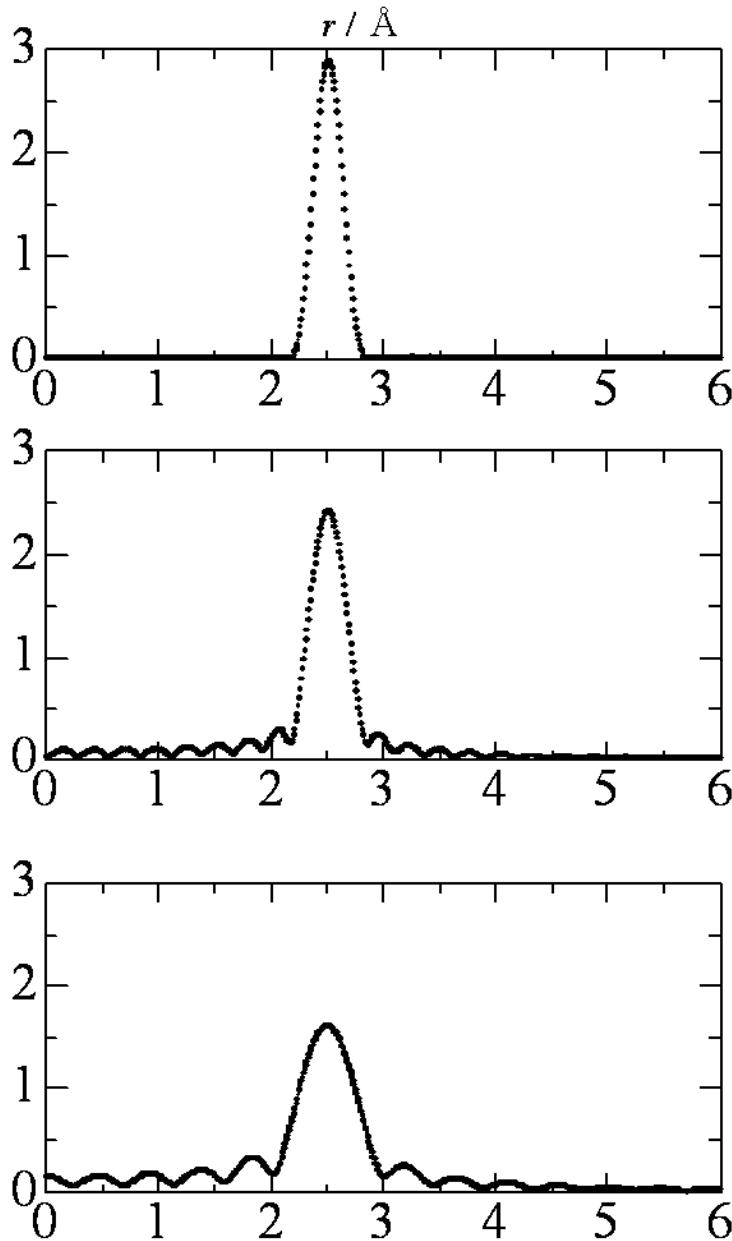
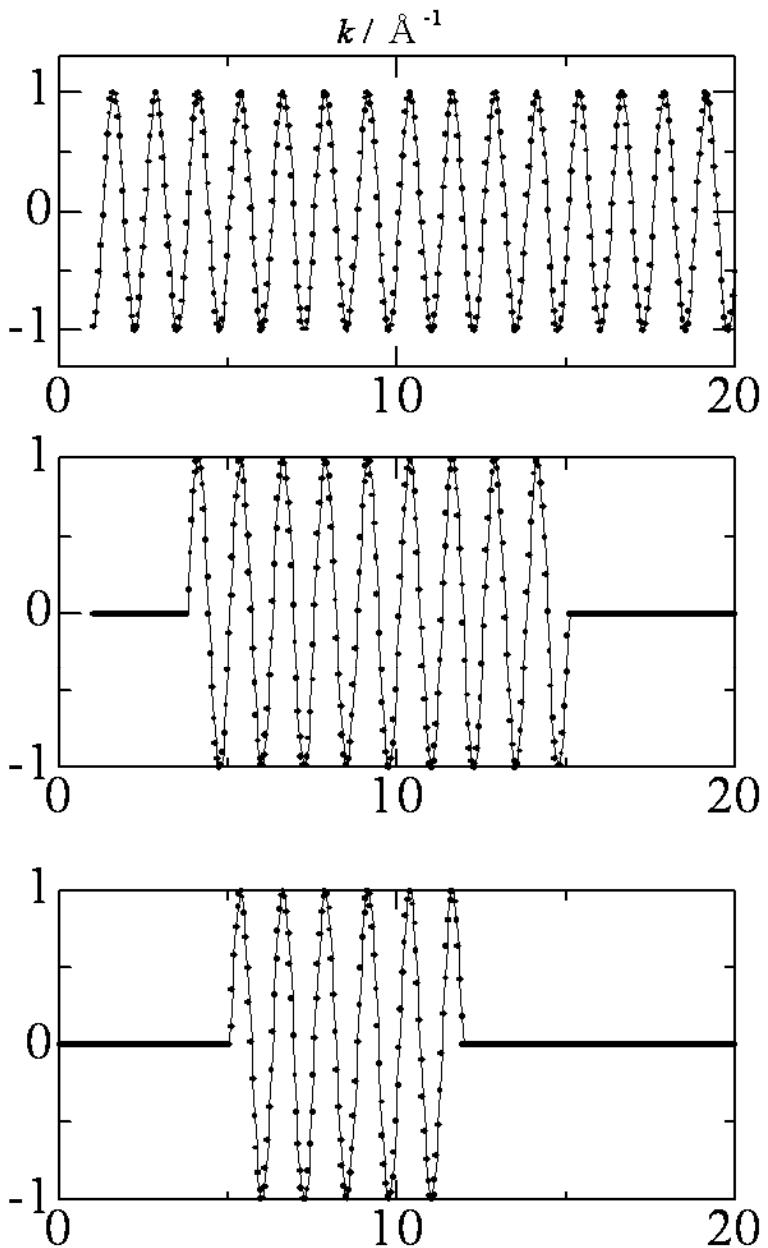


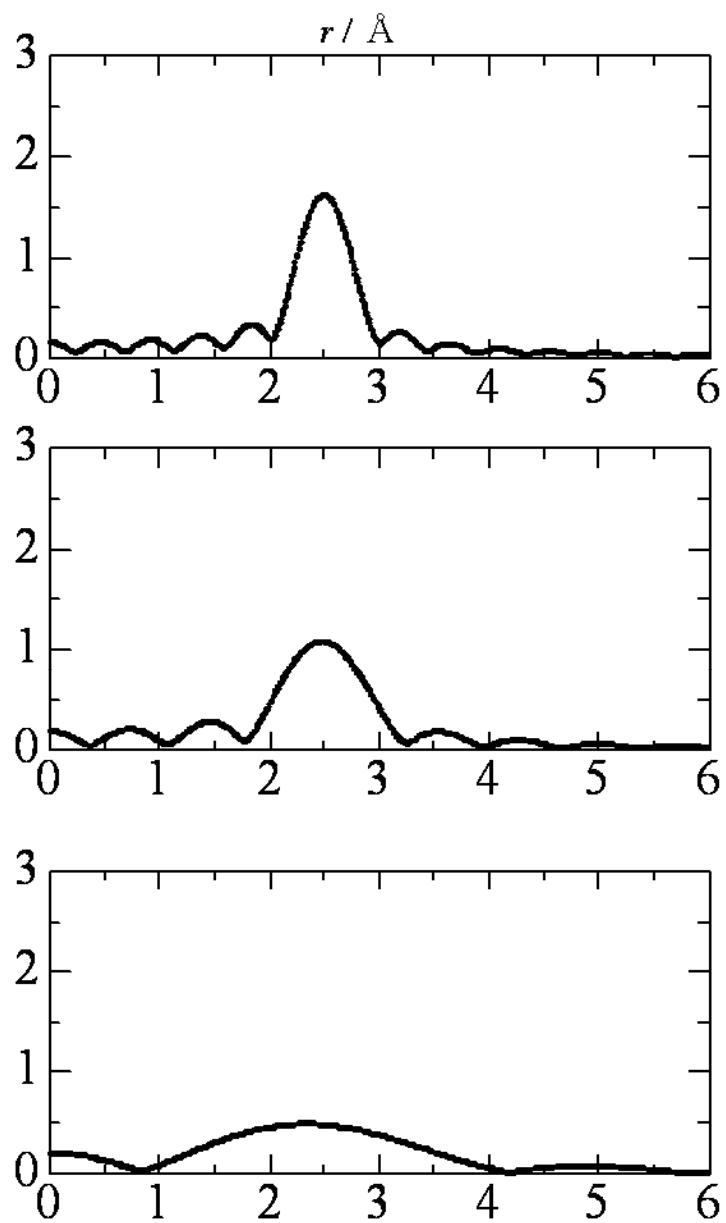
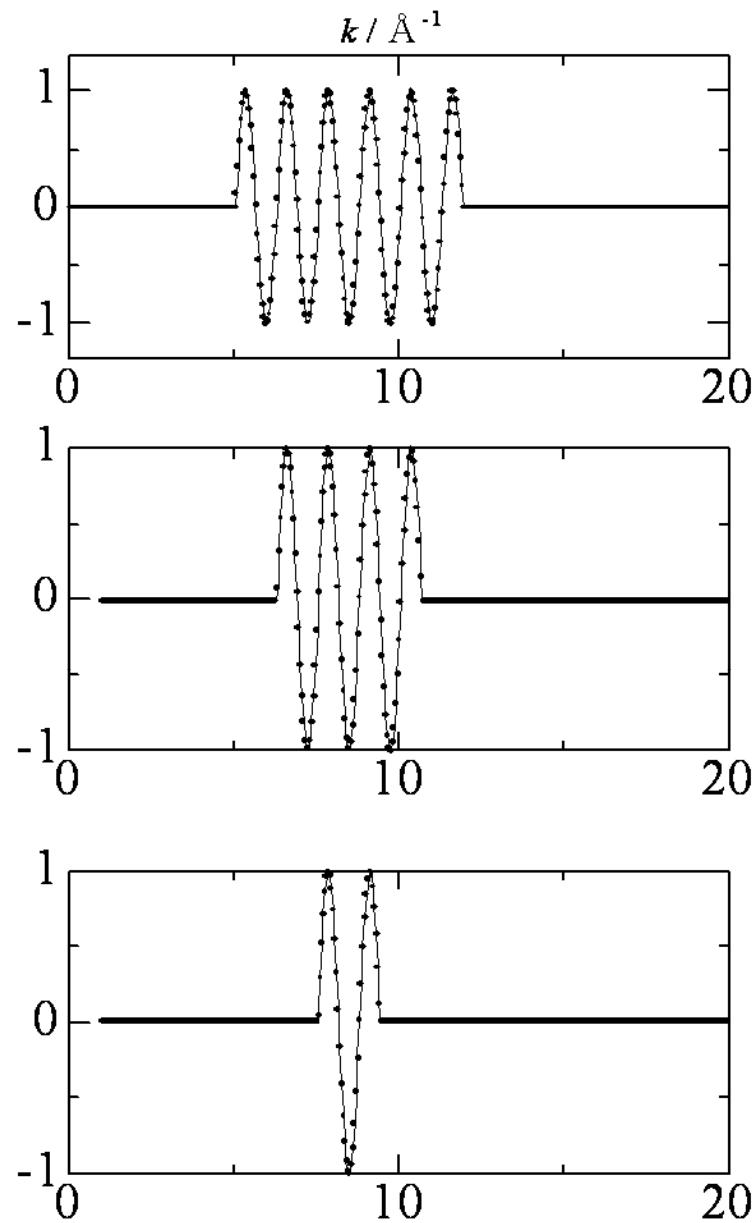


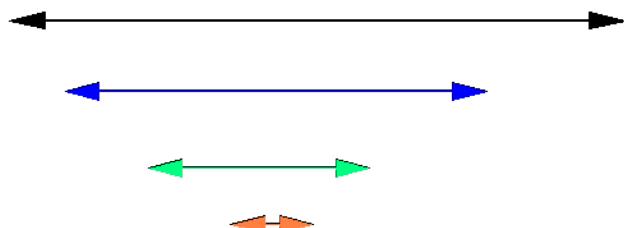
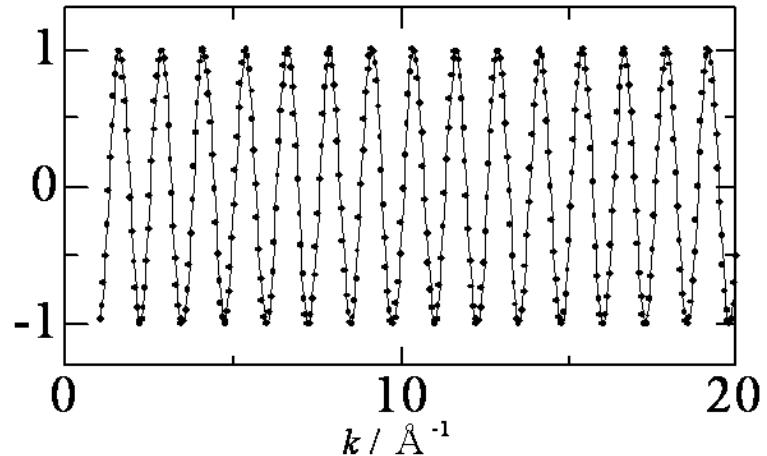
Fourier Transform for a three-shell model



This must be a BACKGROUND structure, not corresponding to a real atom-atom distance.



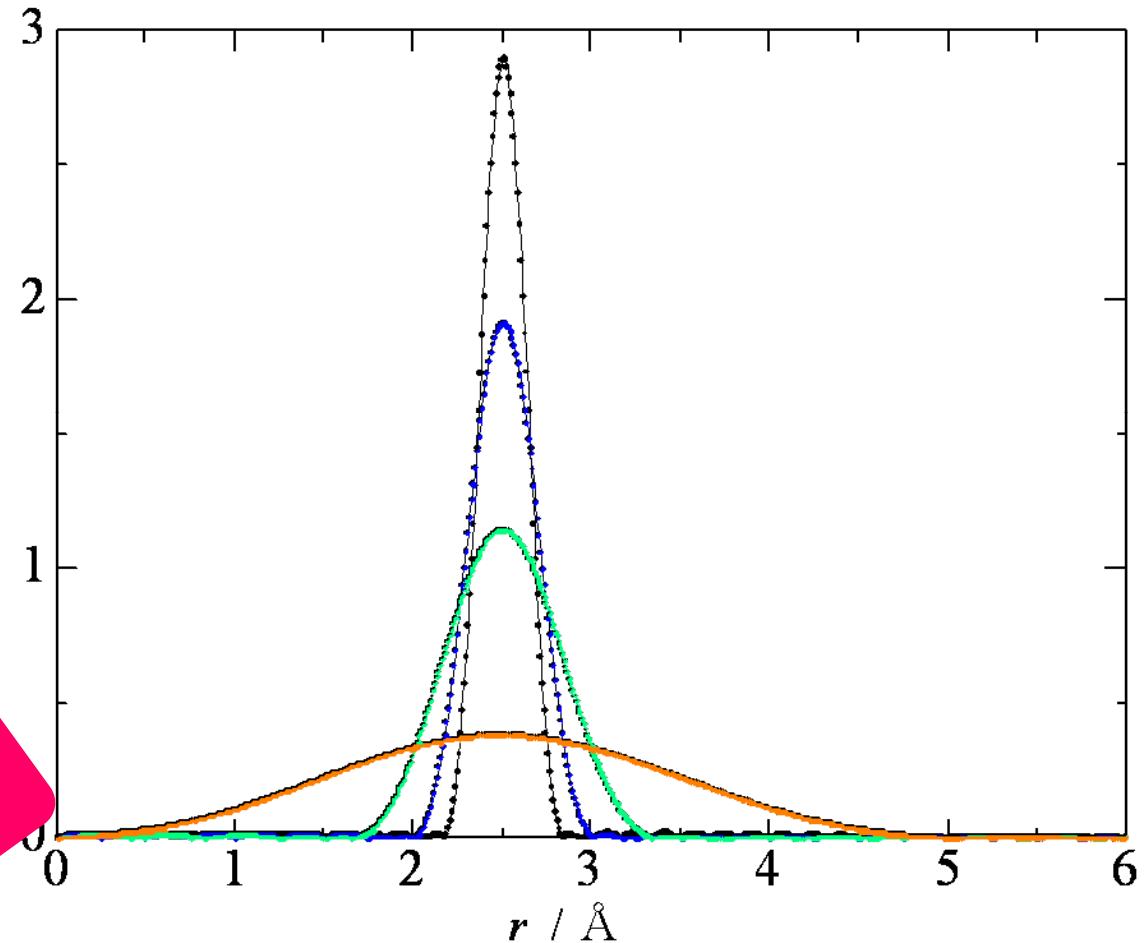




If you have a small number of cycles in k ,

Problem !

Fourier Transform for different k ranges



BASIC EXAFS equation

$$\chi(k) = -\sum_i \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

amplitude part

oscillation part

By comparing the theoretical EXAFS $\chi(k)$ and experimental $\chi(k)$, you can determine;

N coordination number

r bond length

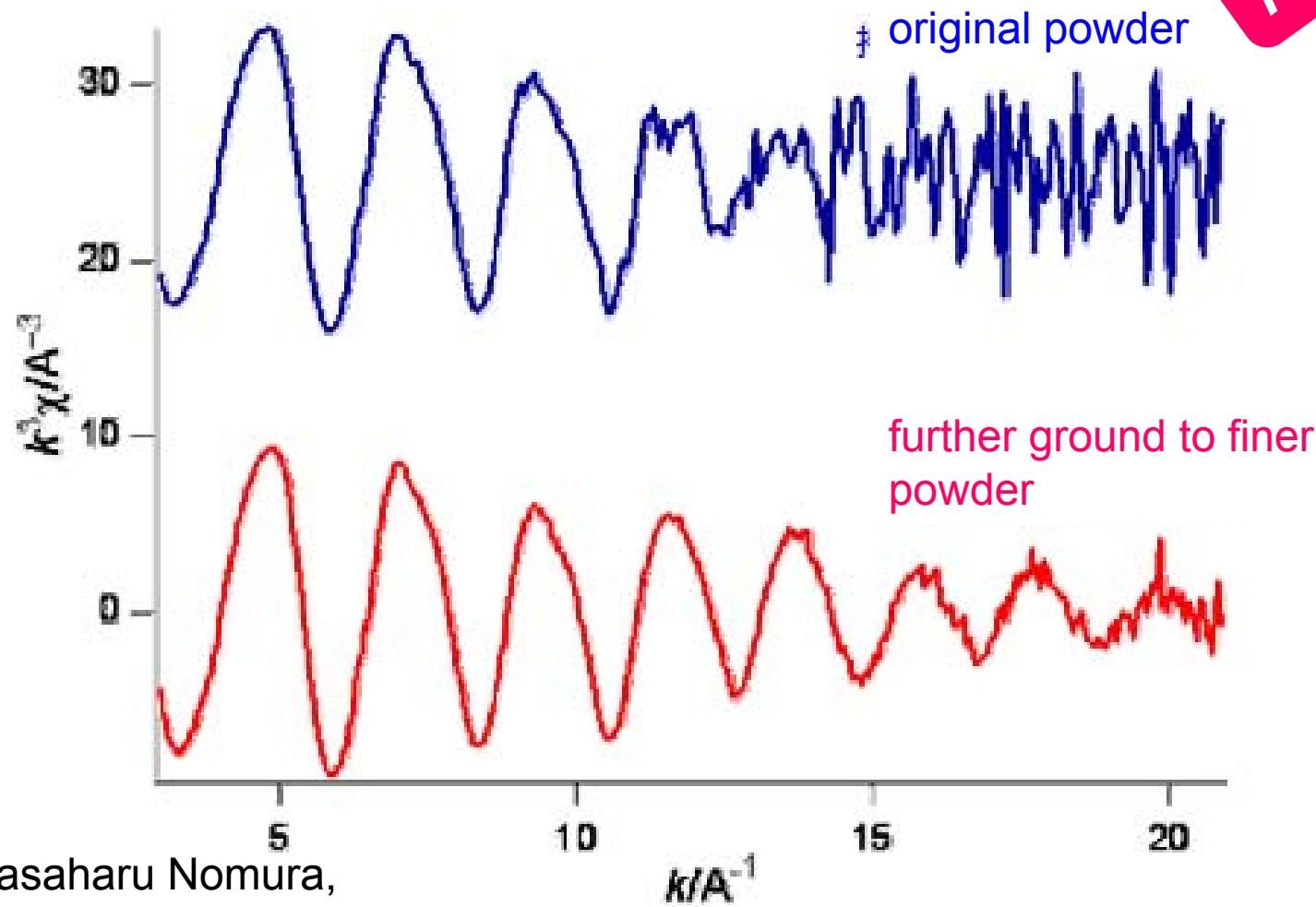
$f(k)$ and $\phi(k)$ are element specific
atomic type of coordination

You may get in trouble with the data quality taken by transmission method

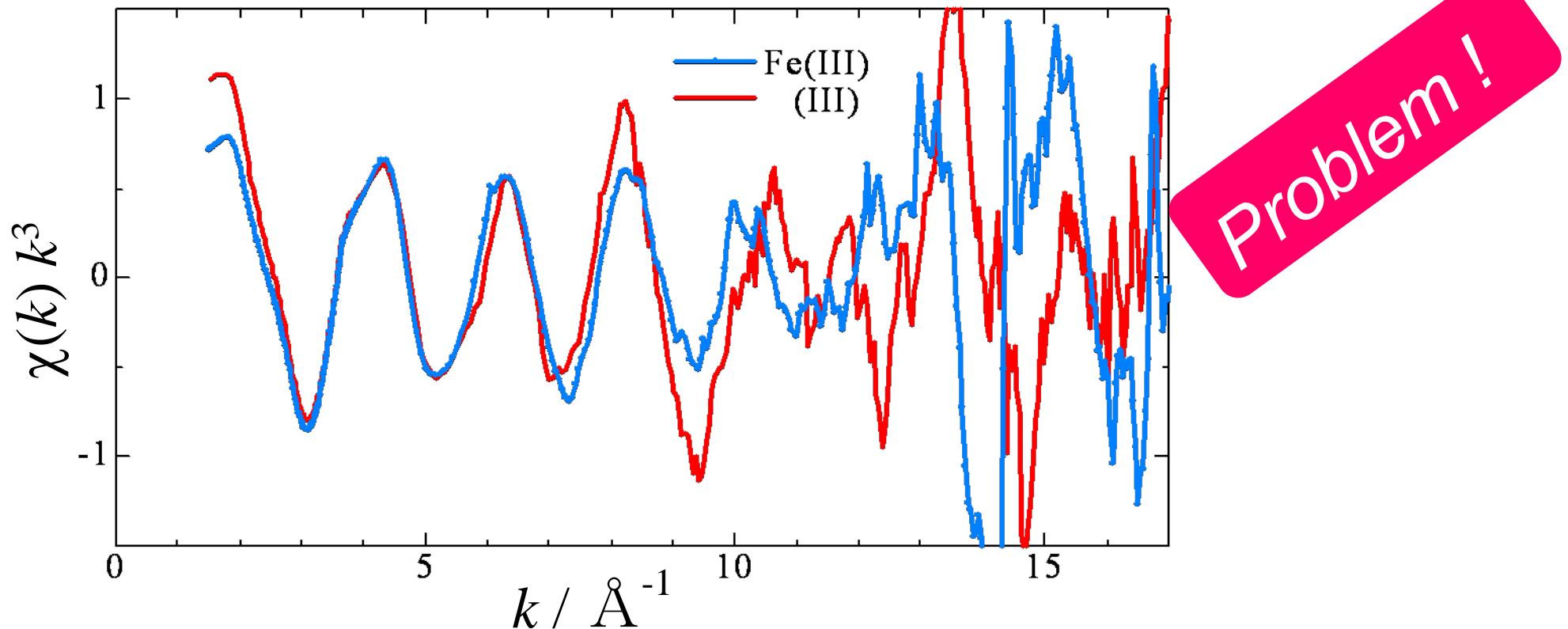
Transmission method

Problem!

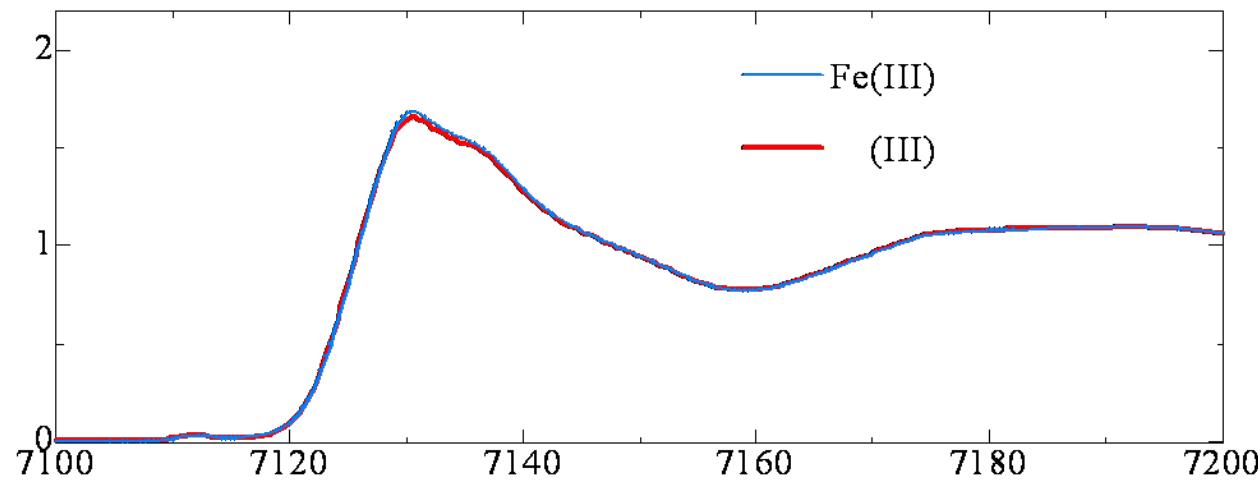
Sample: Ge-Si powder



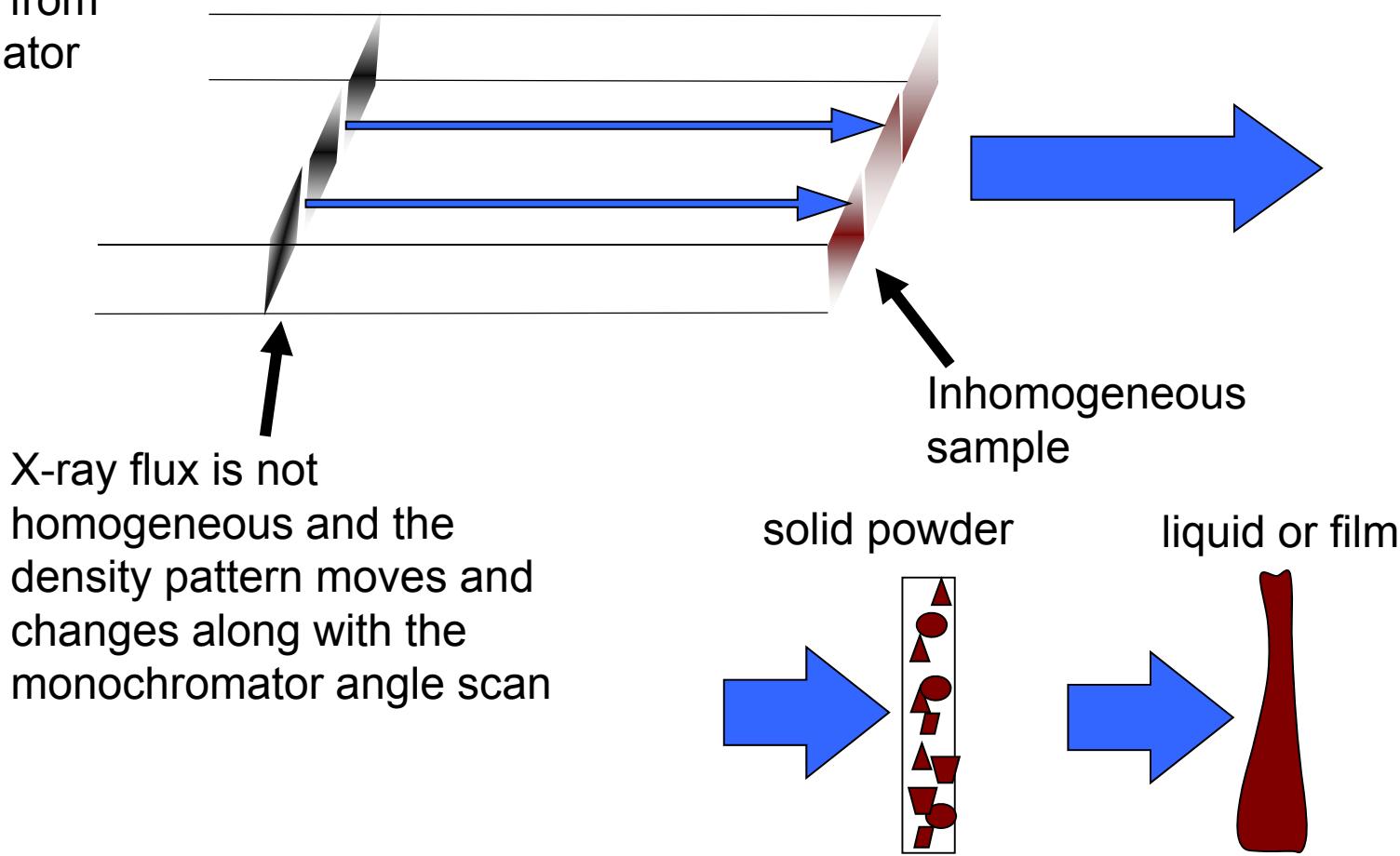
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Photon Factory, KEK



Fe(III) ions in aqueous
solution
possibly, inhomogeneous
sample thickness



X-ray beam from monochromator



Leads to weaker EXAFS oscillation amplitude and noisy spectrum

Si(311) double-crystal monochromator
Output pattern

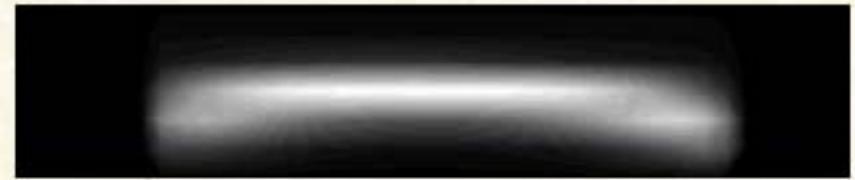
5 deg



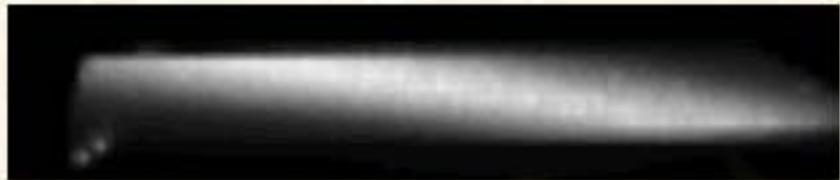
10 deg



15 deg



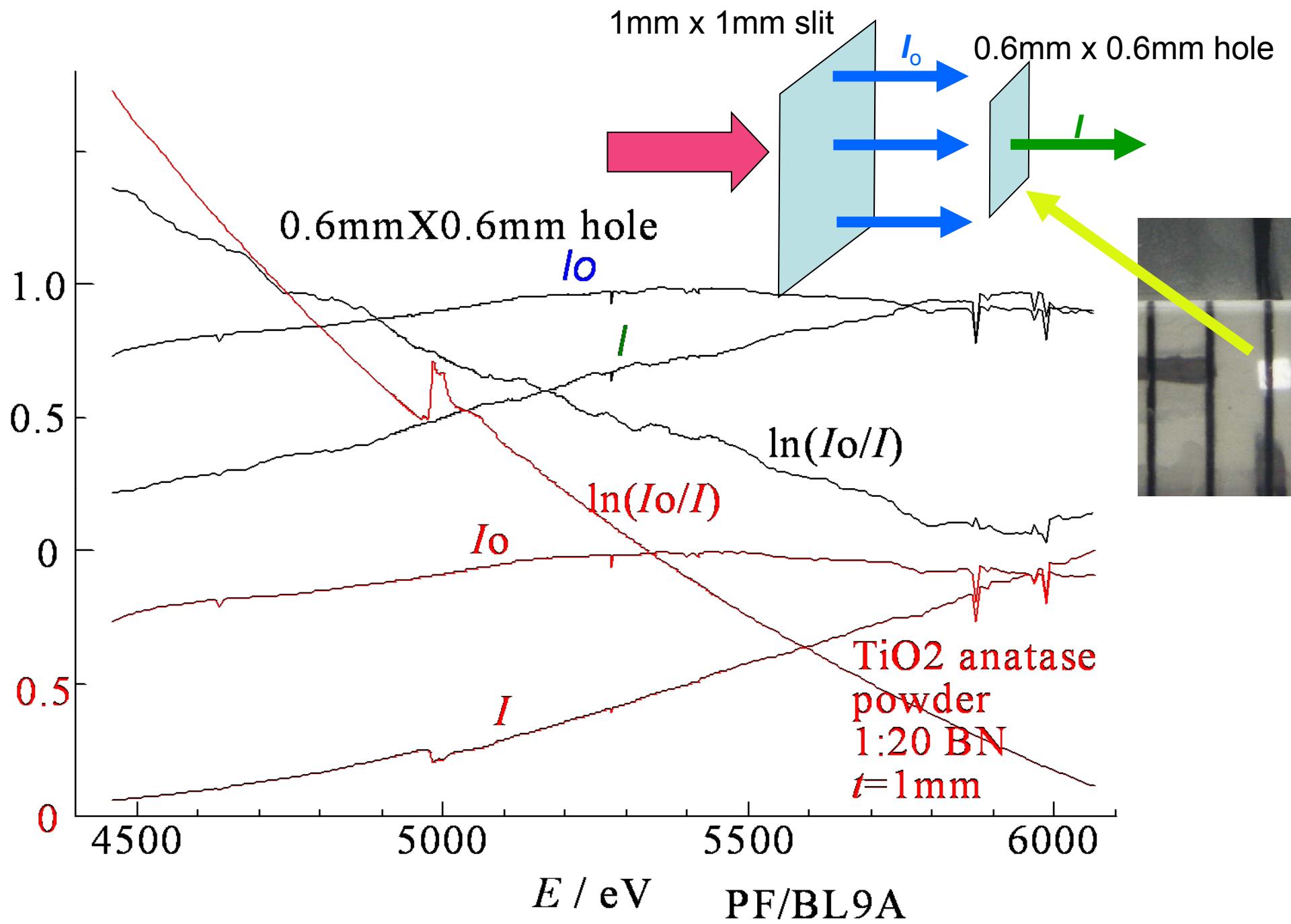
20 deg



before improvements on the crystal
holding method

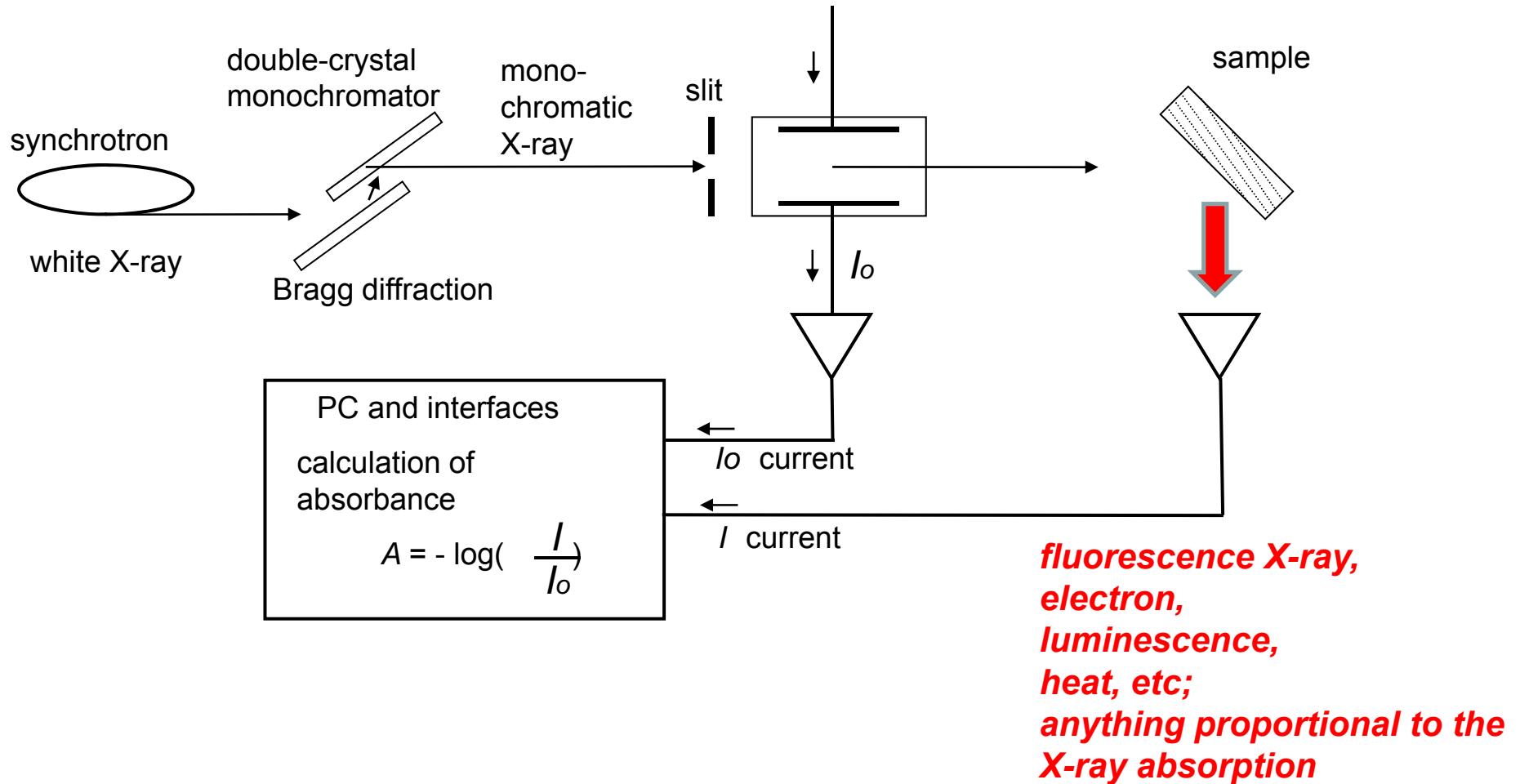
after improvements

mm

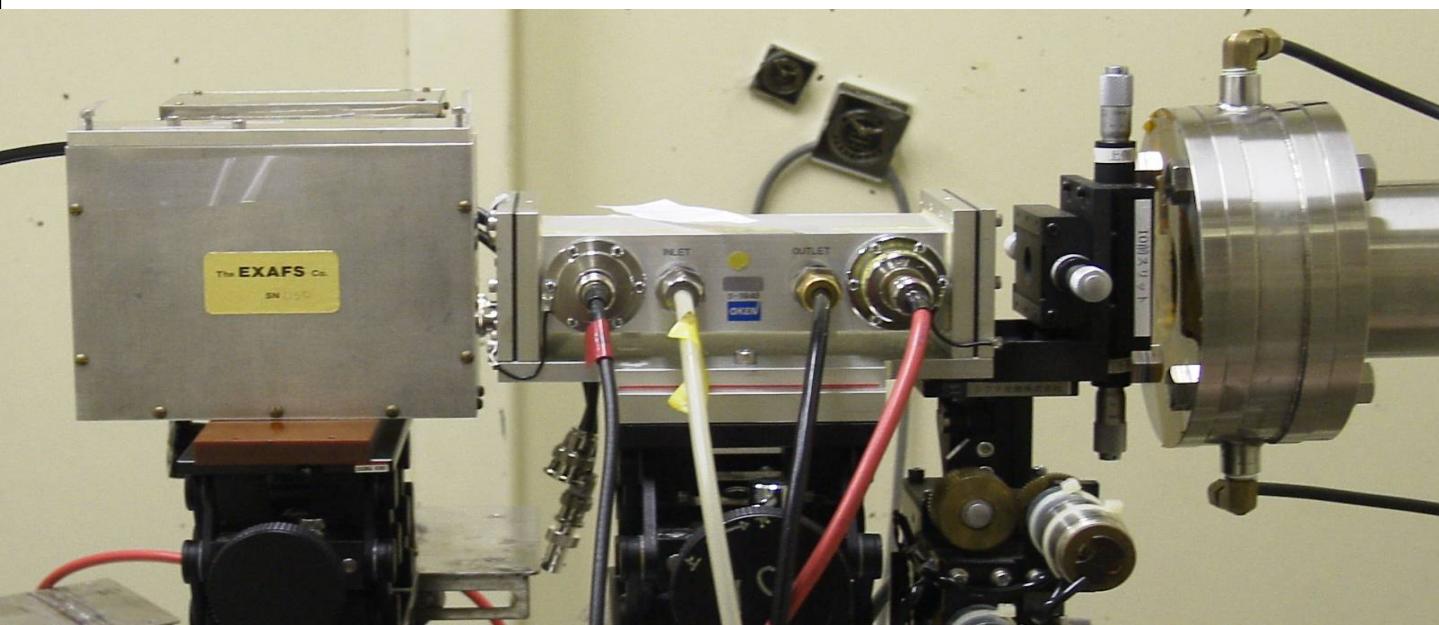
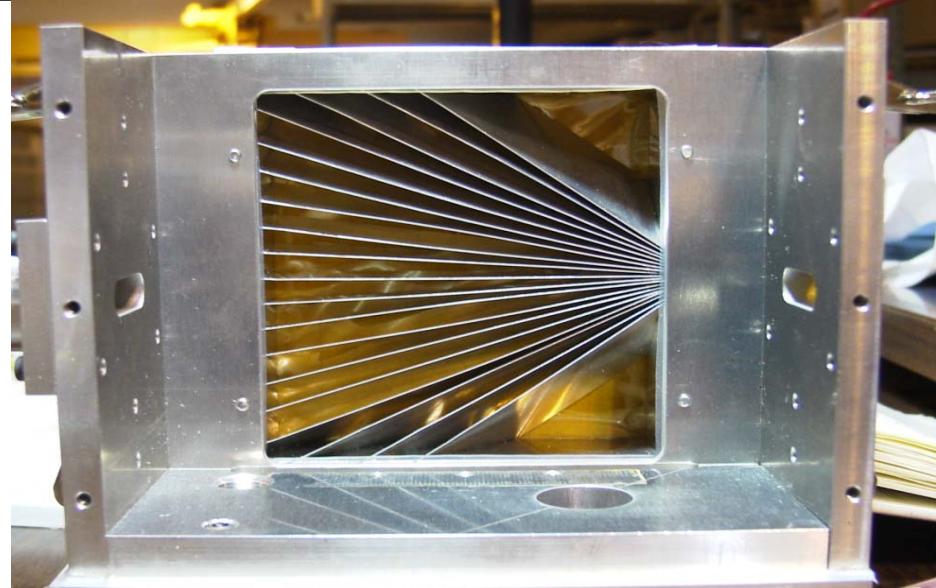
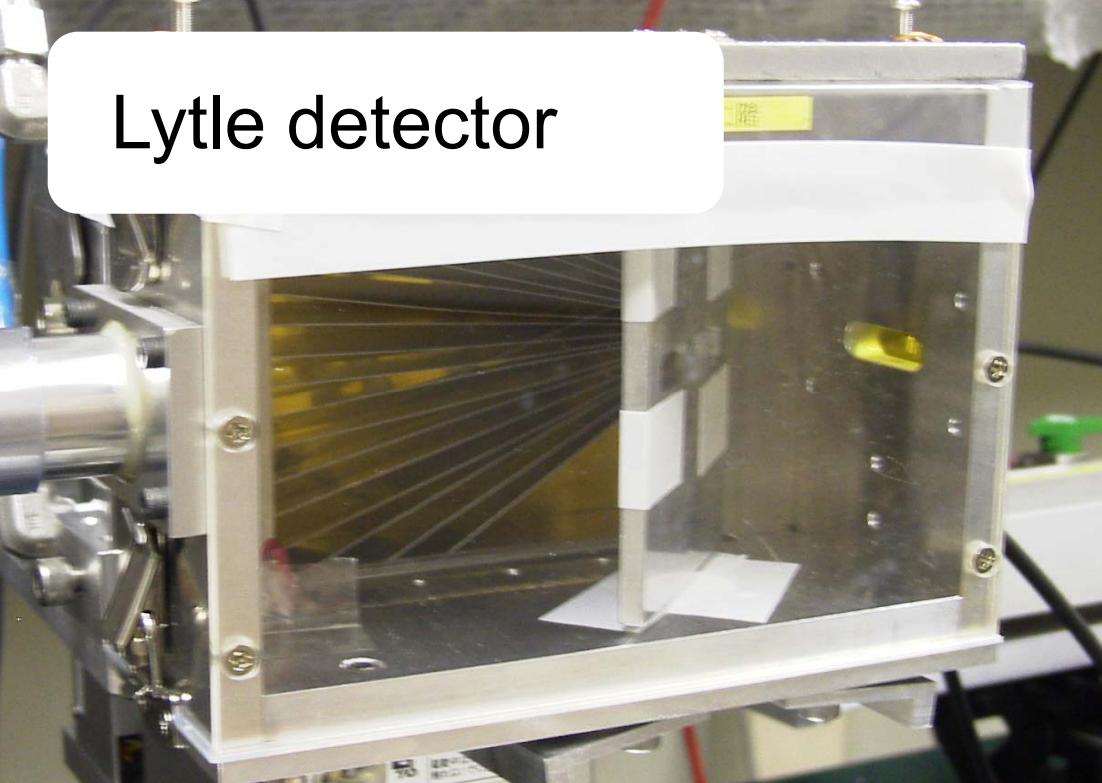


Yield methods:
Fluorescence yield
and
Total-conversion-electron-yield

X-ray absorption measurement by *yield* methods

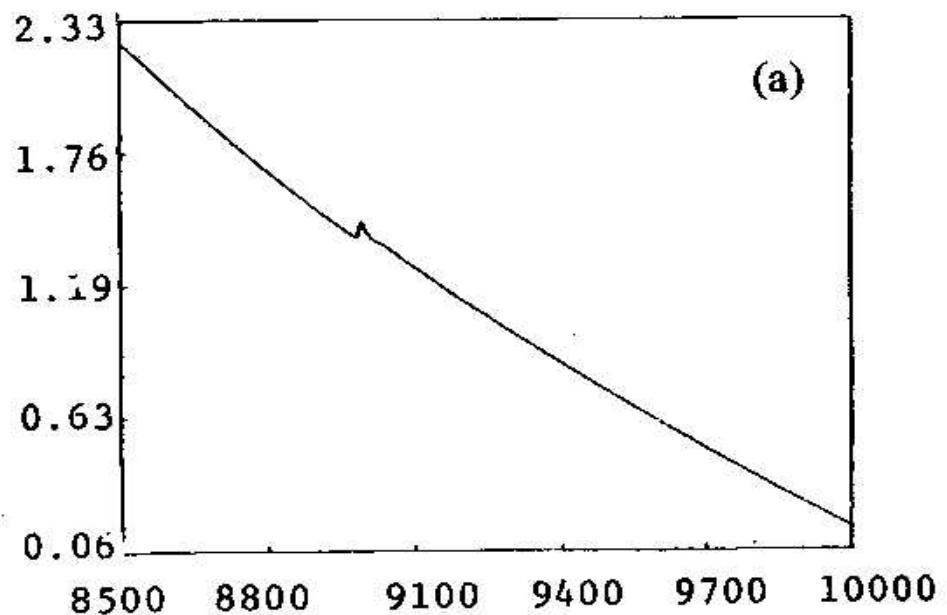


Lytle detector

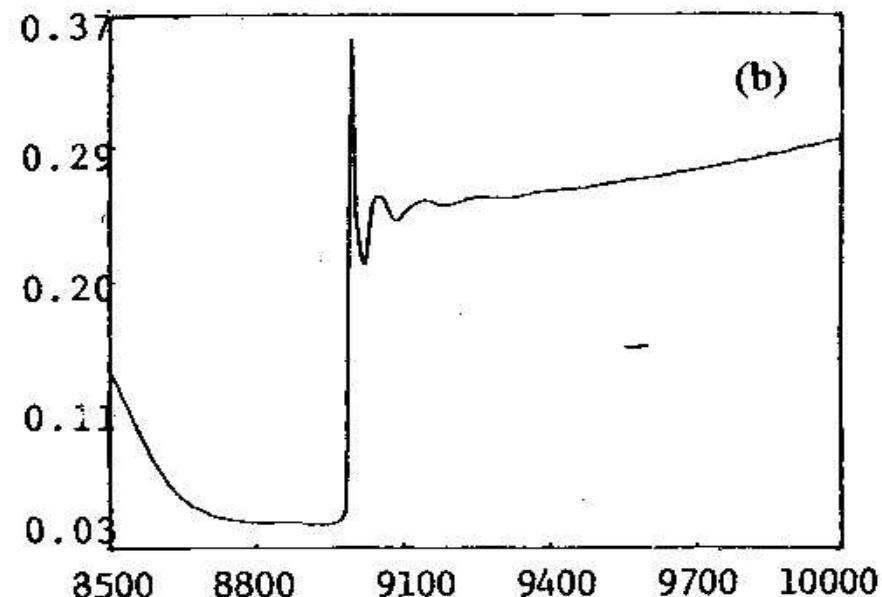


Sample: 0.01 mol dm^{-3} Cu(II) solution

transmittance



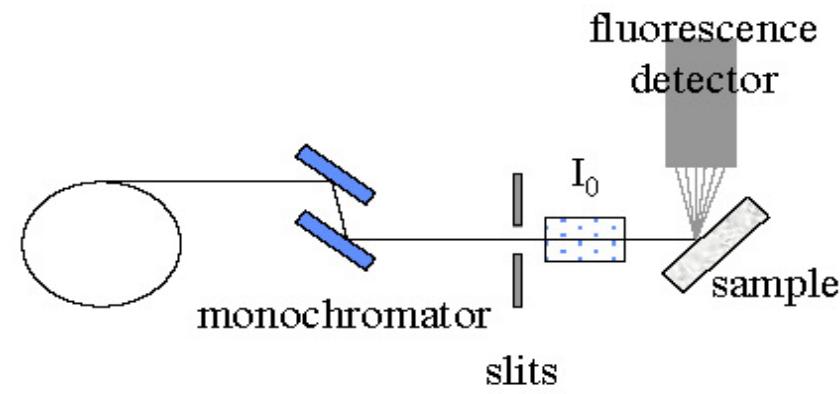
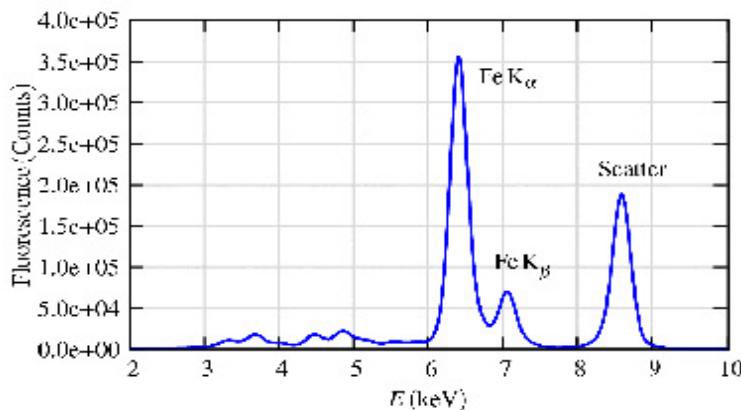
fluorescence

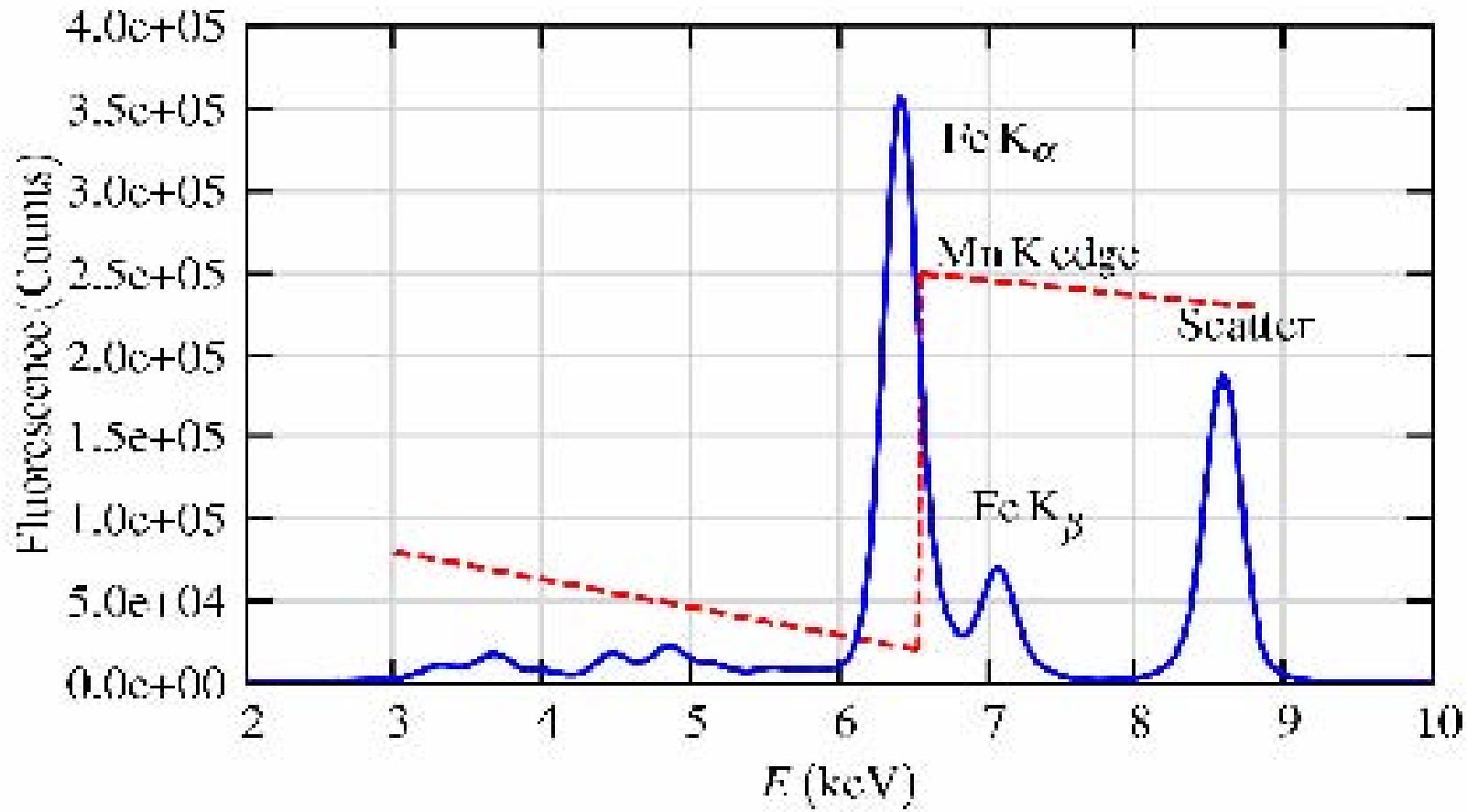


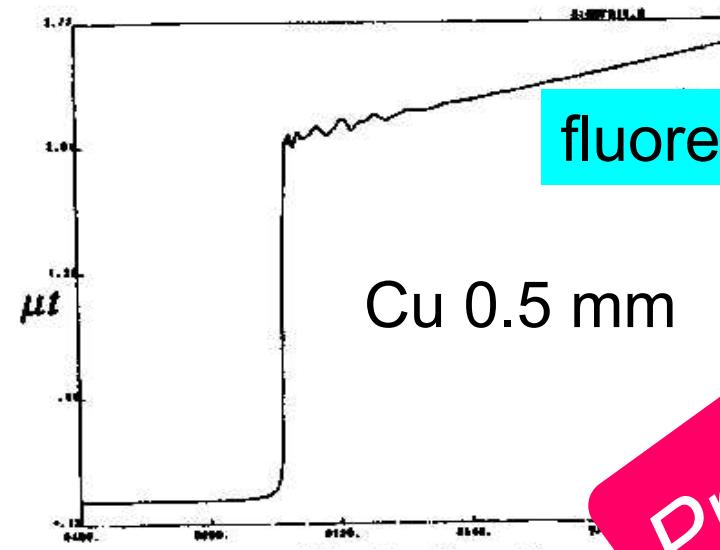
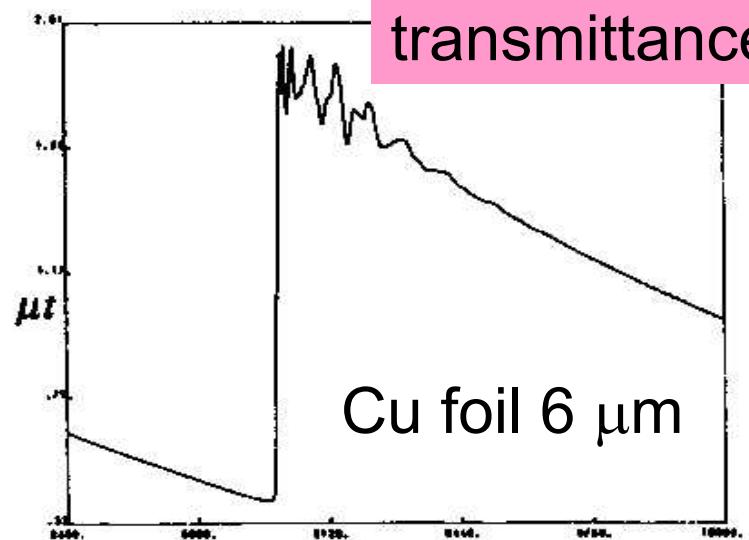
By Masaharu Nomura,
Photon Factory, KEK

Fluorescence XAFS Experiment: Solid State Detectors

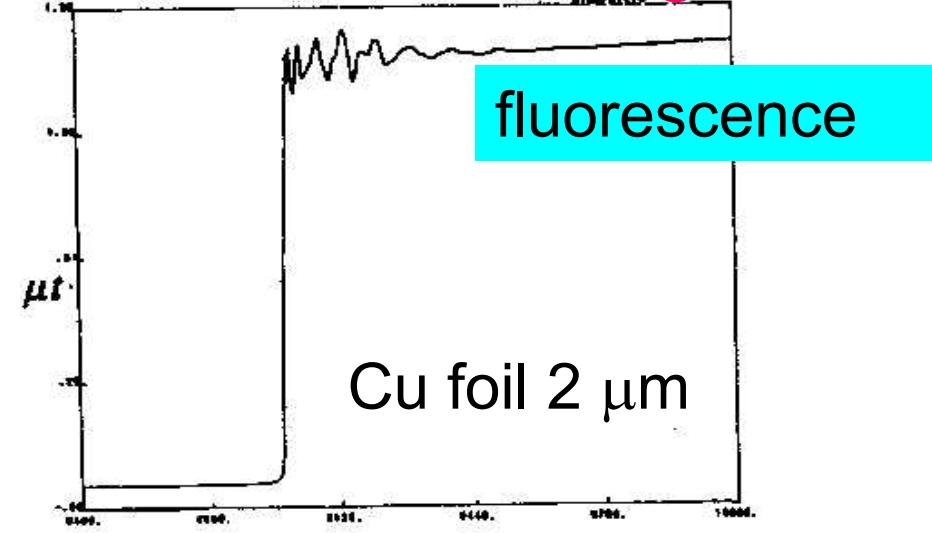
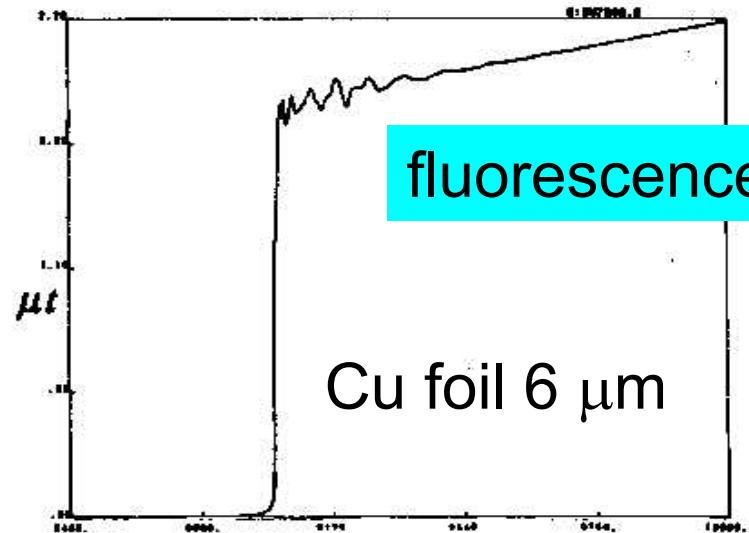
- Alternative is to use a solid state detector with active element of Ge or Si as the x-ray absorber. This uses electronic energy discrimination.
- Typical energy resolution 200-300 eV.
- Has advantage of measuring the full x-ray fluorescence spectrum, so useful for identifying other elements in sample.
- Can be used for XAFS measurements with concentration to 10's of ppm.







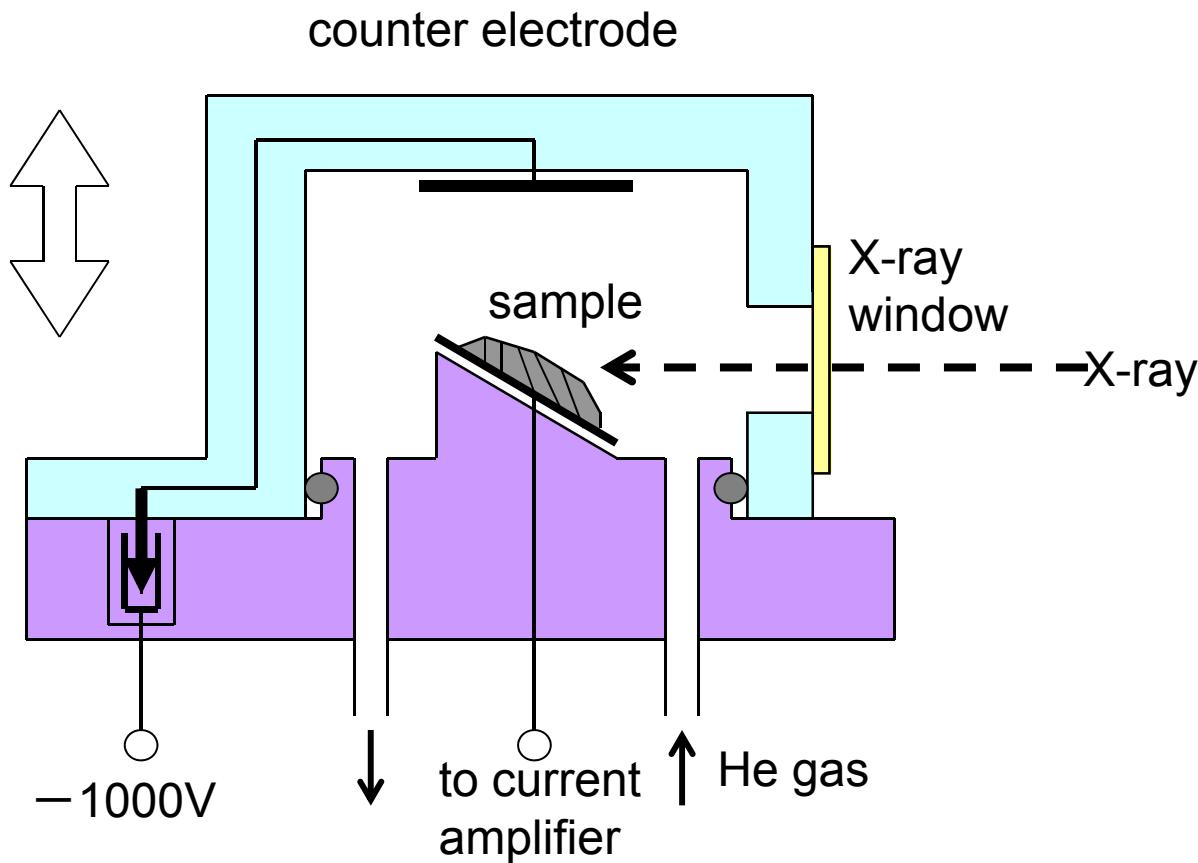
Problem !

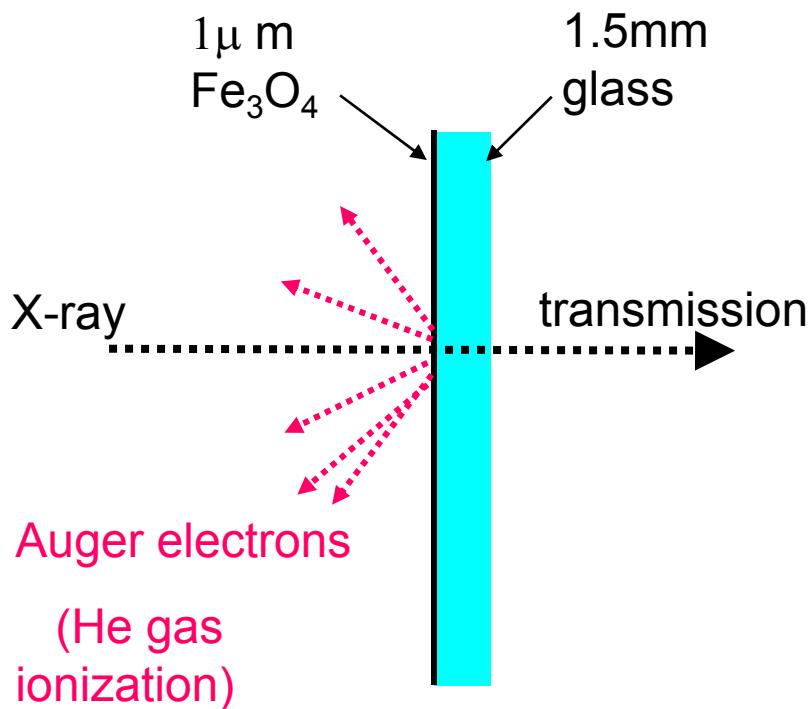


By Masaharu Nomura,
Photon Factory, KEK

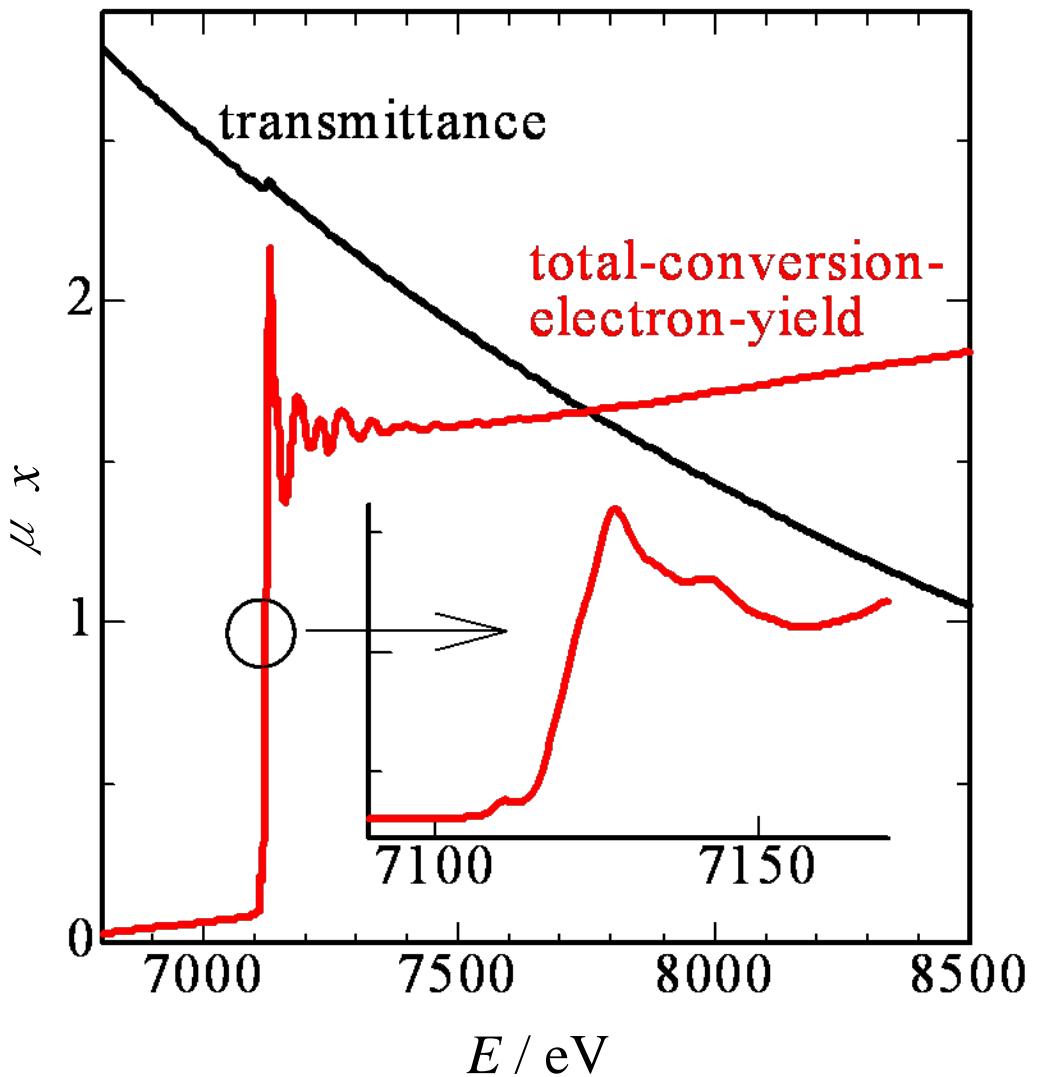
Self-absorption effect → incorrect N

Total-Conversion-Electron-Yield method

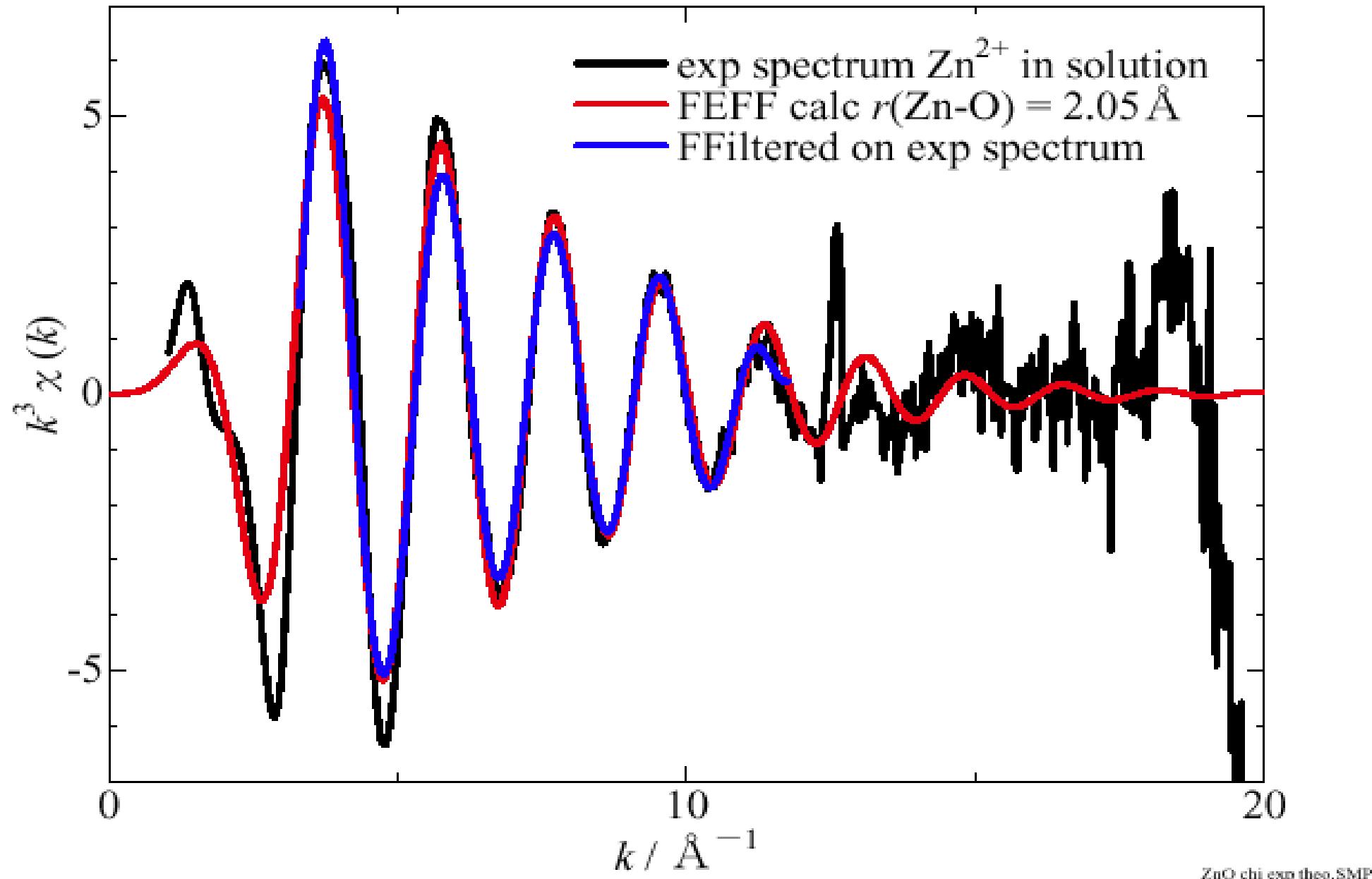


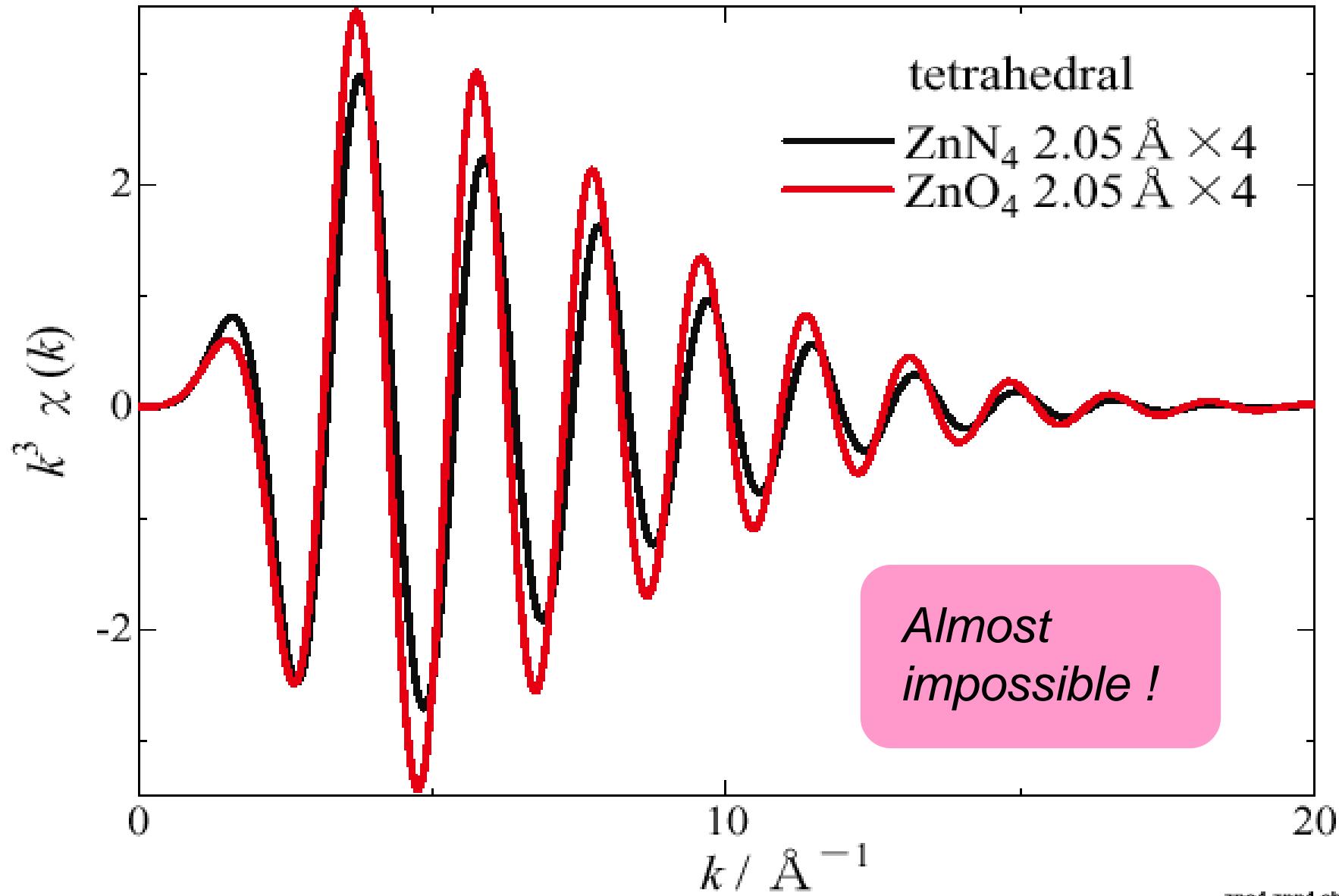


This method can be applied to thick samples owing to the short escape depth of Auger electron.



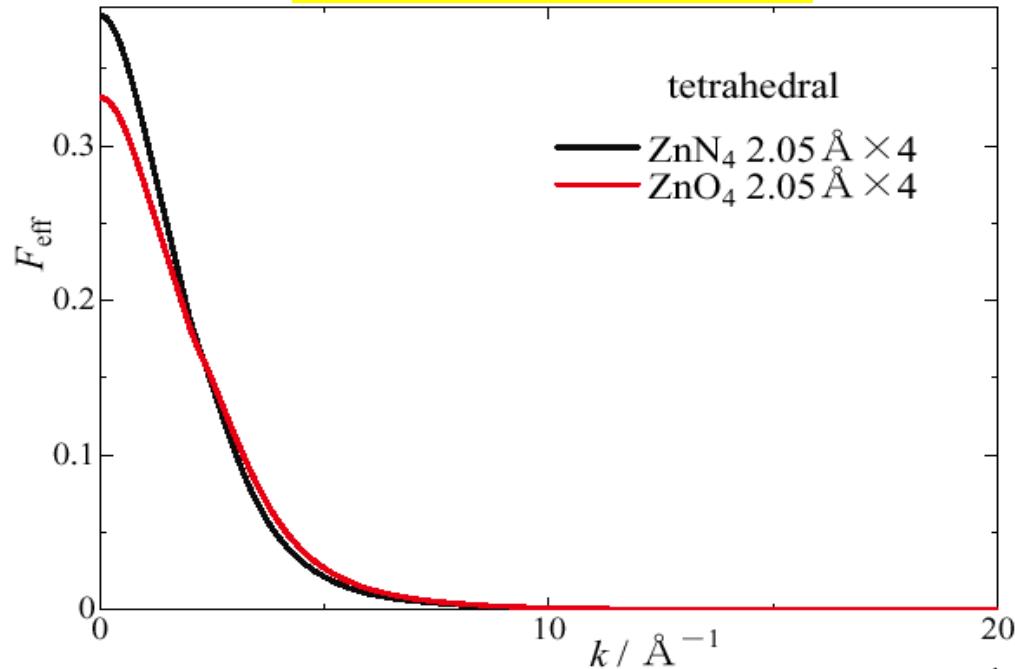
*Can we distinguish oxygen from
nitrogen by EXAFS?*



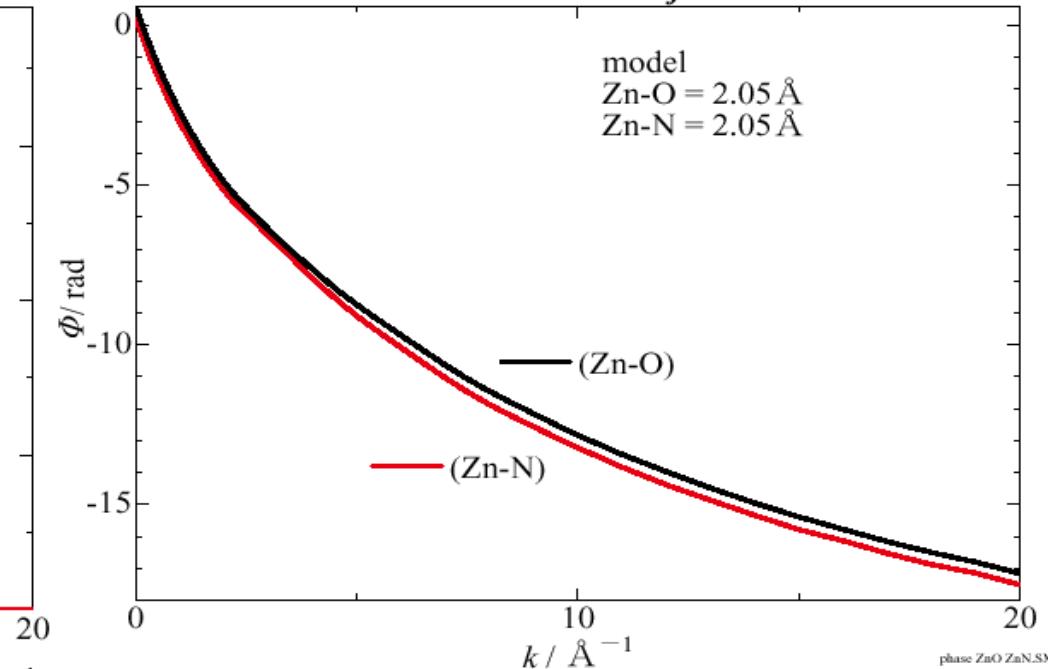


zno4 znn4 chi.smp

Scattering amplitude



Scattering phase shift



$$\chi(k) = -\sum_i \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

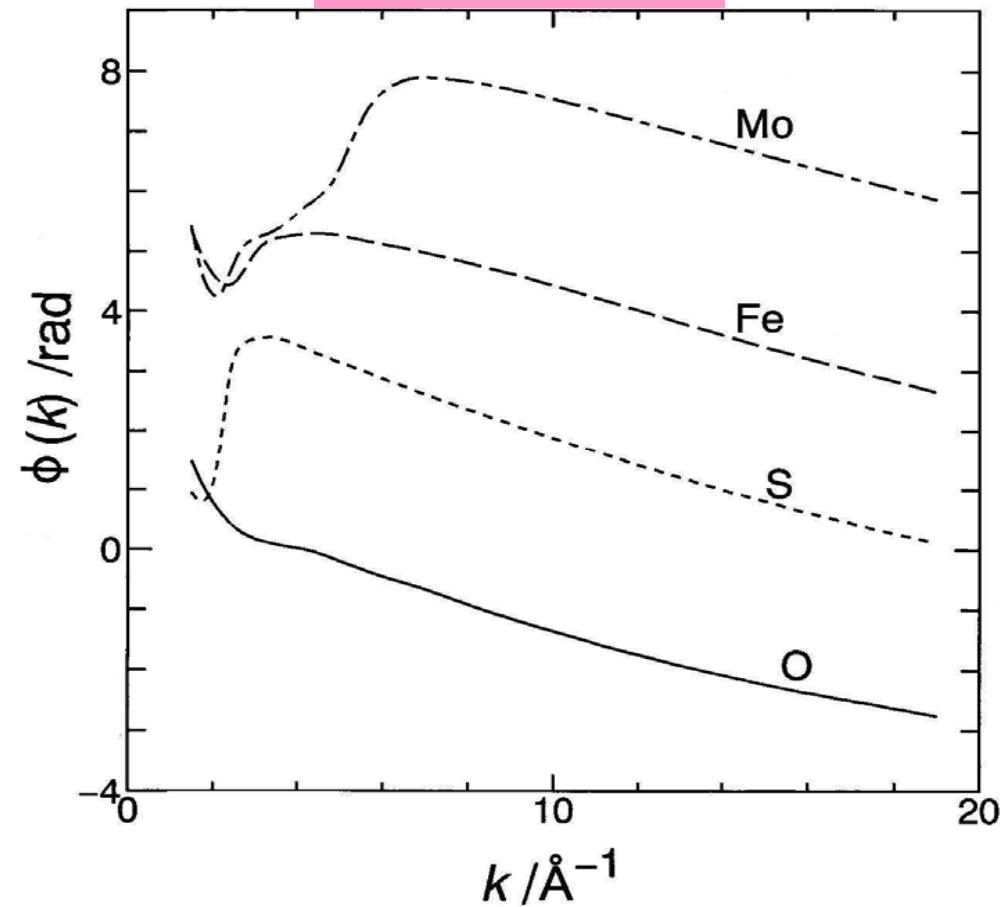
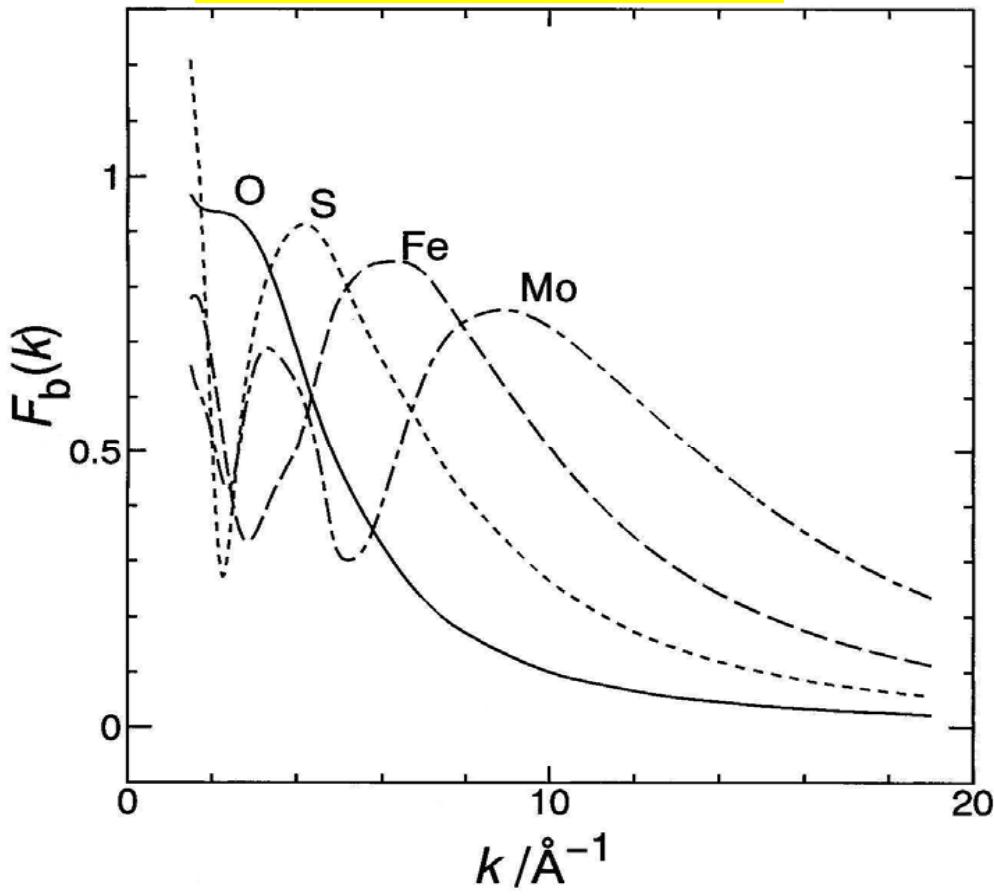
$$\chi(k) = -\sum_i \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

amplitude part

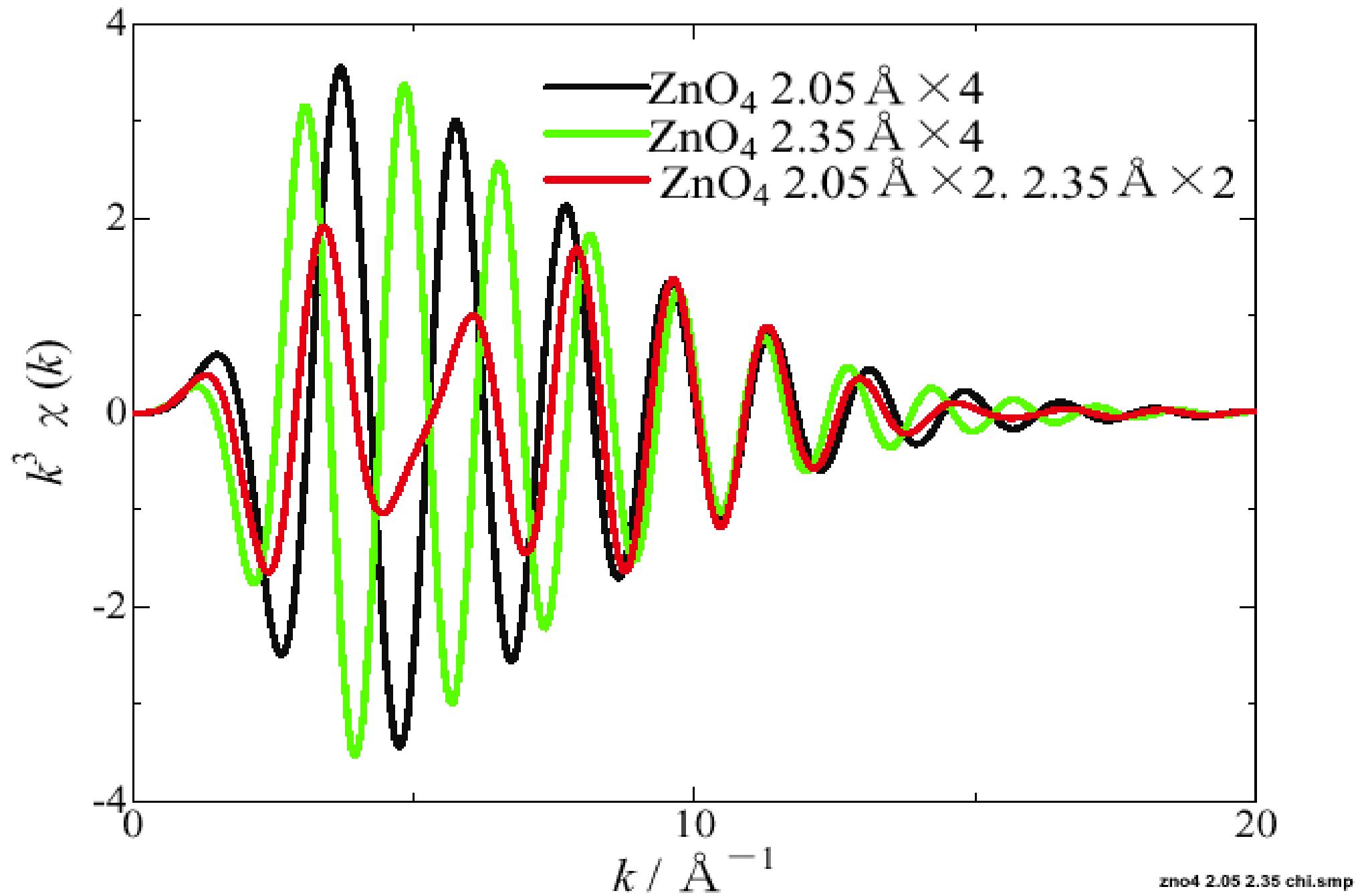
oscillation part

f scattering amplitude

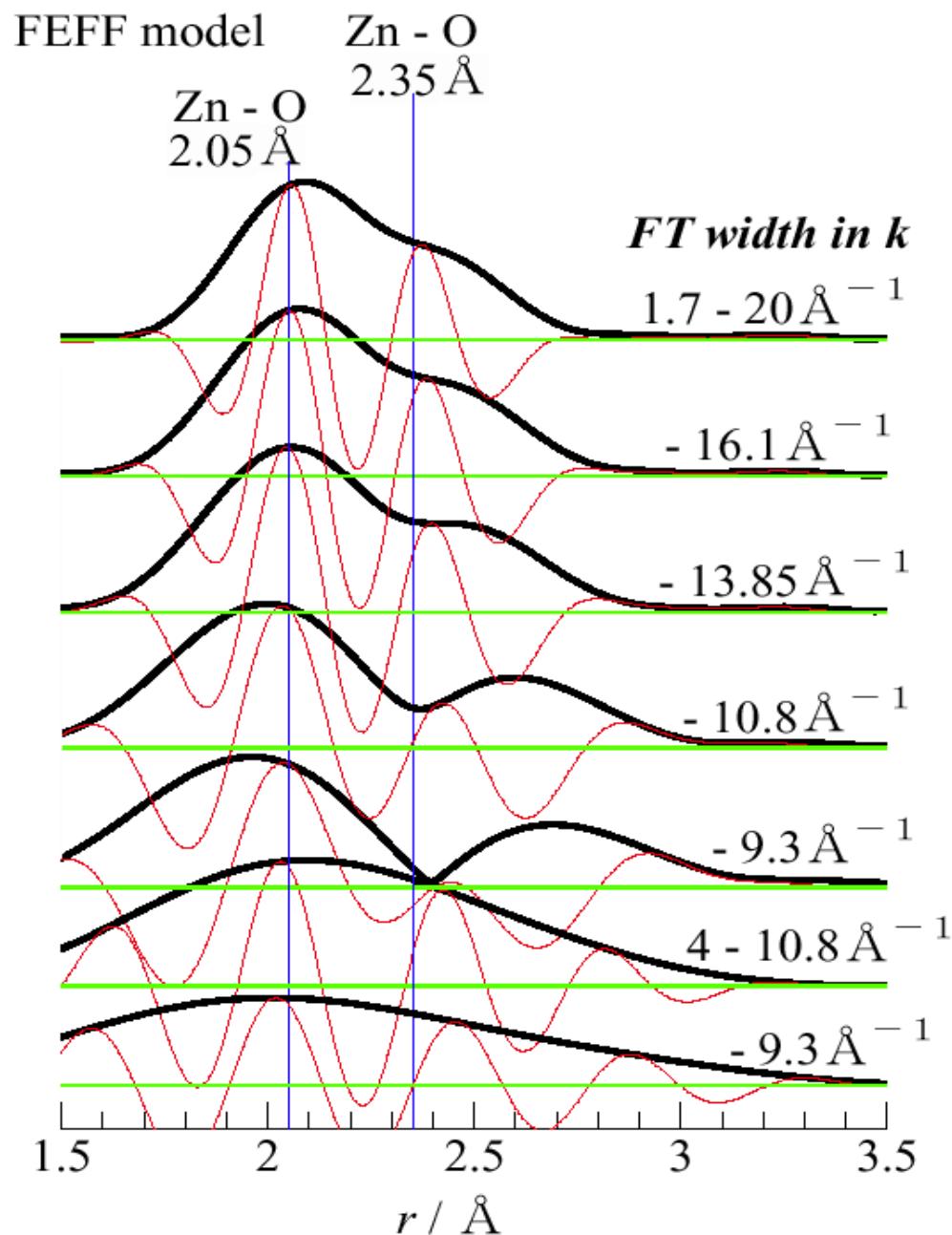
ϕ phase shift



*Can we distinguish oxygen atoms 15%
distant from others by EXAFS?*

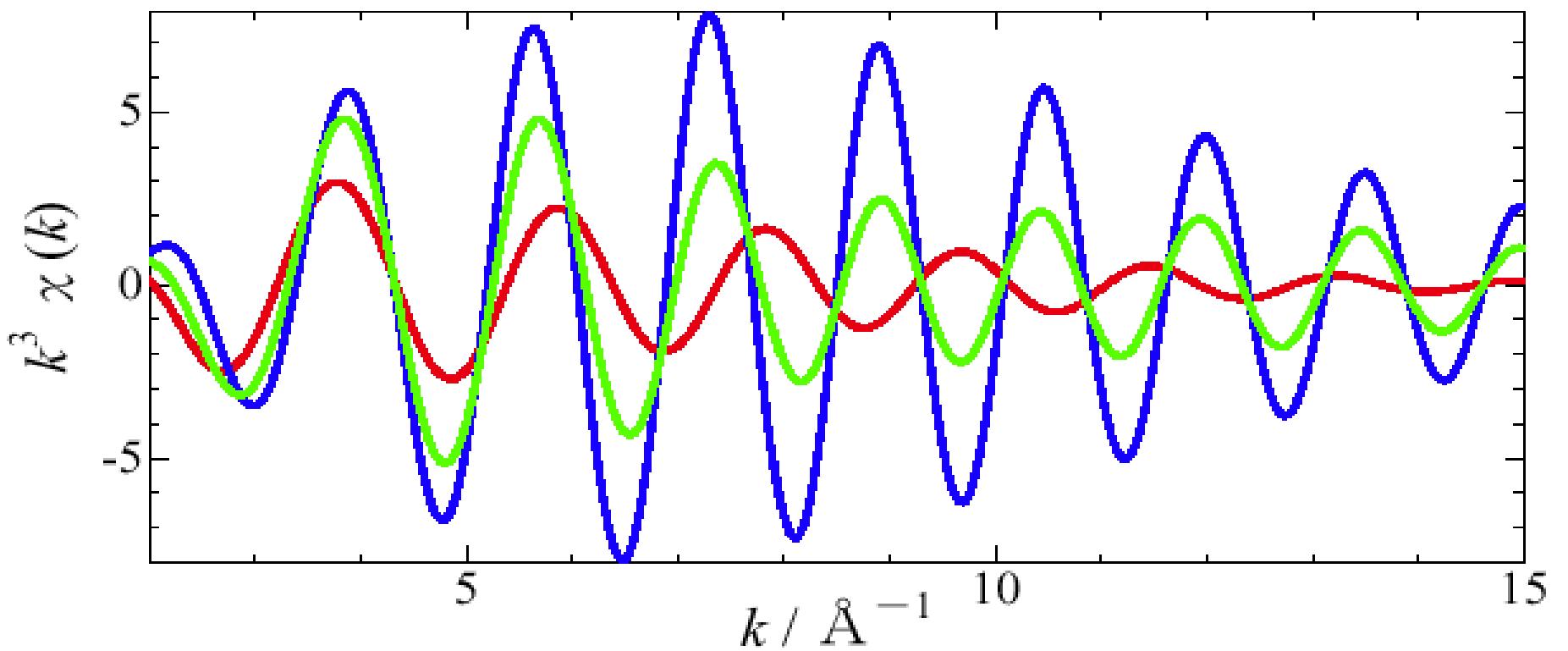


Parameters used for Fourier Trans: O



James E. Penner-Hahn J. Am. Chem. Soc. 1998, **120**, 8401

*Can we distinguish sulfur from
nitrogen (or oxygen) by EXAFS?*

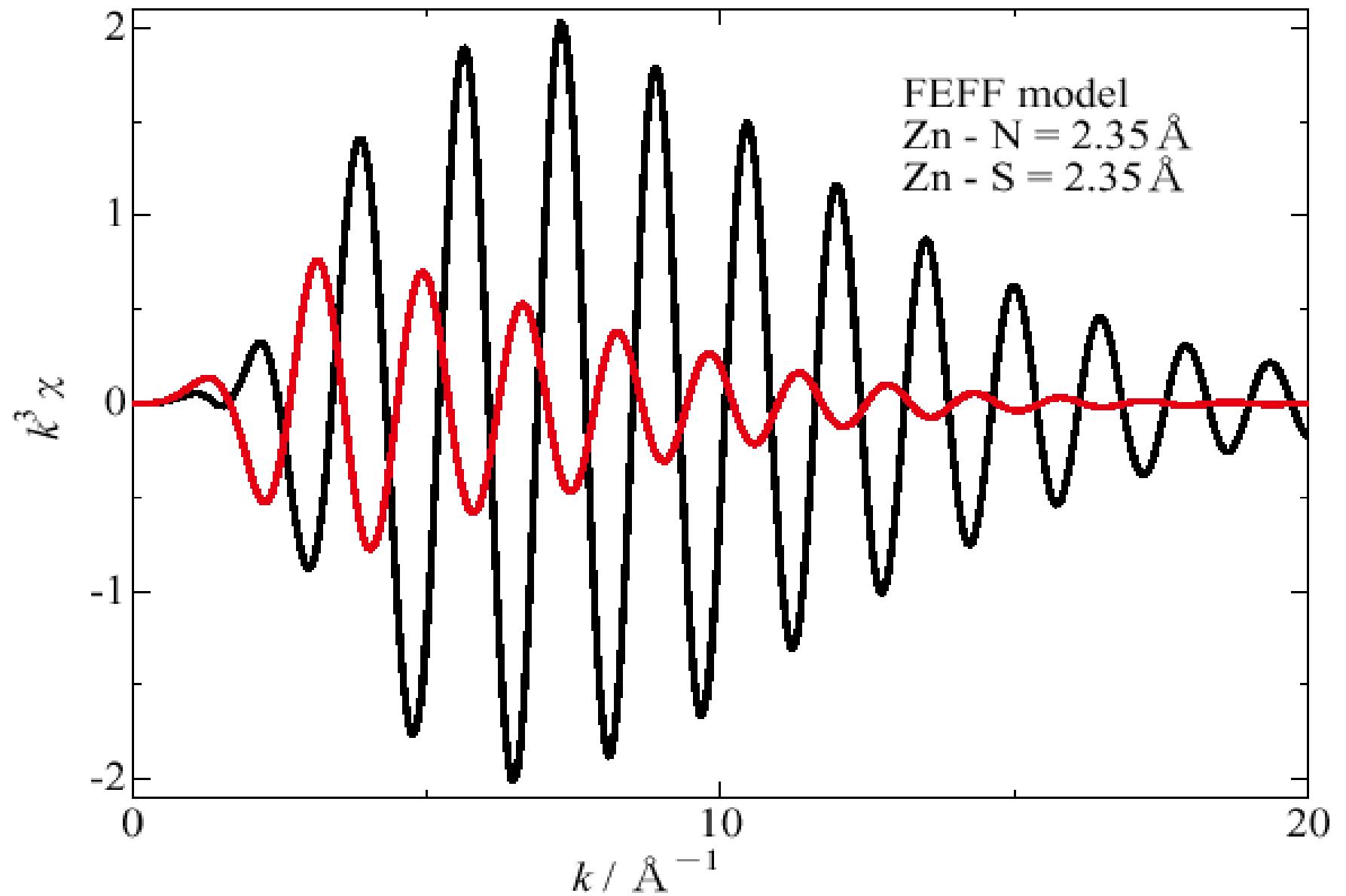


tetrahedral

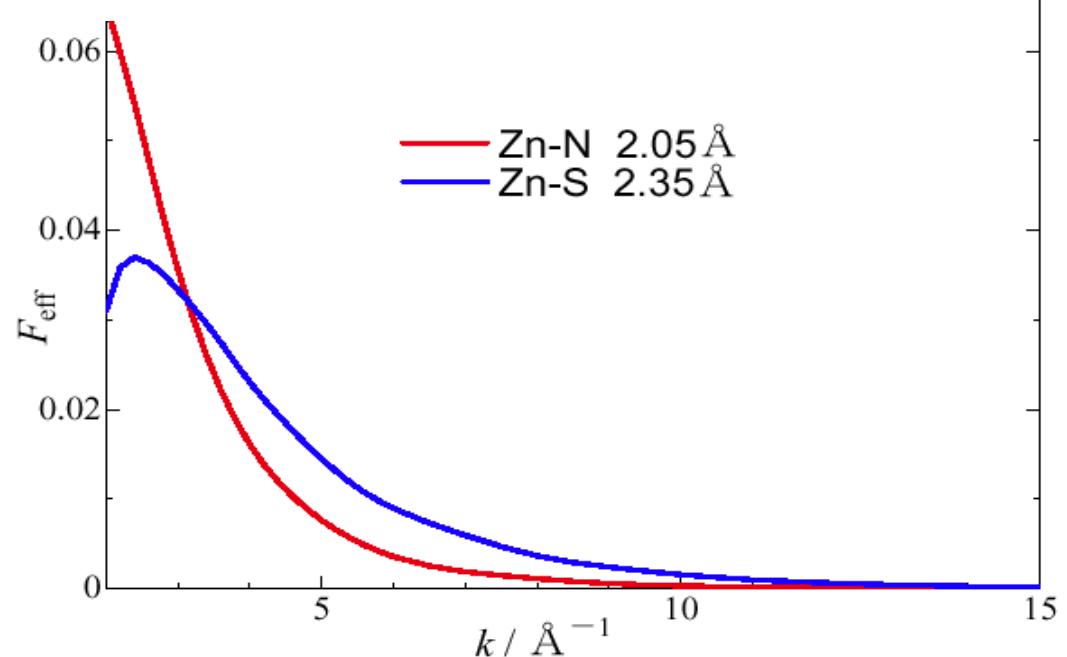
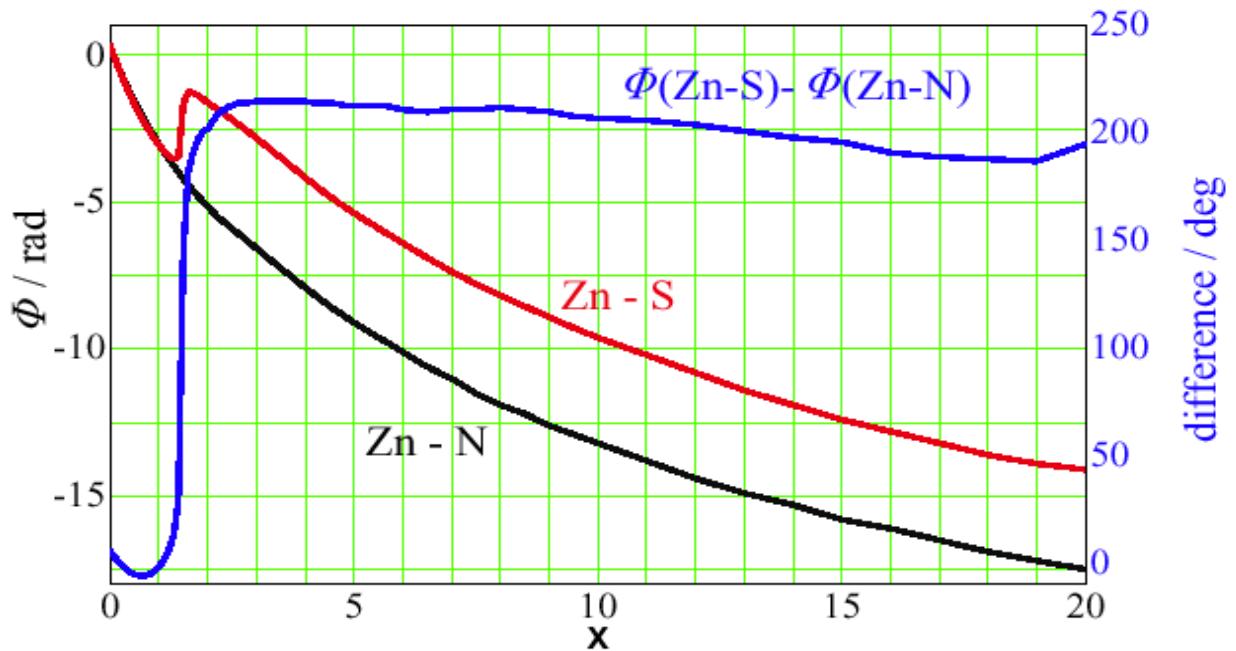
- ZnN_4
- ZnS_4
- ZnS_2N_2

$$r(\text{Zn-N})=2.05 \text{\AA}$$

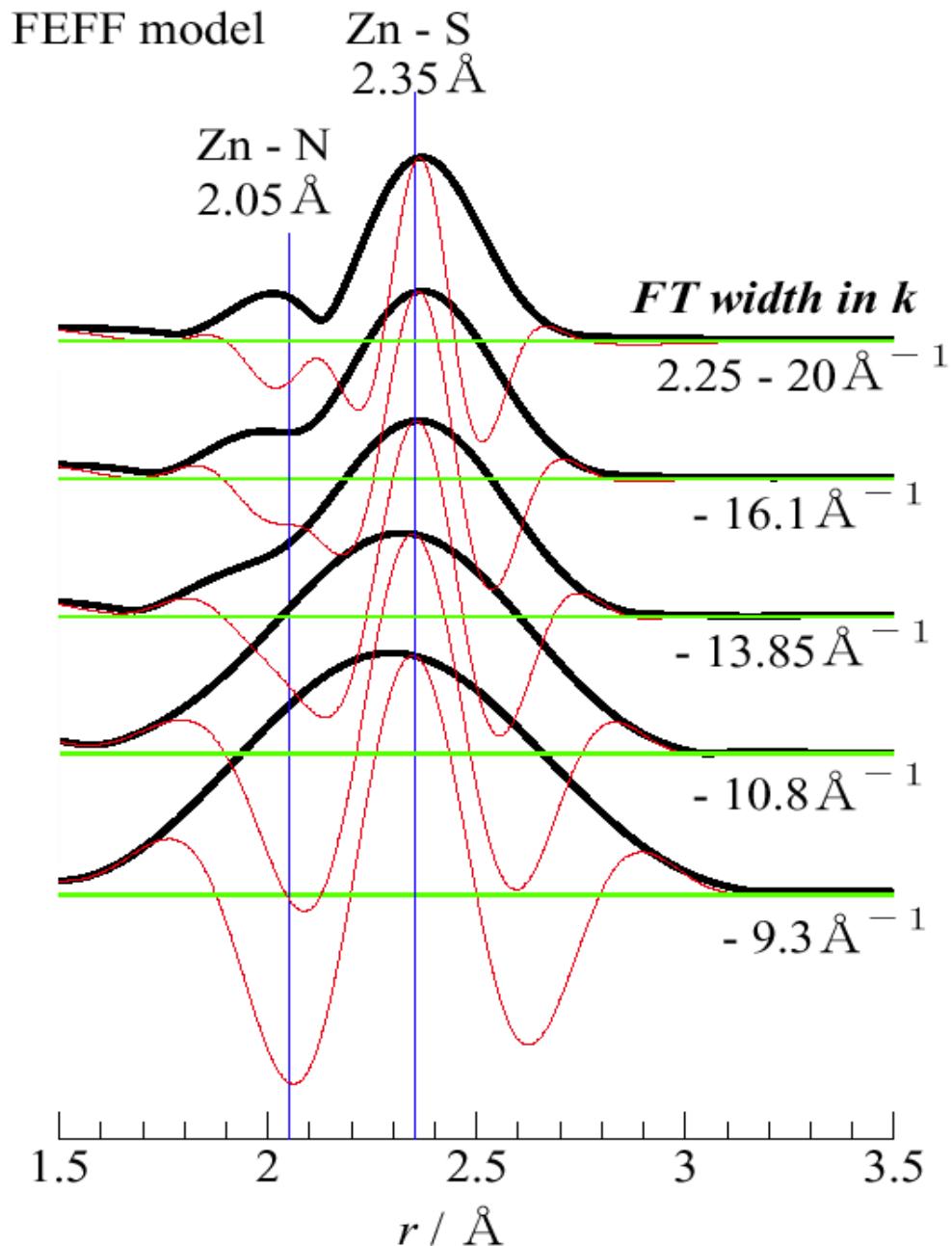
$$r(\text{Zn-S})=2.35 \text{\AA}$$



zns 2.35 znn 2.35.smp



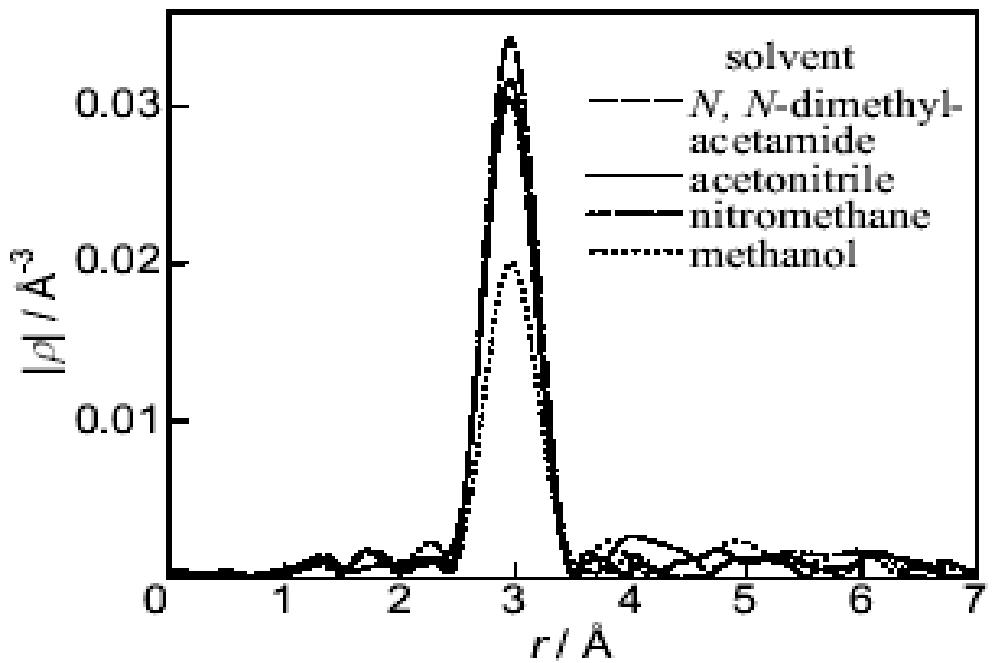
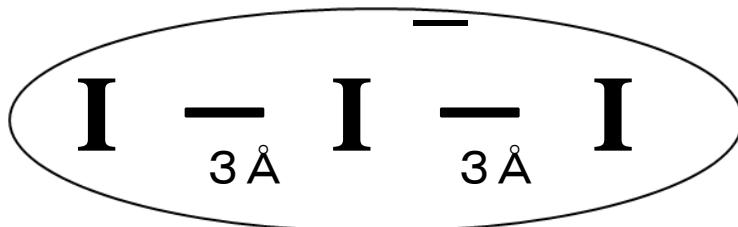
Parameters used for Fourier Trans: S



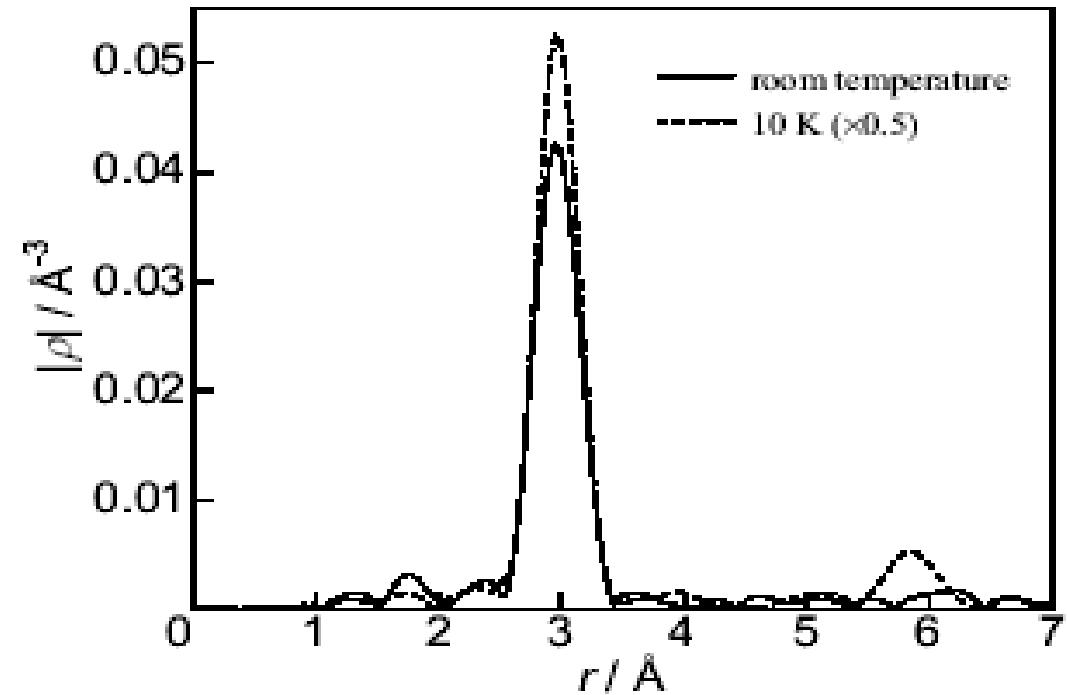
*Almost
impossible !*

Can we detect the end-end atomic interaction in I-I-I molecule (I_3^-) by EXAFS?

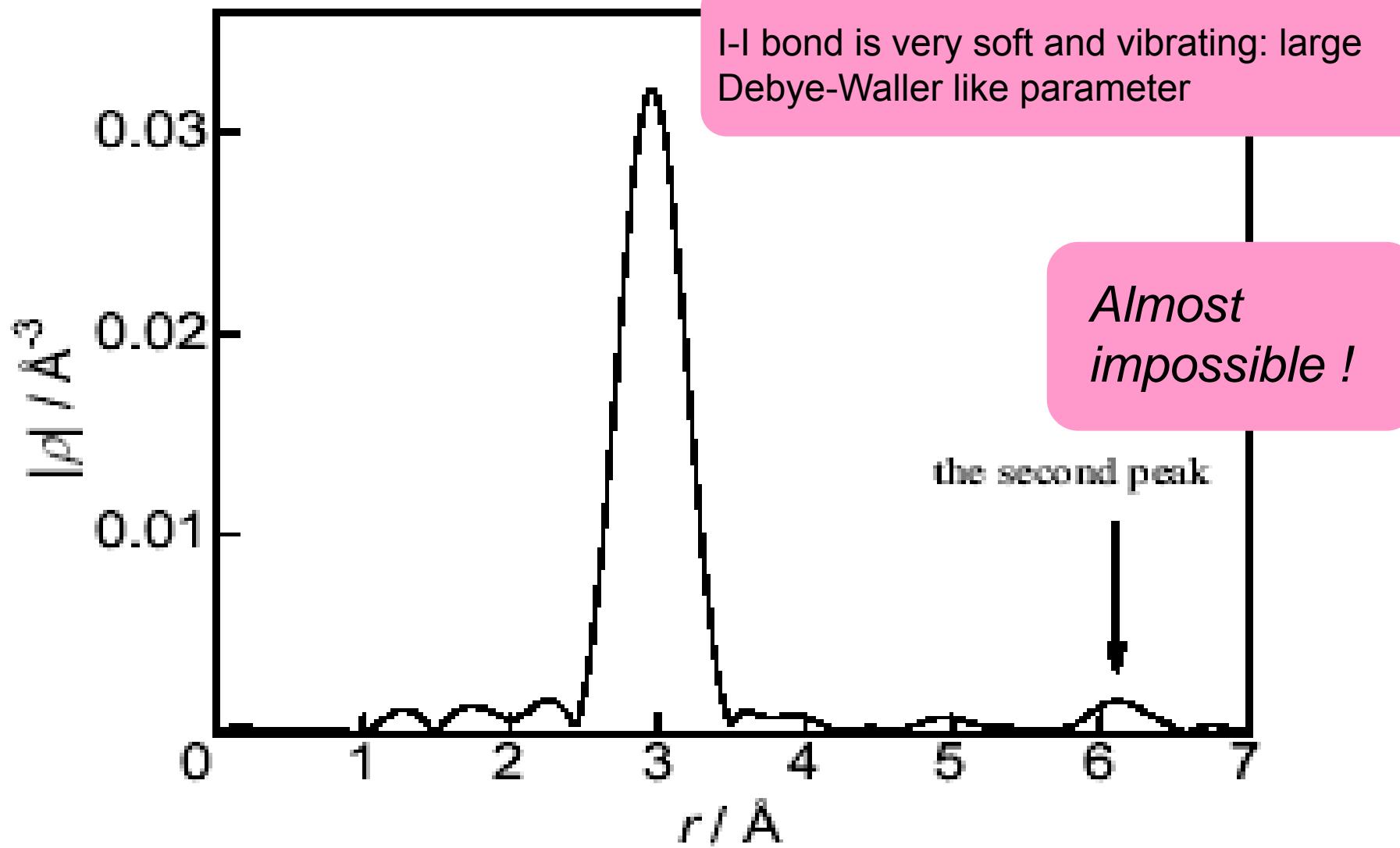
I K-edge EXAFS FT for I₃



Dissolved in organic solvents



(n-C₃H₇)₄N I₃ powder

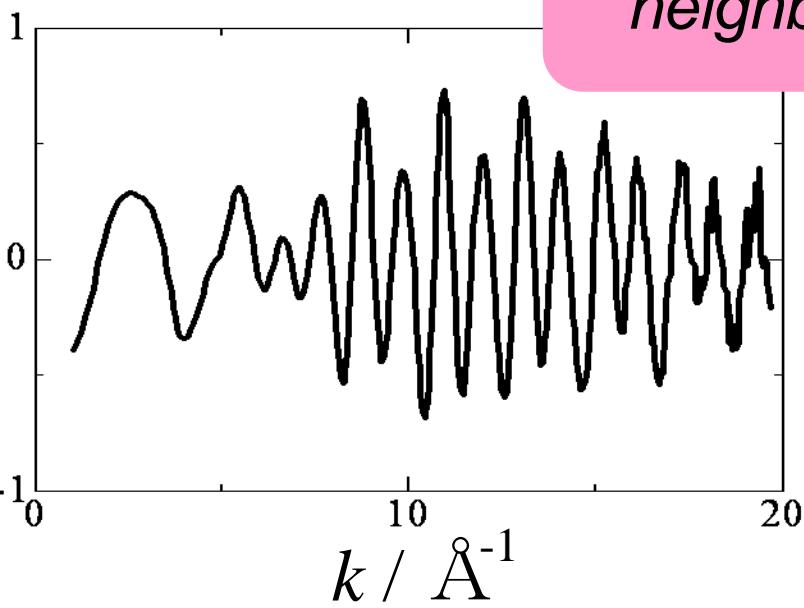
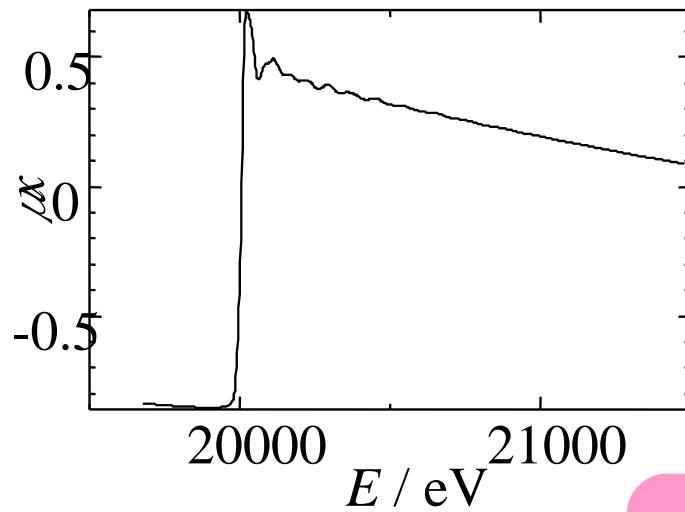


Iodine K-edge EXAFS Fourier transform for the compound spectrum made up from 12 independent spectra for organic solvent solutions.

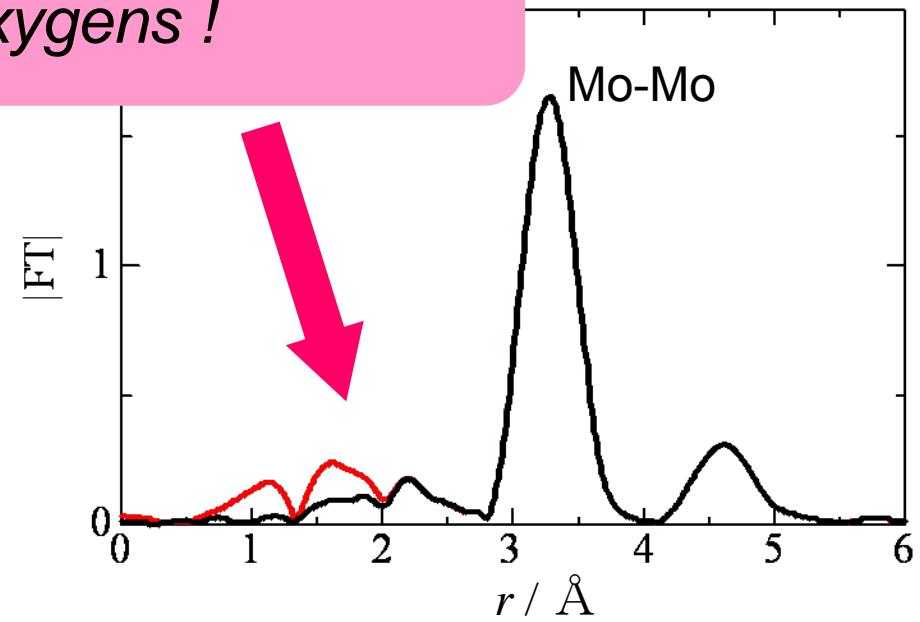
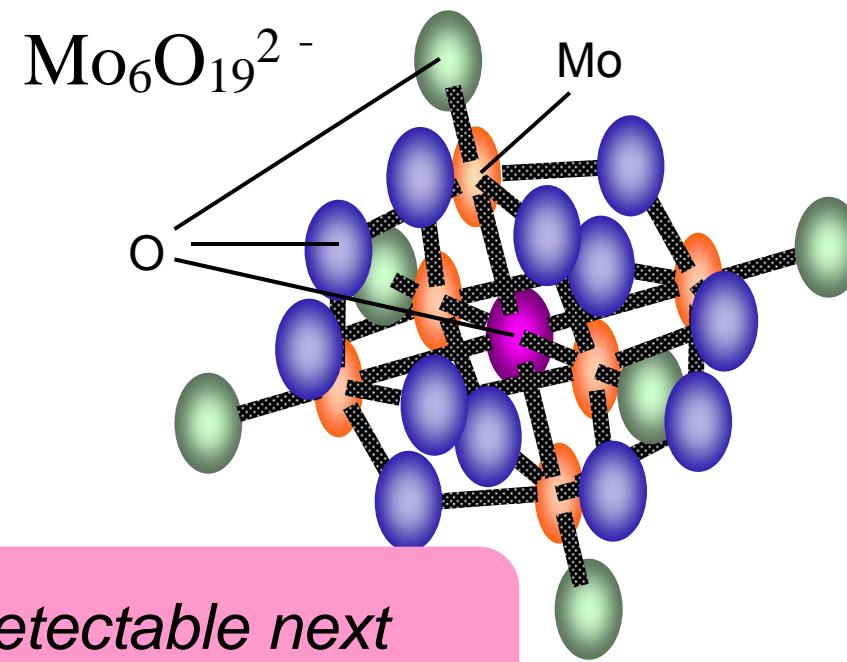
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

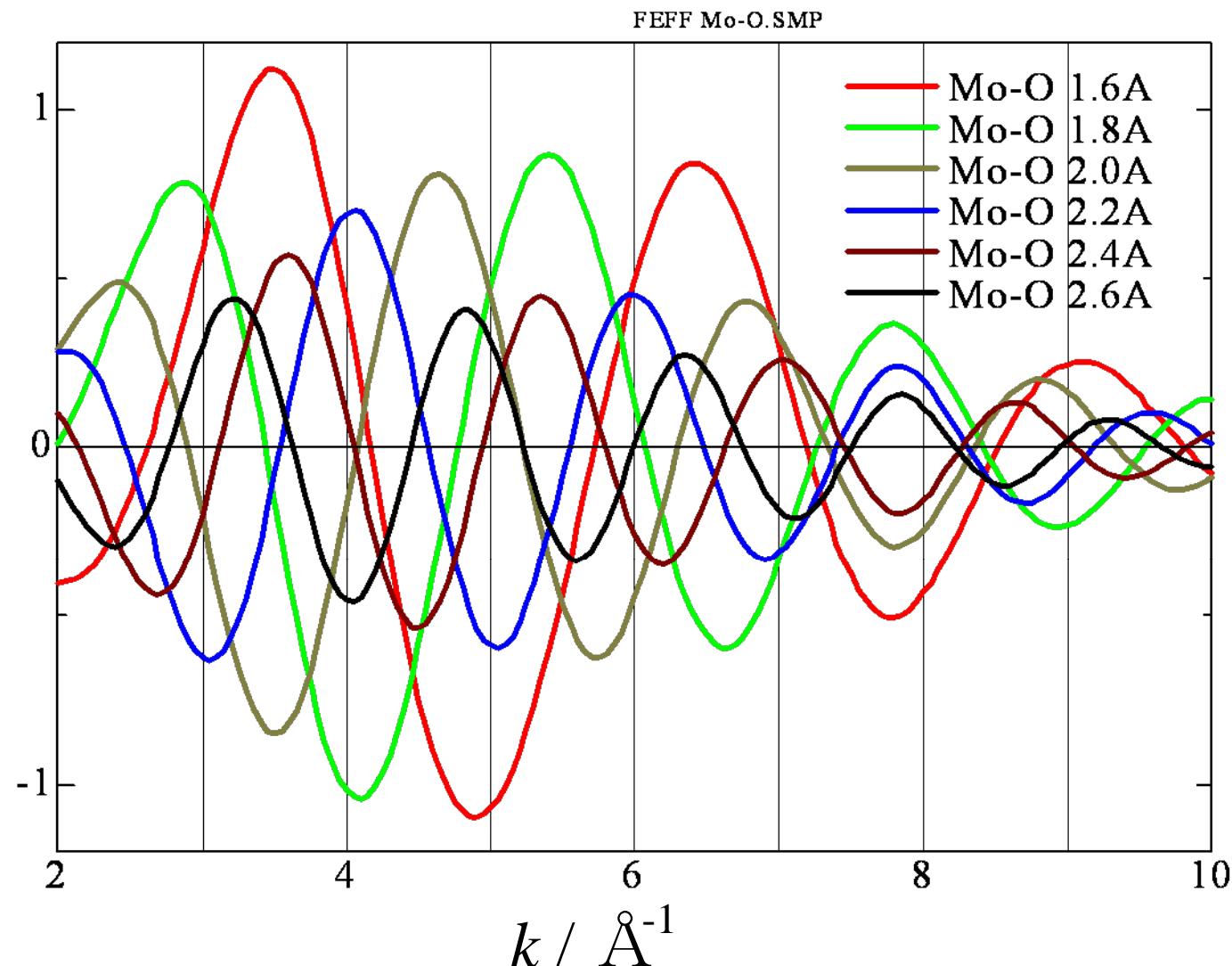
*Large symmetrical cluster of
molybdenum oxide complex*

Mo K-edge XAFS



Almost undetectable next neighbor oxygens !





EXAFS

Extended X-ray Absorption Fine Structure

Theory; very difficult.

Experiment; looks easy.

Data analysis; looks straight forward.

*Thanks to the advanced data
analysis software.*

EXAFS

In reality,

Theory; becomes even more and more complex and difficult to understand.

Experiment; to obtain CORRECT spectral data is NOT an easy task.

Data analysis; no one except for the GOD knows whether the conclusion from the EXAFS analysis is CORRECT.

EXAFS is a tricky technique.

Then, what do we have to do ?

Use

- ★ *other analytical methods,*
- ★ *knowledge of chemistry and physics,*

and

- ★ *good sense as a scientist*

*and combine them together with
the EXAFS analysis.*

XAS Analysis Software Using IFEFFIT

free software



Current release: 0.8.059
Release date: 1 July, 2009

ATHENA is an interactive graphical utility for processing EXAFS data. It handles most of the common data handling chores of interest, including deglitching, aligning, merging, background removal, Fourier transforms, and much more.



Current release: 0.8.013
Release date: 15 December, 2008

ARTEMIS is an interactive graphical utility for fitting EXAFS data using theoretical standards from FEFF and sophisticated data modelling along with flexible data visualization and statistical analysis. ARTEMIS includes interfaces to ATOMS and FEFF.