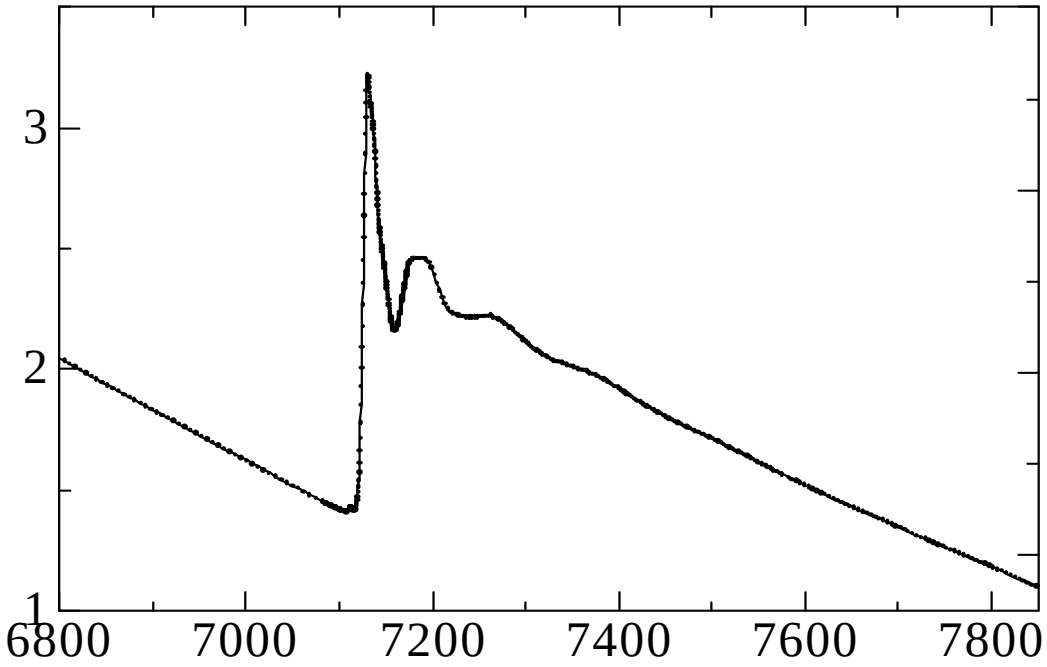
AOFSRR Cheiron School 2011, SPring-8

Oct. 2nd, 2011

XAFS

X-ray Absorption Fine Structure



Iwao Watanabe

Ritsumeikan University

XAFS

Theory

- Quantum Mechanics
- Models
- Approximations

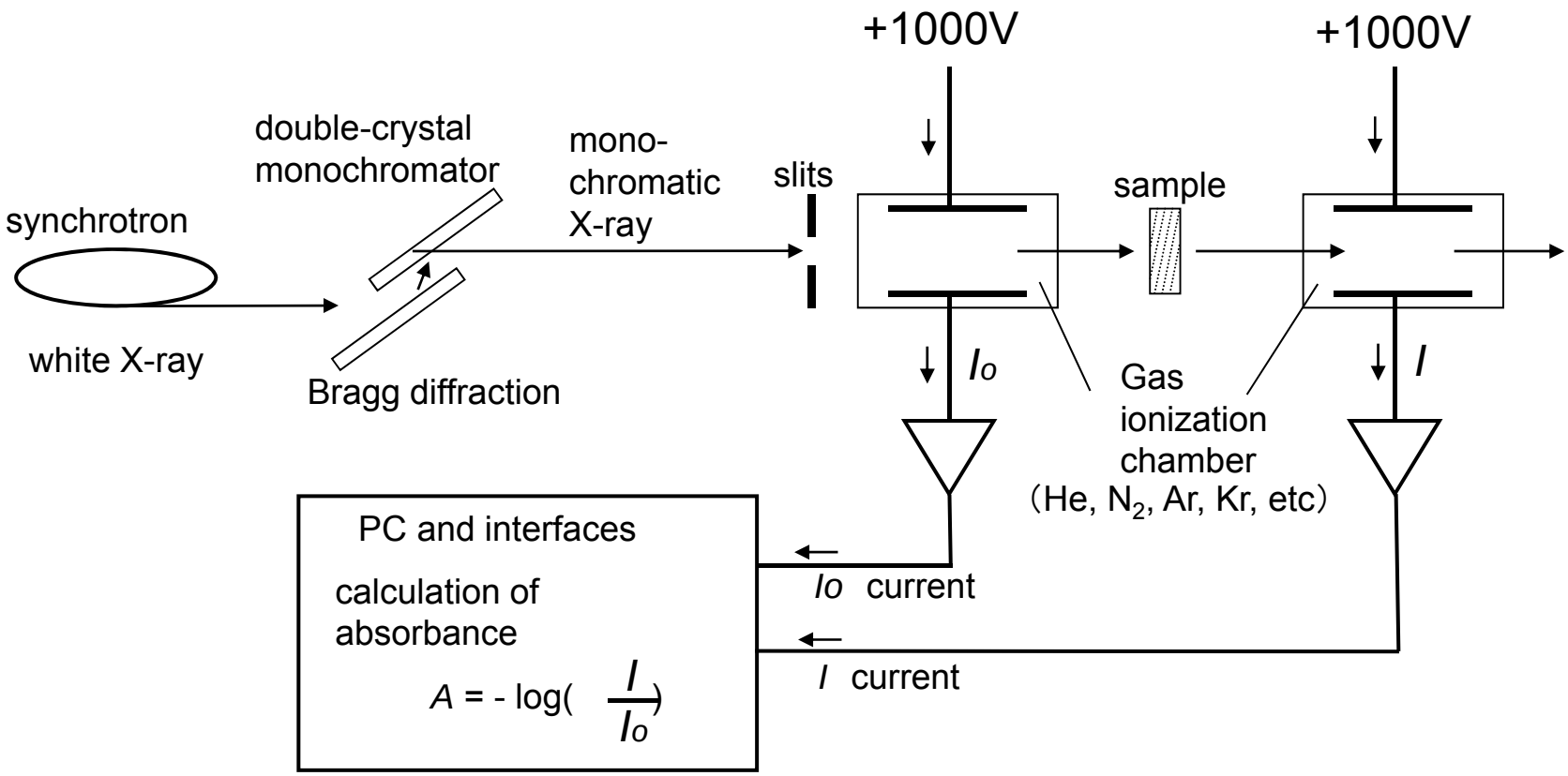
Experiment

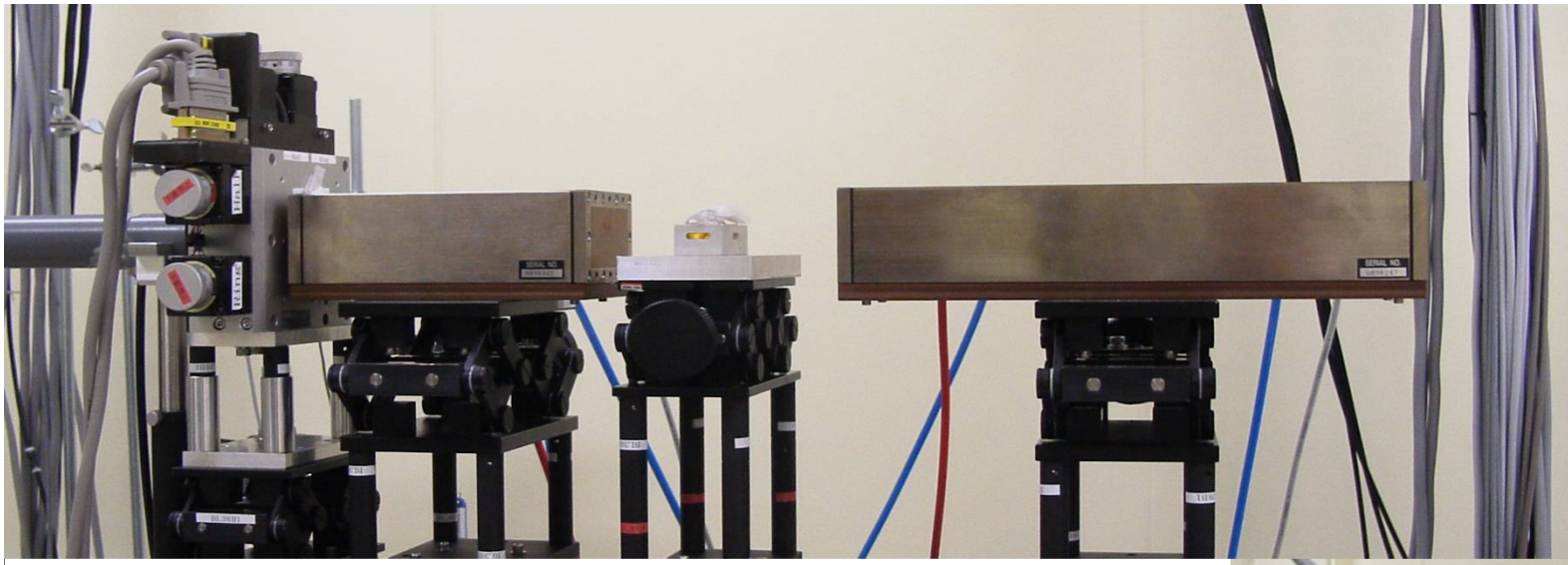
- Light Source
- Monochromator
- Higher Harmonics Rejection
- Sample Preparation
- Detection Methods
- Polarization XAFS

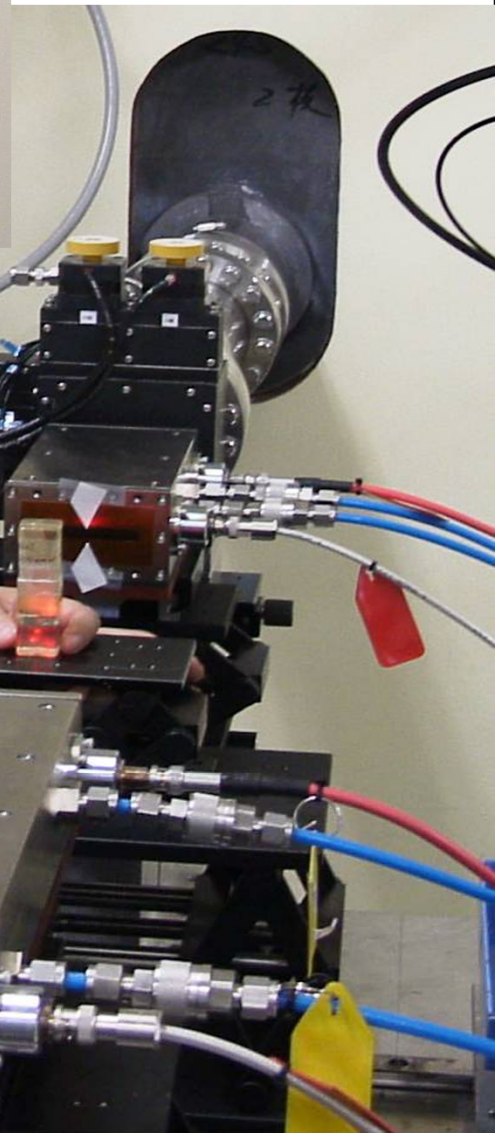
Data Analysis

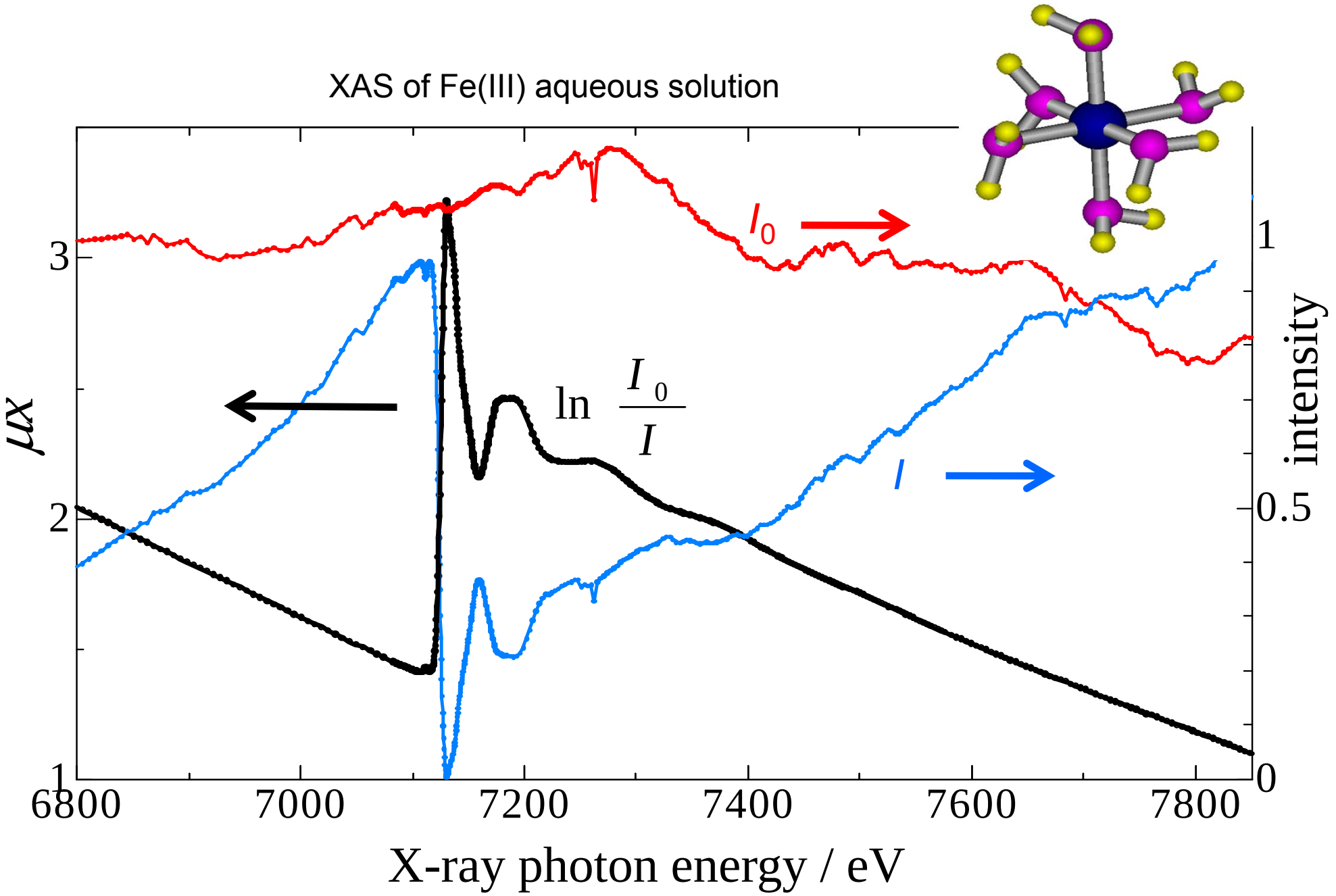
- Limited Usable Range in Experimental Data
- Estimation of Background Curves
- Fourier Transform
- Multi-Scattering
- Curve Fitting Procedure
- Phase Problems
- Debye-Waller-Like Parameter
- Anharmonicity in Potential

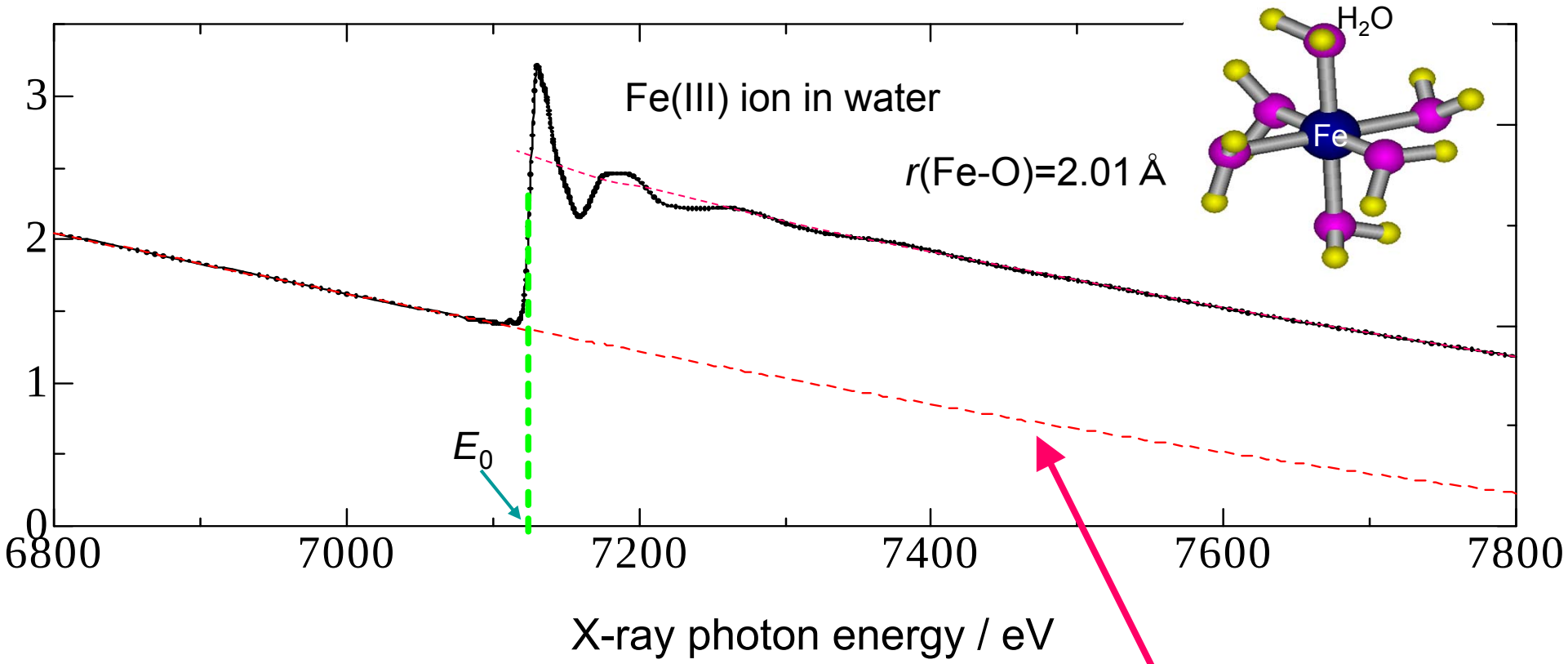
X-ray absorption measurement by transmission method
The most reliable and basic method








XAS of Fe(III) aqueous solution
I_0
μx
$\ln \frac{I_0}{I}$
I
intensity
3
2
1
1
0.5
0
6800
7000
7200
7400
7600
7800
X-ray photon energy / eV



Focusing on K shell (1s electron) excitation

Background absorption due to other atoms and other shell electrons

Fermi's Golden Rule

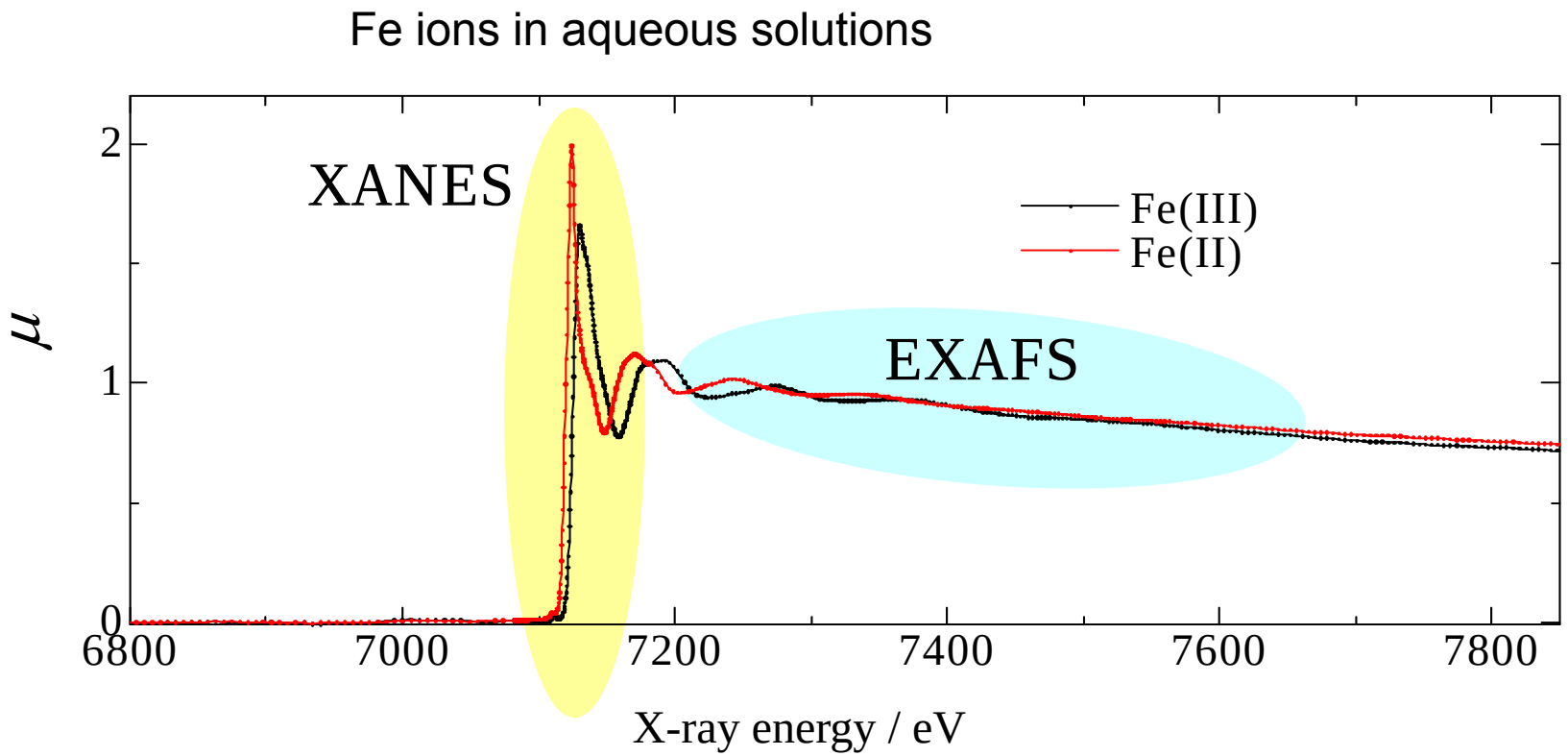
In XAS we measure the dipole mediated transition of an electron in a deep core state $|i\rangle$ into an unoccupied state $|f\rangle$:

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left|\langle f|\hat{\epsilon}\cdot\mathbf{r}|i\rangle\right|^2 \delta(E_f)$$

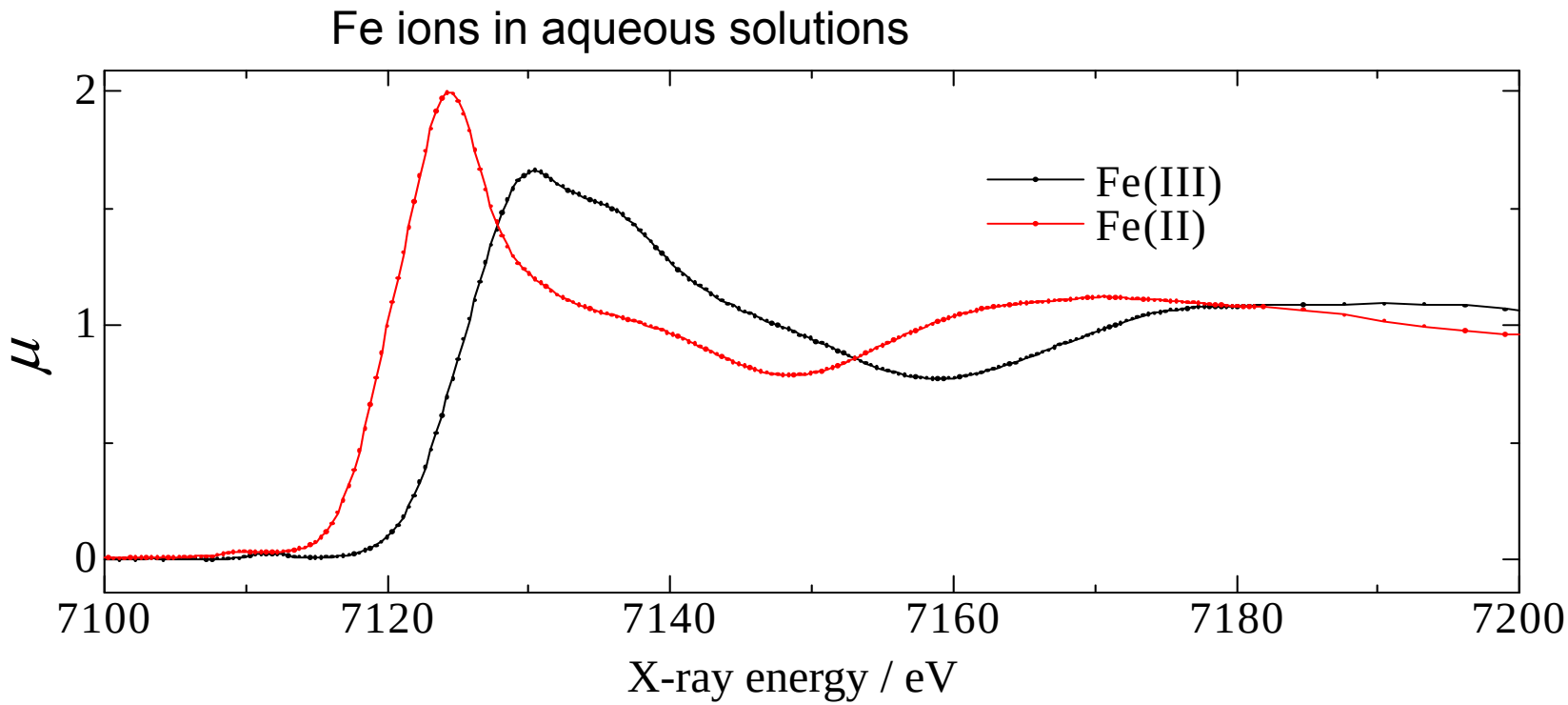
There are two ways to solve this equation:

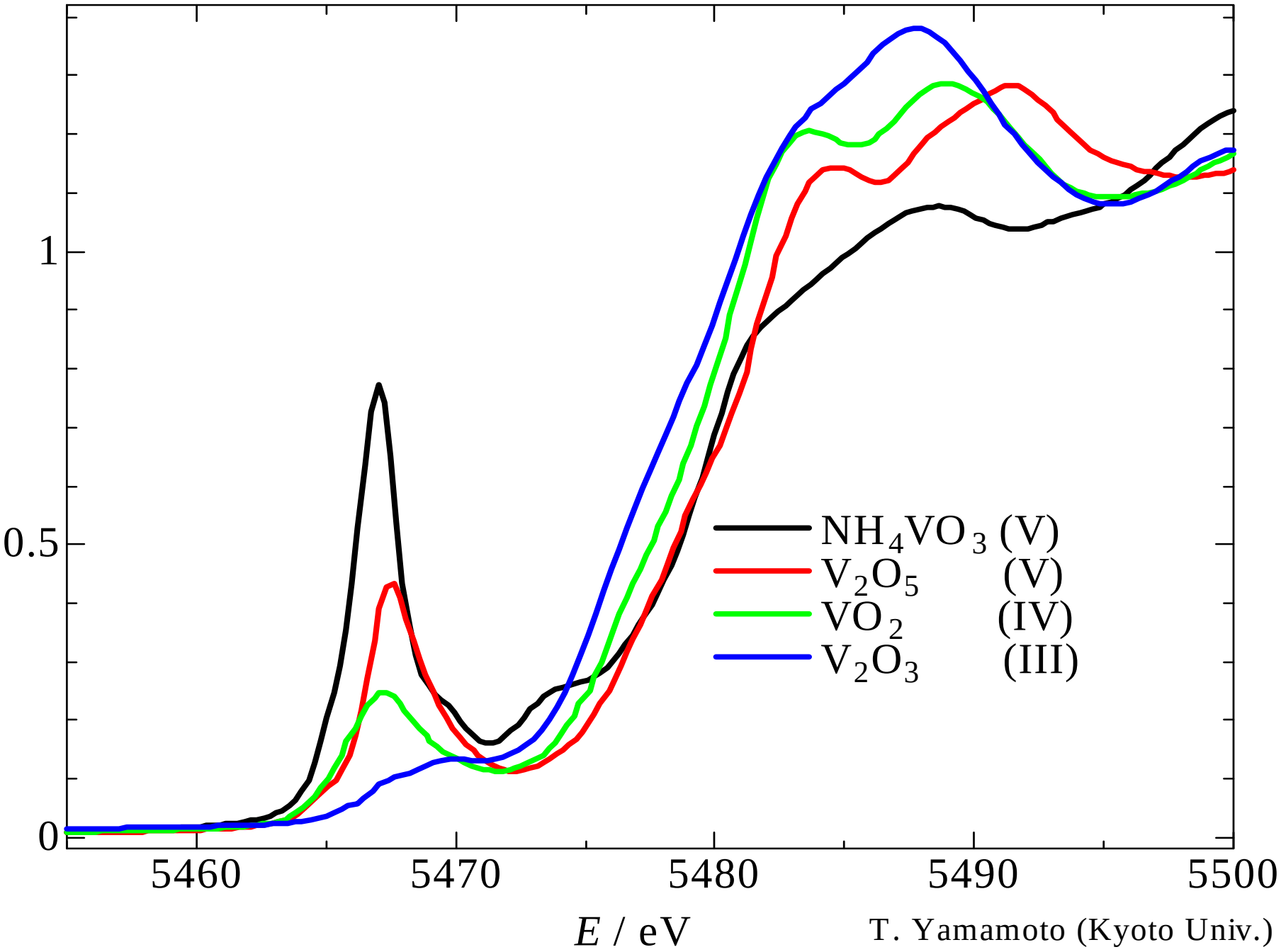
1. Accurately represent $|i\rangle$ and $|f\rangle$, then evaluate the integral directly. This is the approach taken, for example, by molecular orbital theory.
2. Use multiple scattering theory:
   This is the approach taken by FEFF and, by extension, by analysis programs which use FEFF.

XAFS: X-ray Absorption Fine Structure



XANES: X-ray Absorption Near Edge Structure




1
0.5
0
5460
5470
5480
5490
5500
E / eV
NH4VO3 (V)
V2O5 (V)
VO2 (IV)
V2O3 (III)
T. Yamamoto (Kyoto Univ.)

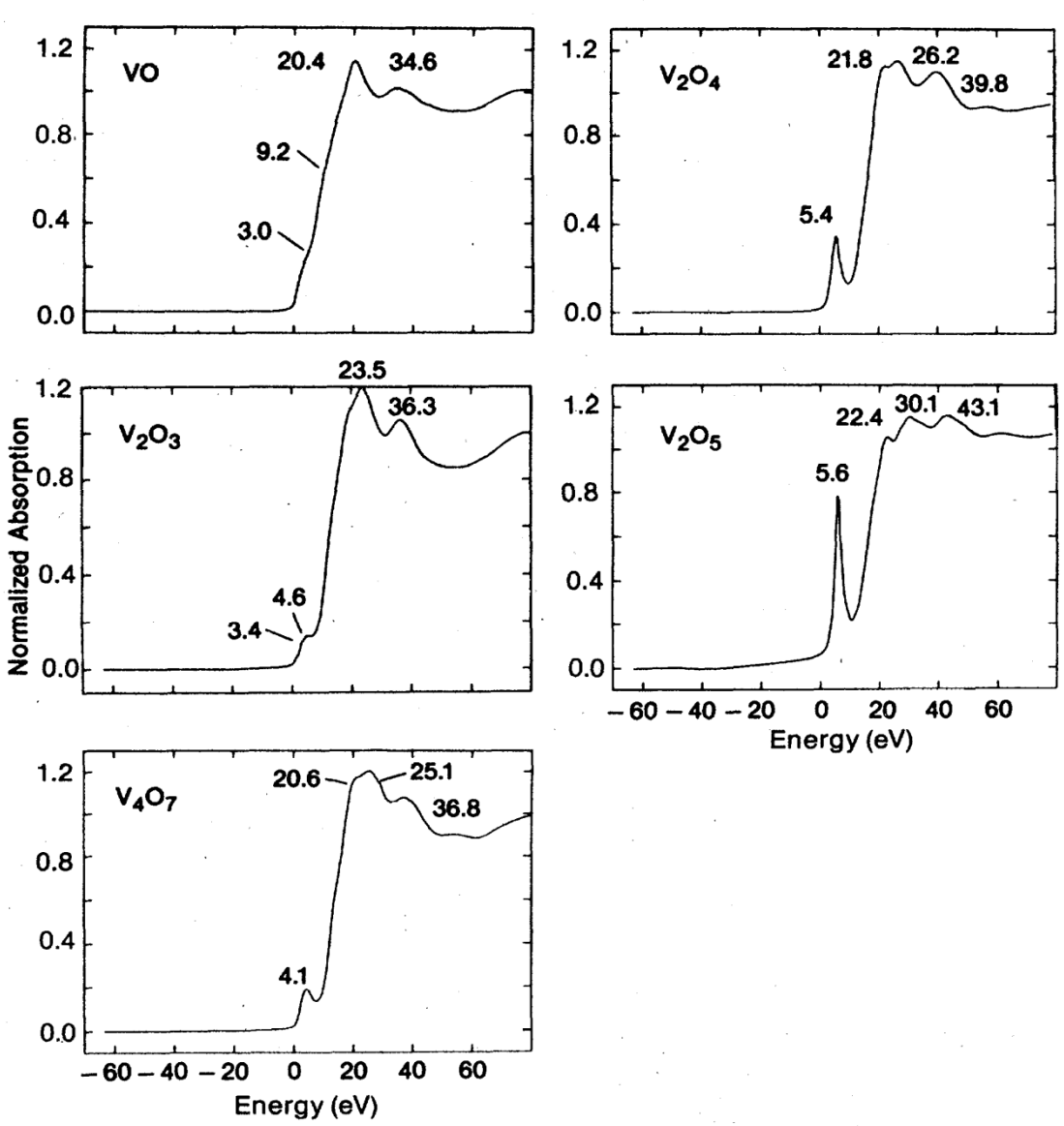
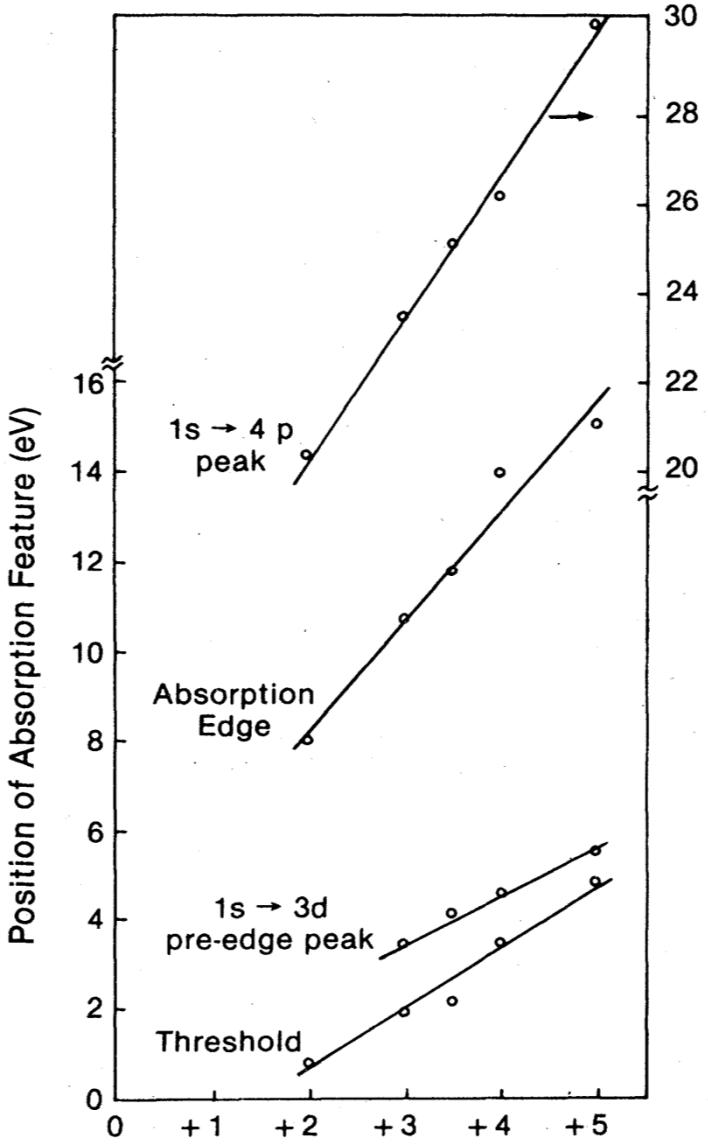
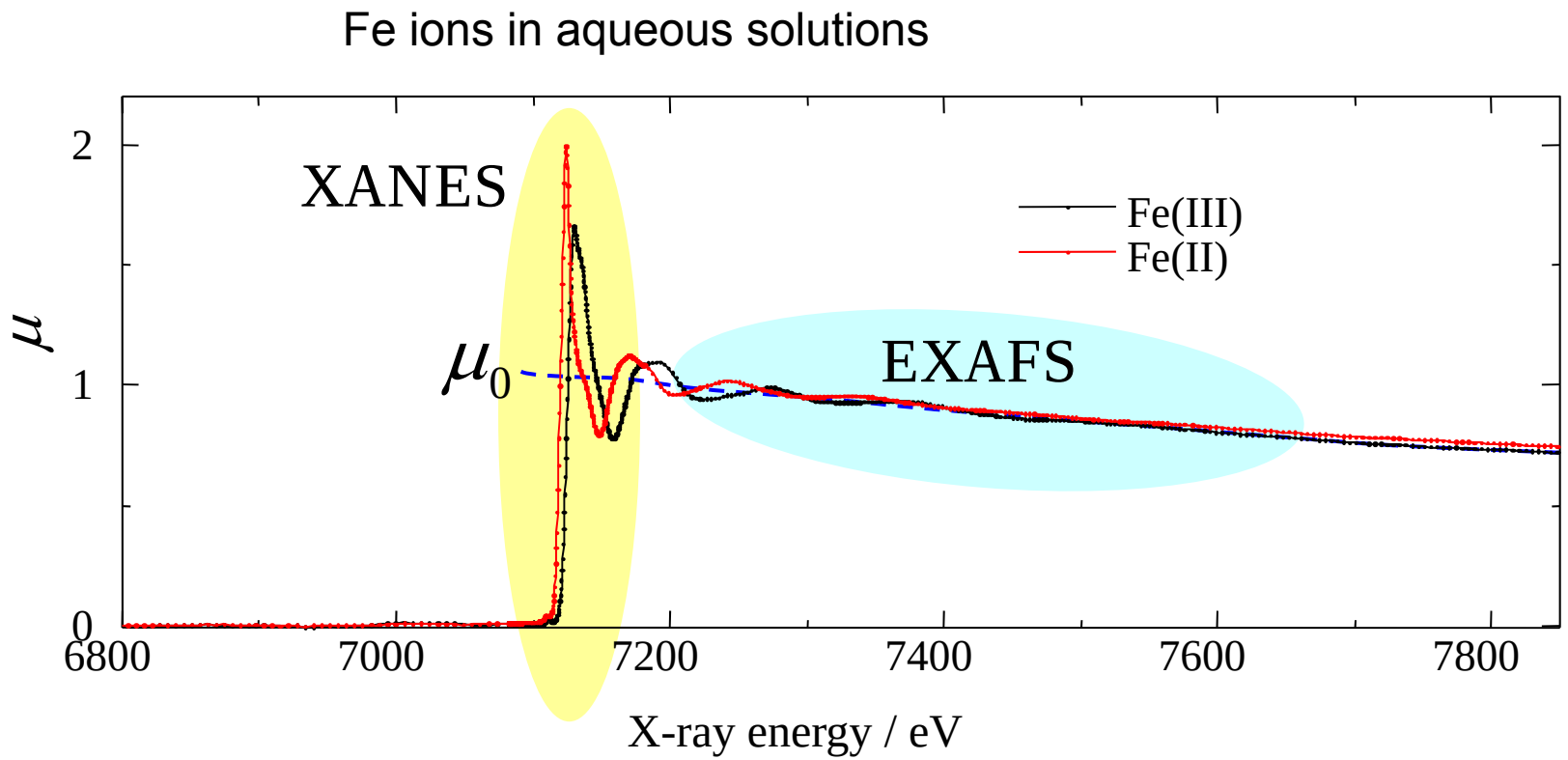


FIG. 3. Normalized *K*-edge XANES spectra of vanadium oxides, the zero of energy taken at 5465 eV.



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

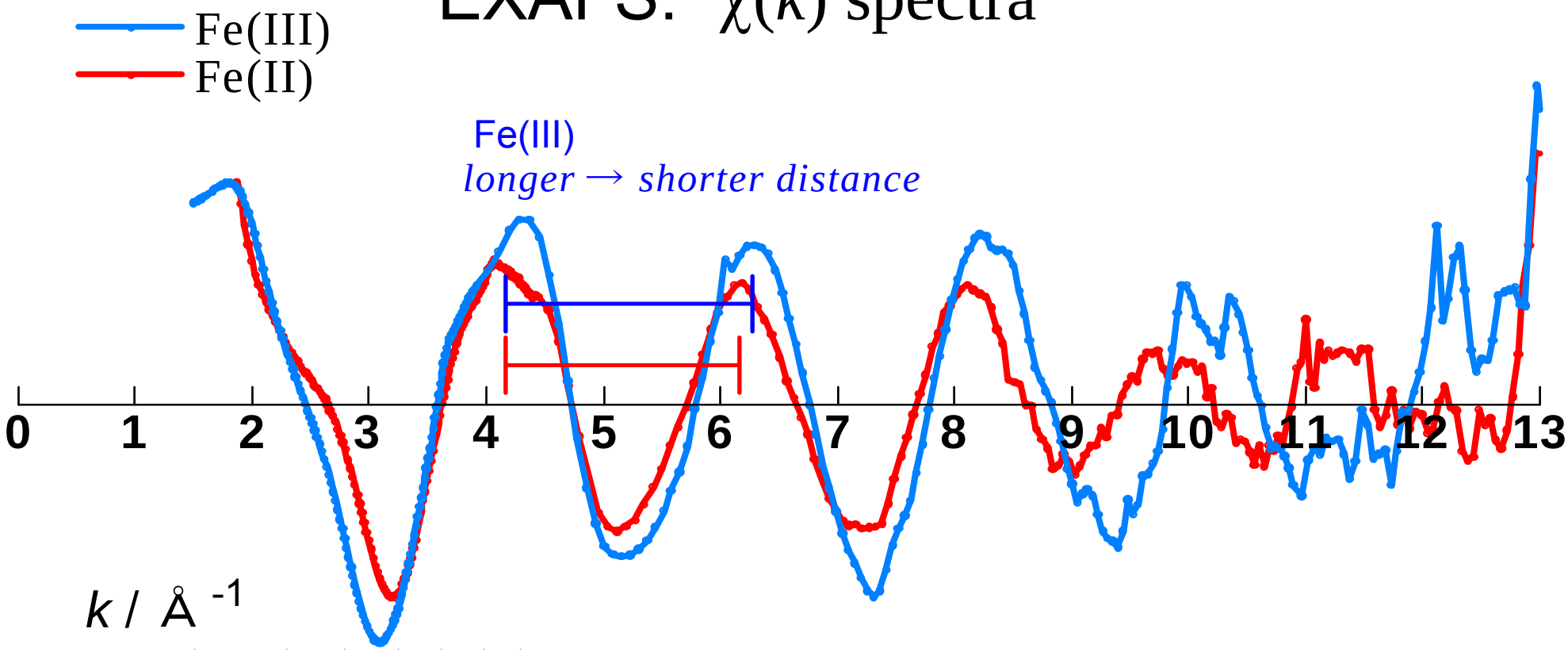
EXAFS: Extended X-ray Absorption Fine Structure



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

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

EXAFS: $\chi(k)$ spectra

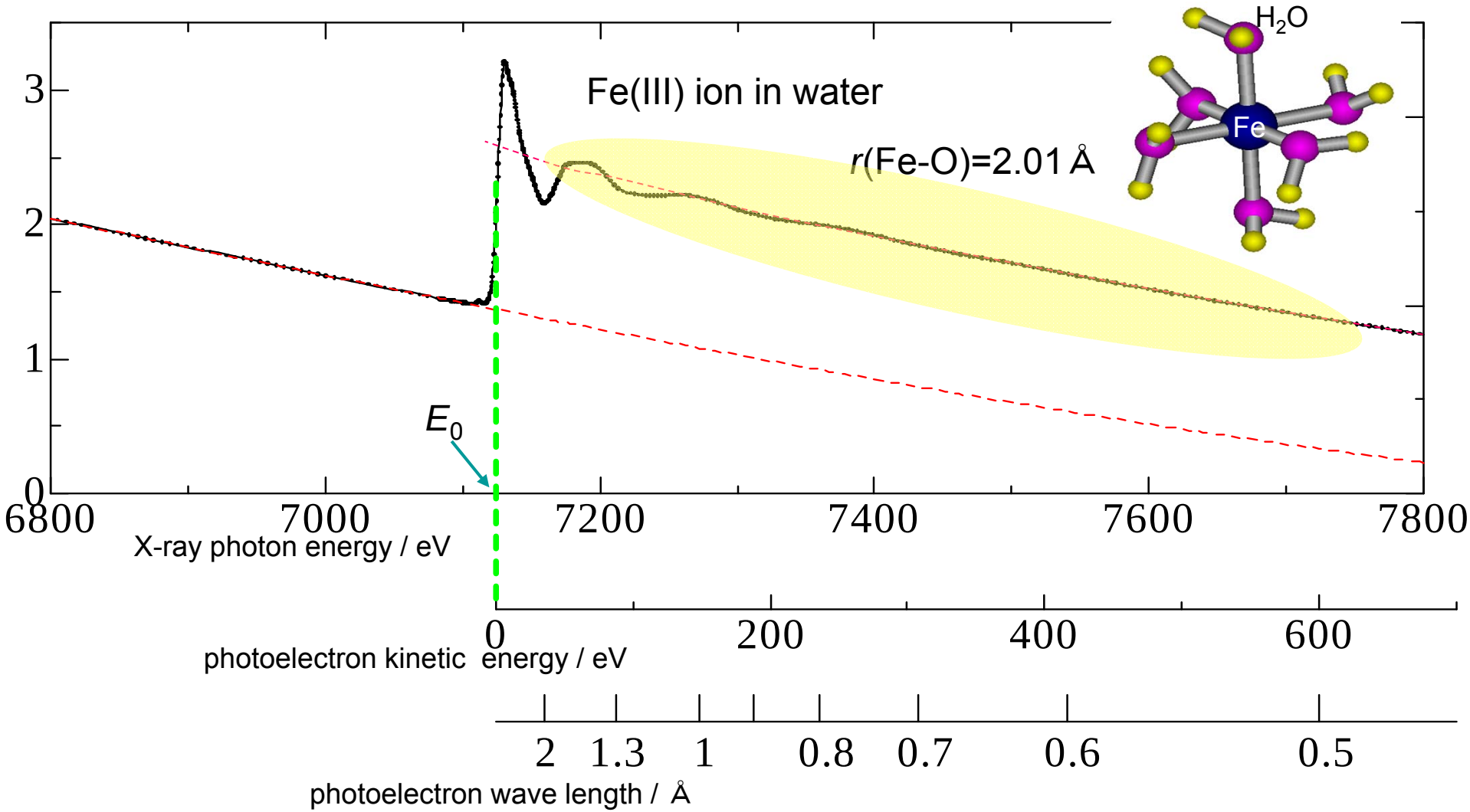


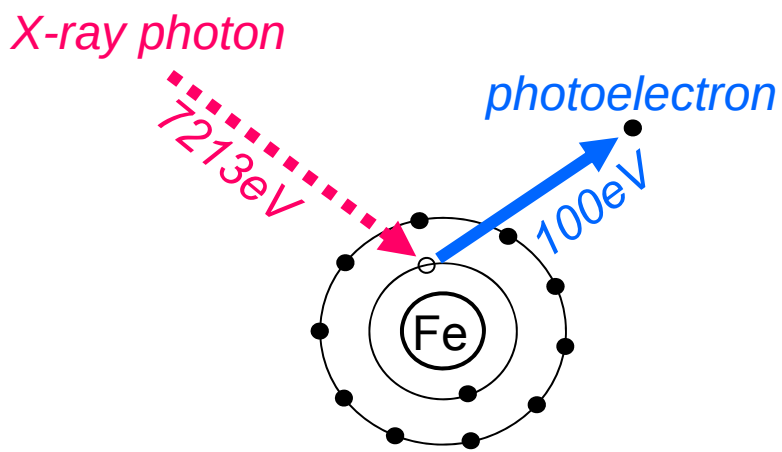
k : wave number, wave vector

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

$(E - E_0)$
kinetic energy of photoelectron

Simplest model to explain how the EXAFS oscillation occurs


Fe(III) ion in water
r(Fe-O)=2.01 Å
H2O
Fe
E0
3
2
1
0
6800
7000
7200
7400
7600
7800
X-ray photon energy / eV
0
200
400
600
photoelectron kinetic energy / eV
2
1.3
1
0.8
0.7
0.6
0.5
photoelectron wave length / Å

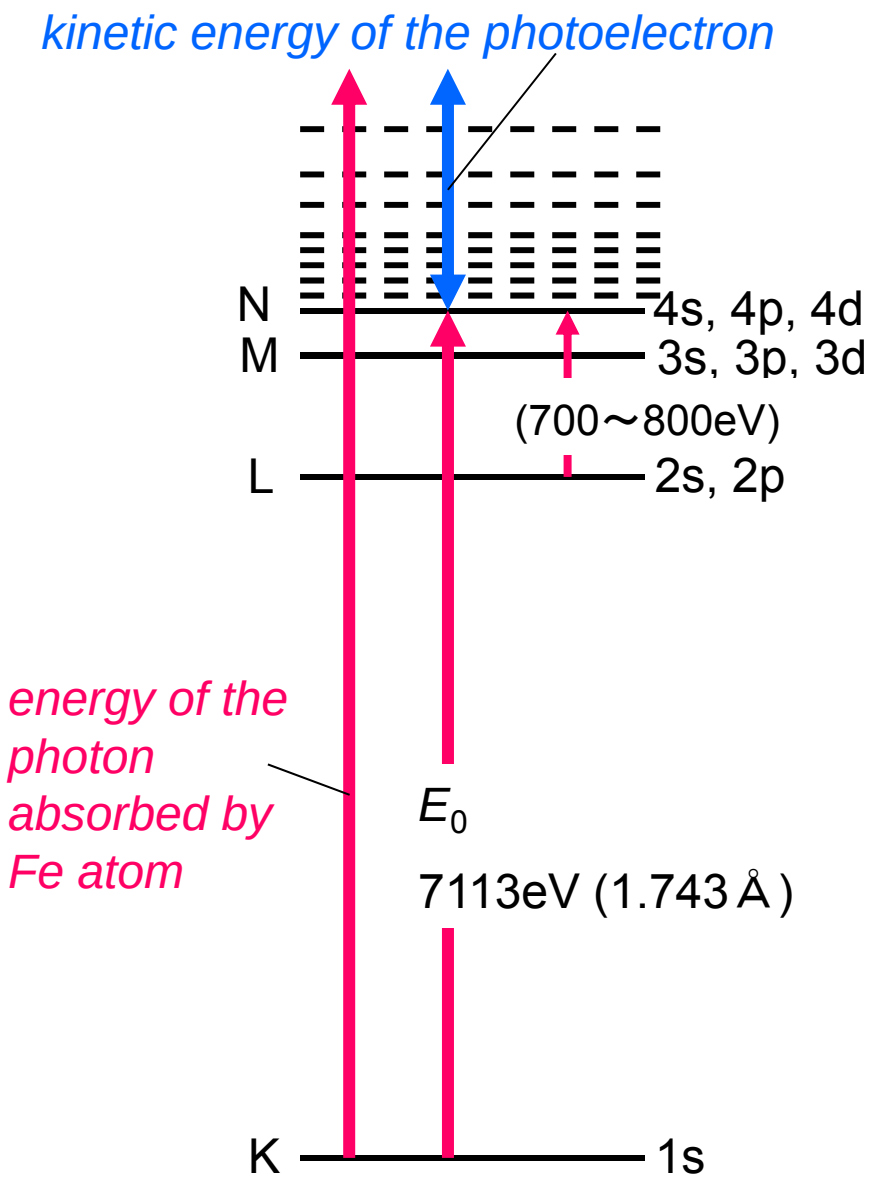


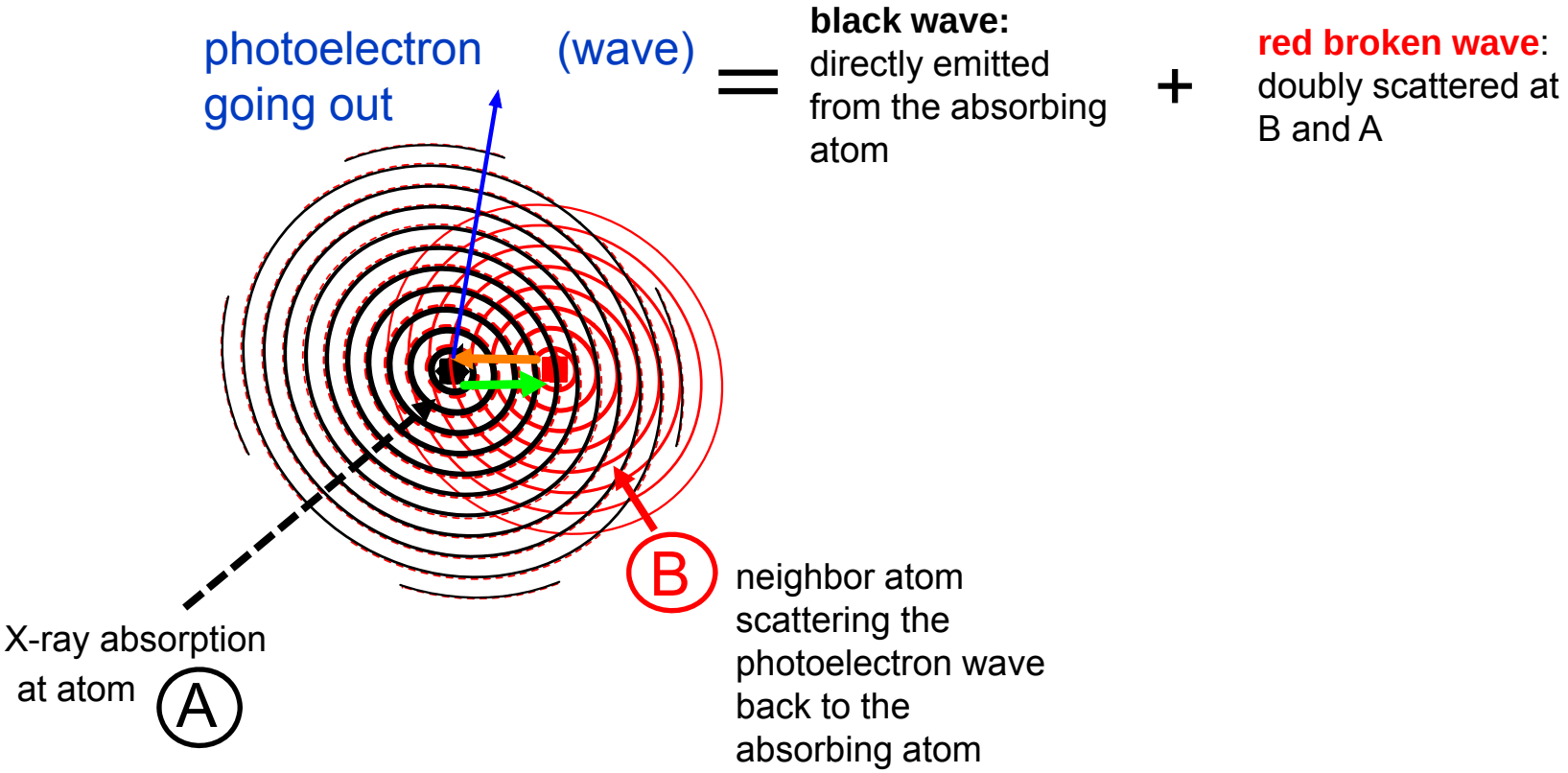
an electron with E_k=100eV behaves as a wave with λ=1.2 Å

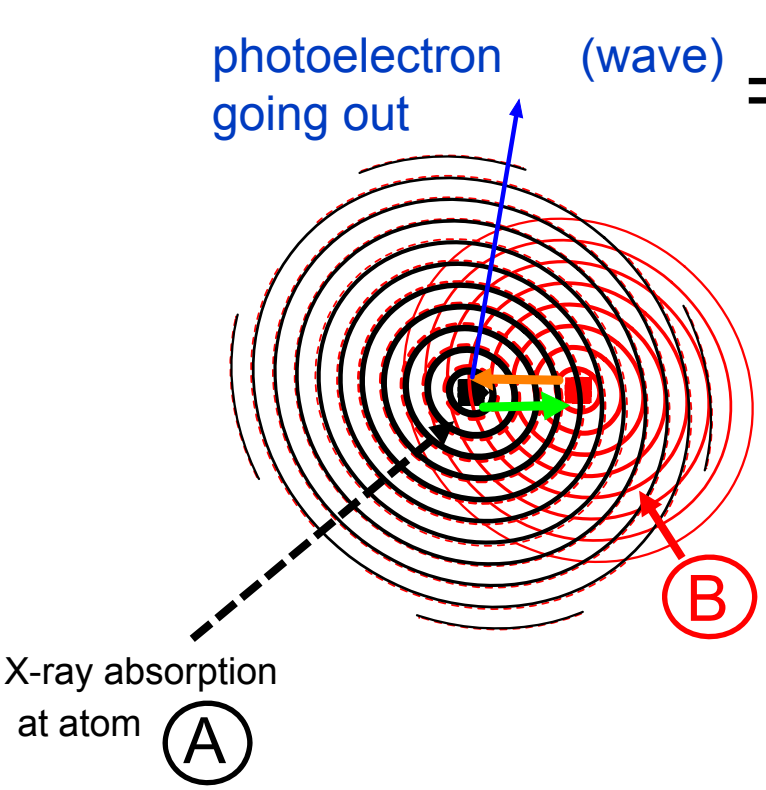
$$\lambda = \frac{h}{p}$$: *de Broglie*

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

The cause for EXAFS appearance !!!




photoelectron
going out
(wave)
=
black wave:
directly emitted
from the absorbing
atom
+
red broken wave:
doubly scattered at
B and A
B
neighbor atom
scattering the
photoelectron wave
back to the
absorbing atom
X-ray absorption
at atom
A



= **black wave:** directly emitted from the absorbing atom + **red broken wave:** doubly scattered at B and A

If they are ***in phase*** , $(2r)k=2n\pi$ ($k=2\pi/\lambda$) or $2r=n\lambda$,

→ larger photoelectron wave

→ larger probability of finding photoelectrons

(amplitude squared).

If they are ***out of phase*** , $(2r)k=(2n+1)\pi$, and equal amplitudes,

→ photoelectron waves disappear

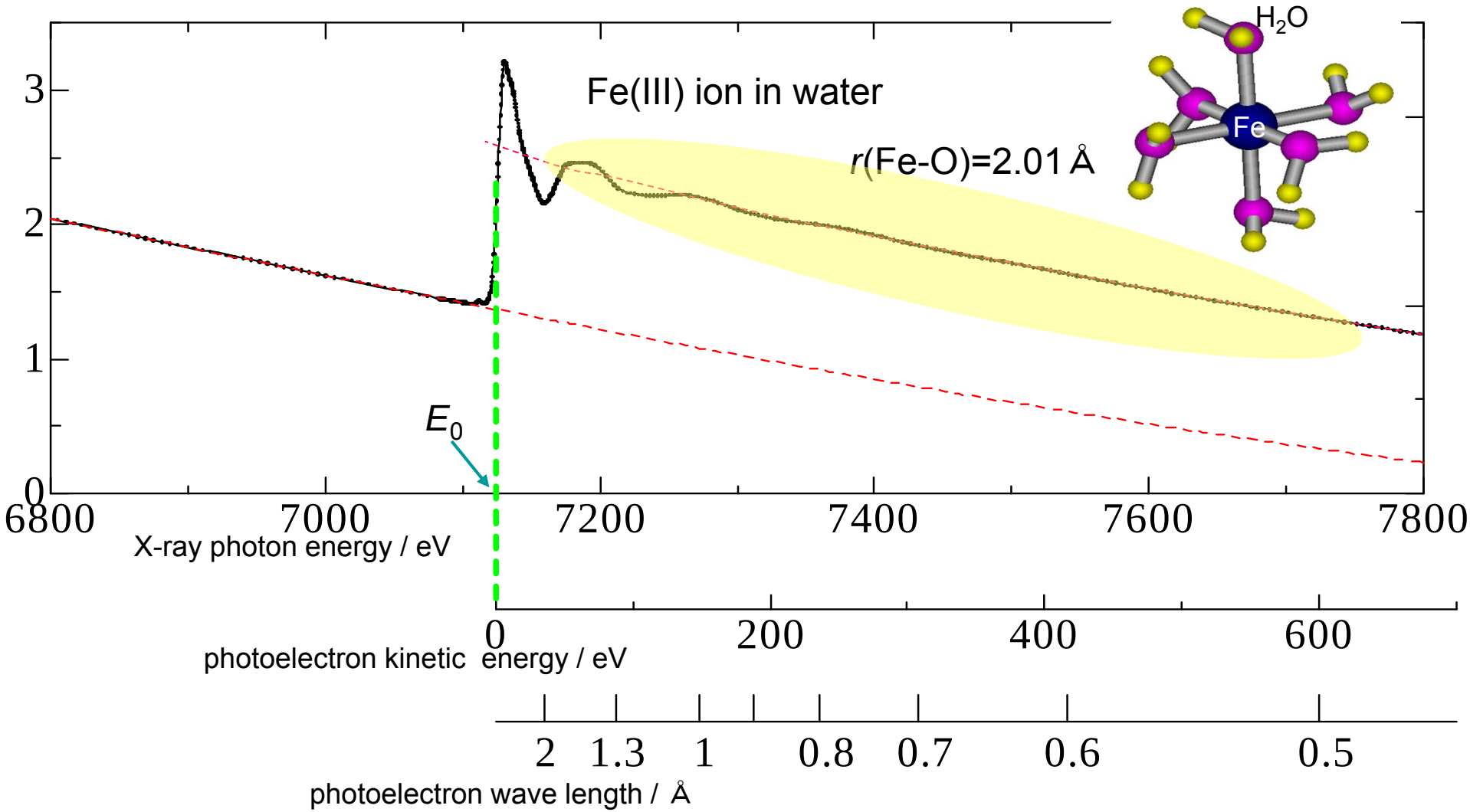
→ no photoelectrons found outside.

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

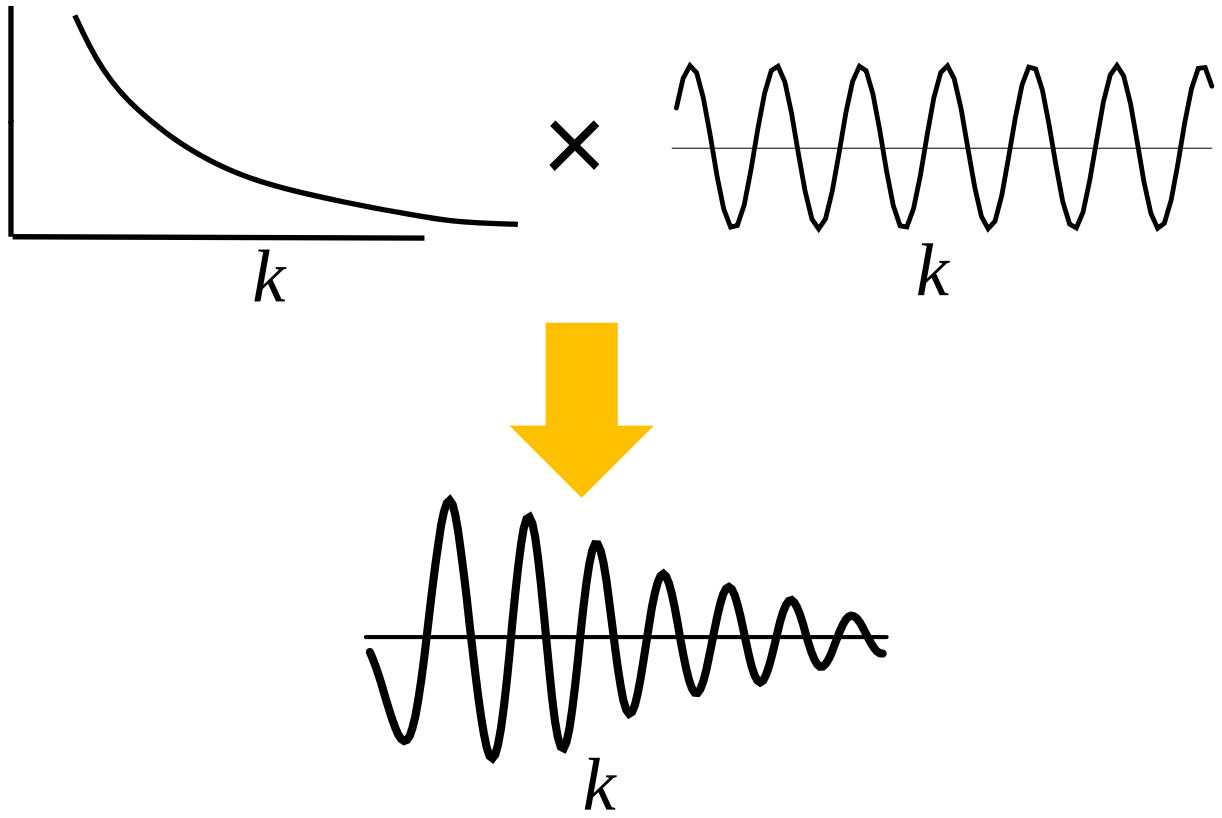
$$\chi(k) = \sum_i \frac{N_i}{k\, r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

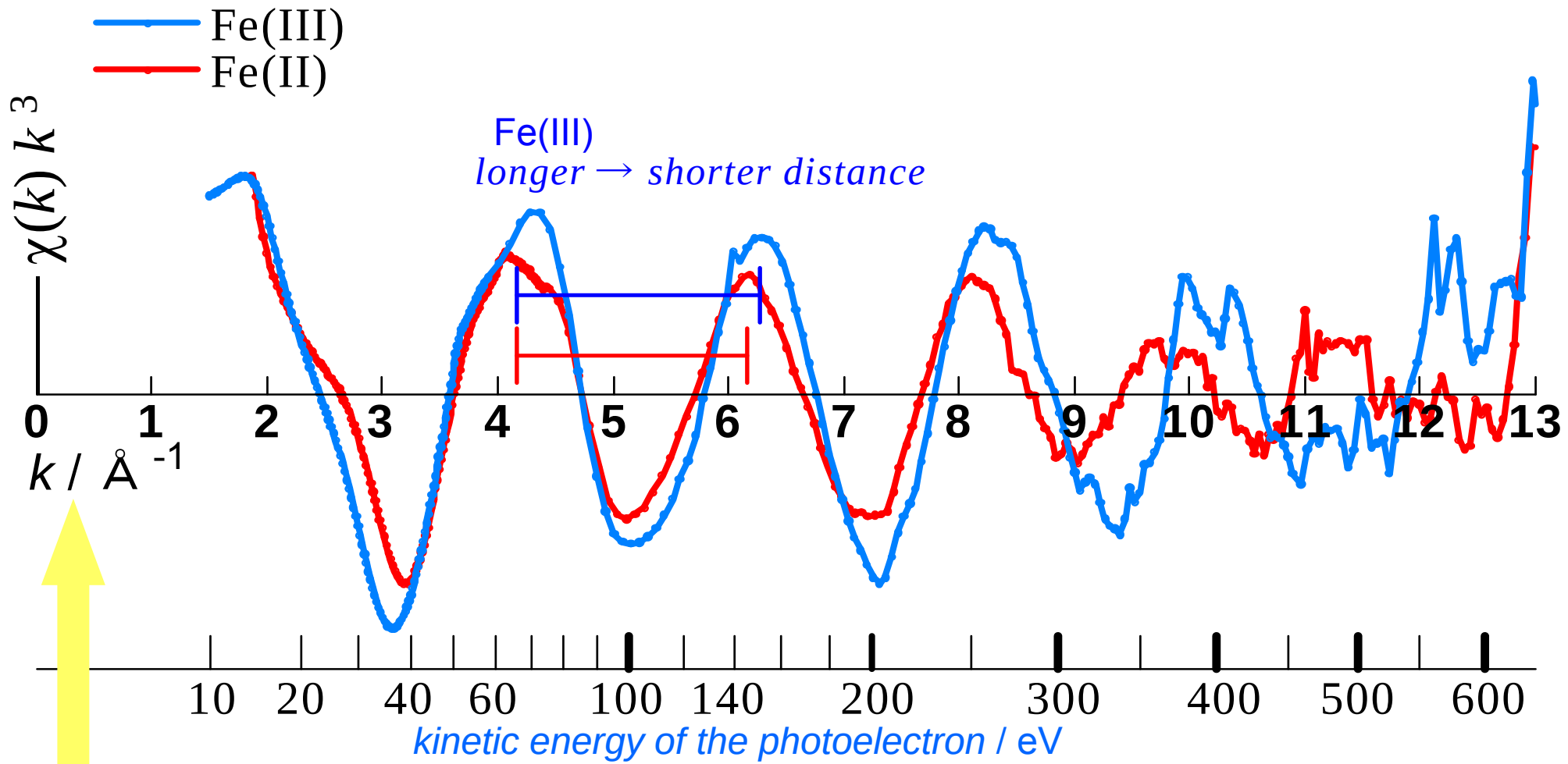
BASIC EXAFS equation

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

amplitude part

oscillation part



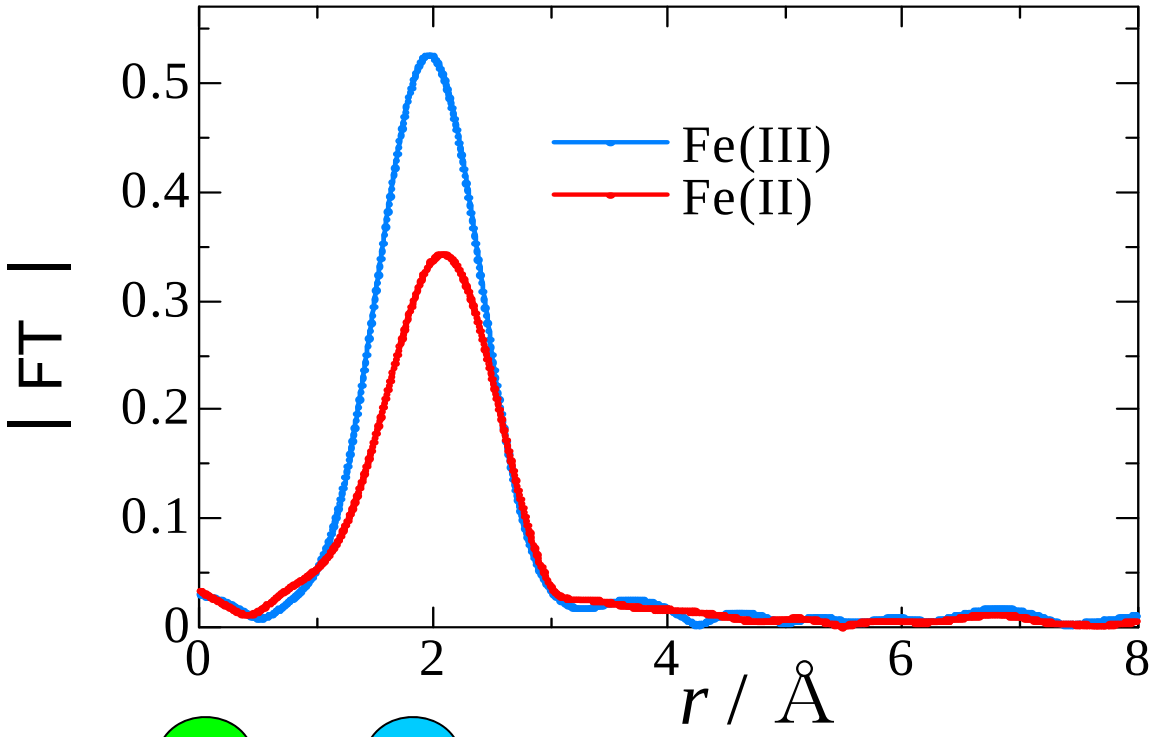


photoelectron wave number (vector)

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

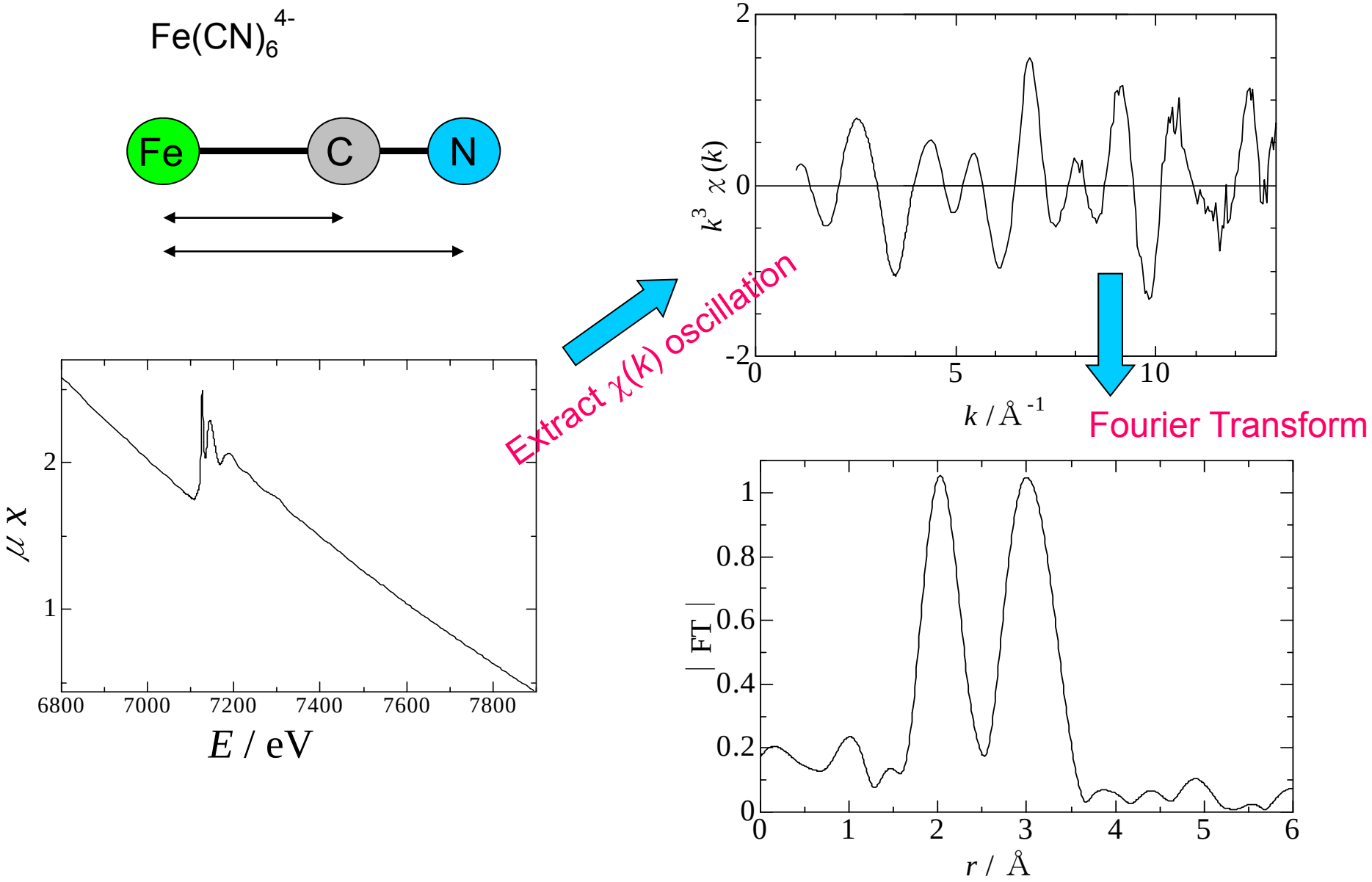
Fourier Transform: Simplest way to analyze the EXAFS oscillation

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



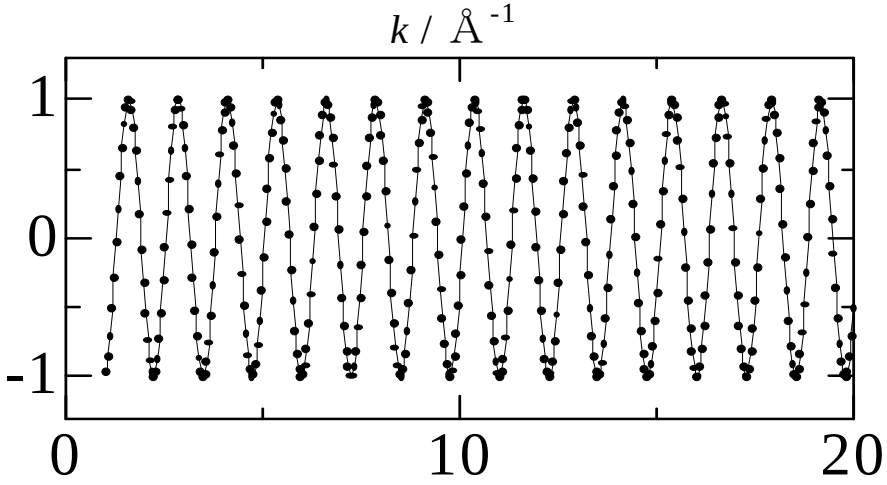
Fe(III) shoter

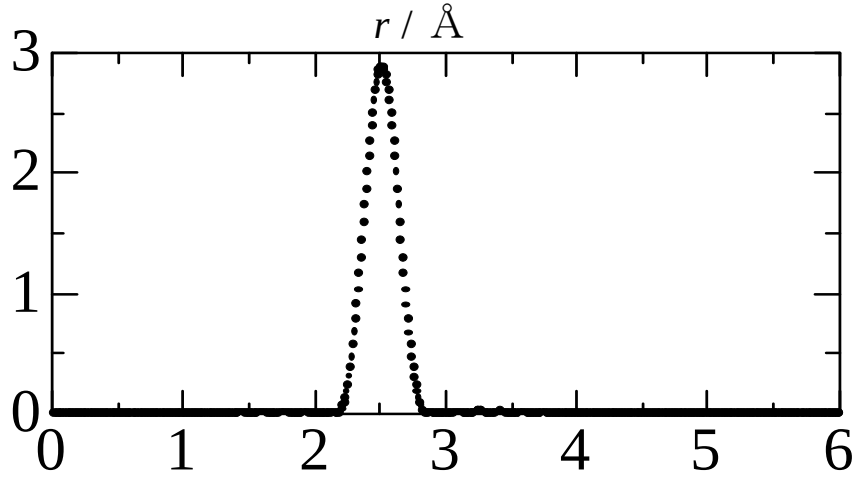
Fe(II) longer


Fe(CN)6 4-
Fe
C
N
μ x
E / eV
Extract χ(k) oscillation
k3 χ (k)
k / Å -1
Fourier Transform
| FT |
r / Å

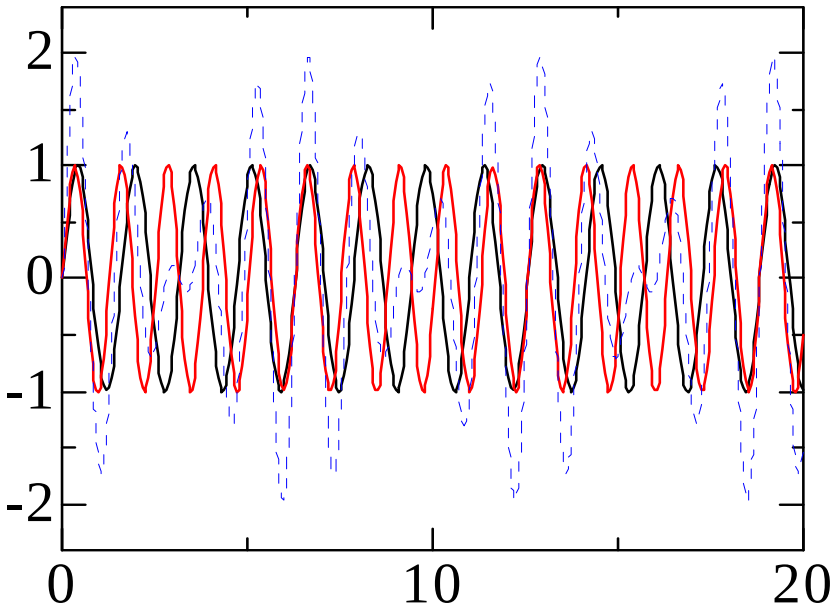
Fourier Transform (Frequency Filter)

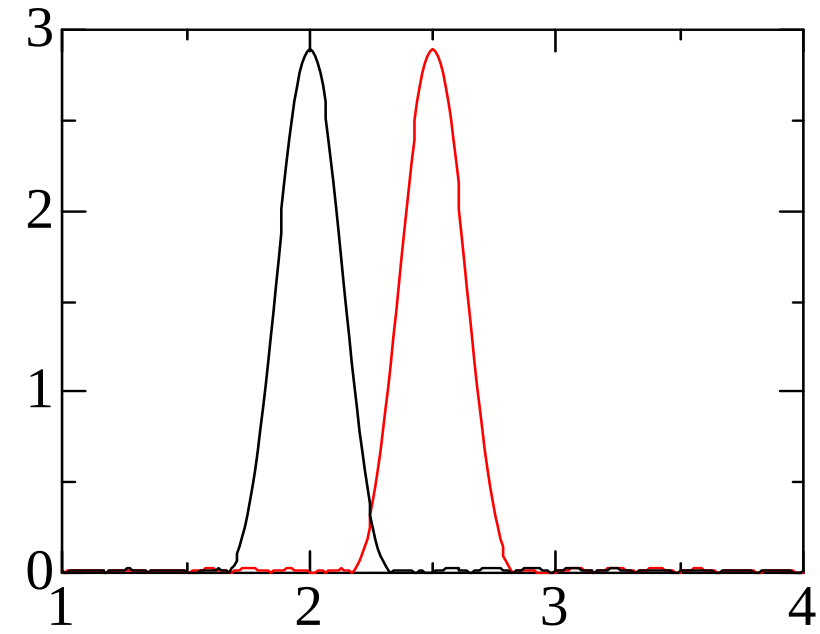
will let you know the frequencies of the waves

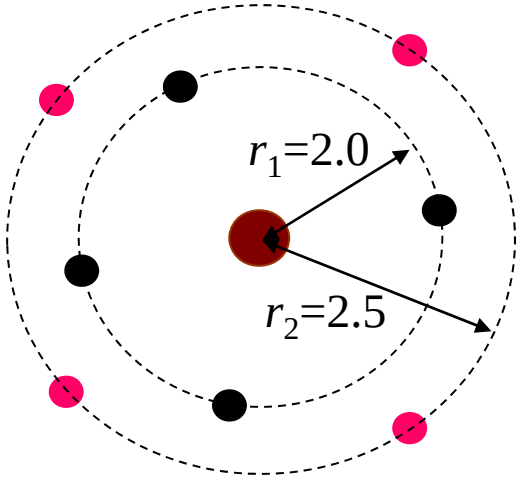




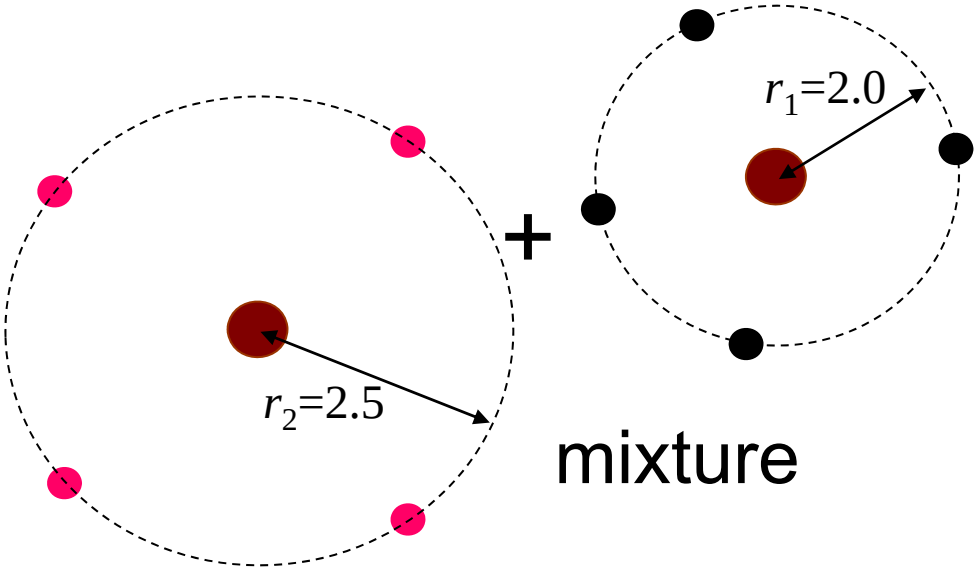
$$\sin(kr)$$





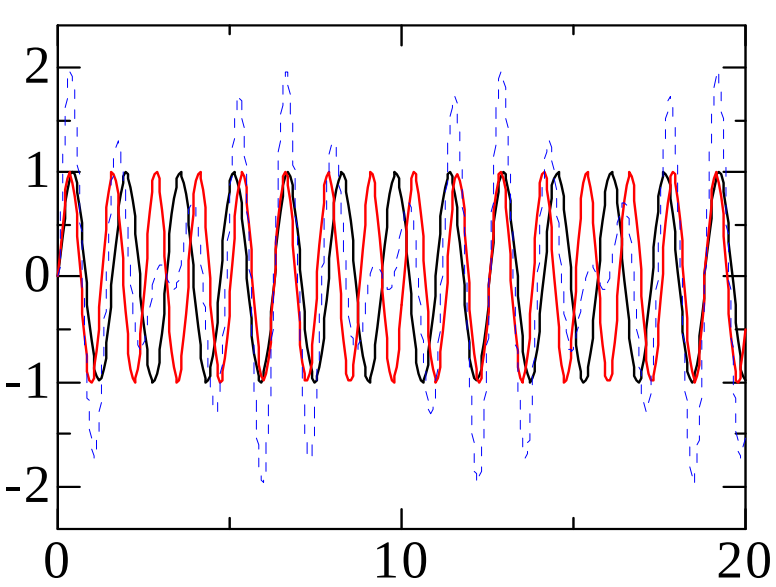


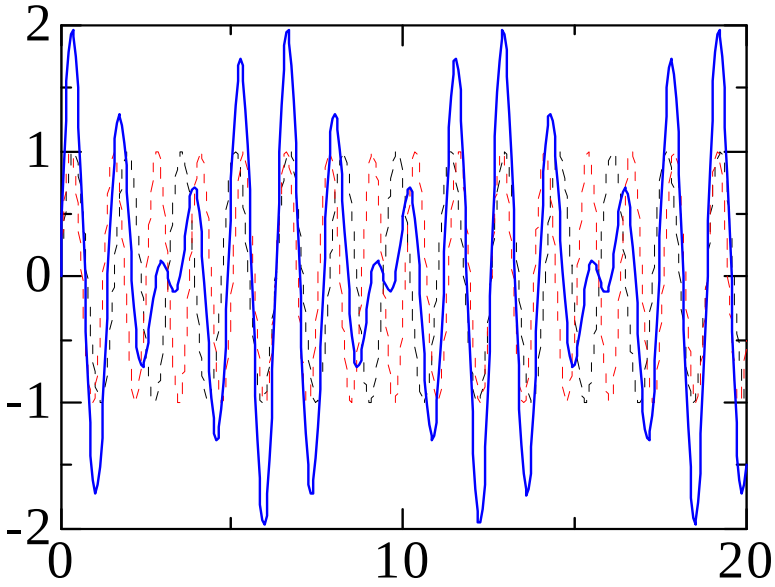
or

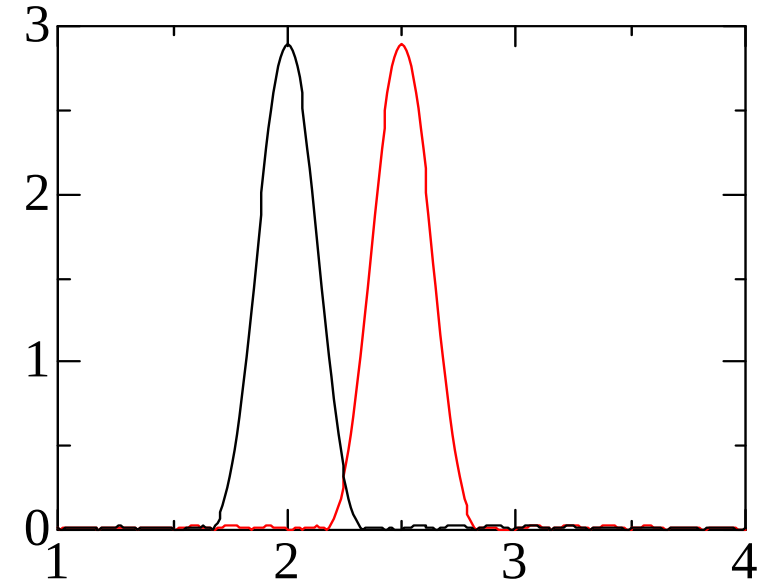


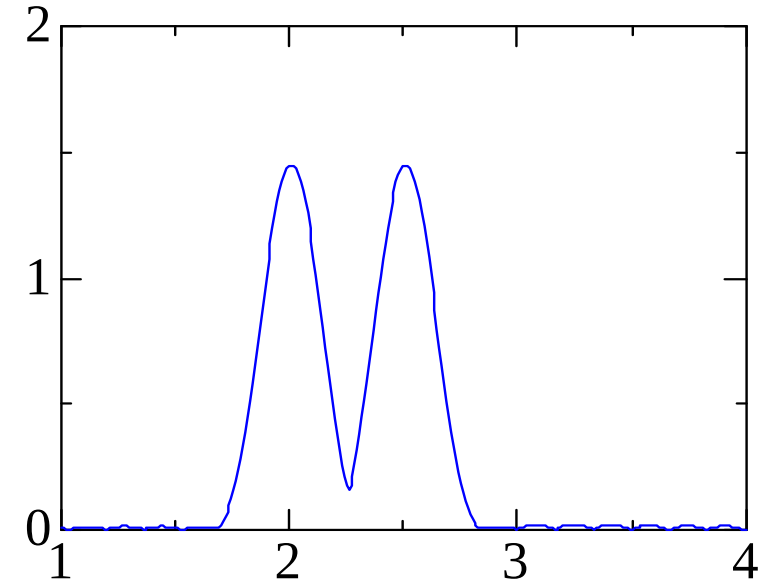
mixture

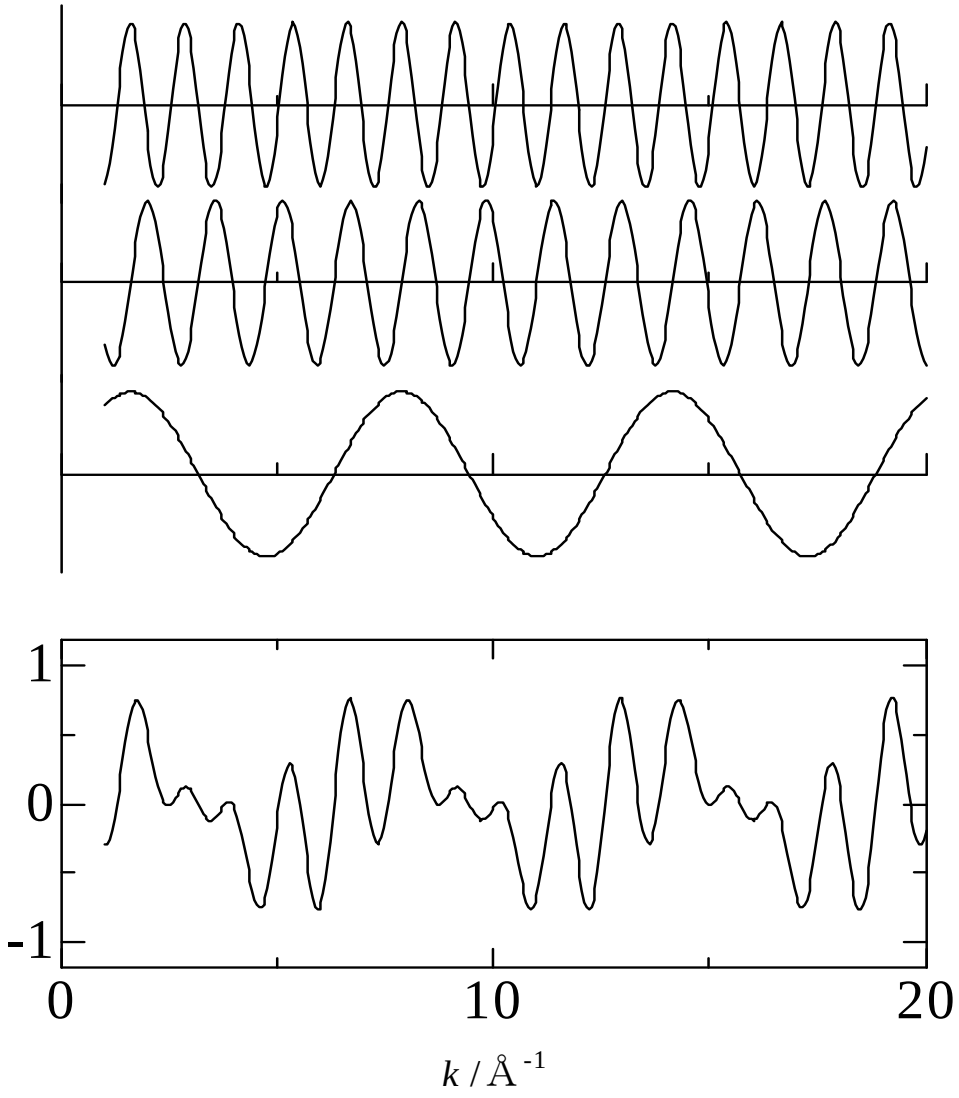
Fourier Transform for two-shell model



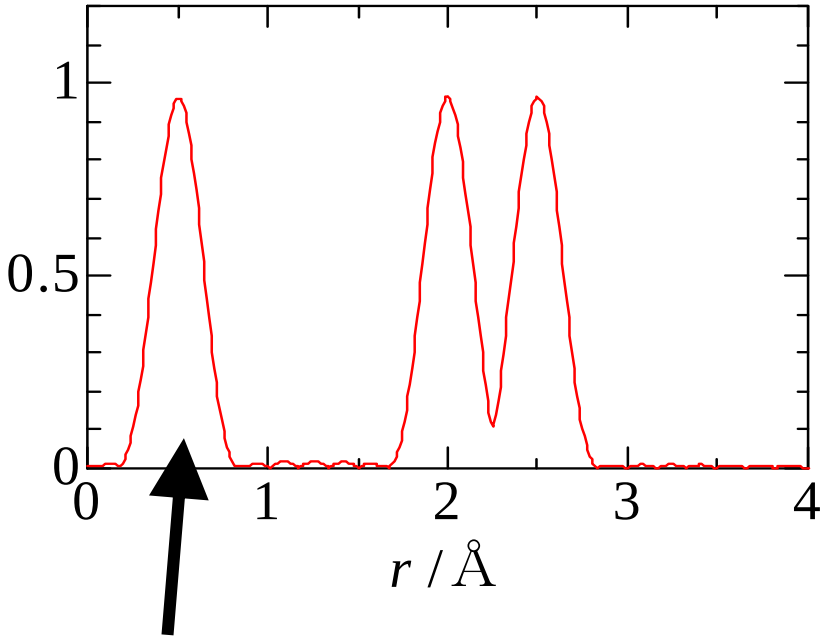




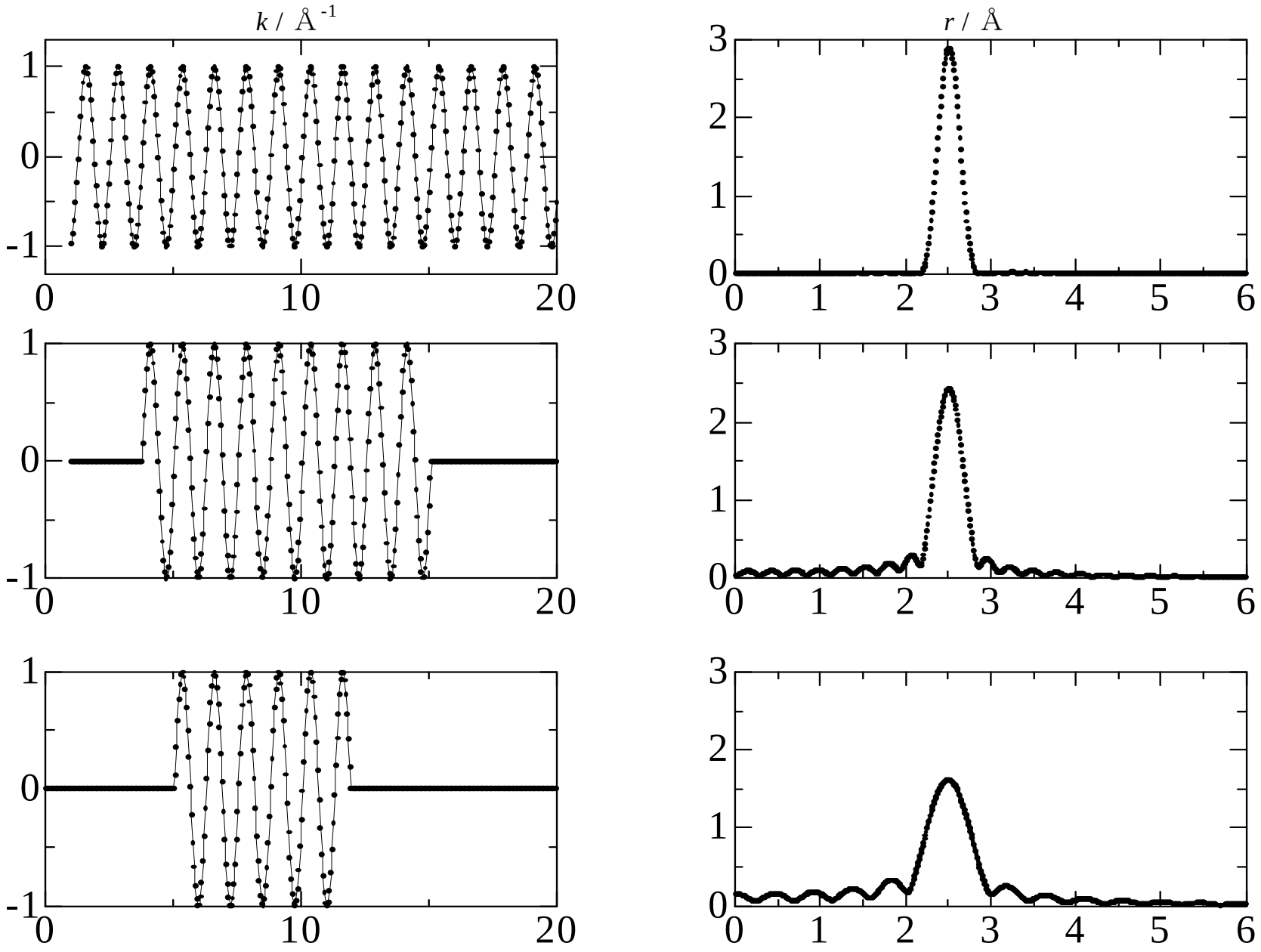


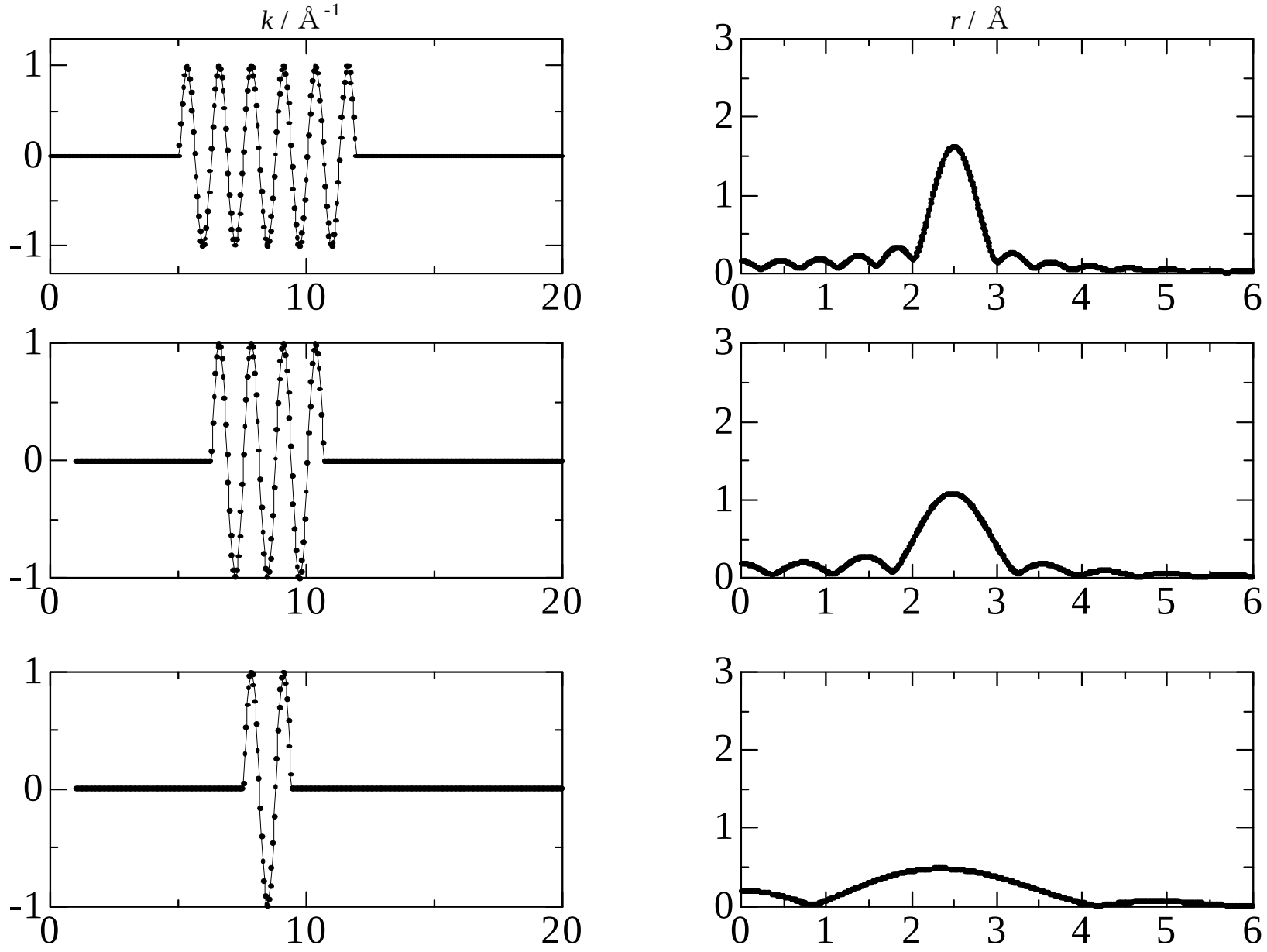


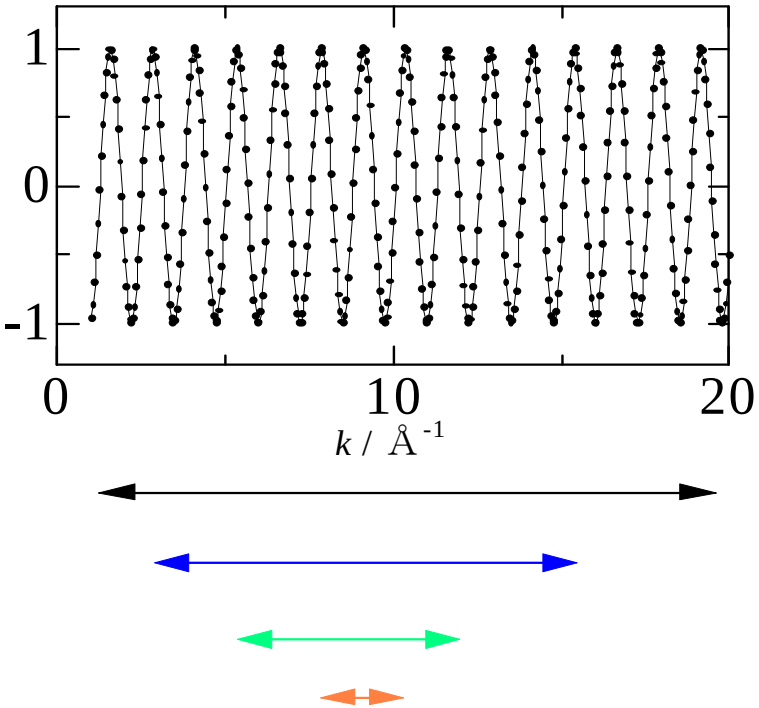
Fourier Transform for a three-shell model



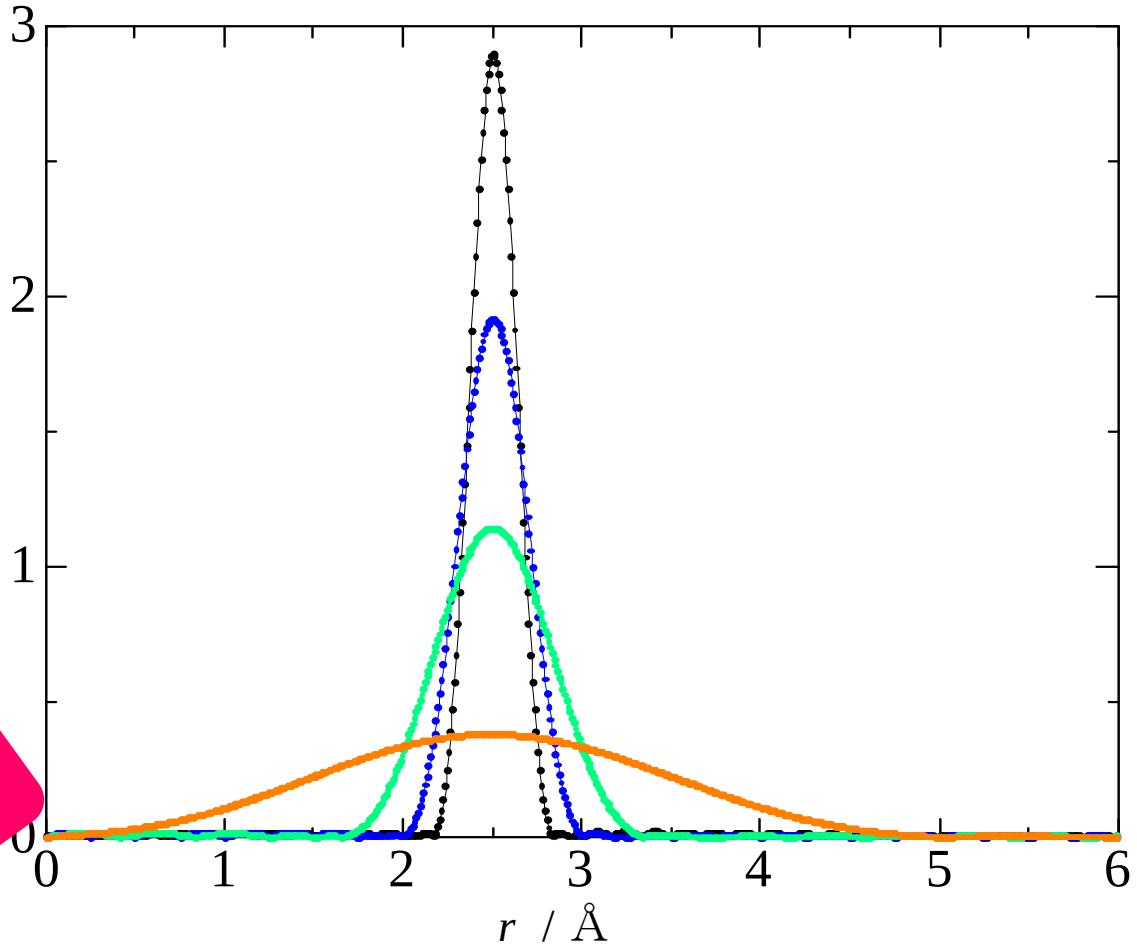
This must be a BACKGROUND structure, not corresponding to a real atom-atom distance.


k / Å -1
r / Å
1
0
-1
0
10
20
3
2
1
0
0
1
2
3
4
5
6


k / Å -1
r / Å
1
0
-1
0
10
20
3
2
1
0
0
1
2
3
4
5
6



Fourier Transform for different *k* ranges



If you have a small number of cycles in k,

Problem !

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

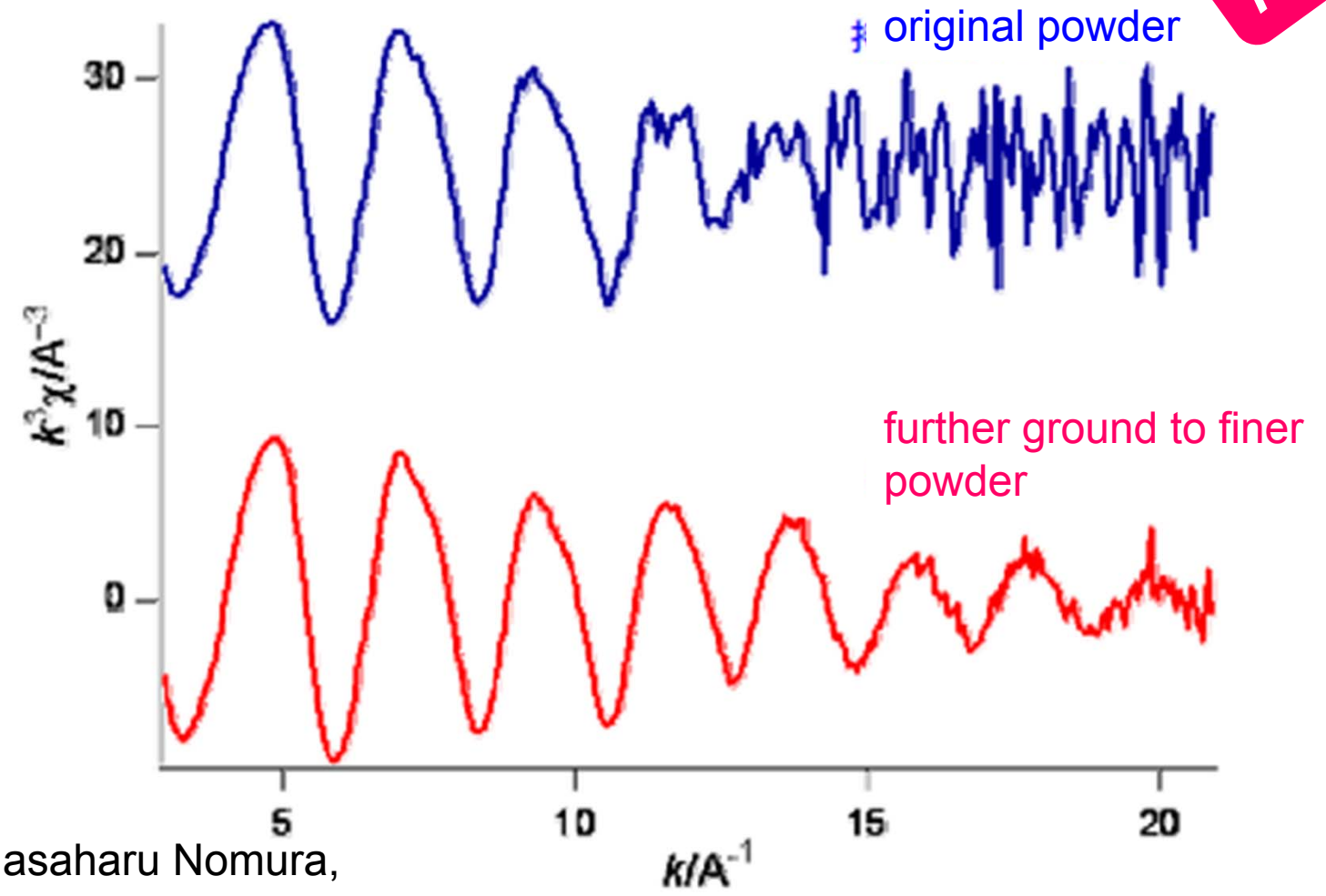
$f(k)$ and $\phi(k)$ are element specific atomic type of coordination

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

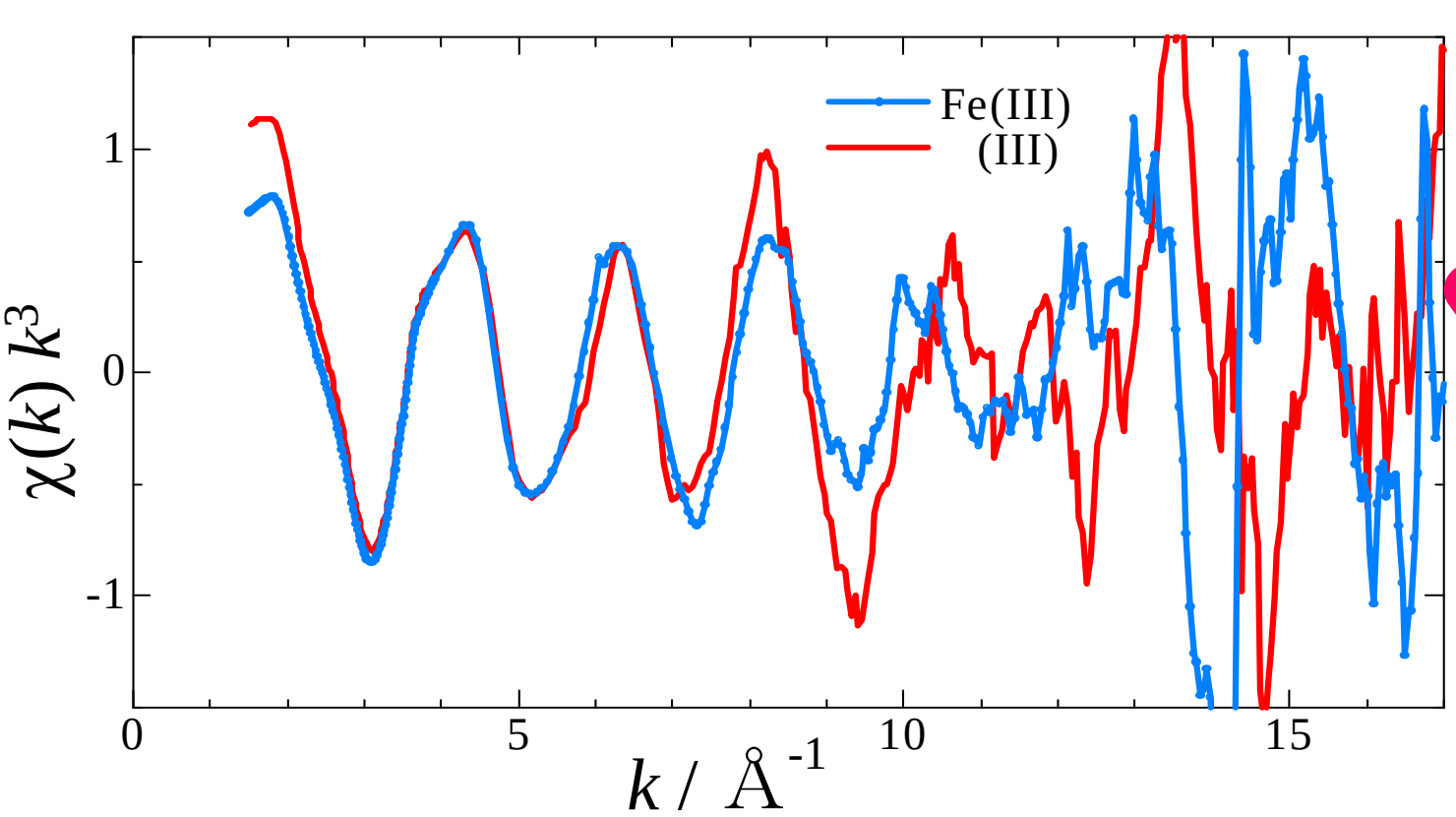
Transmission method

Problem !

Sample: Ge-Si powder



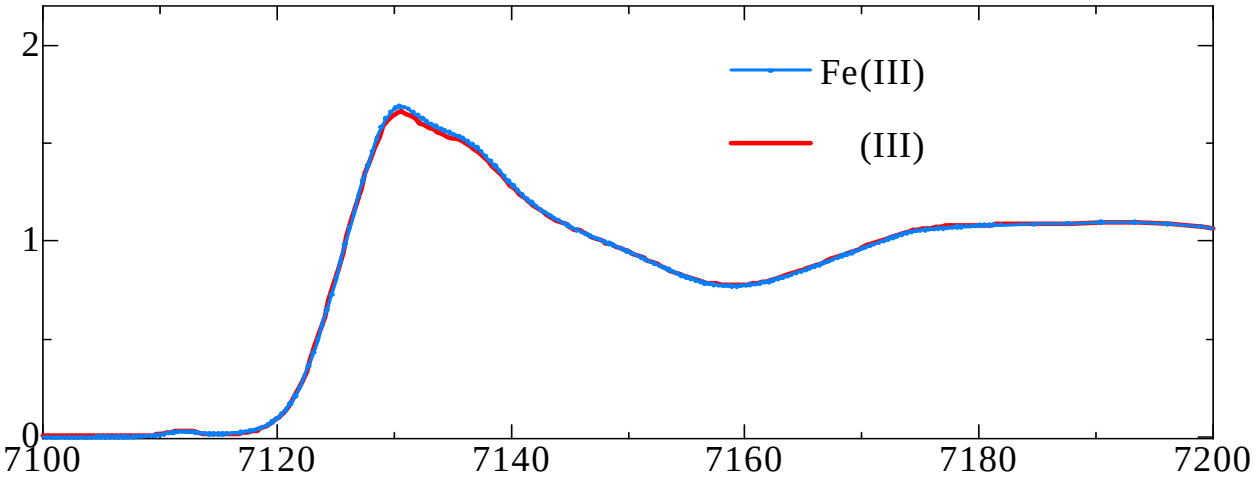
By Masaharu Nomura,
Photon Factory, KEK

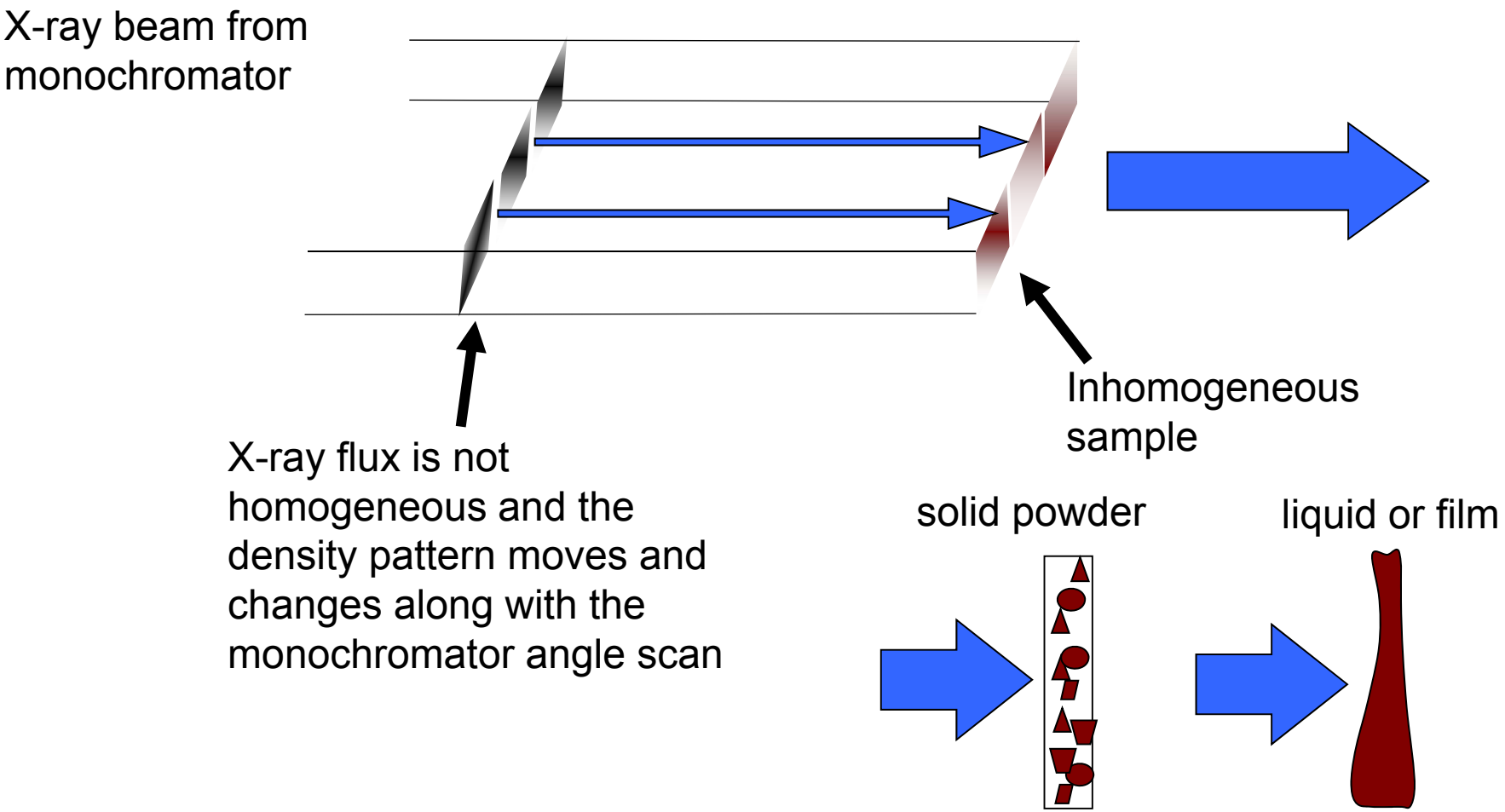


Problem !

Fe(III) ions in aqueous solution

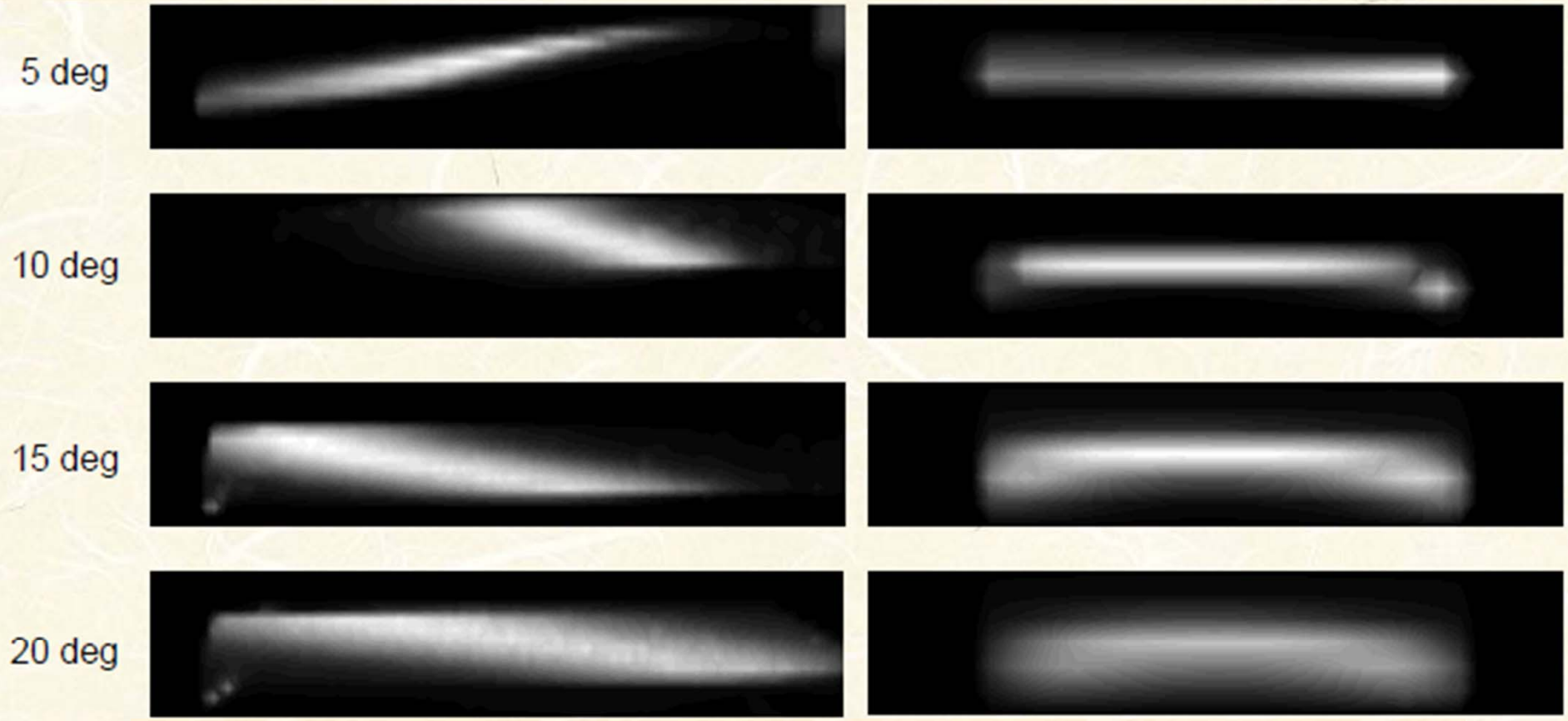
possibly, inhomogeneous sample thickness

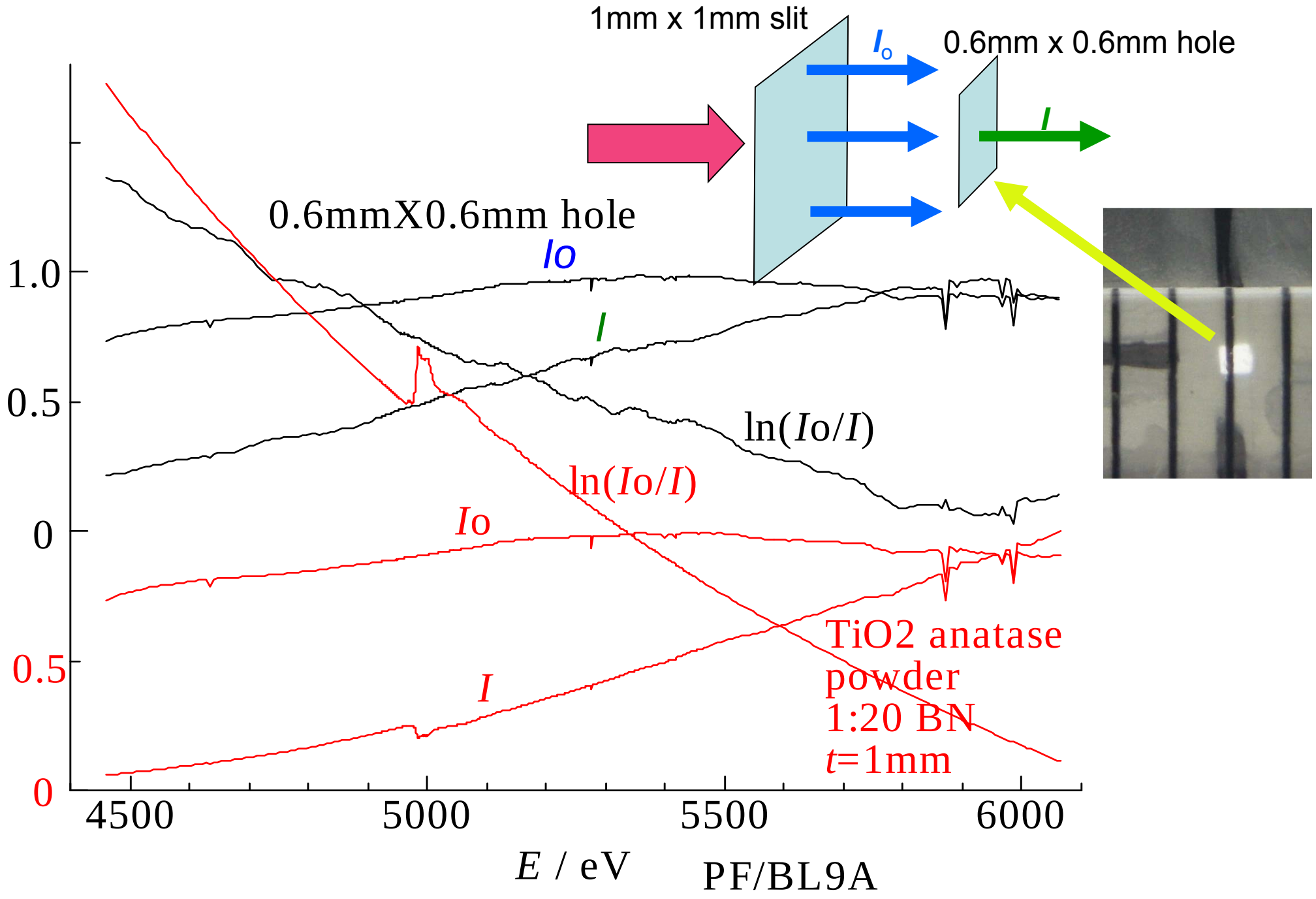




Leads to weaker EXAFS oscillation amplitude and noisy spectrum

Si(311) double-crystal monochromator
Output pattern

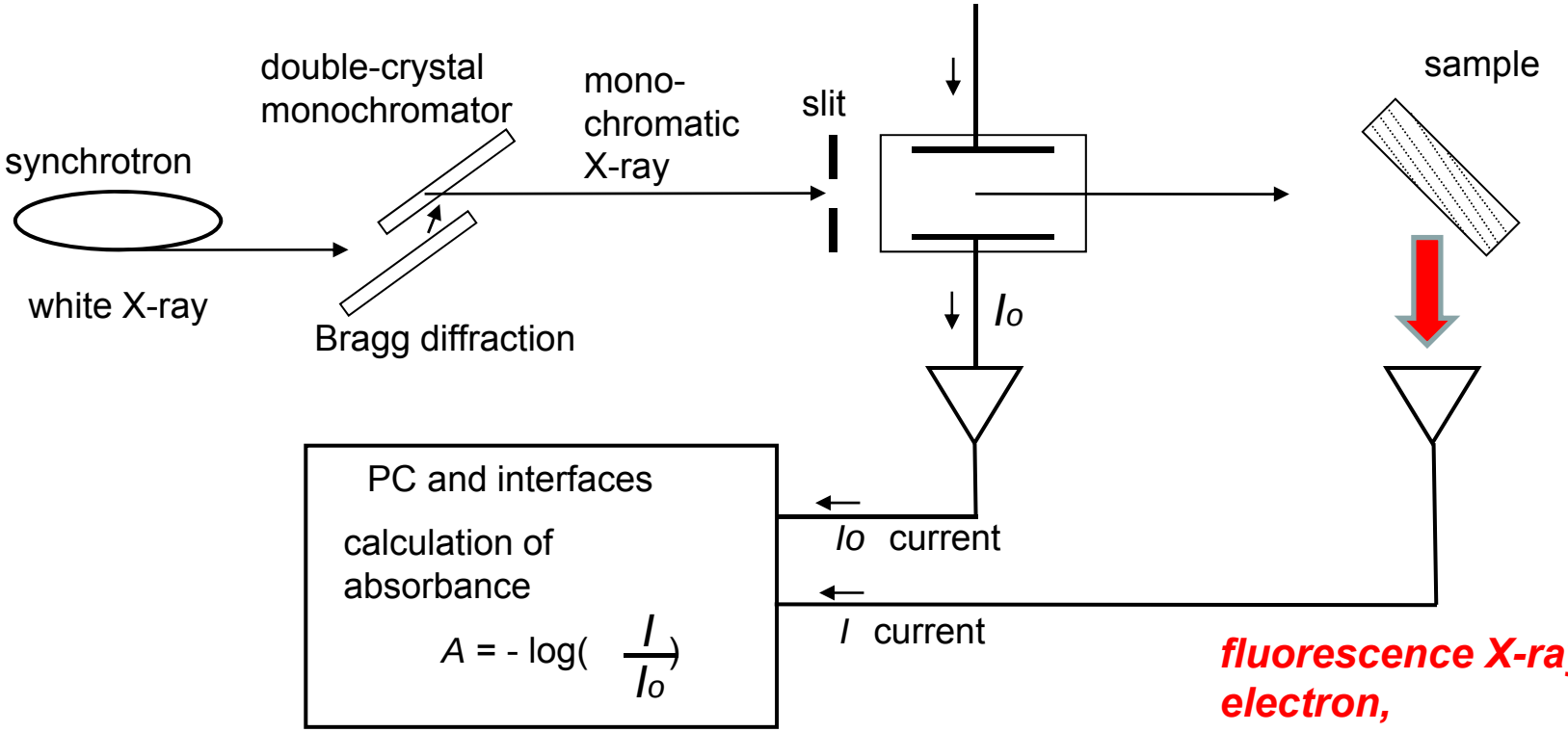



1mm x 1mm slit
I_o
0.6mm x 0.6mm hole
I
0.6mmX0.6mm hole
Io
I
ln(Io/I)
ln(Io/I)
Io
I
TiO2 anatase
powder
1:20 BN
t=1mm
1.0
0.5
0
0.5
0
4500
5000
5500
6000
E / eV
PF/BL9A

Yield methods:

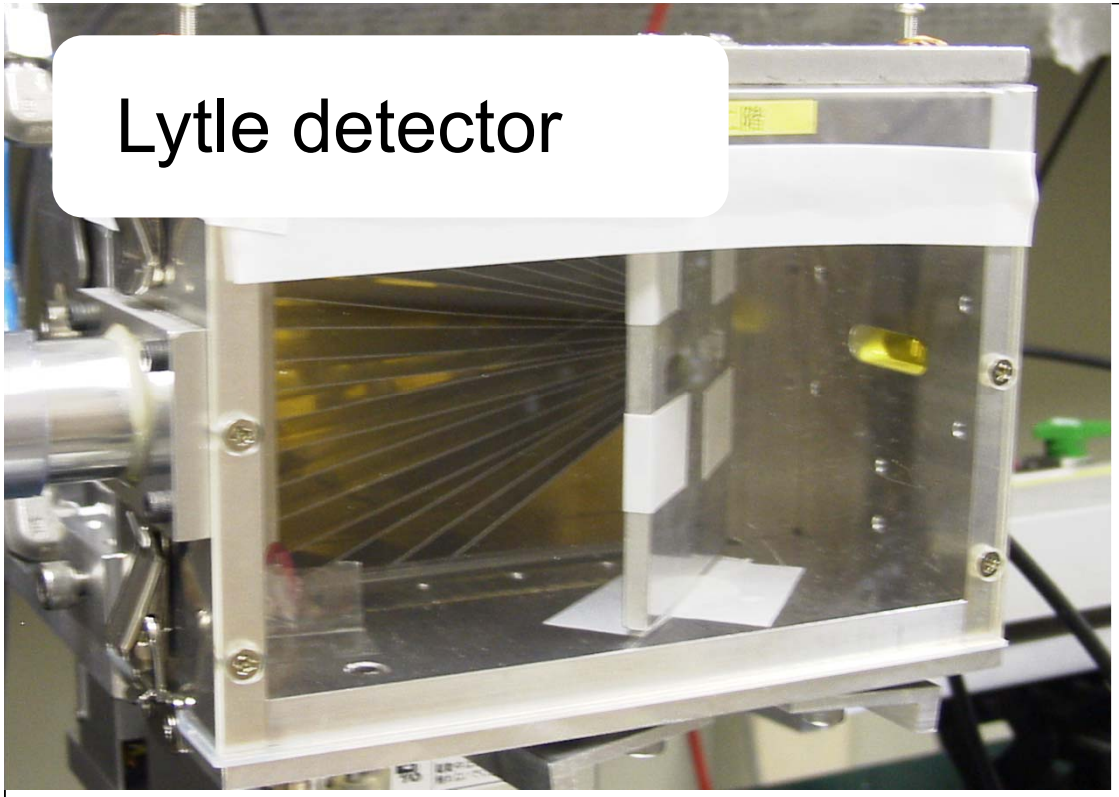
Fluorescence yield
and
Total-conversion-electron-yield

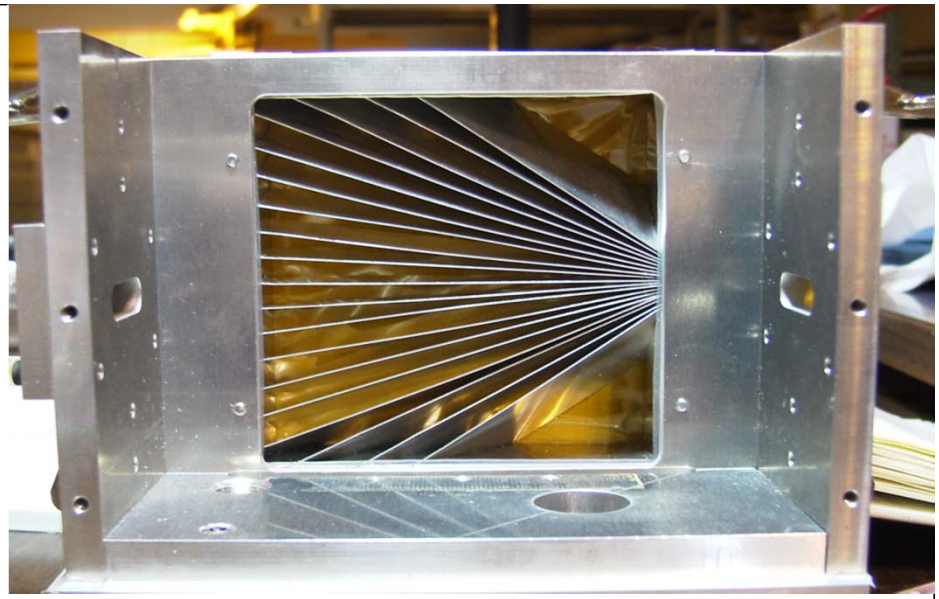
X-ray absorption measurement by yield methods

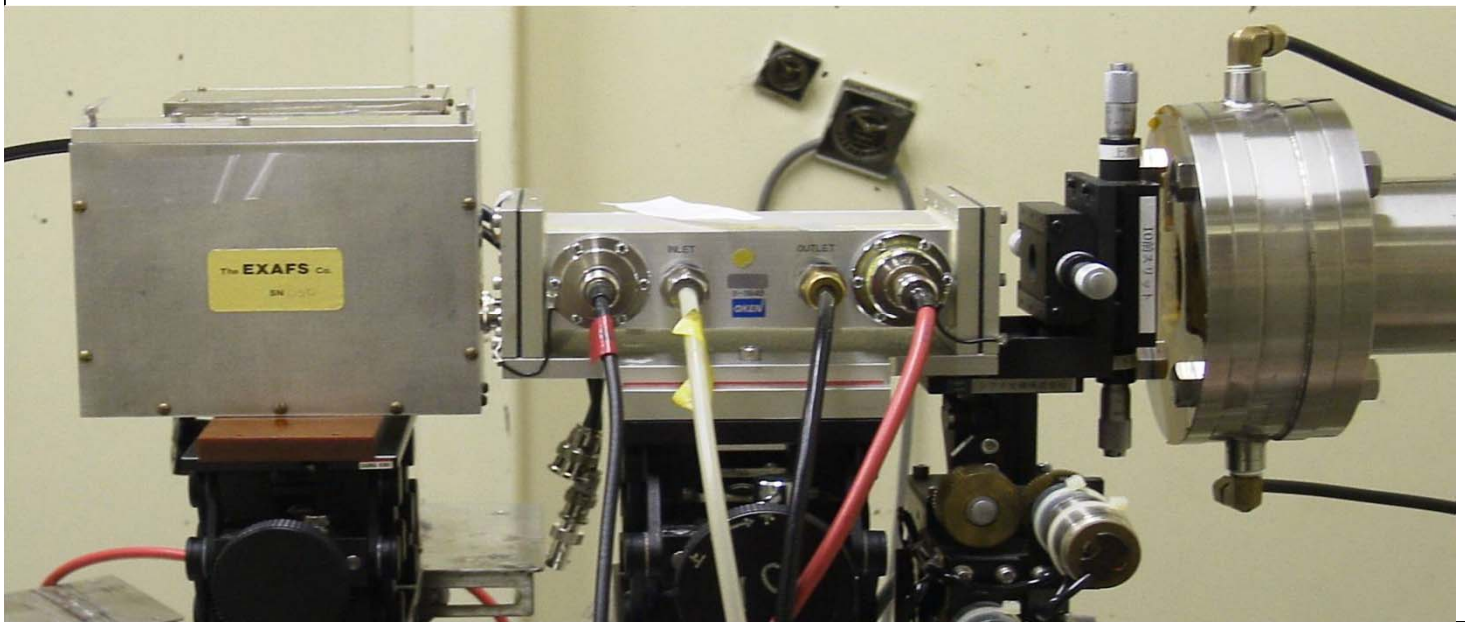


fluorescence X-ray,
electron,
luminescence,
heat, etc;
anything proportional to the X-ray absorption

Lytle detector

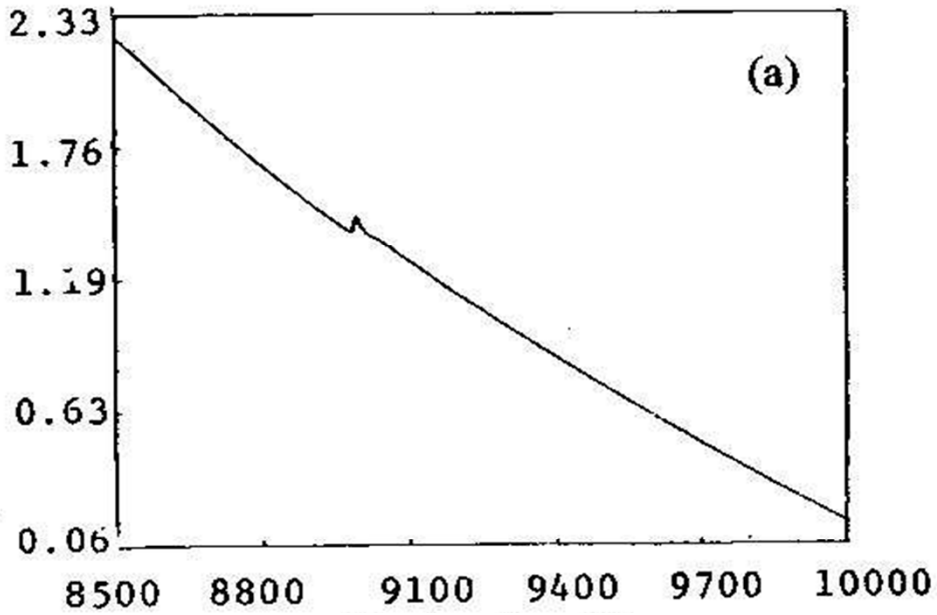




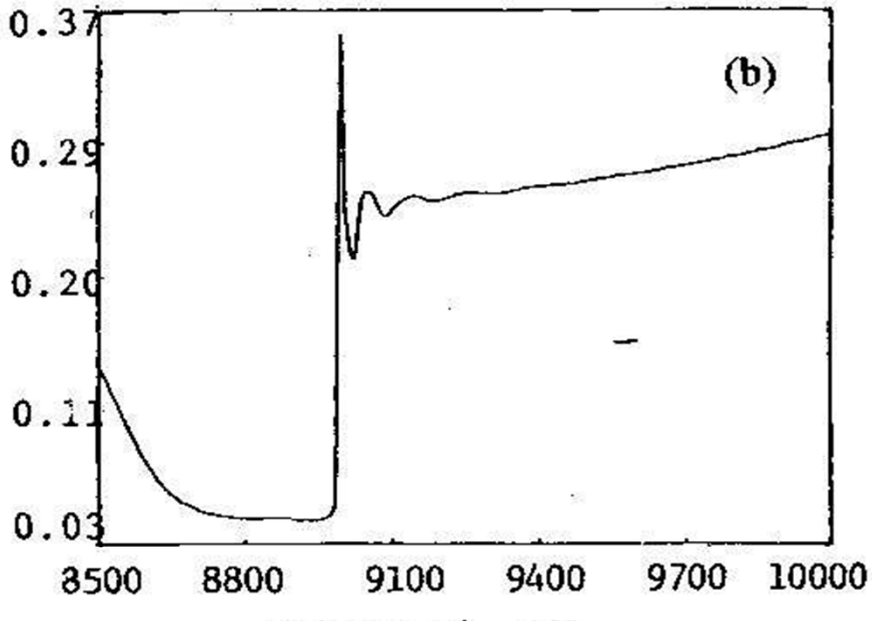


Sample: 0.01 mol dm^{-3} Cu(II) solution

transmittance



fluorescence

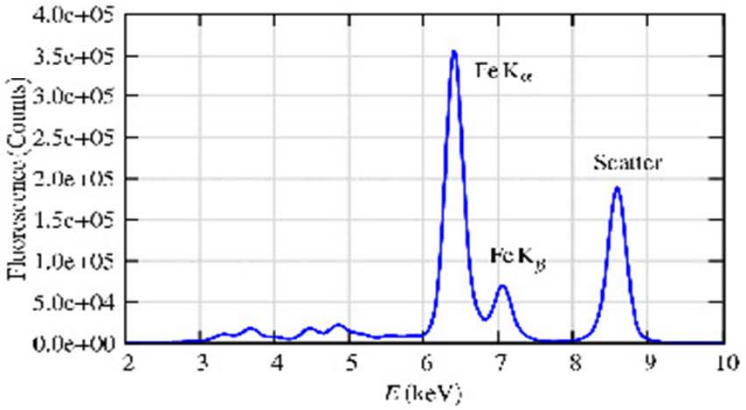


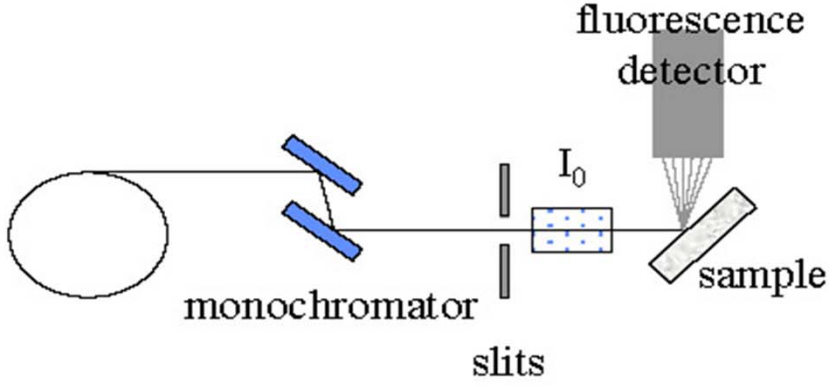
By Masaharu Nomura,
Photon Factory, KEK

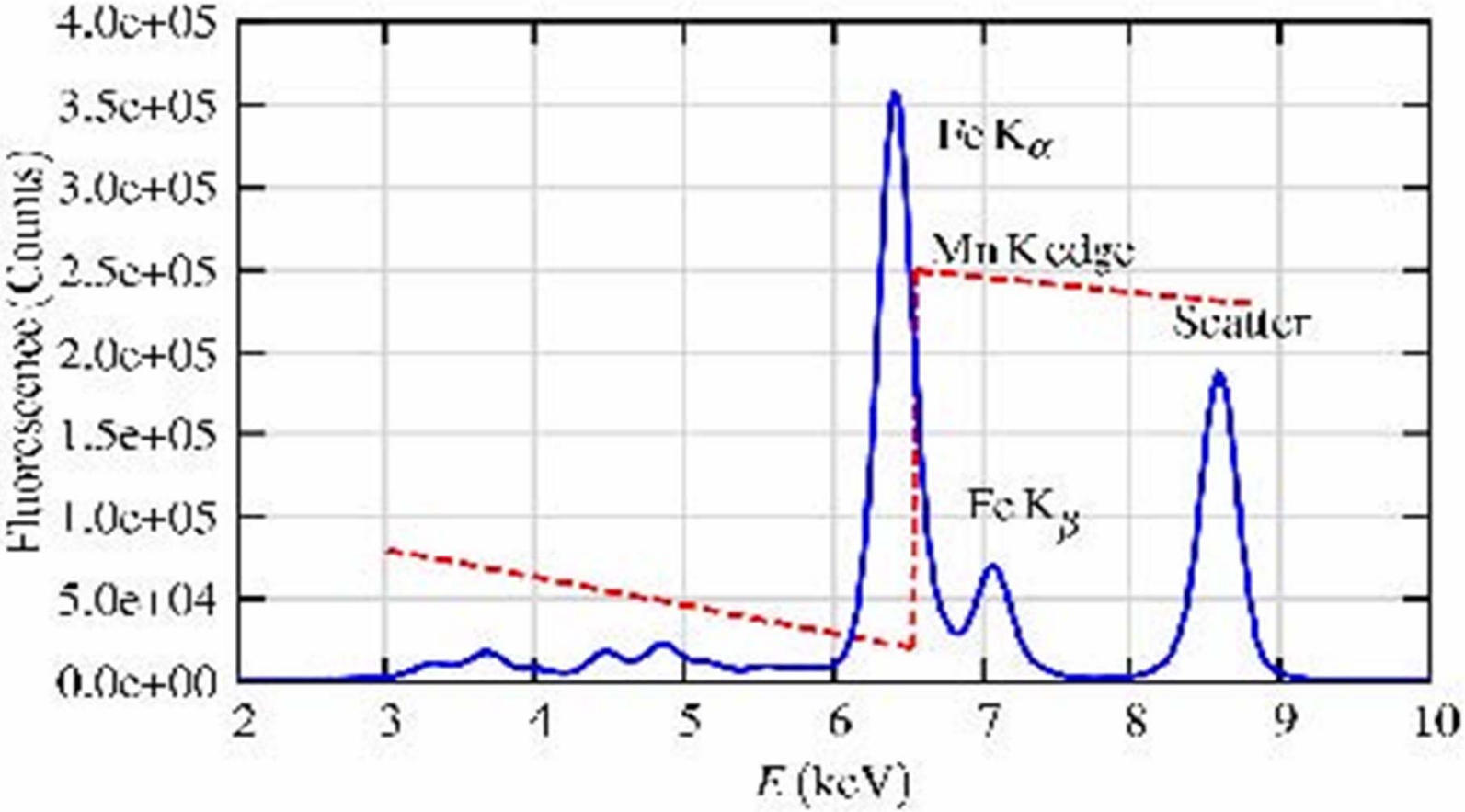
Fluorescence XAFS Experiment: Solid State Detectors

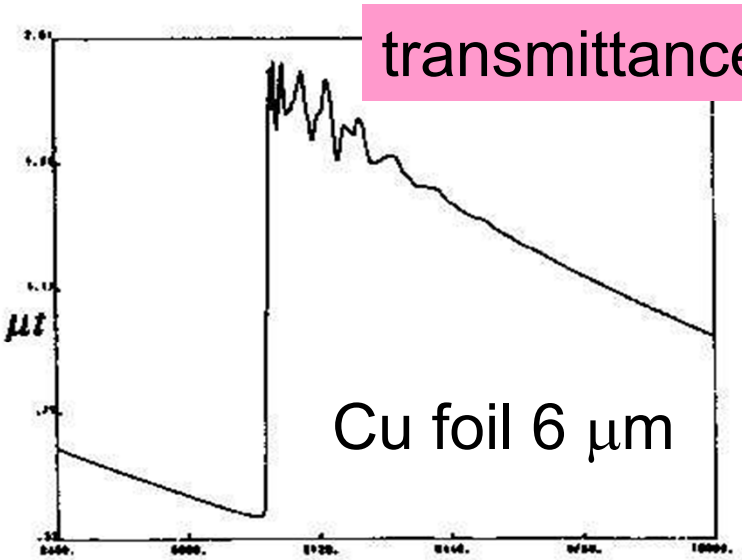
uop
A Honeywell Company

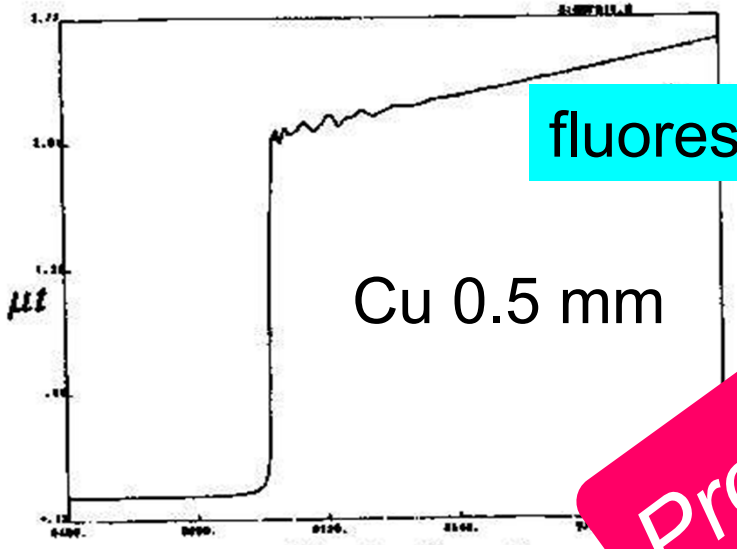
- Alternative is to use a solid state detector with active element of Ge or Si as the x-ray absorber. This uses electronic energy discrimination.
- Typical energy resolution 200-300 eV.
- Has advantage of measuring the full x-ray fluorescence spectrum, so useful for identifying other elements in sample.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



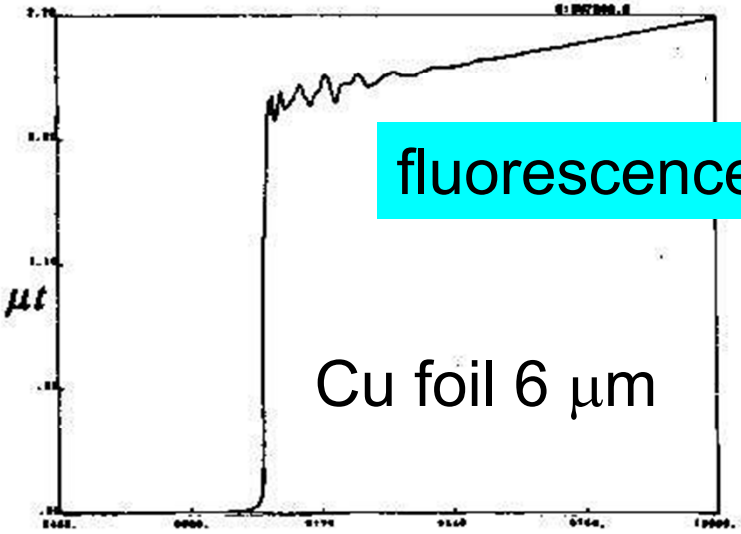


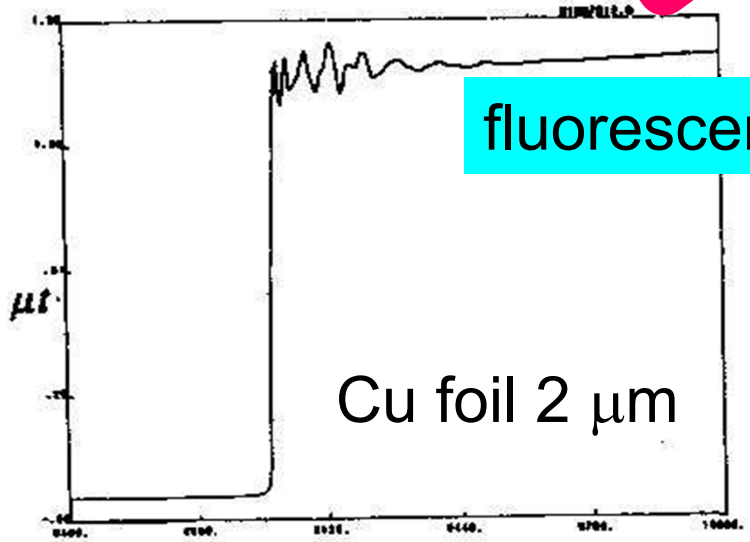

4.0e+05
3.5e+05
3.0e+05
2.5e+05
2.0e+05
1.5e+05
1.0e+05
5.0e+04
0.0e+00
Fluorescence (Counts)
2
3
4
5
6
7
8
9
10
E (keV)
Fe Kα
Mn K edge
Scatter
Fe Kβ





Problem !

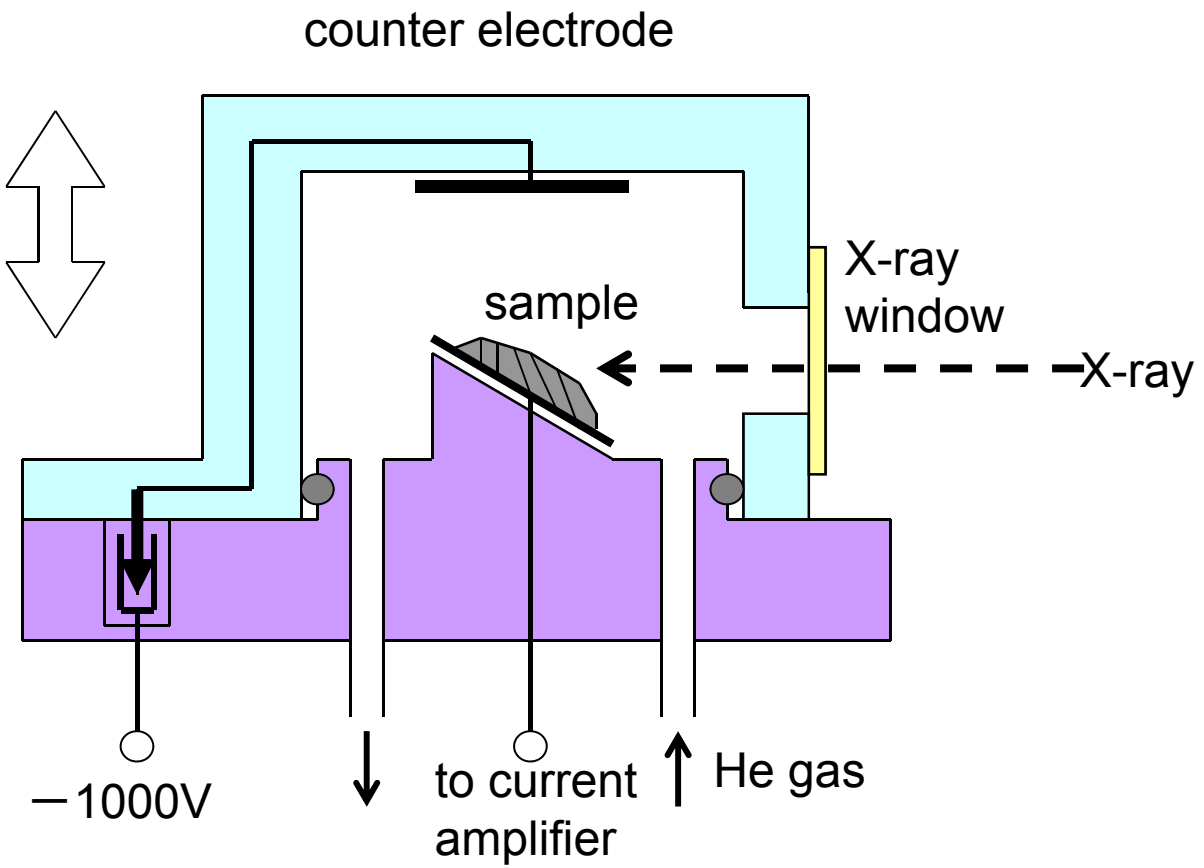


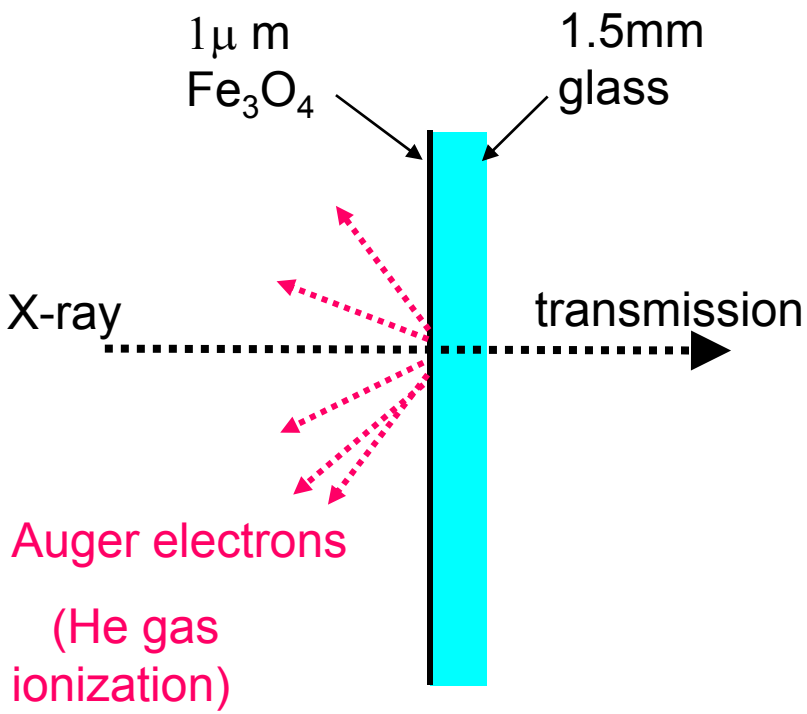


By Masaharu Nomura,
Photon Factory, KEK

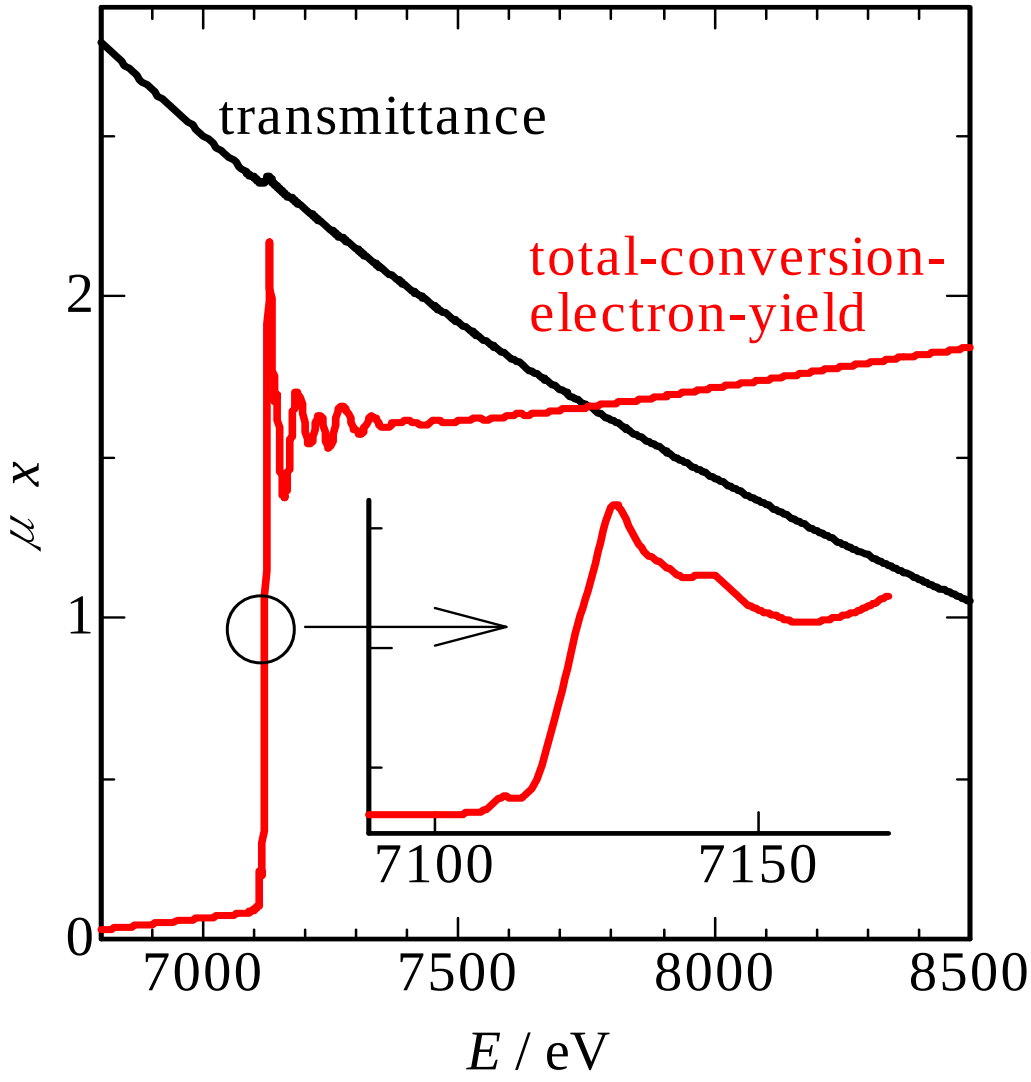
Self-absorption effect → incorrect *N*

Total-Conversion-Electron-Yield method

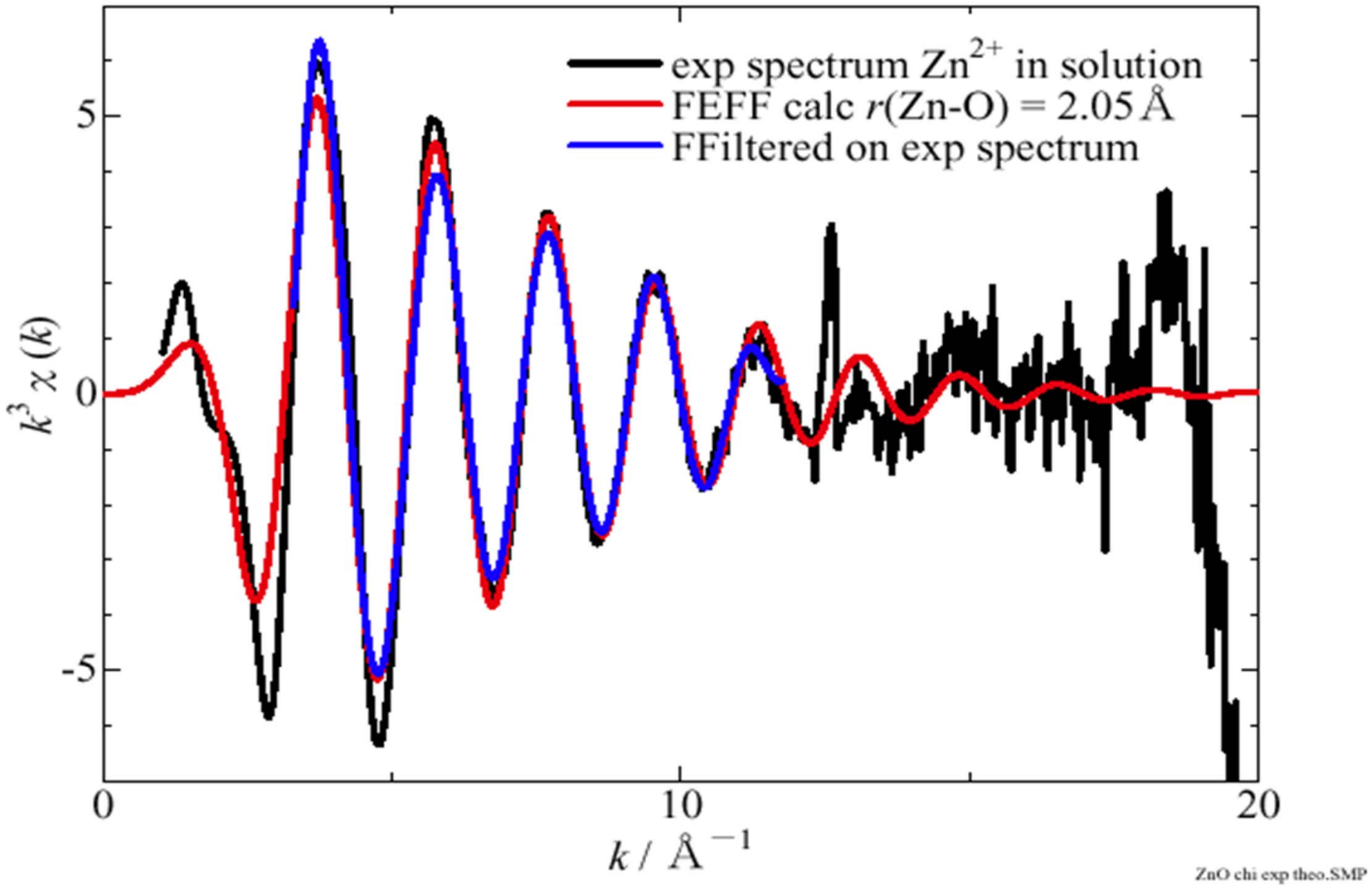


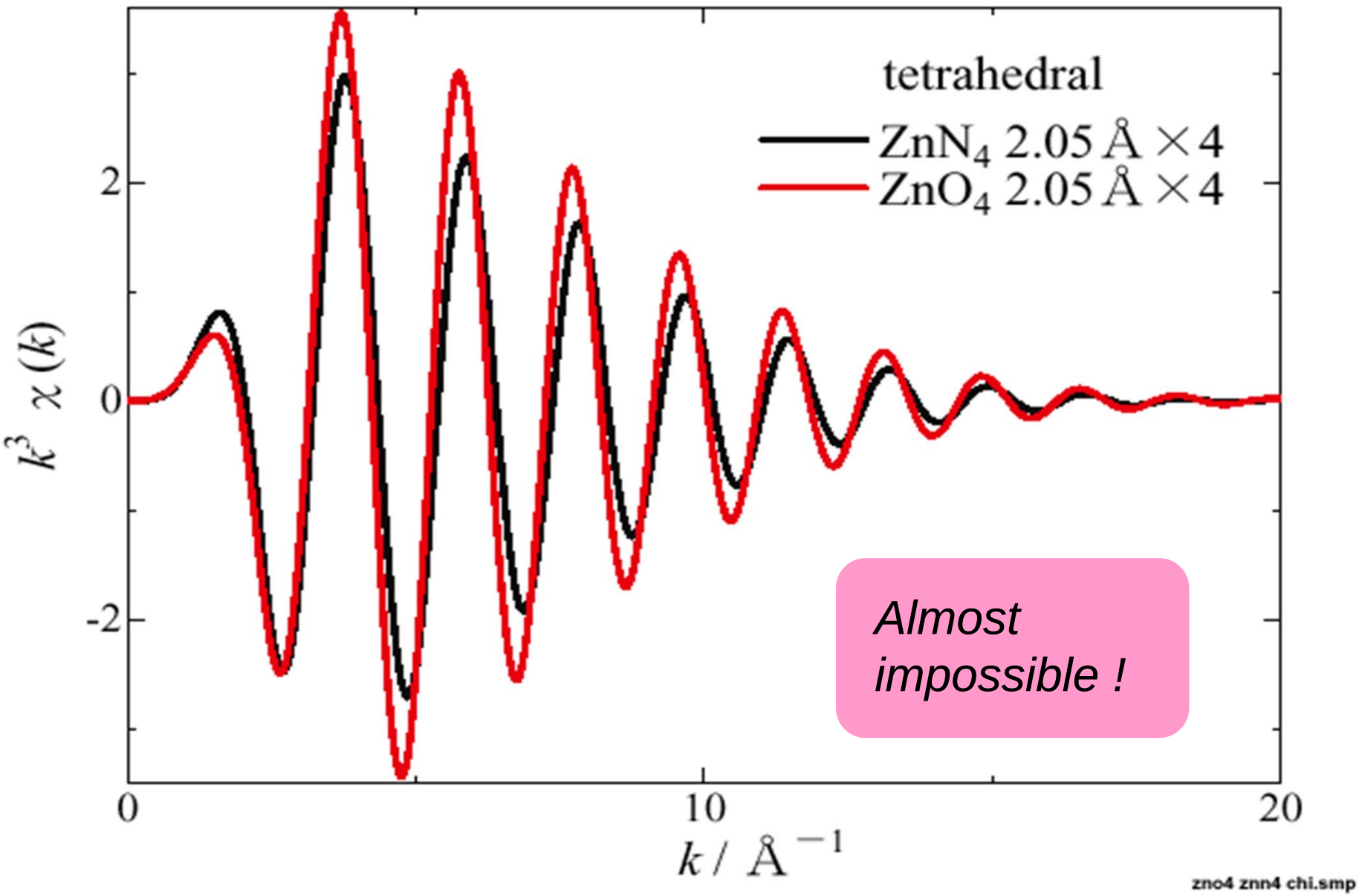


This method can be applied to thick samples owing to the short escape depth of Auger electron.

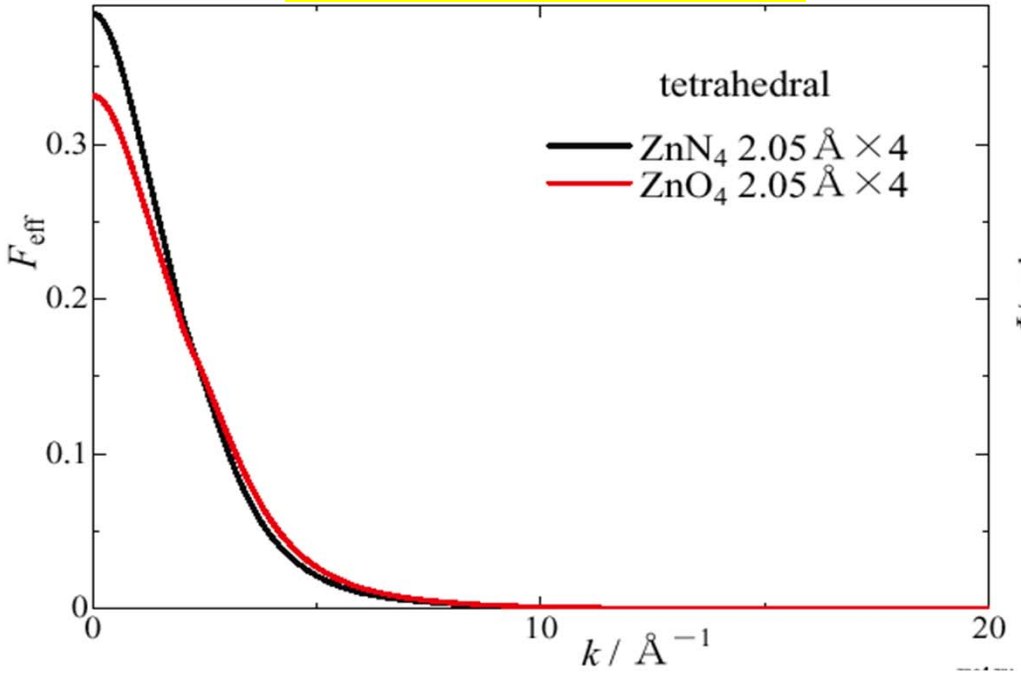


Can we distinguish oxygen from nitrogen by EXAFS?

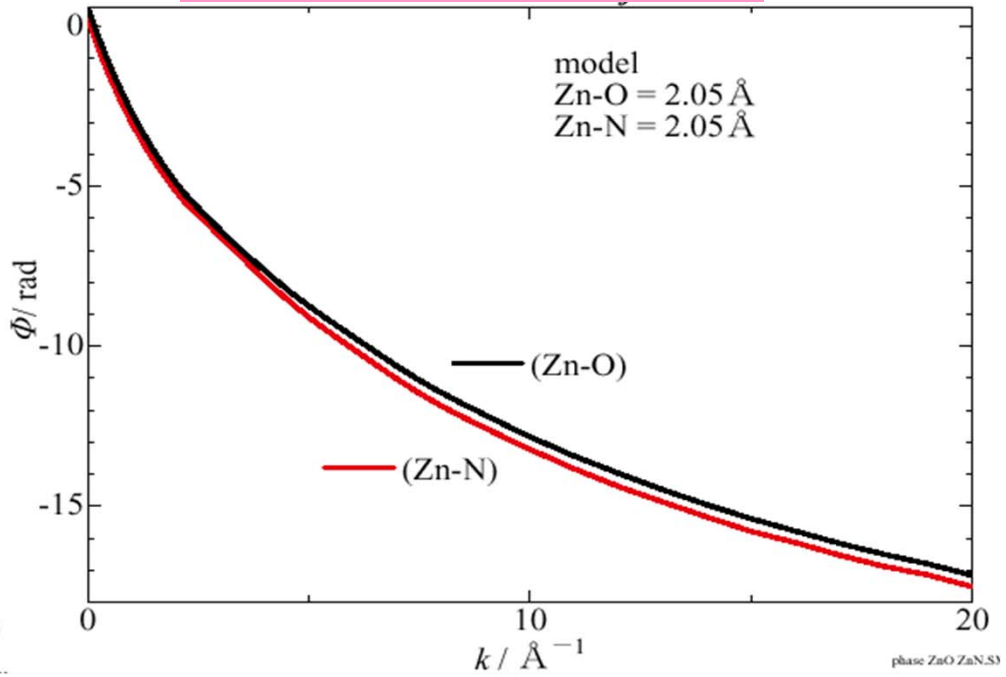

exp spectrum Zn2+ in solution
FEFF calc r(Zn-O) = 2.05 Å
FFiltered on exp spectrum
5
0
-5
k3 χ (k)
0
10
20
k / Å −1
ZnO chi exp theo.SMP


tetrahedral
ZnN4 2.05 Å ×4
ZnO4 2.05 Å ×4
Almost impossible !
2
0
-2
0
10
20
k / Å −1
k3 χ (k)
zno4 znn4 chi.smp

Scattering amplitude



Scattering phase shift



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

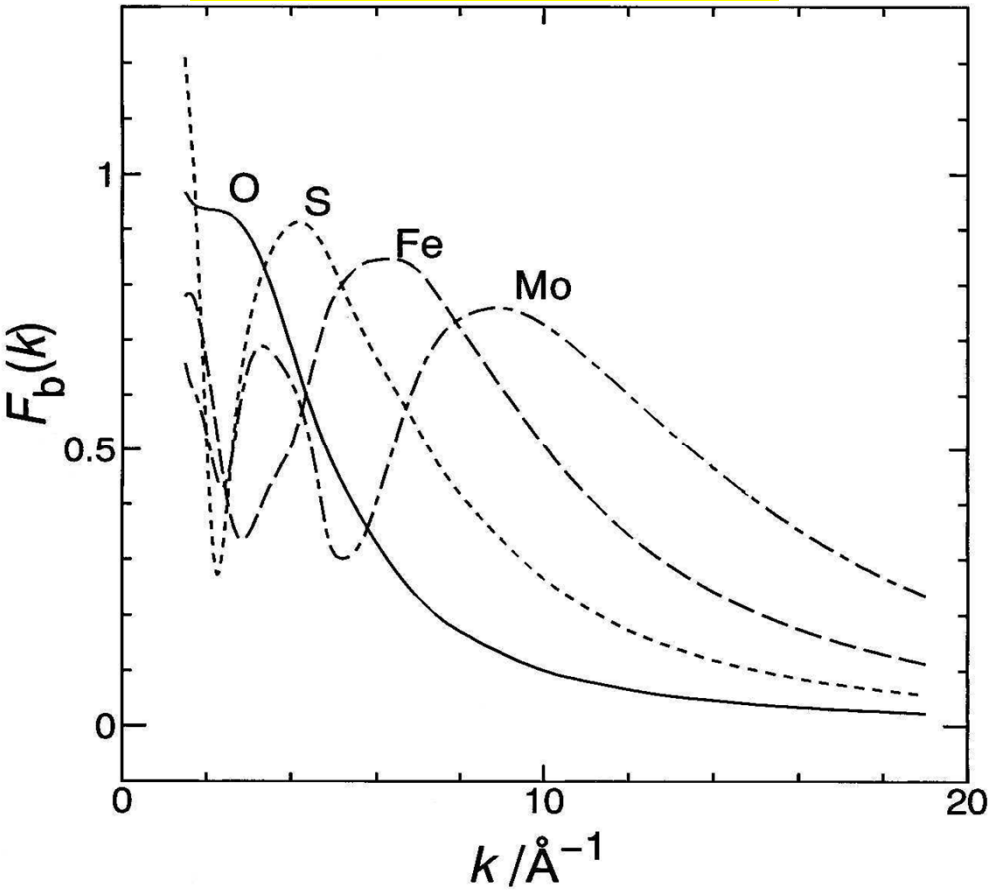
$$\chi(k) = \sum_i \frac{N_i}{k\, r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

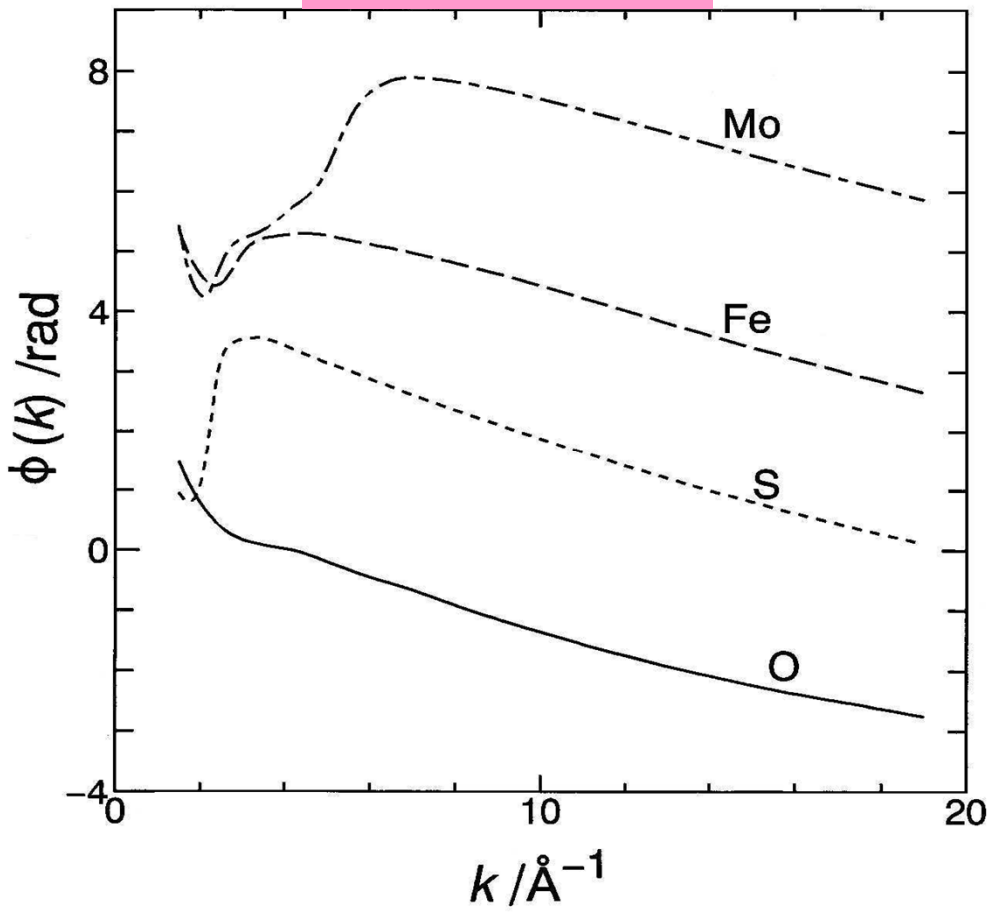
amplitude part

oscillation part

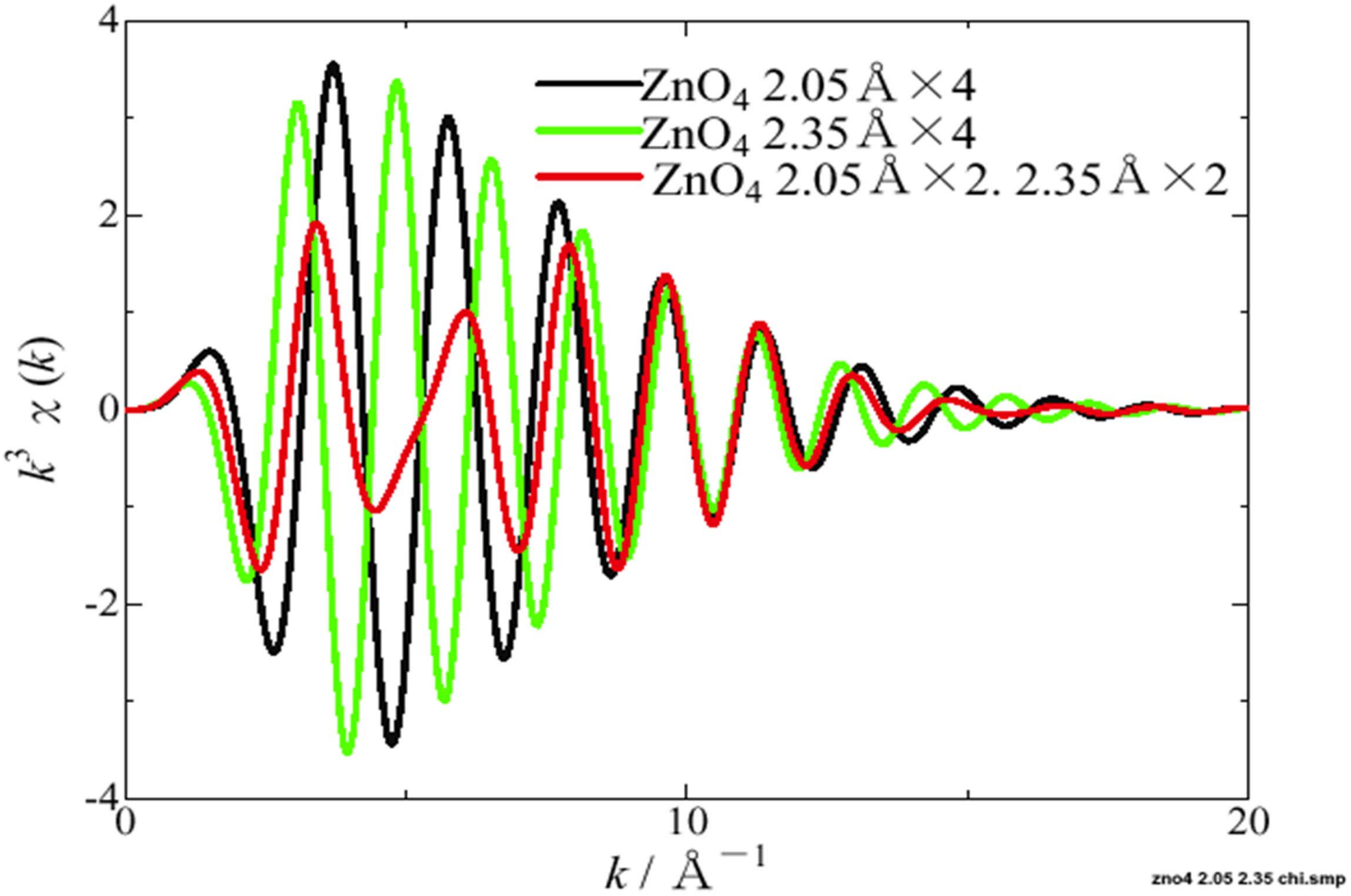
f scattering amplitude

ϕ phase shift

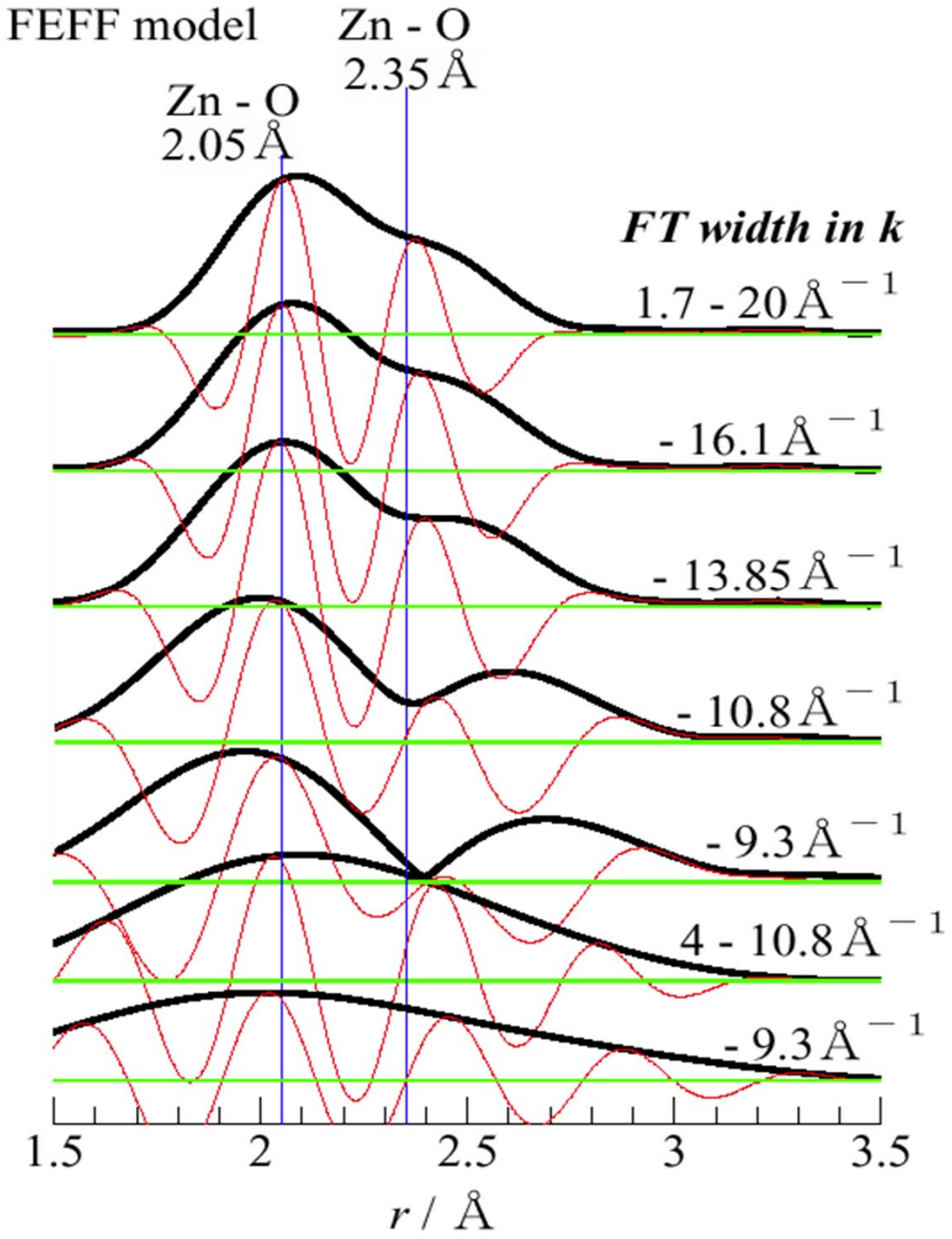




Can we distinguish oxygen atoms 15% distant from others by EXAFS?

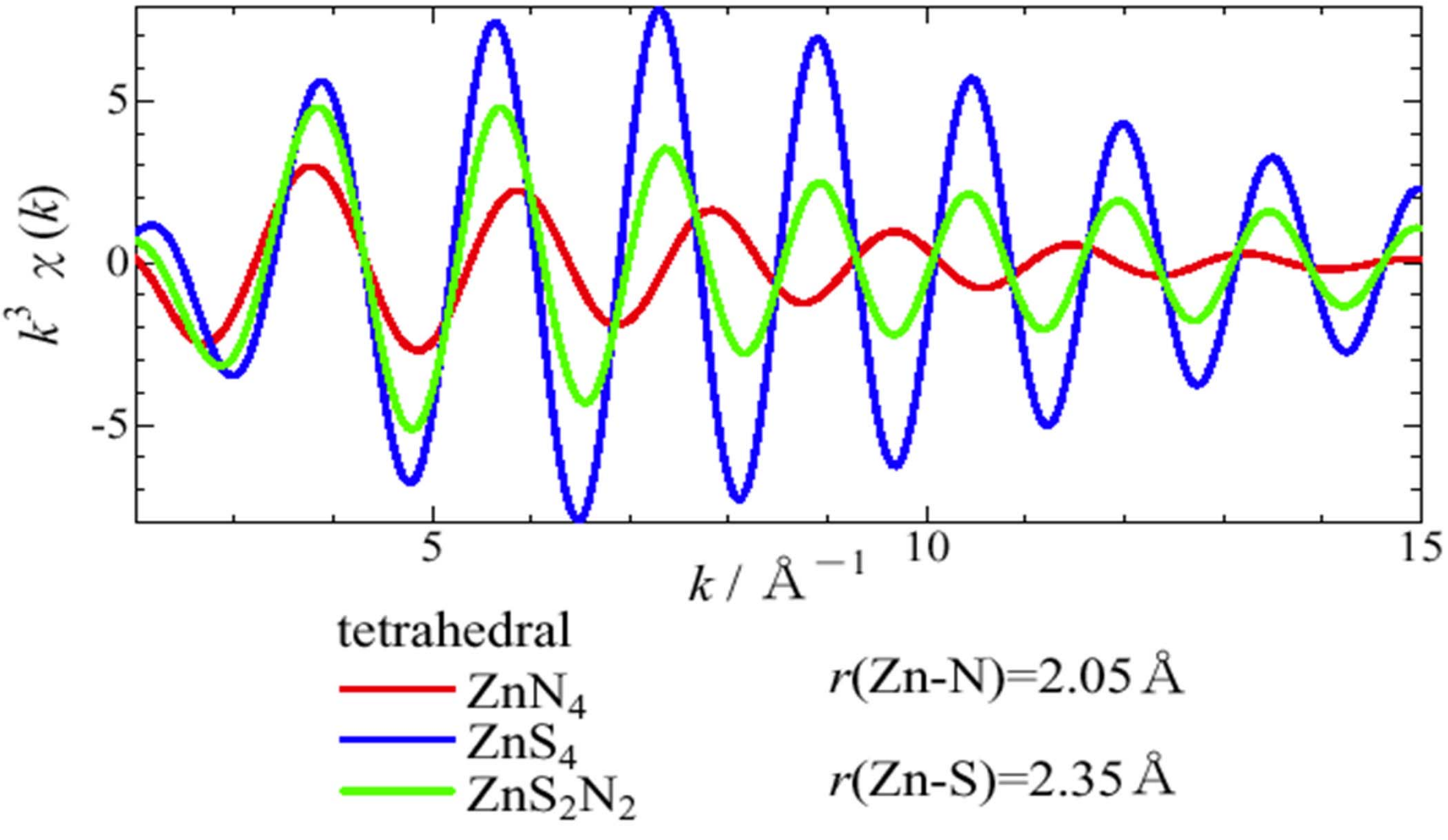

ZnO4 2.05 Å ×4
ZnO4 2.35 Å ×4
ZnO4 2.05 Å ×2. 2.35 Å ×2
4
2
0
-2
-4
0
10
20
k^3 χ (k)
k / Å^-1
zno4 2.05 2.35 chi.smp

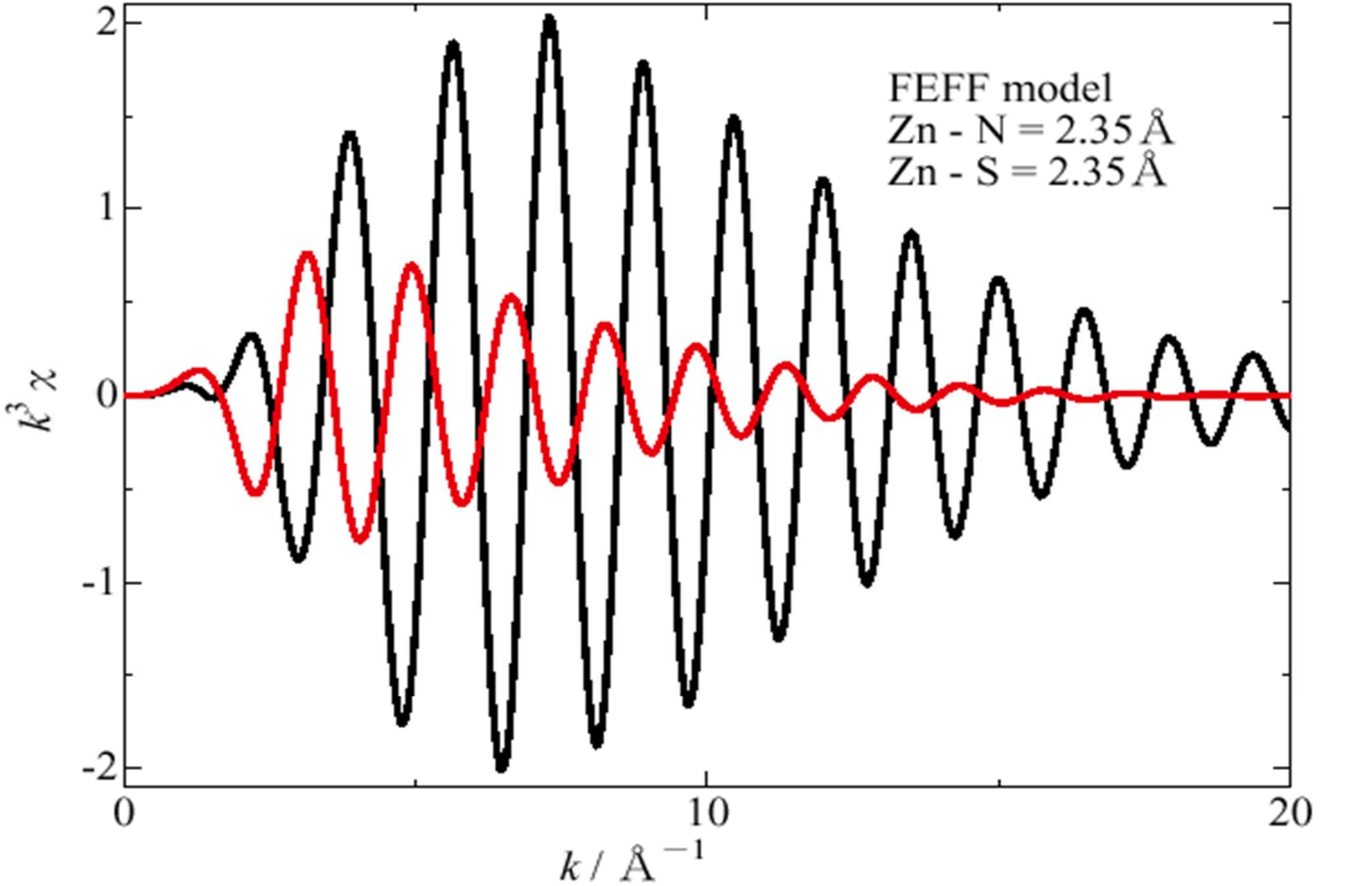
Parameters used for Fourier Trans: O



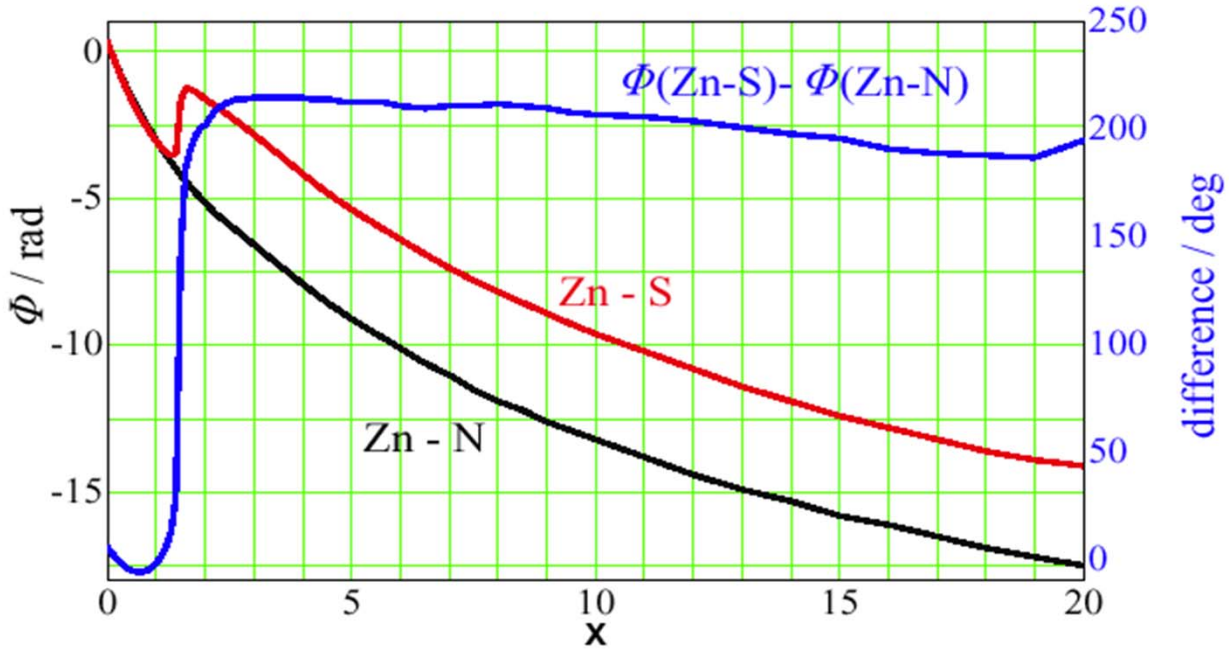
James E. Penner-Hahn J. Am. Chem. Soc. 1998,**120**,8401

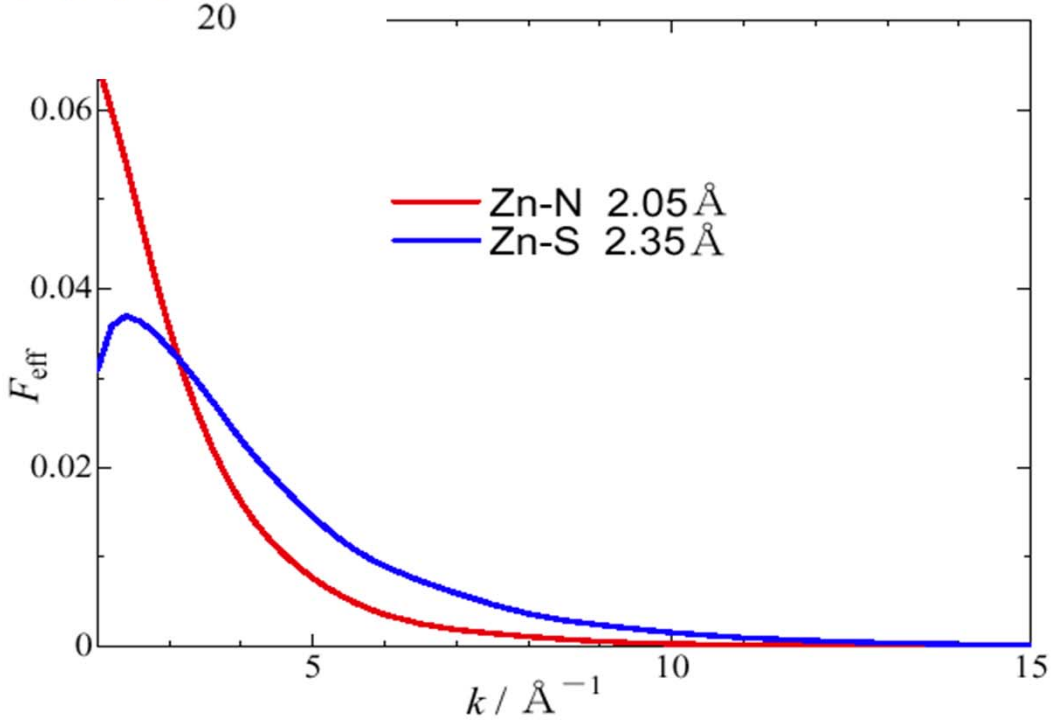
Can we distinguish sulfur from nitrogen (or oxygen) by EXAFS?


5
0
-5
$k^3\ \chi\ (k)$
5
10
15
k / Å $^{-1}$
tetrahedral
ZnN_4
ZnS_4
ZnS_2N_2
r(Zn-N)=2.05 Å
r(Zn-S)=2.35 Å



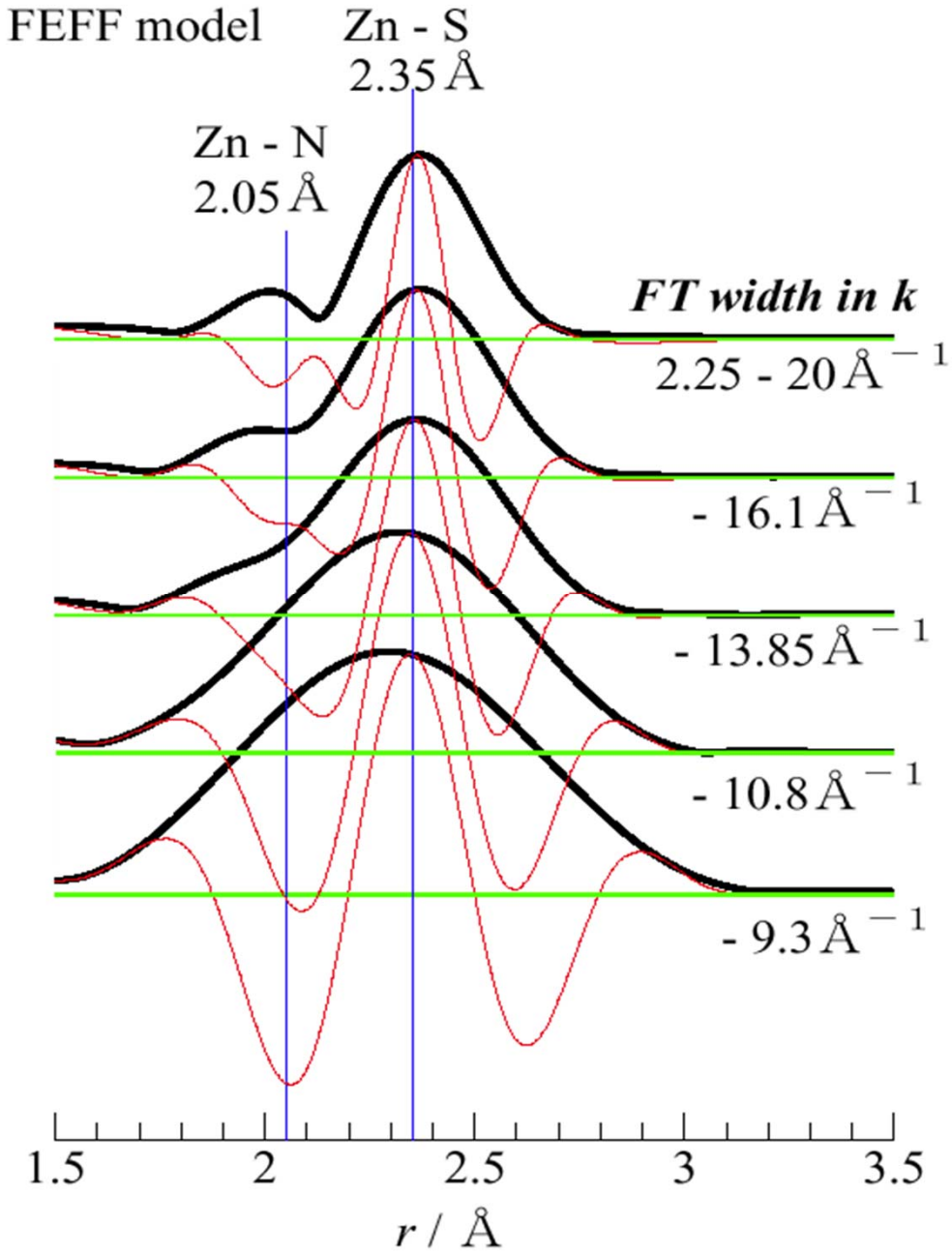
zns 2.35 znn 2.35.smp


Φ(Zn-S)- Φ(Zn-N)
Zn - S
Zn - N
Φ / rad
difference / deg
x
0
-5
-10
-15
250
200
150
100
50
0
0
5
10
15
20


Zn-N 2.05 Å
Zn-S 2.35 Å
F_{eff}
k / Å^{-1}
0.06
0.04
0.02
0
5
10
15

f zns znn.smp

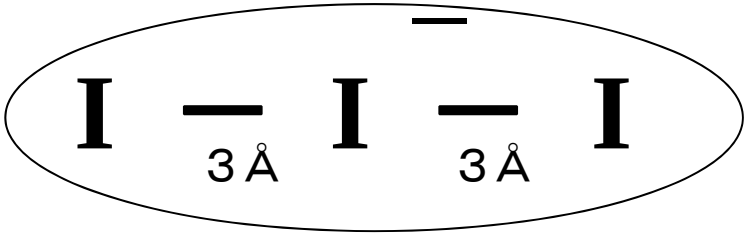
Parameters used for Fourier Trans: S

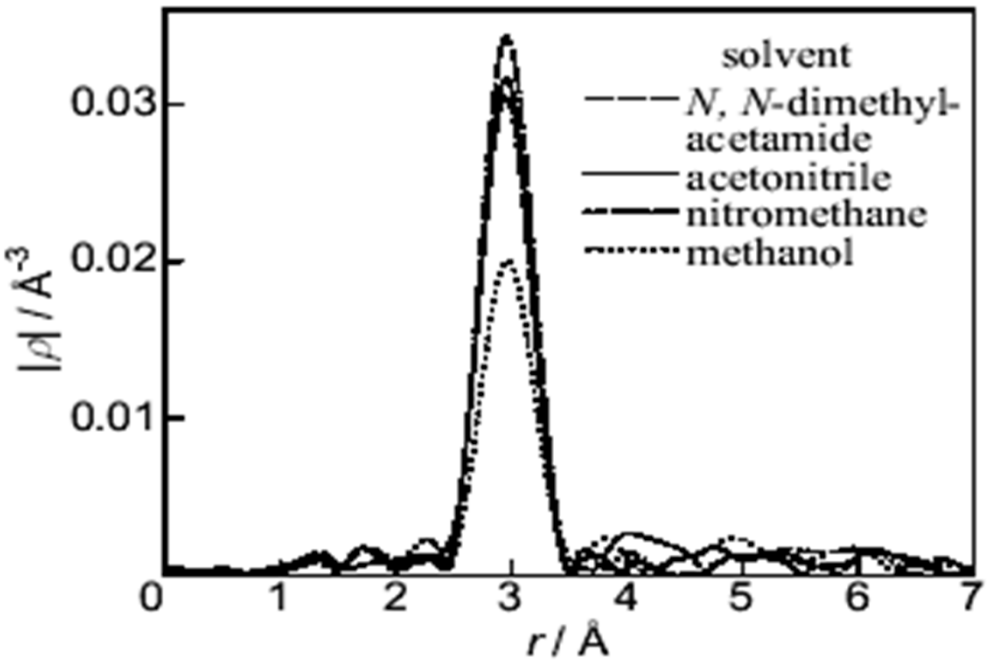


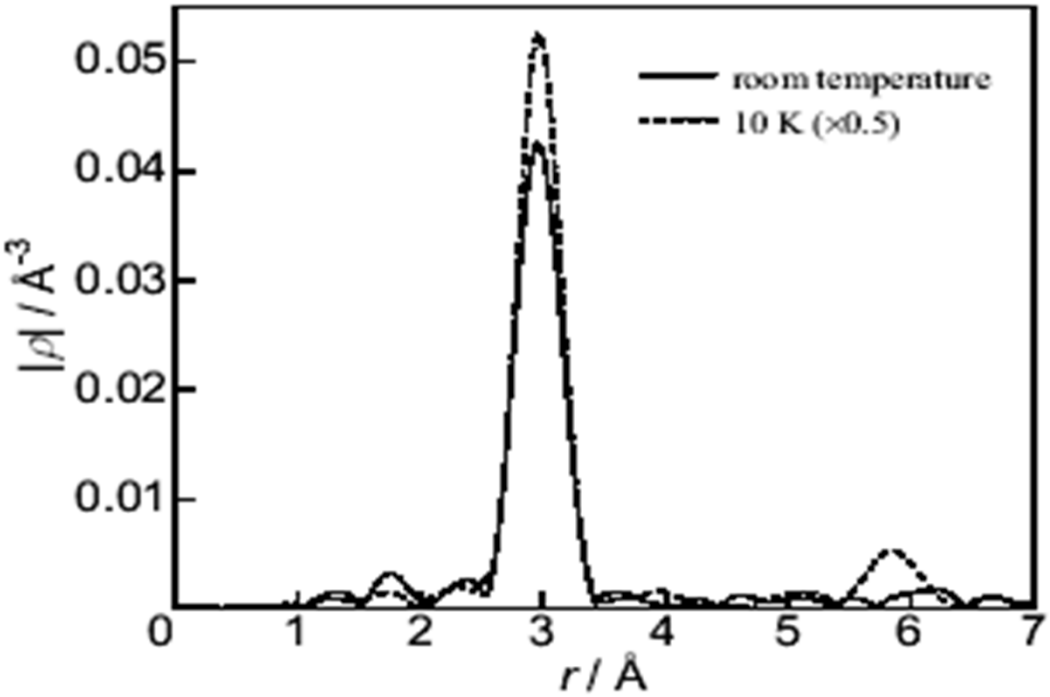
Almost impossible !

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

I K-edge EXAFS FT for I_3^-



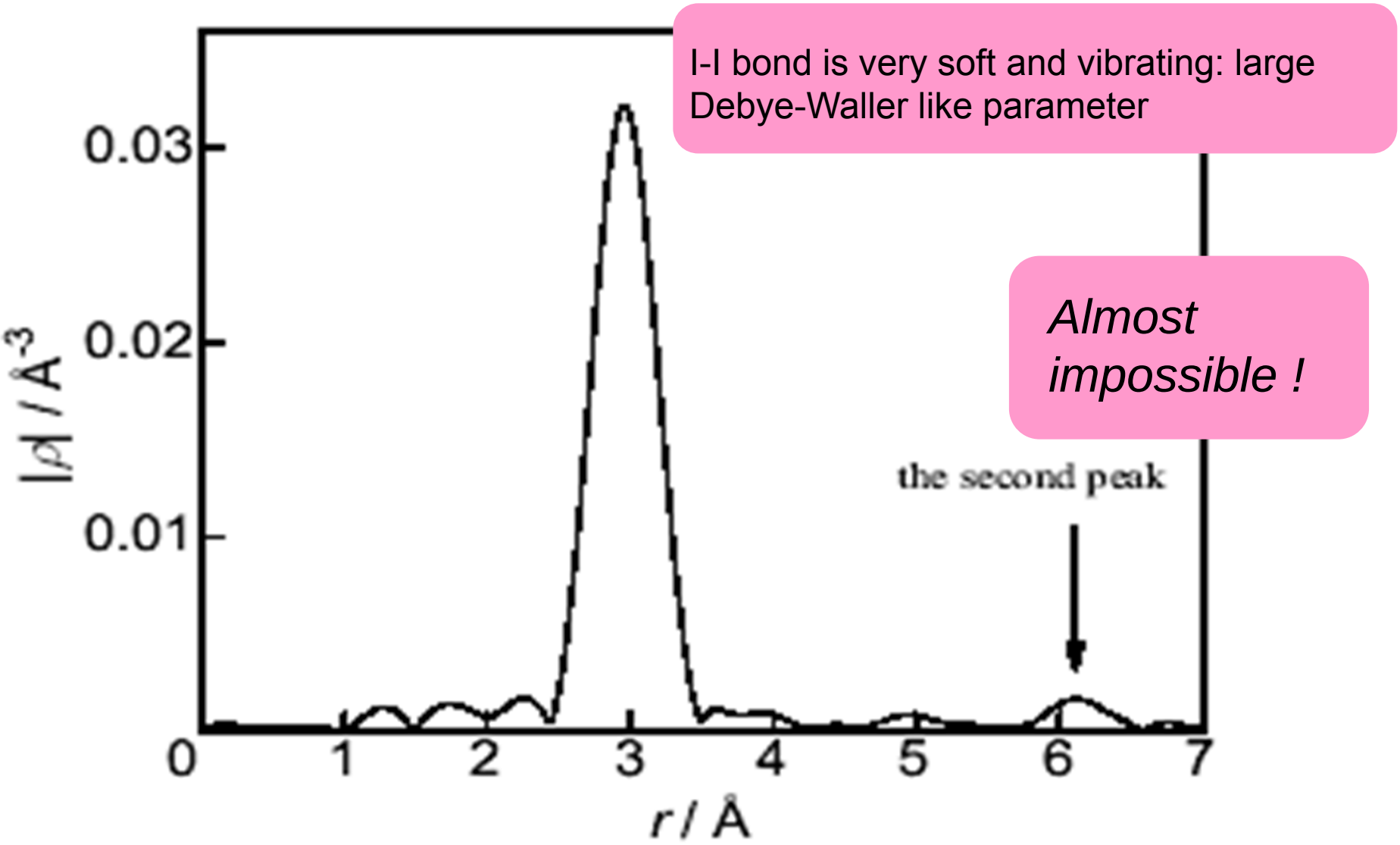




Dissolved in organic solvents

$(n\text{-}C_3H_7)_4N\ I_3$ powder

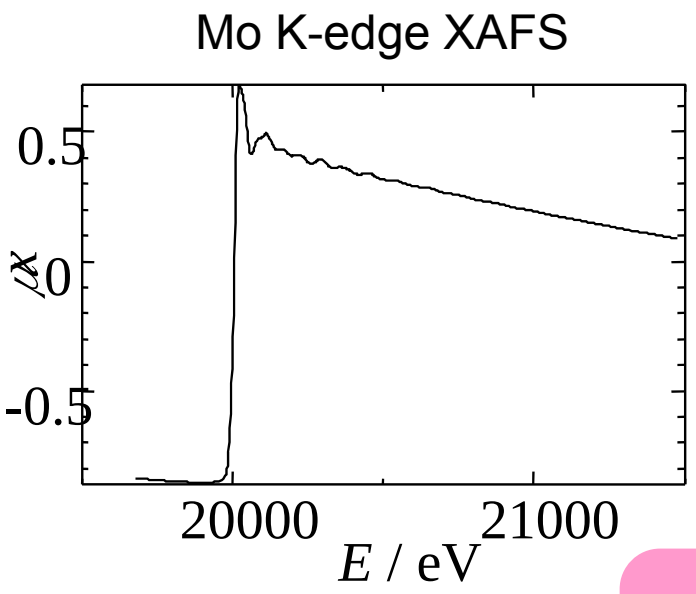
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

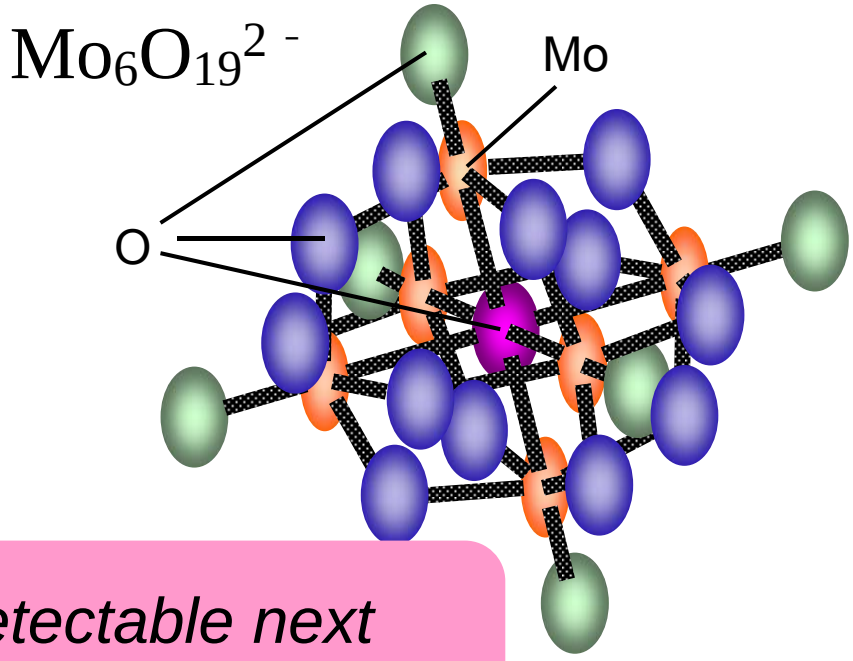


Iodine K-edge EXAFS Fourier transform for the compound spectrum made up from 12 independent spectra for organic solvent solutions.

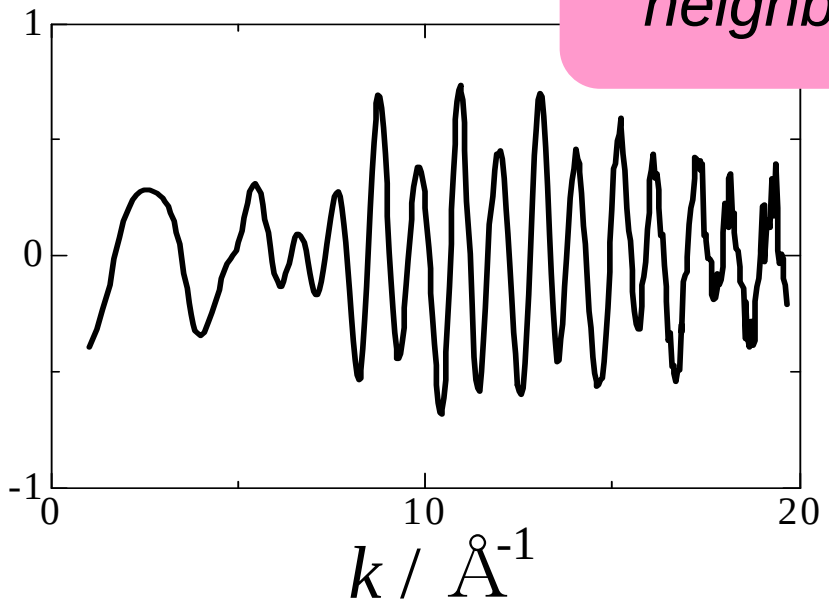
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

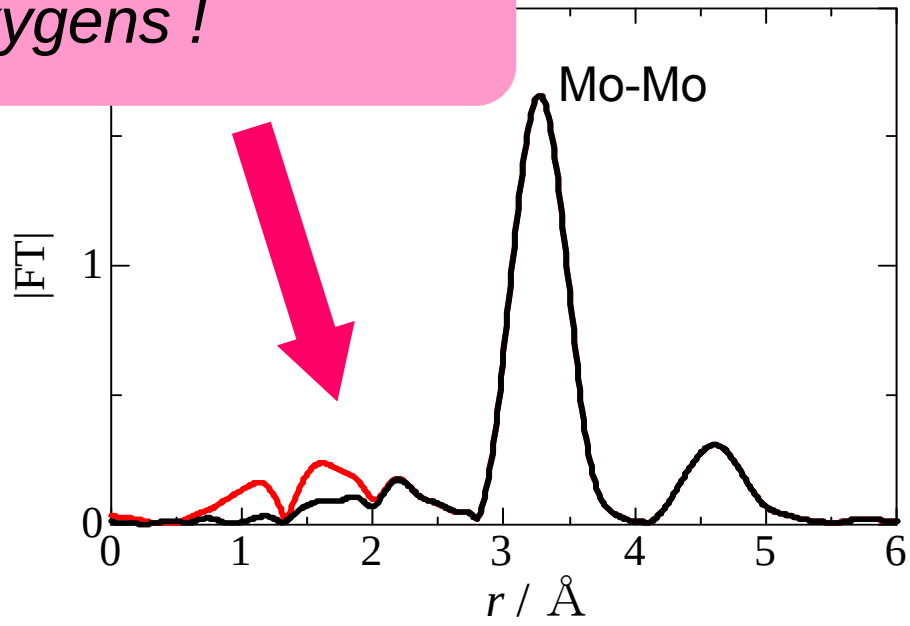
Large symmetrical cluster of molybdenum oxide complex

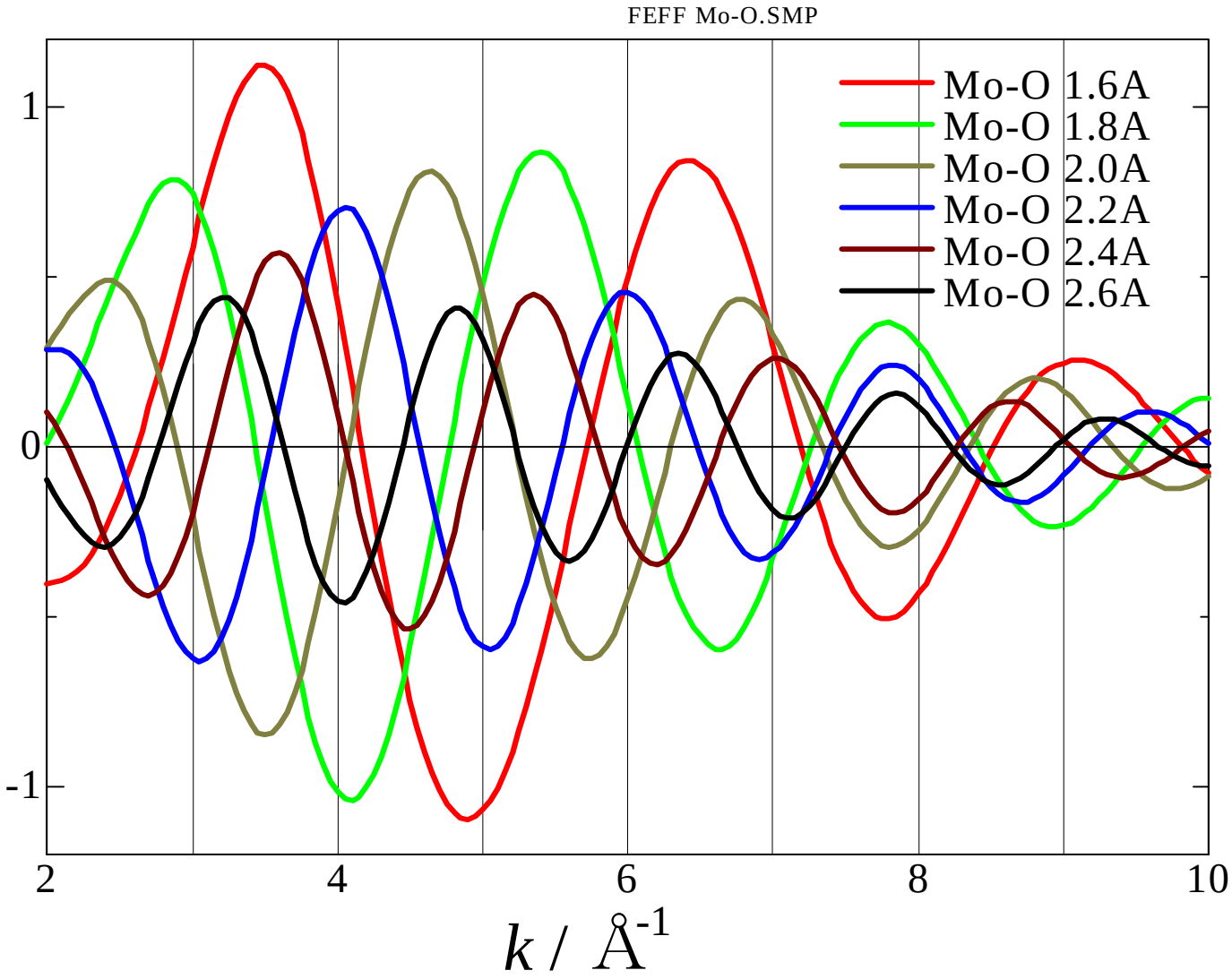




Almost undetectable next neighbor oxygens !






FEFF Mo-O.SMP
Mo-O 1.6A
Mo-O 1.8A
Mo-O 2.0A
Mo-O 2.2A
Mo-O 2.4A
Mo-O 2.6A
1
0
-1
2
4
6
8
10
k / Å-1

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.

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

free software

XAS Analysis Software Using IFEFFIT

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.