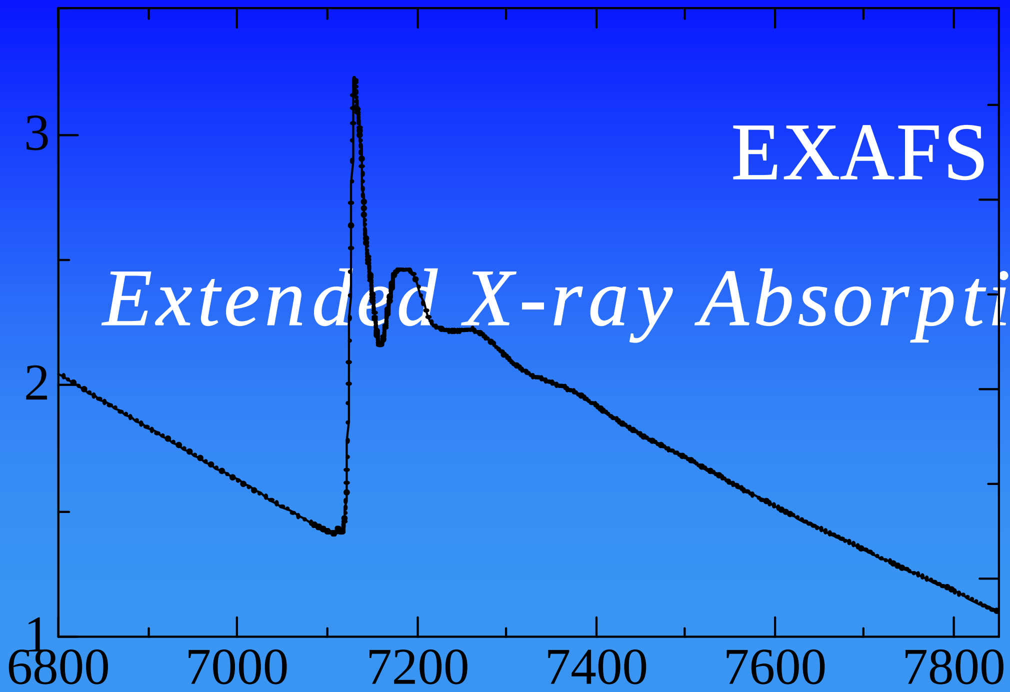


EXAFS

The 2nd AOFSRR Summer School
- Cheiron School 2008 –
SPring-8
Sept. 30th, 2008

Extended X-ray Absorption Fine Structure

Iwao Watanabe

Ritsumeikan University

EXAFS

Theory

- Quantum Mechanics
- Models
- Approximations

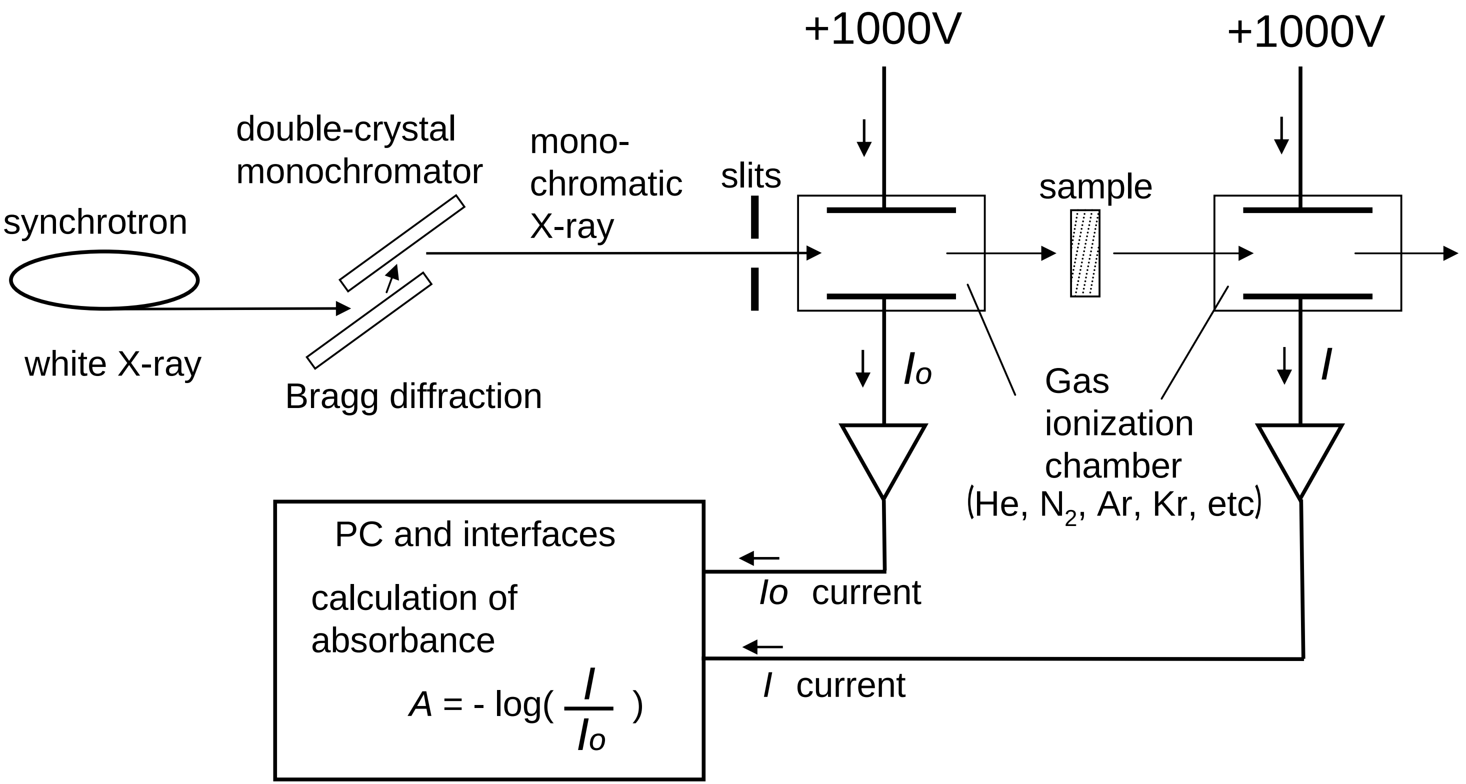
Experiment

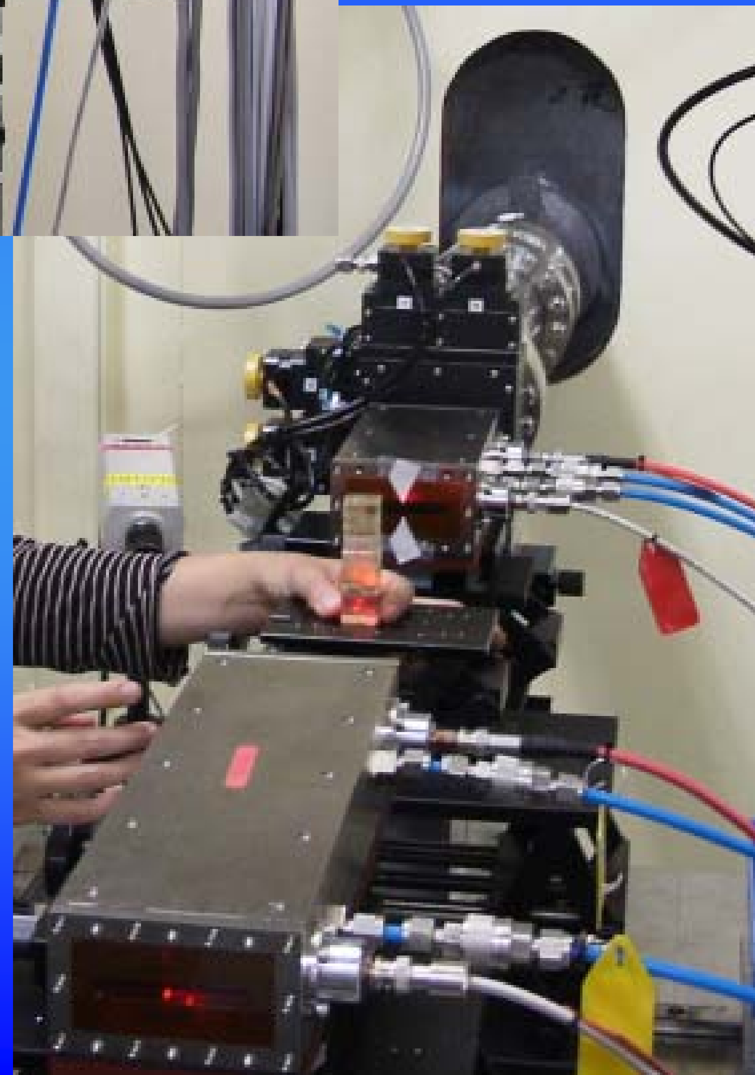
- Light Source
- Monochromator
- Higher Harmonics Rejection
- Sample Preparation
- Detection Methods
- Polarization XAFS

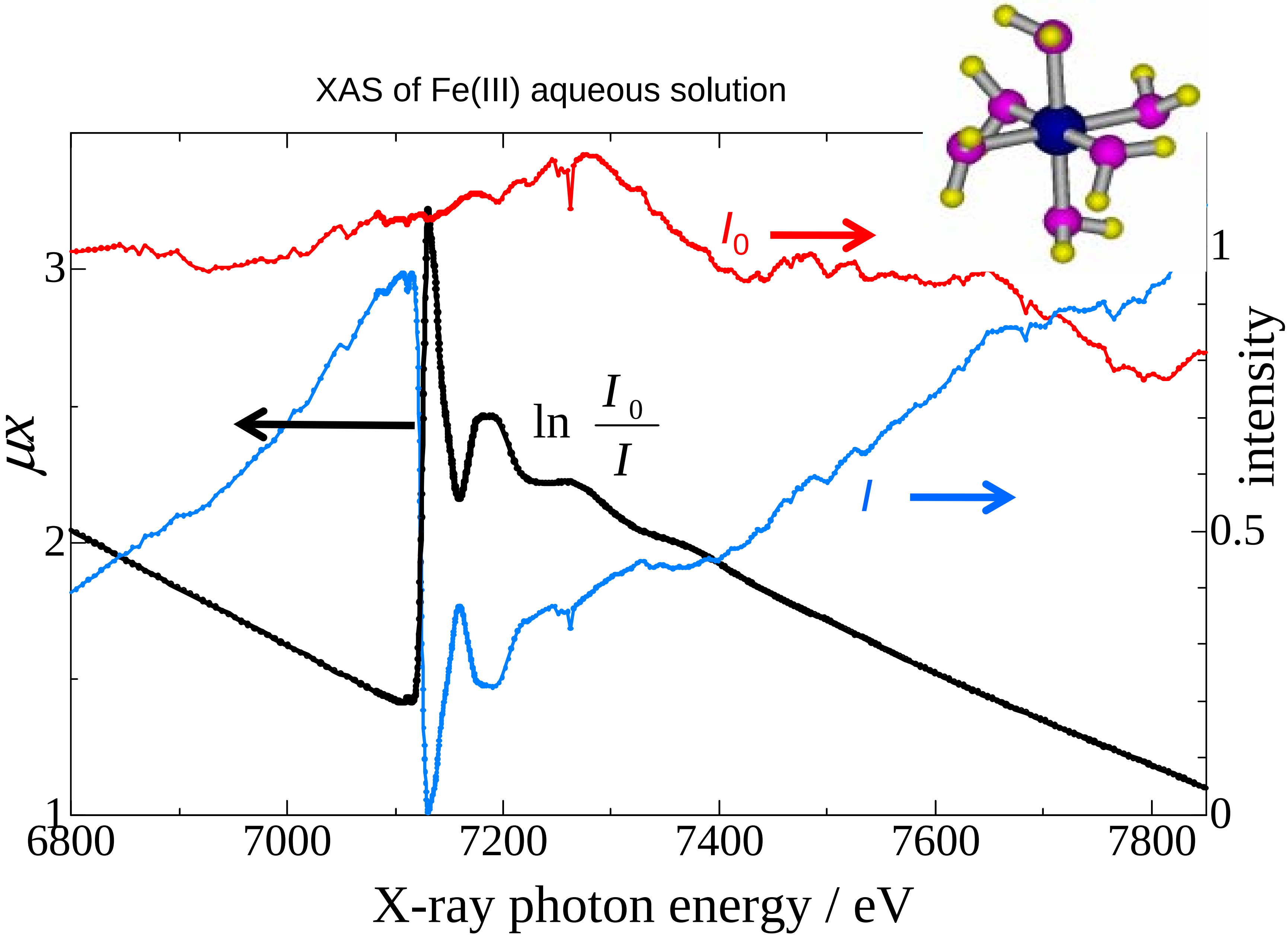
Data Analysis

- 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

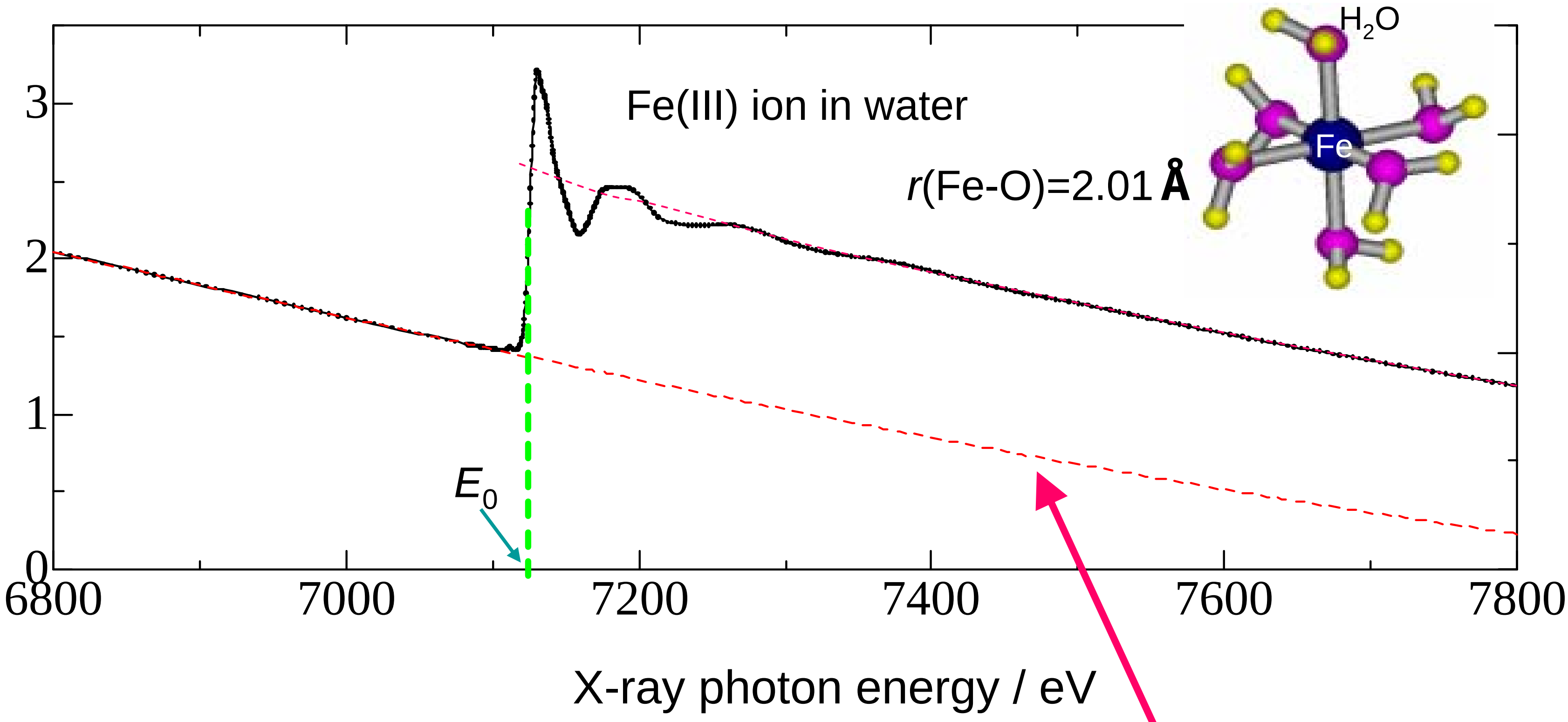
X-ray absorption measurement by transmission method
The most reliable and basic method





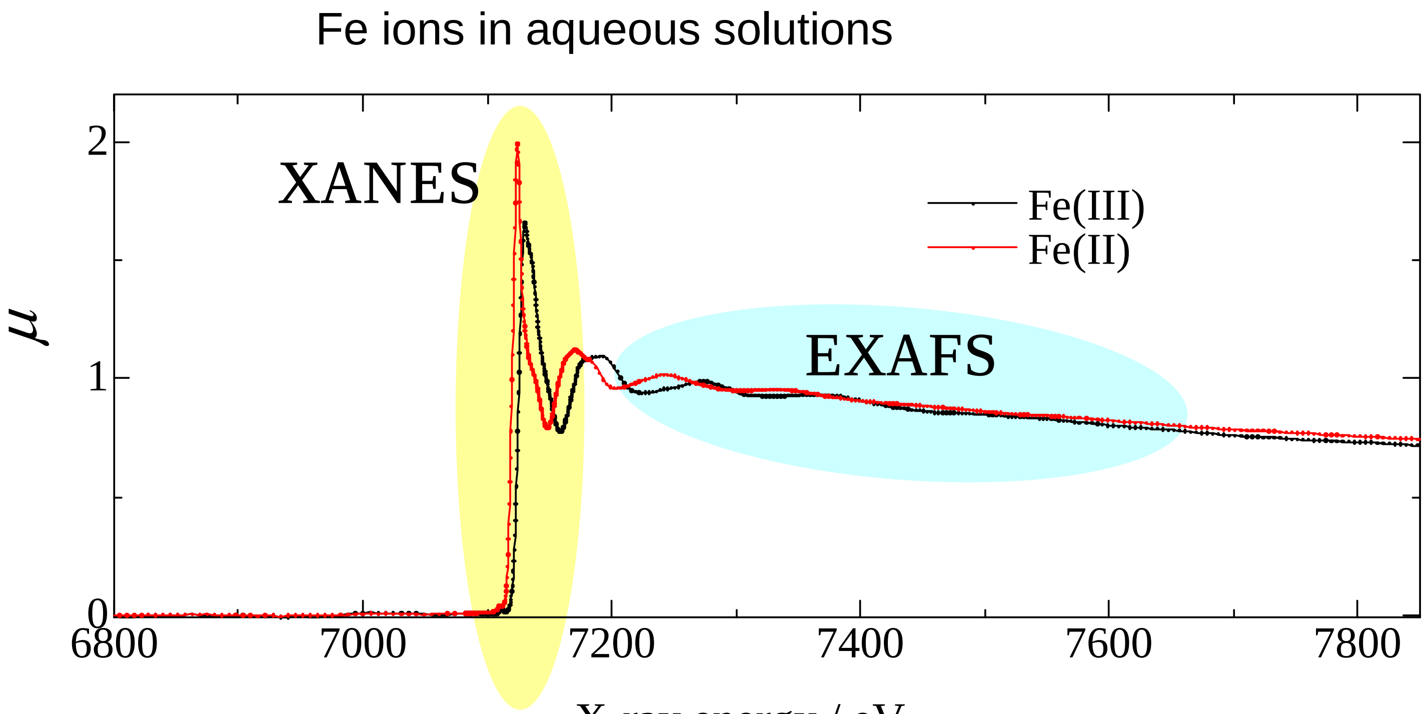
XAS of Fe(III) aqueous solution
μx
intensity
$\ln \frac{I_0}{I}$
I_0
I
3
2
1
1
0.5
0
6800
7000
7200
7400
7600
7800
X-ray photon energy / eV



Focusing on K shell (1s electron) excitation

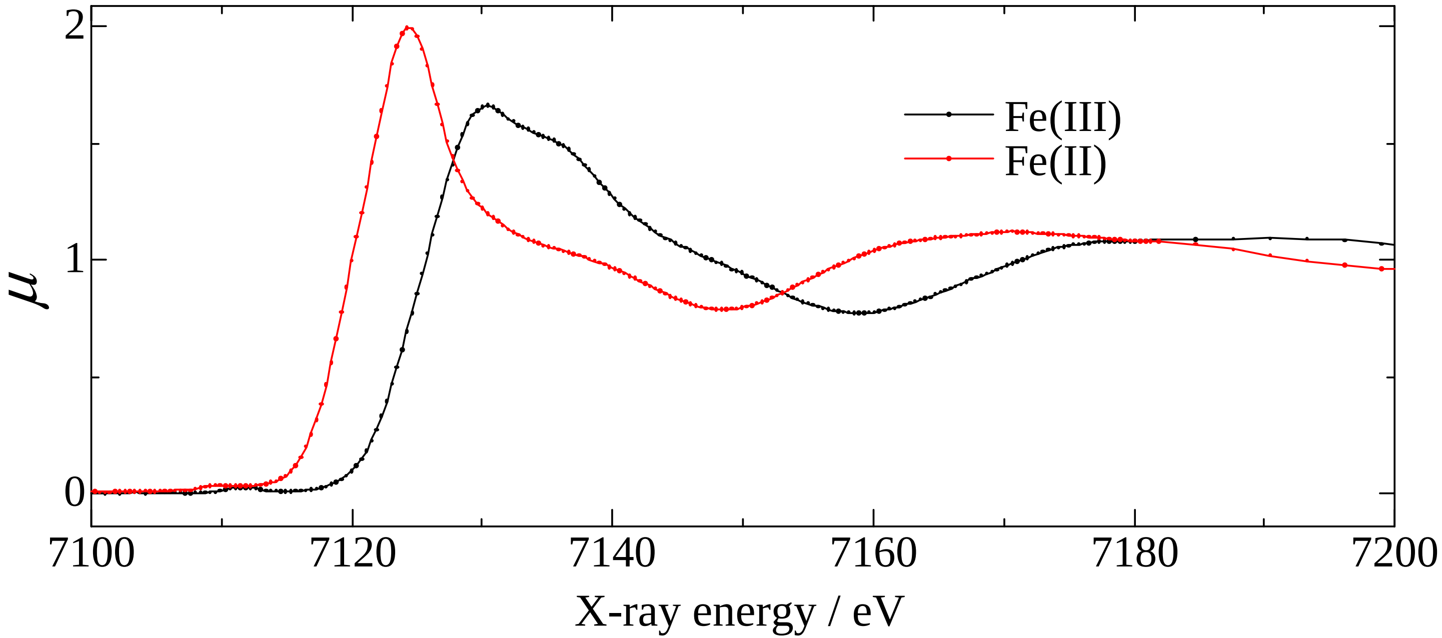
Background absorption due to other atoms and other shell electrons

XAFS: X-ray Absorption Fine Structure



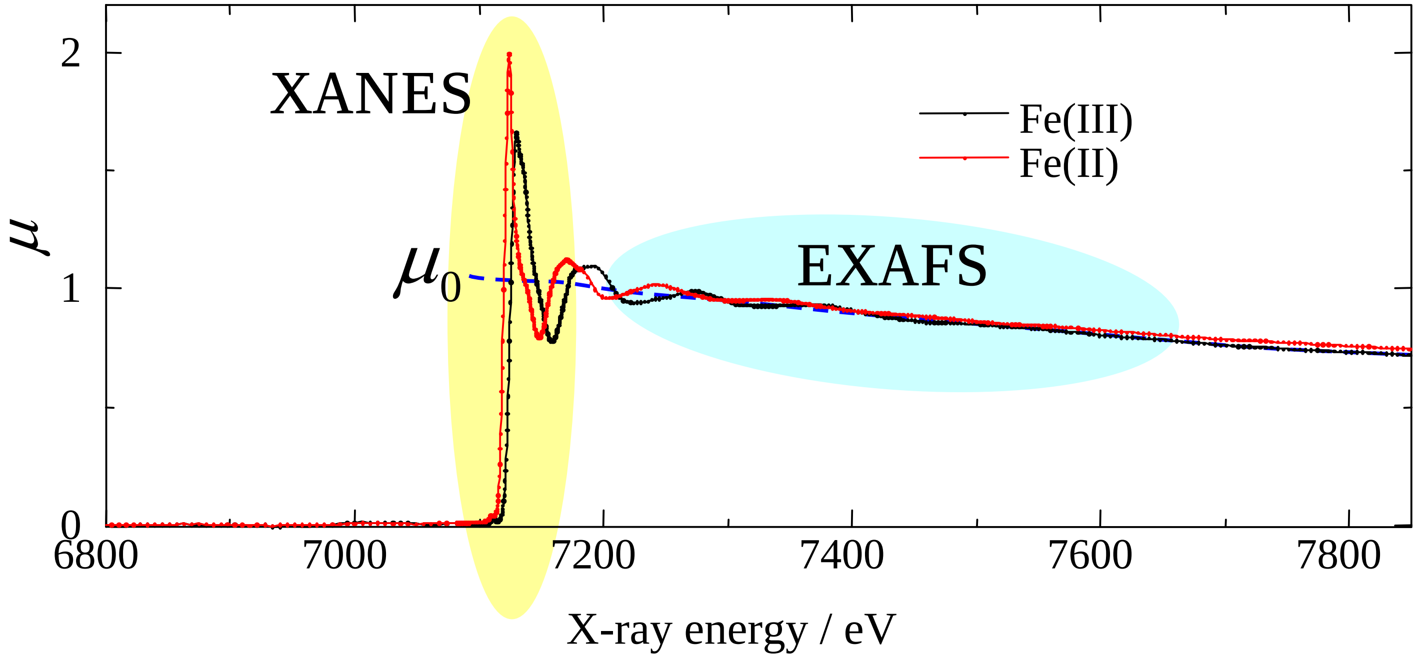
XANES: X-ray Absorption Near Edge Structure

Fe ions in aqueous solutions



EXAFS: Extended X-ray Absorption Fine Structure

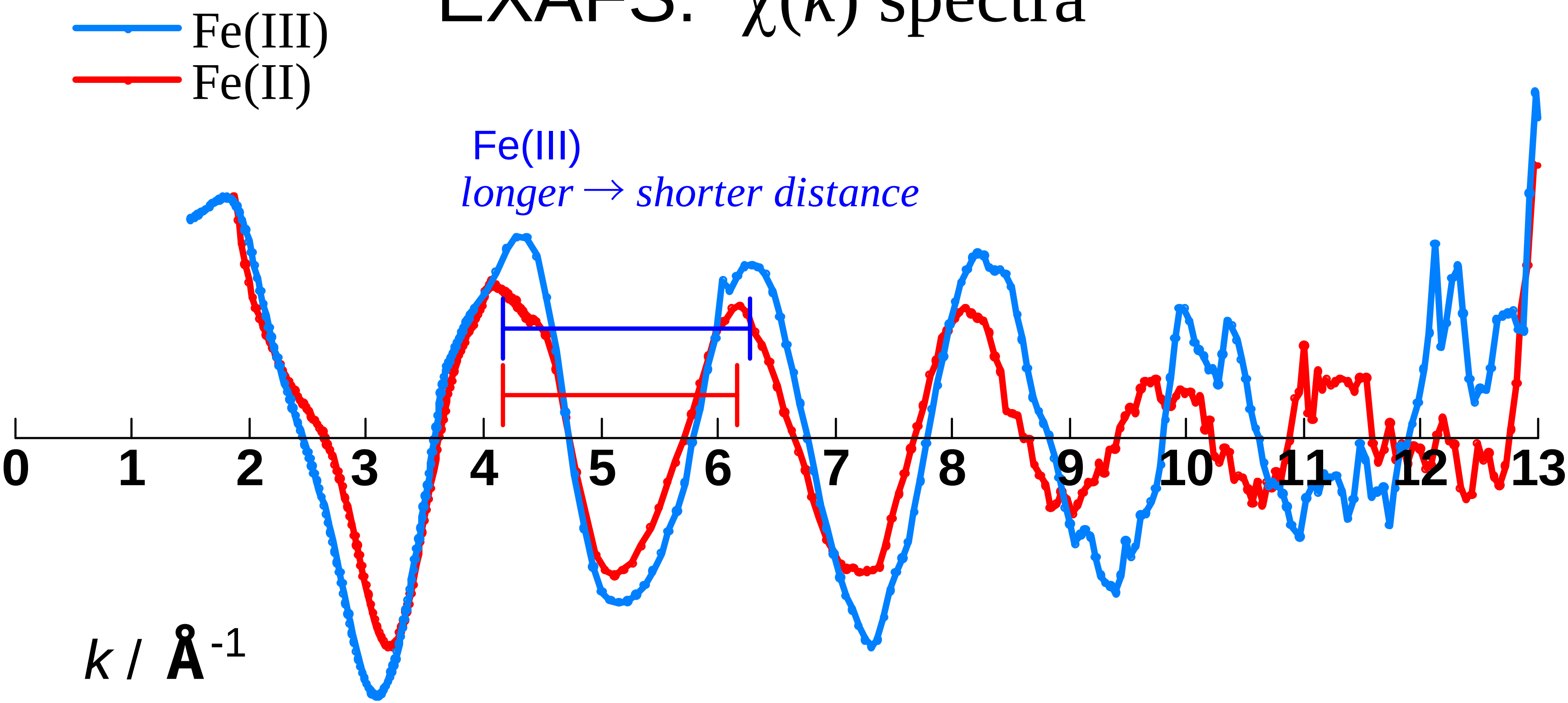
Fe ions in aqueous solutions



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

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

EXAFS: $\chi(k)$ spectra



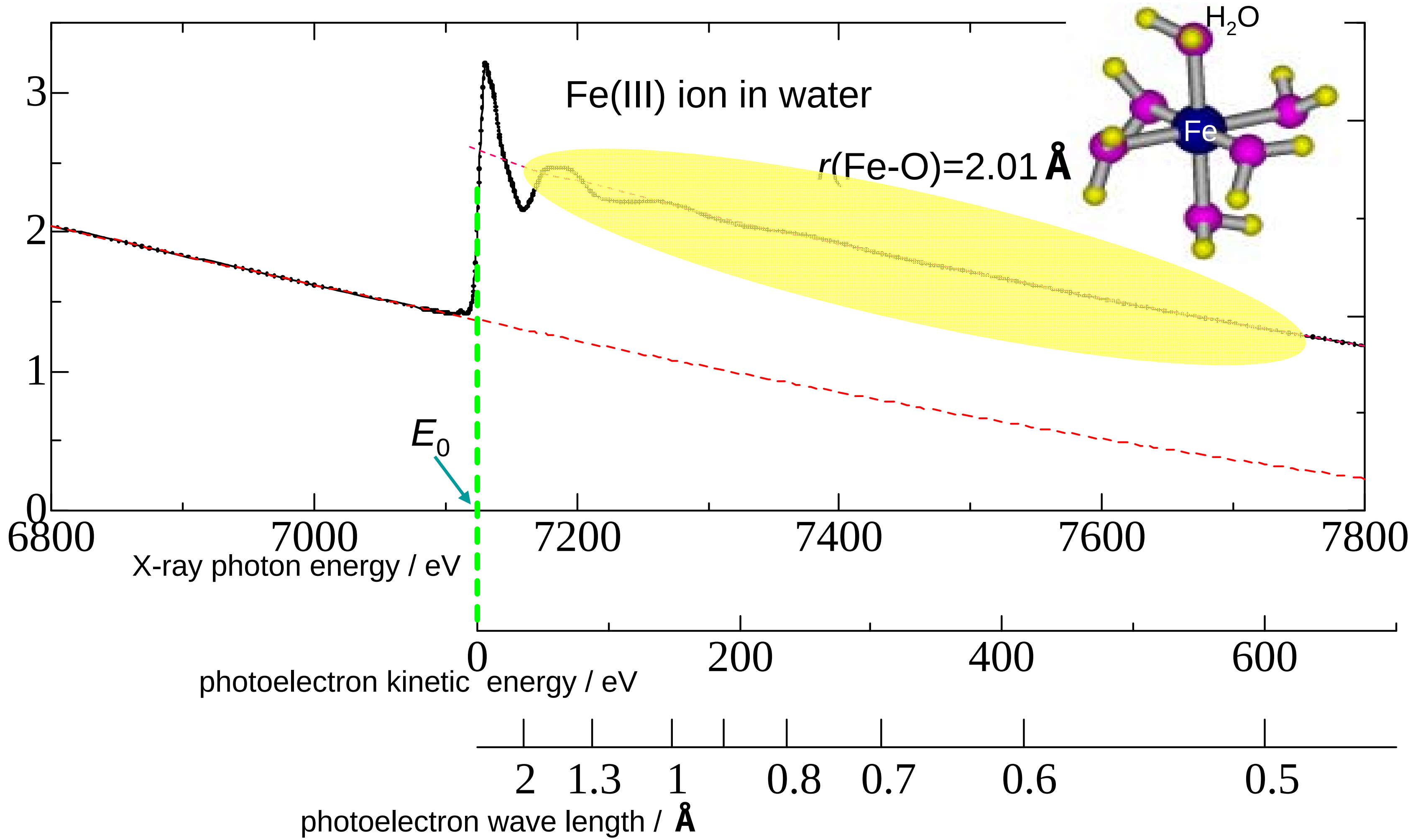
k : wave number, wave vector

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

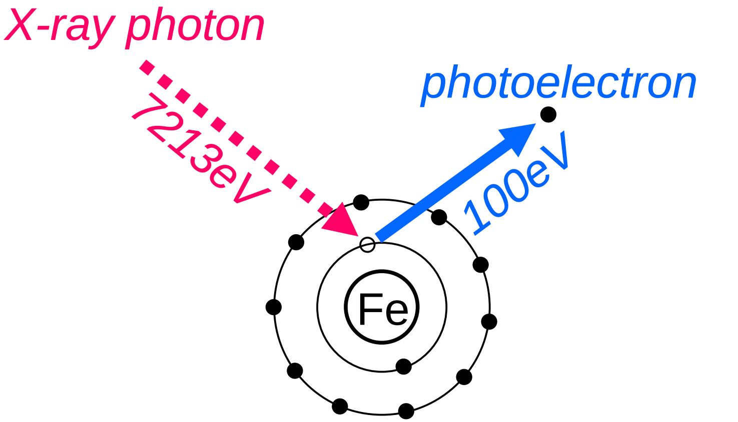
$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

$(E - E_0)$ kinetic energy of photoelectron

Simplest model to explain how the EXAFS oscillation occurs



Fe(III) ion in water
H2O
Fe
r(Fe-O)=2.01 Å
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

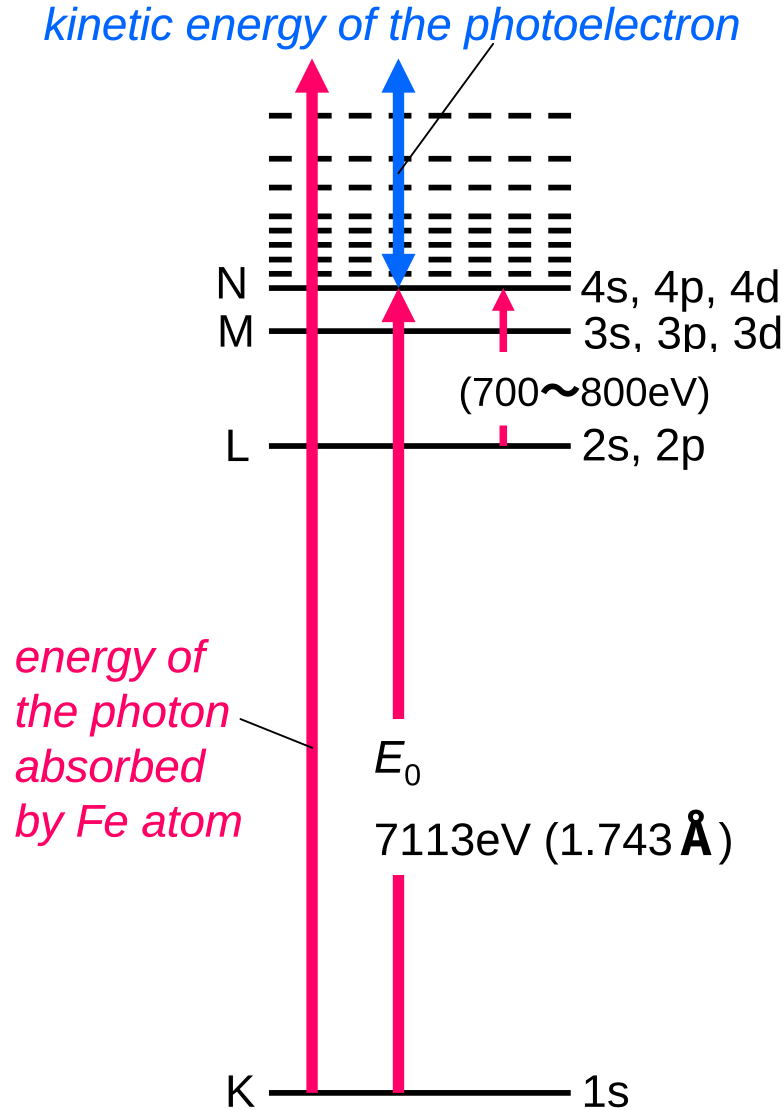


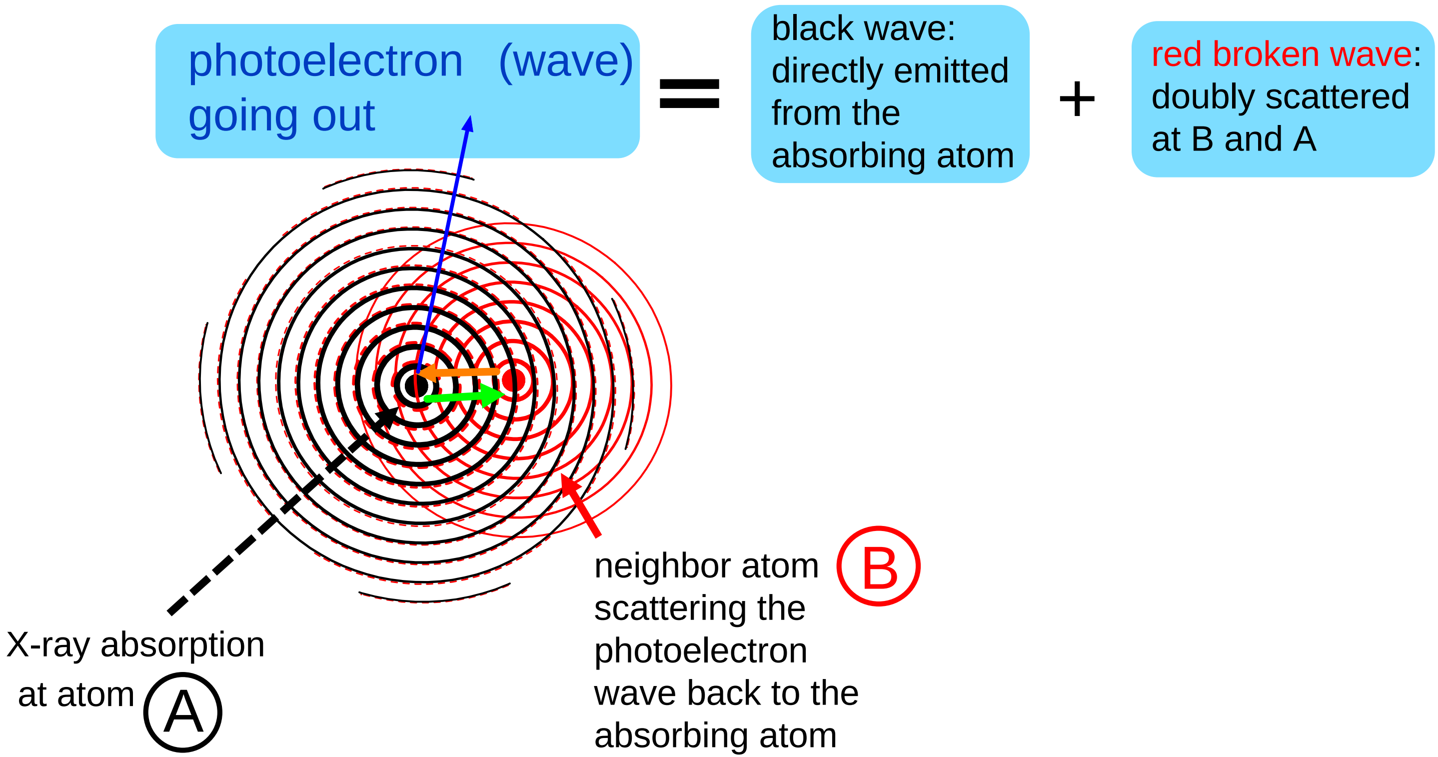
an electron with E_k=100eV behaves as a wave with **λ=1.2 Å**

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

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

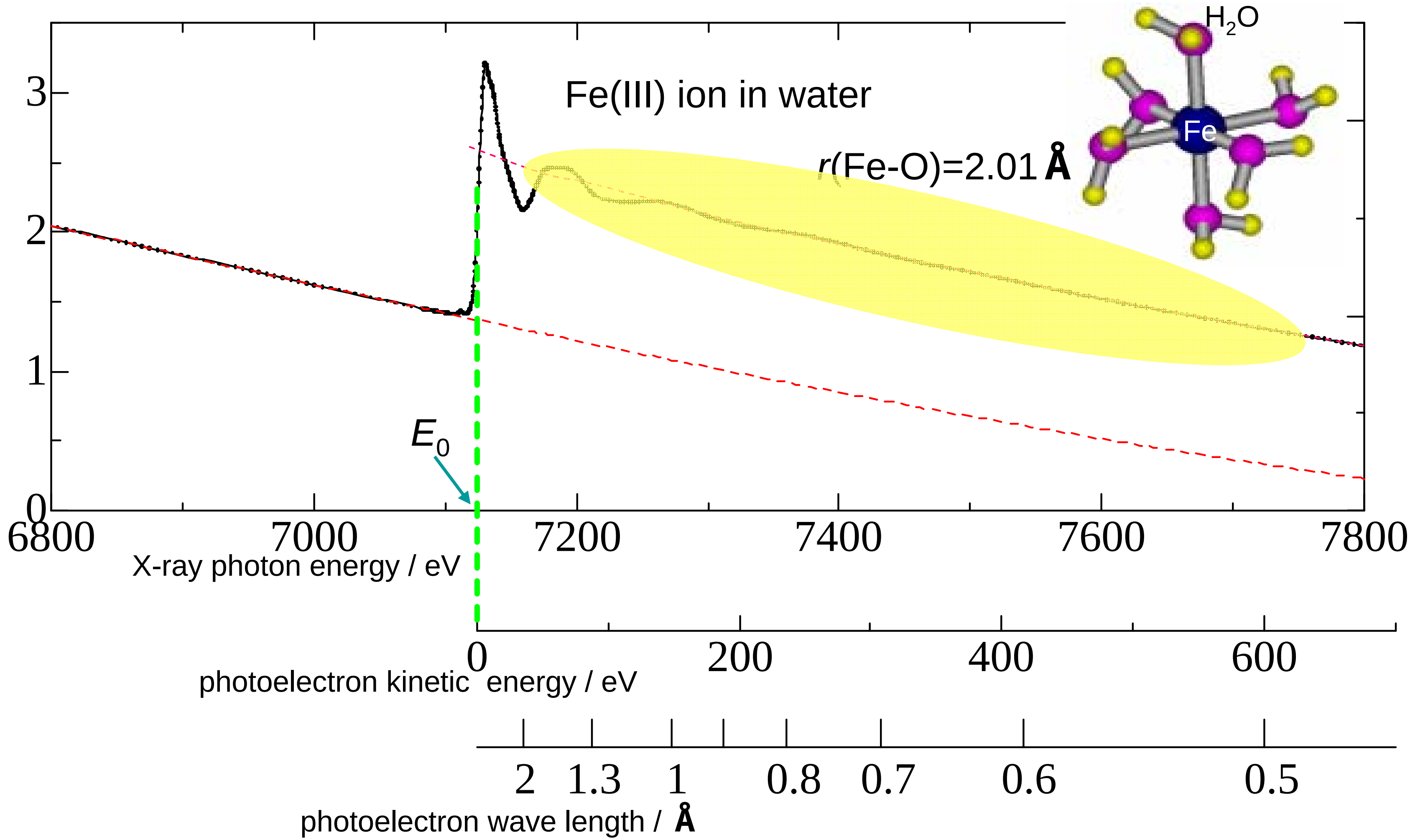
The cause for EXAFS appearance !!!





BASIC EXAFS equation

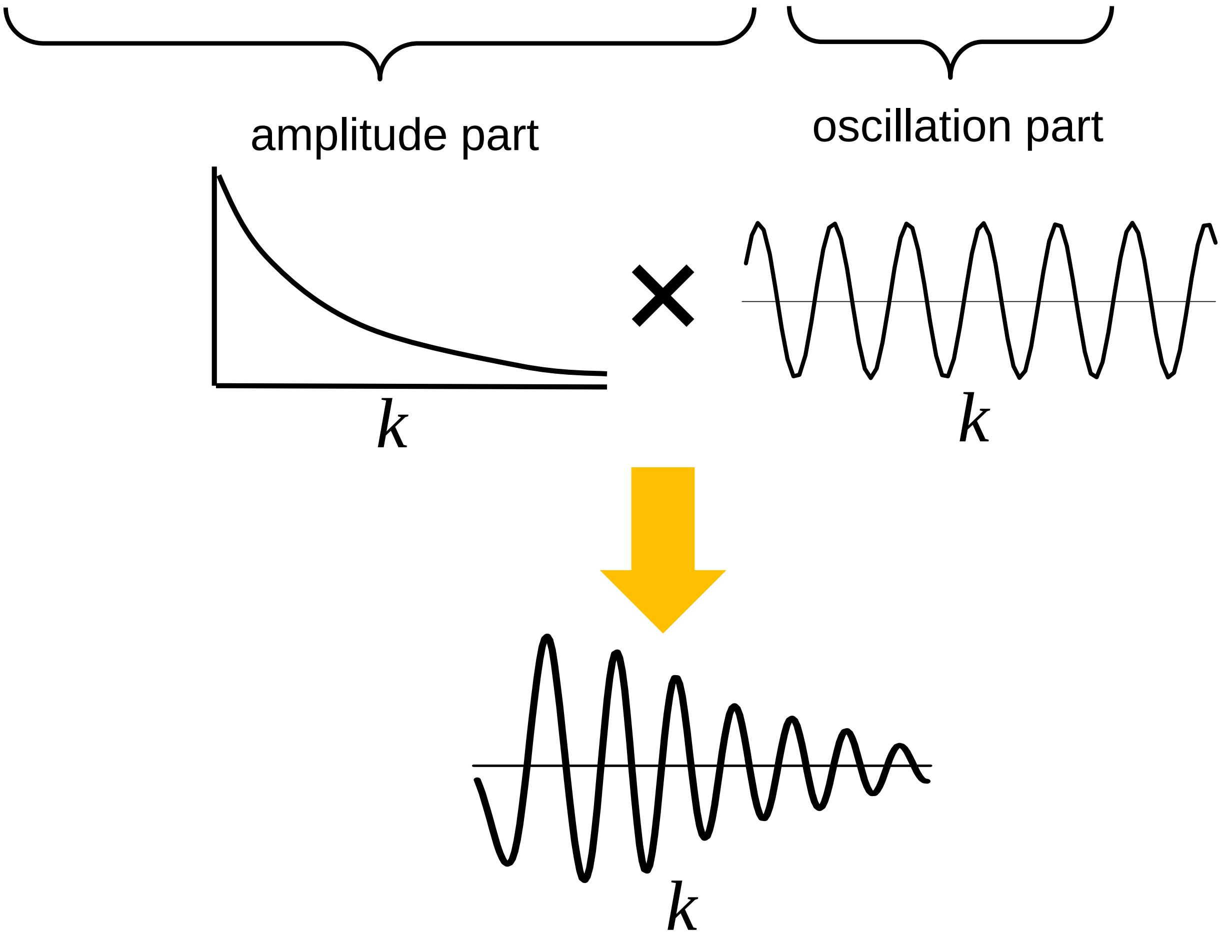
$$\chi(k) = -\sum_{\mathrm{i}} \frac{N_{\mathrm{i}}}{k\, r_{\mathrm{i}}^{2}} f_{\mathrm{i}}(k) \exp(-2\sigma_{\mathrm{i}}^{2} k^{2} - 2r_{\mathrm{i}}/\lambda) S_0^2(k) \sin(2kr_{\mathrm{i}} + \phi_{\mathrm{i}}(k))$$

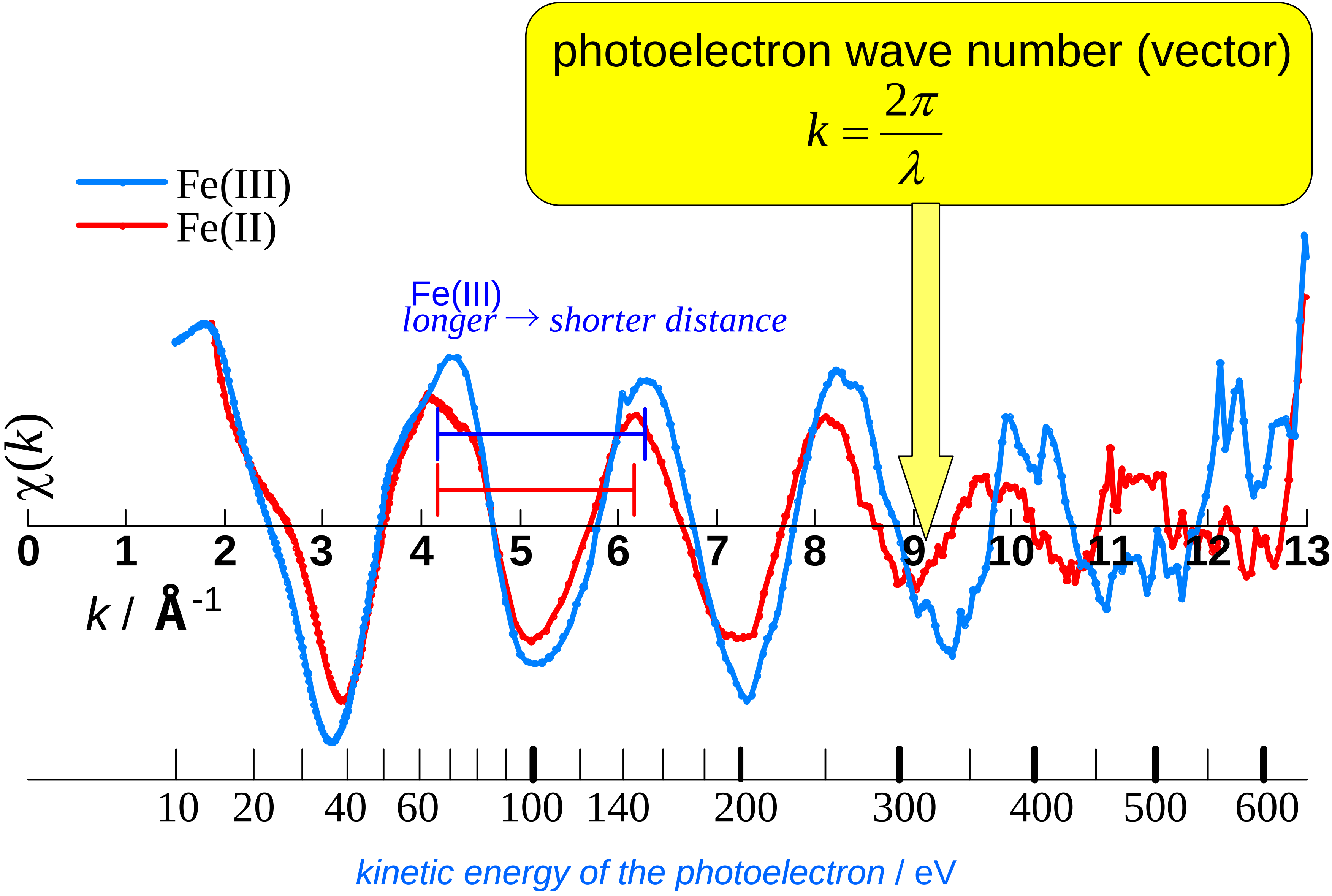


Fe(III) ion in water
H2O
Fe
r(Fe-O)=2.01 Å
3
2
1
0
E0
6800
7000
7200
7400
7600
7800
X-ray photon energy / eV
0
200
400
600
photoelectron kinetic energy / eV
2
1.3
1
0.8
0.7
0.6
0.5
photoelectron wave length / Å

BASIC EXAFS equation

$$\chi(k) = -\sum_{\mathrm{i}} \frac{N_{\mathrm{i}}}{k\, r_{\mathrm{i}}^{2}} f_{\mathrm{i}}(k) \exp(-2\sigma_{\mathrm{i}}^{2} k^{2} - 2r_{\mathrm{i}}/\lambda) \mathrm{S}_{0}^{2}(k) \sin(2kr_{\mathrm{i}} + \phi_{\mathrm{i}}(k))$$





photoelectron wave number (vector)
$k = \frac{2\pi}{\lambda}$
Fe(III)
Fe(II)
Fe(III)
longer → shorter distance
$\chi(k)$
0 1 2 3 4 5 6 7 8 9 10 11 12 13
k / Å^{-1}
10 20 40 60 100 140 200 300 400 500 600
kinetic energy of the photoelectron / eV

BASIC EXAFS equation

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

k photoelectron wave number

N number of coordinating atoms

r distance between atoms A and B

f scattering amplitude

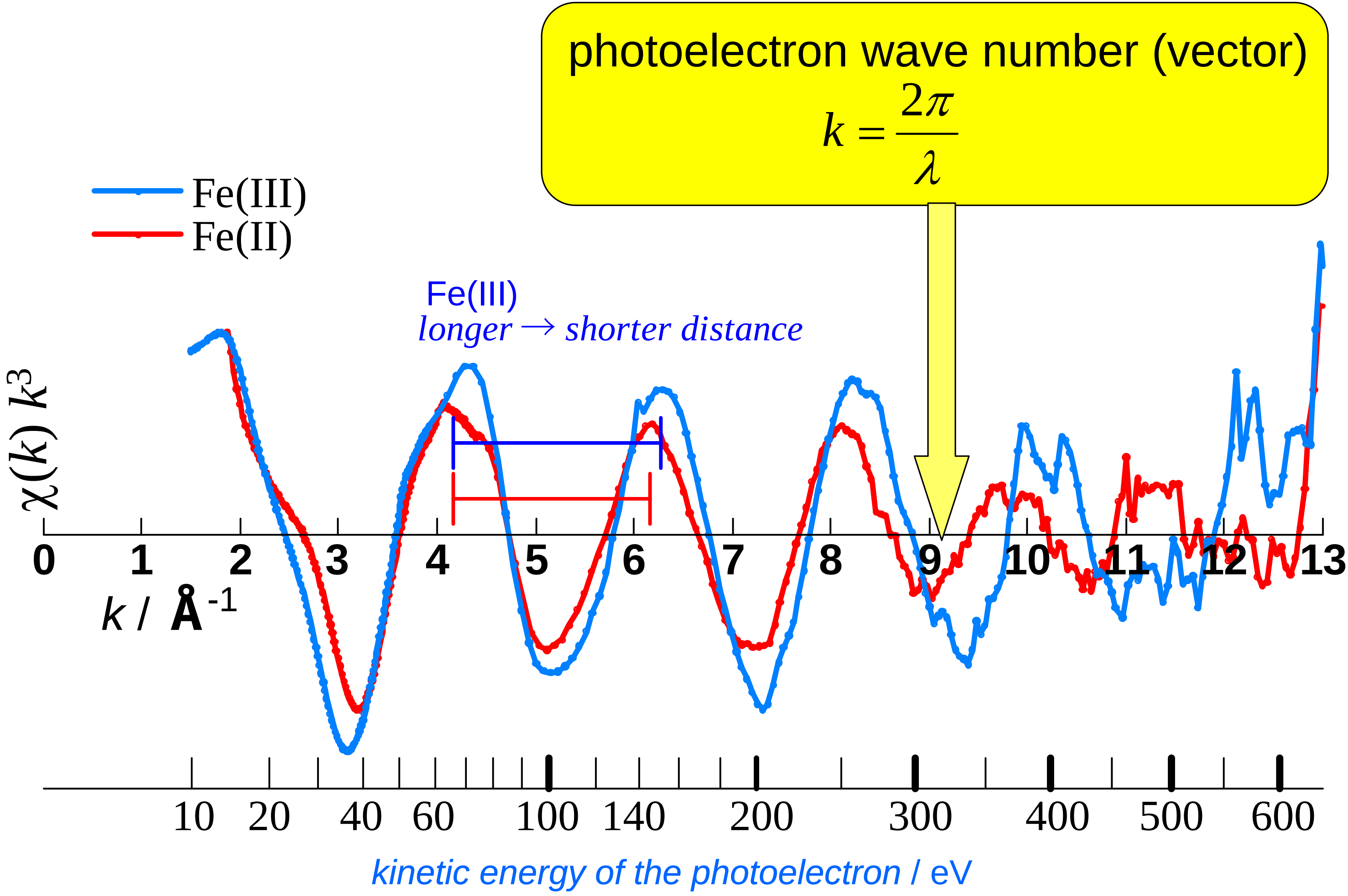
σ^2 mean squared displacement in r (Debye-Waller factor)

λ photoelectron mean path length

S_0^2 reduction factor

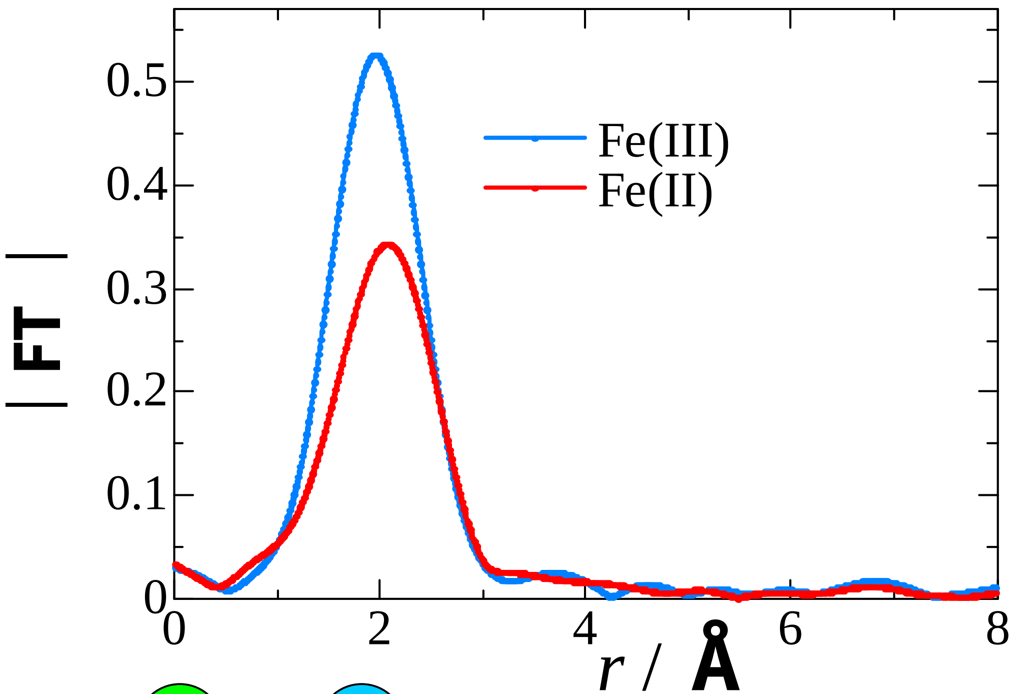
ϕ phase shift

Fourier Transform:
Simplest way to analyze the EXAFS oscillation



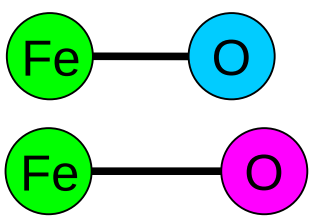
photoelectron wave number (vector)
$k = \frac{2\pi}{\lambda}$
Fe(III)
Fe(II)
Fe(III)
longer → shorter distance
$\chi(k)\, k^3$
0 1 2 3 4 5 6 7 8 9 10 11 12 13
k / Å^{-1}
10 20 40 60 100 140 200 300 400 500 600
kinetic energy of the photoelectron / eV

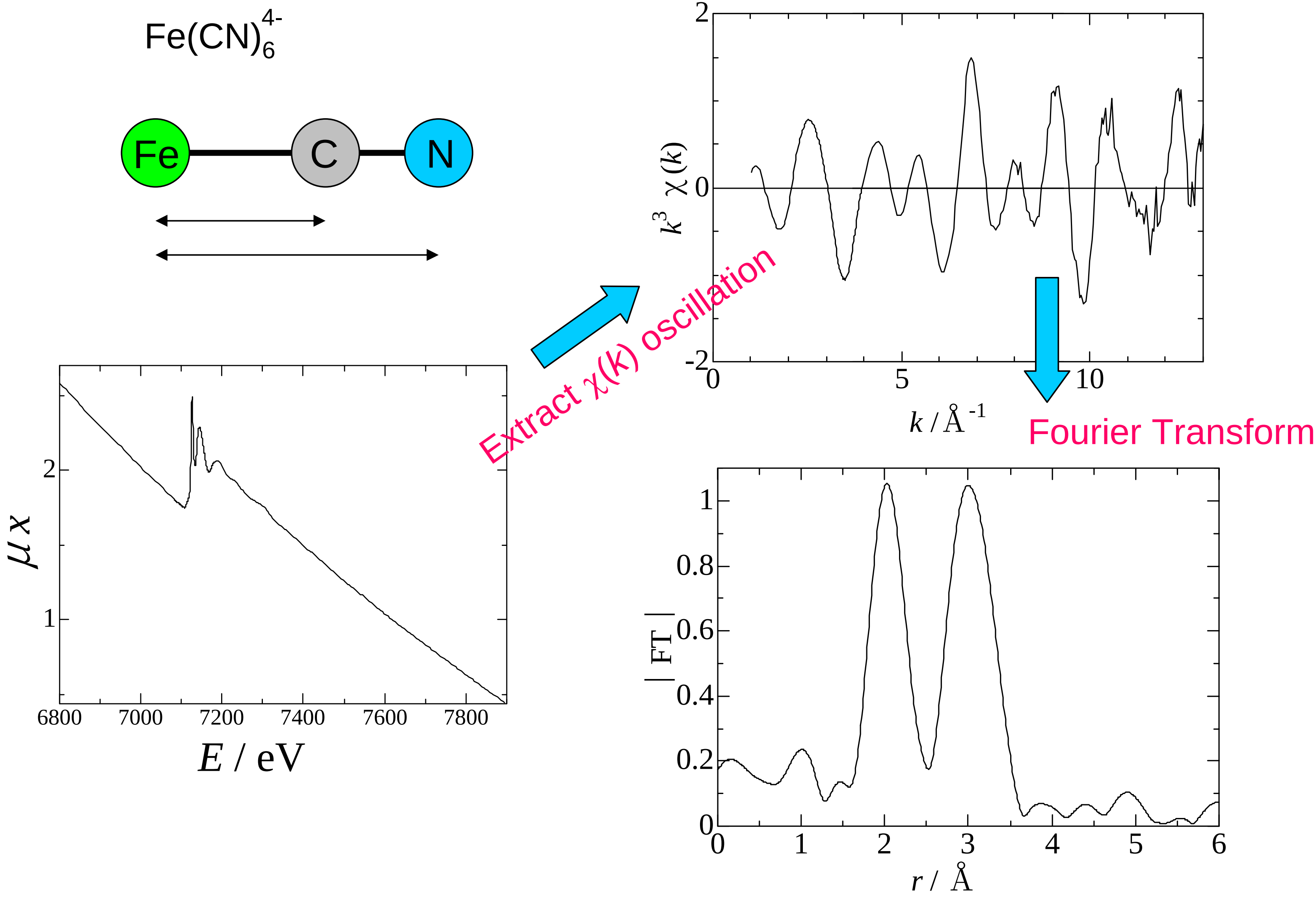
The simplest way of knowing the wave number (corresponding to the distance) is Fourier Transformation of wave on k



Fe(III) shoter

Fe(II) longer

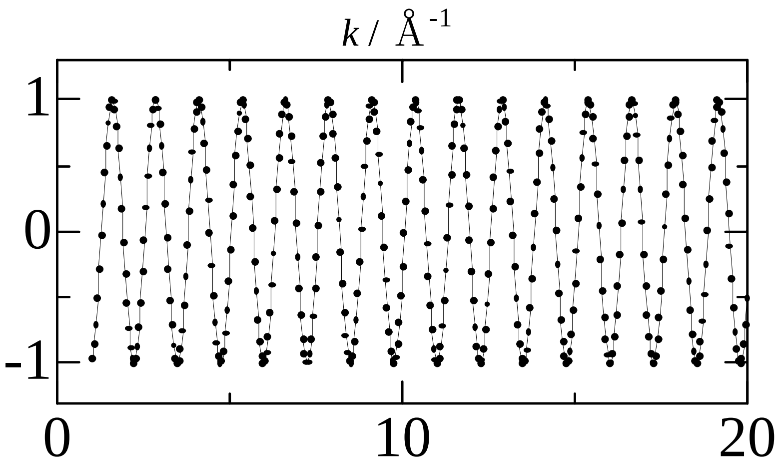


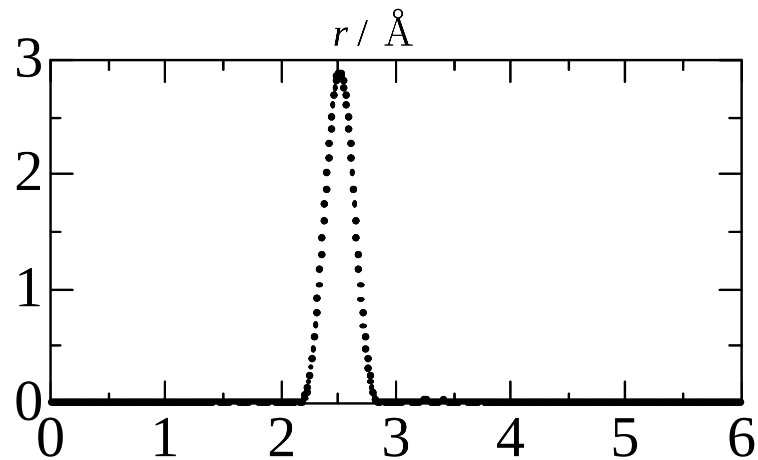


$Fe(CN)_6^{4-}$
Fe
C
N
Extract χ(k) oscillation
Fourier Transform
μx
E / eV
6800
7000
7200
7400
7600
7800
1
2
k³ χ(k)
k / Å⁻¹
0
5
10
-2
0
2
|FT|
r / Å
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5
6

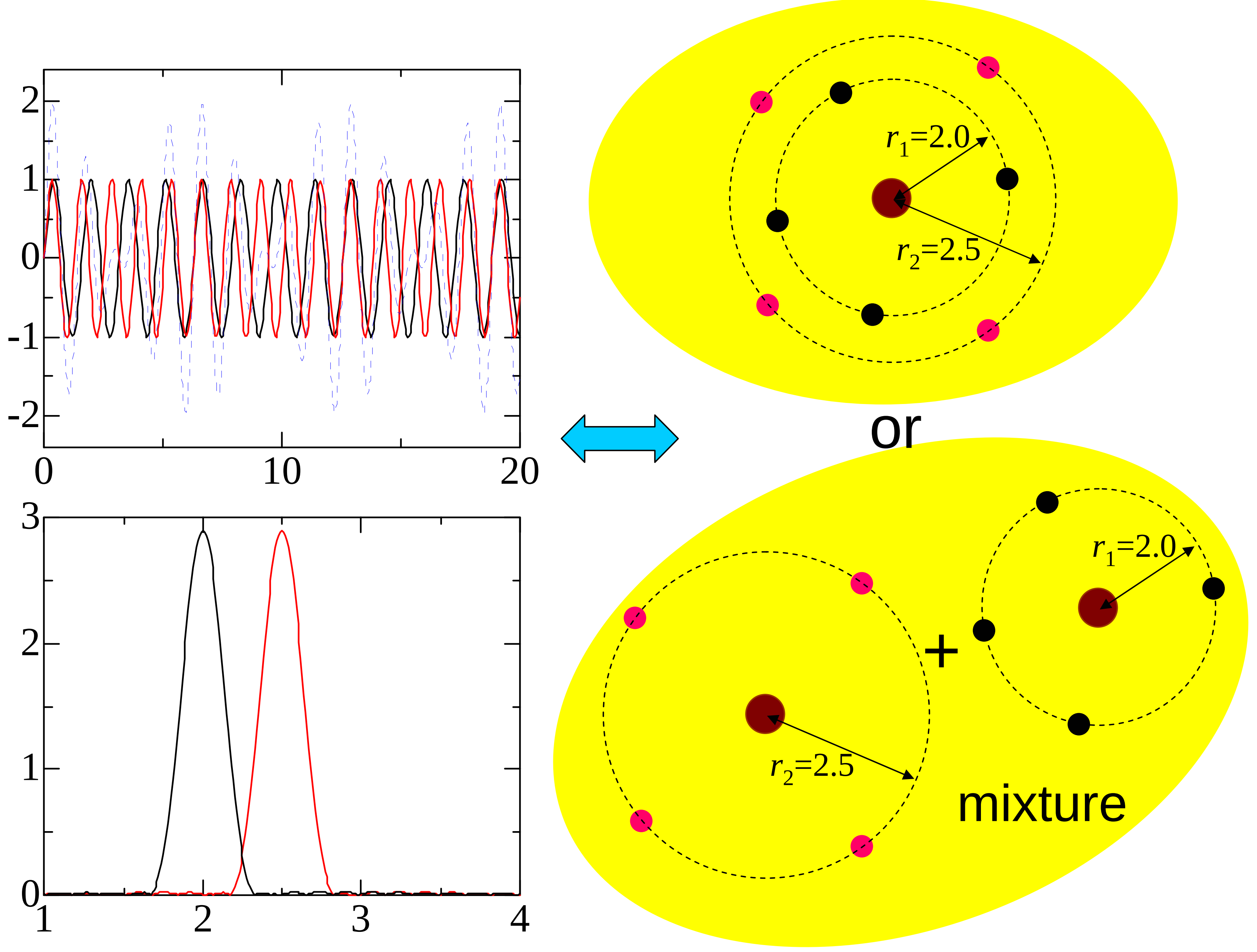
Fourier Transform (Frequency Filter)

will let you know the frequencies of the waves



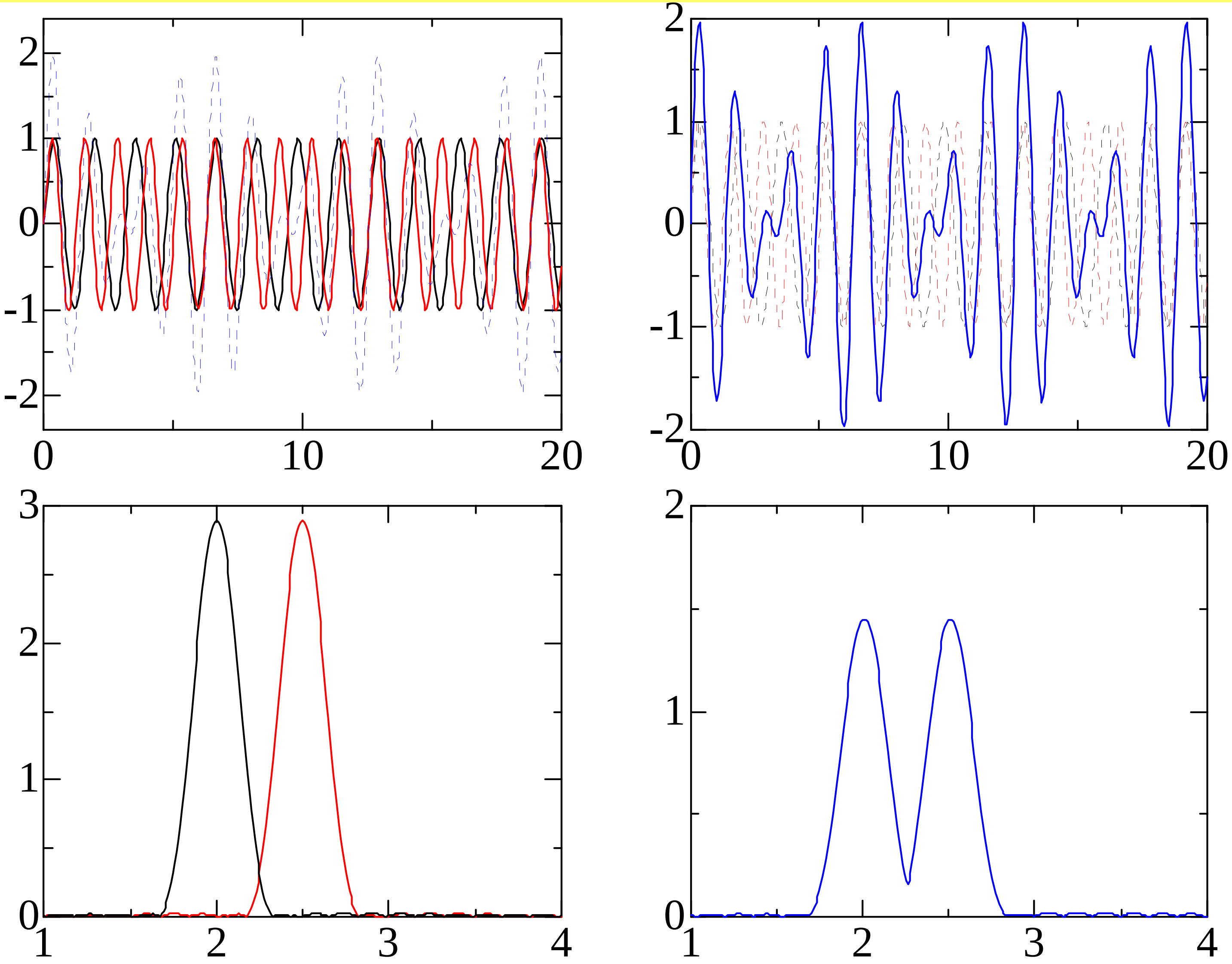


$$\sin(kr)$$

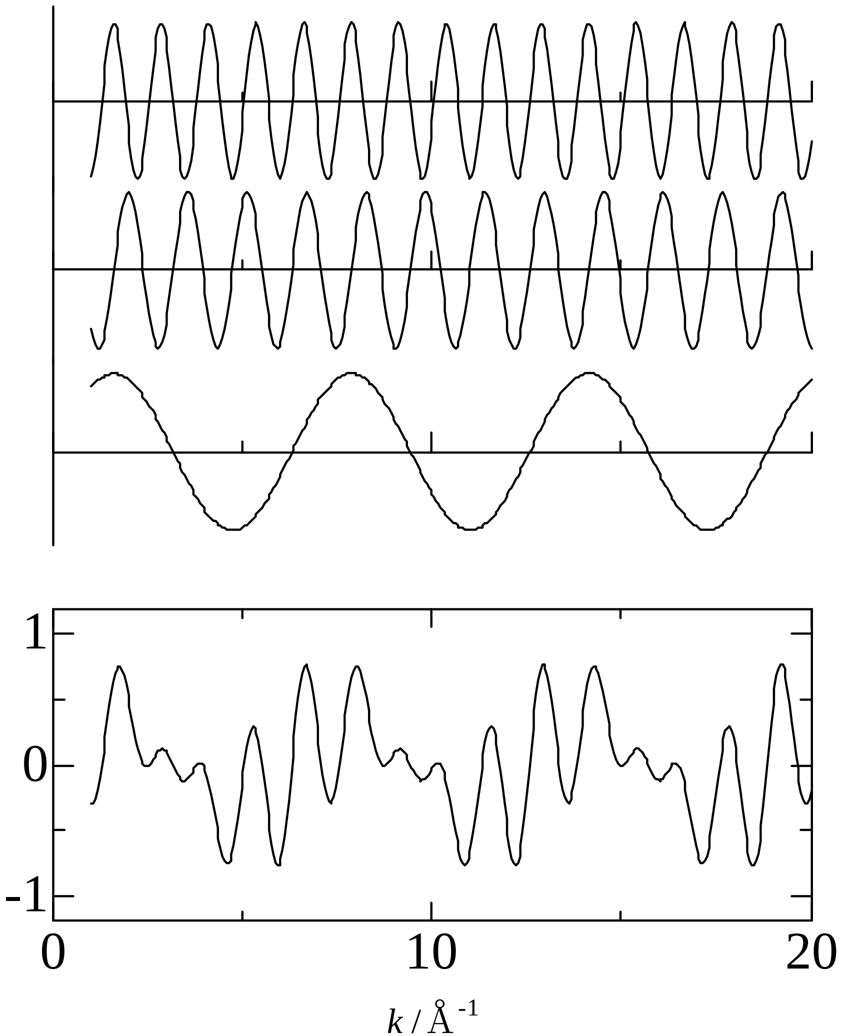


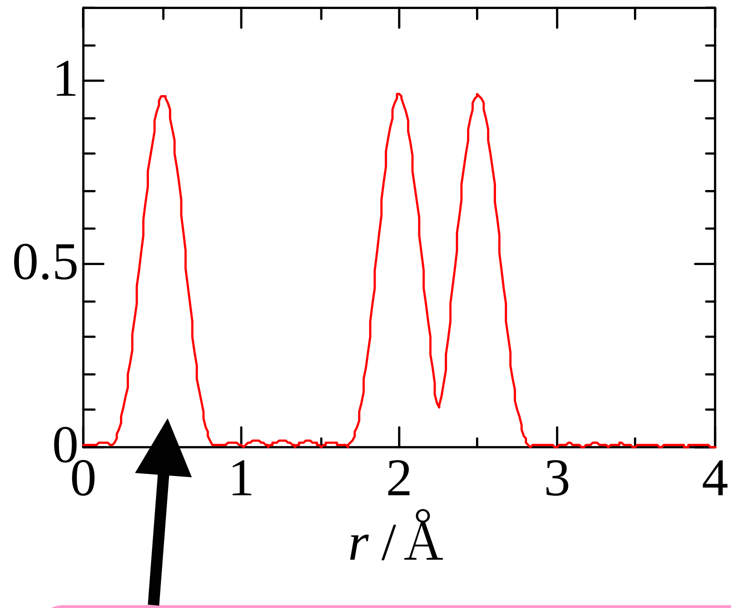
2
1
0
-1
-2
0
10
20
3
2
1
0
1
2
3
4
r1=2.0
r2=2.5
or
r1=2.0
r2=2.5
+
mixture

Fourier Transform for two-shell model

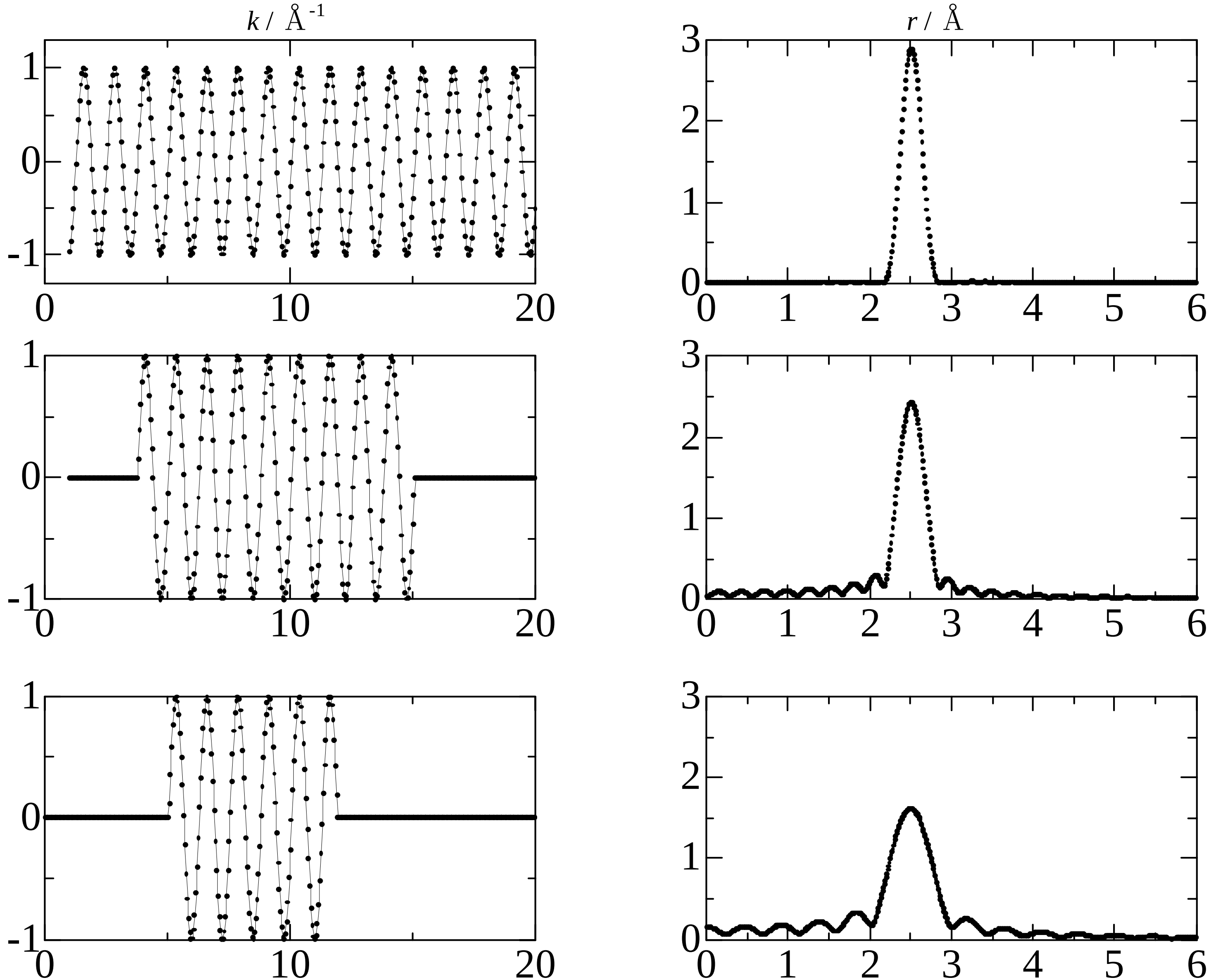


Fourier Transform for a three-shell model

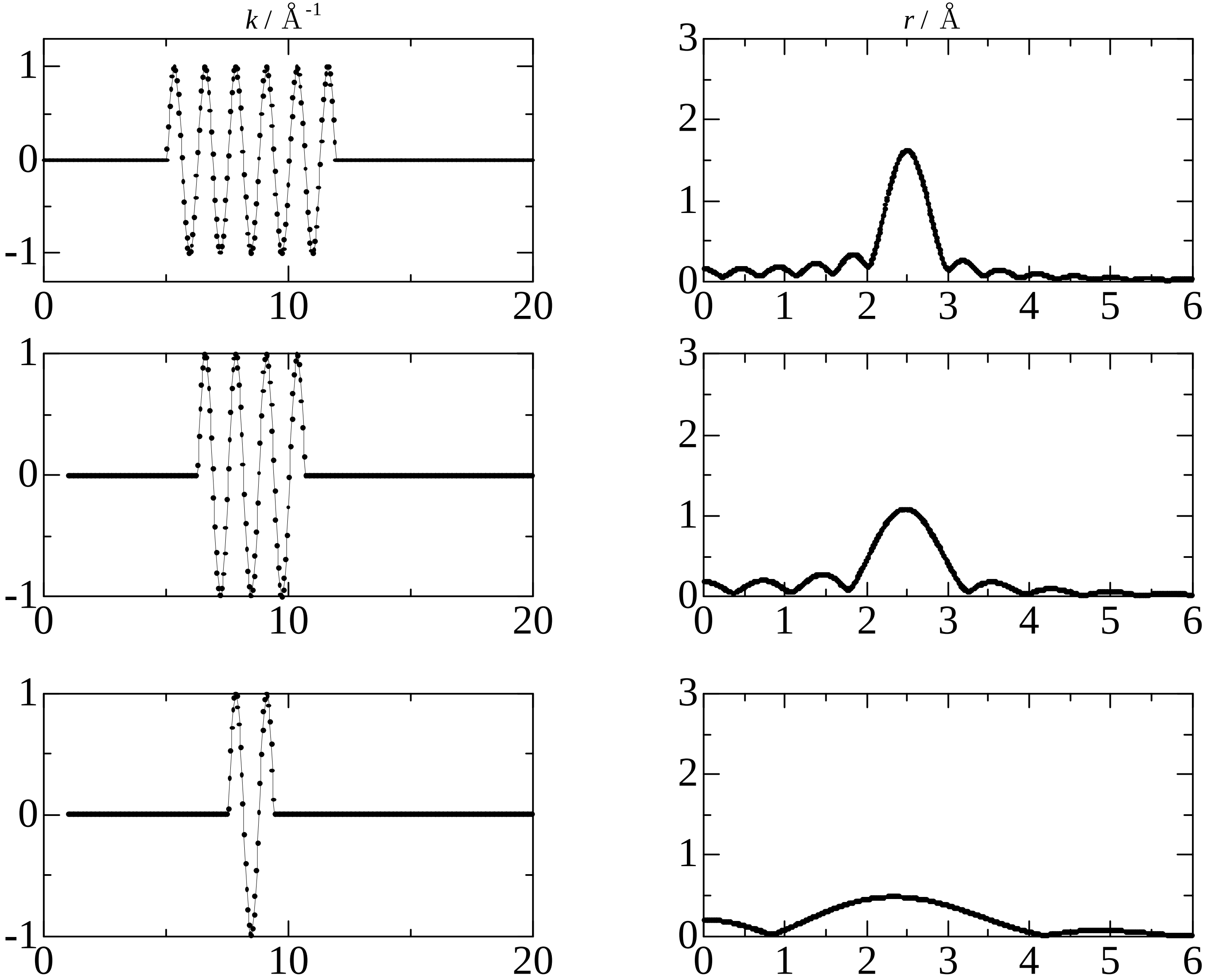




This must be a BACKGROUND structure, not corresponding to a real atom-atom distance.

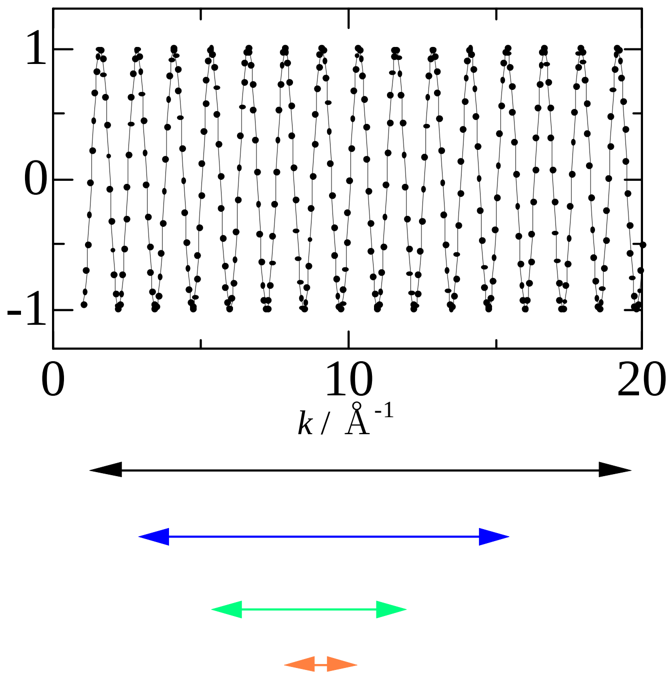


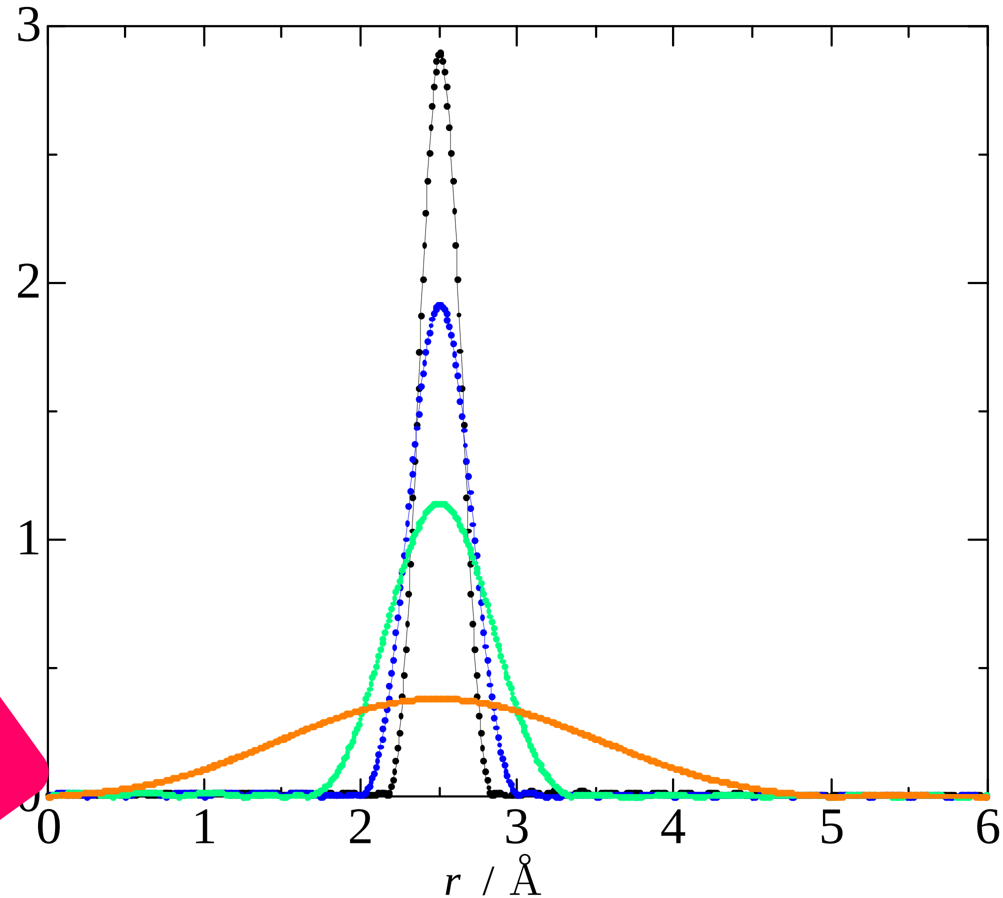
k / Å -1
r / Å
1
0
-1
0
10
20
3
2
1
0
0
1
2
3
4
5
6



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

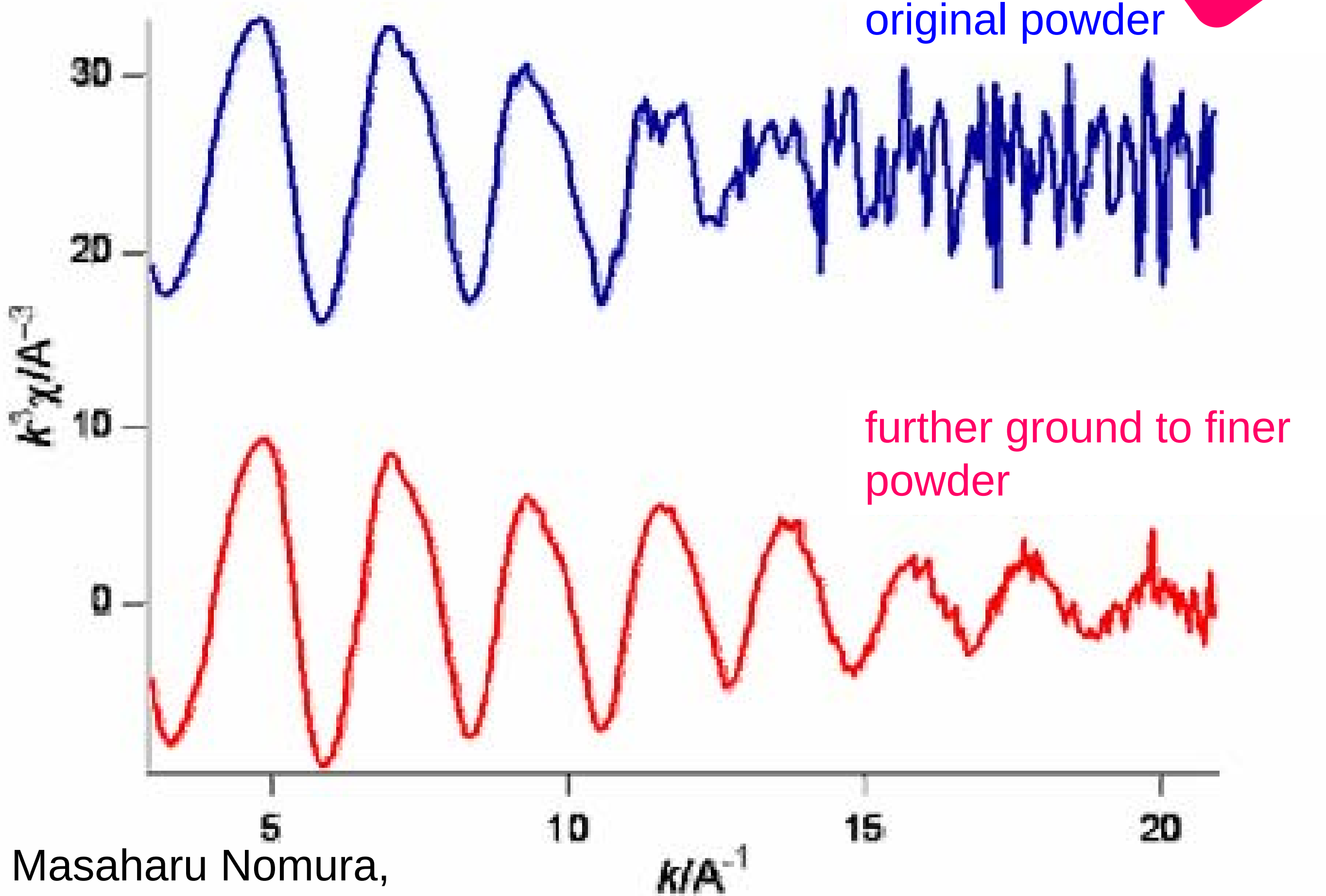
atomic type of coordination

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

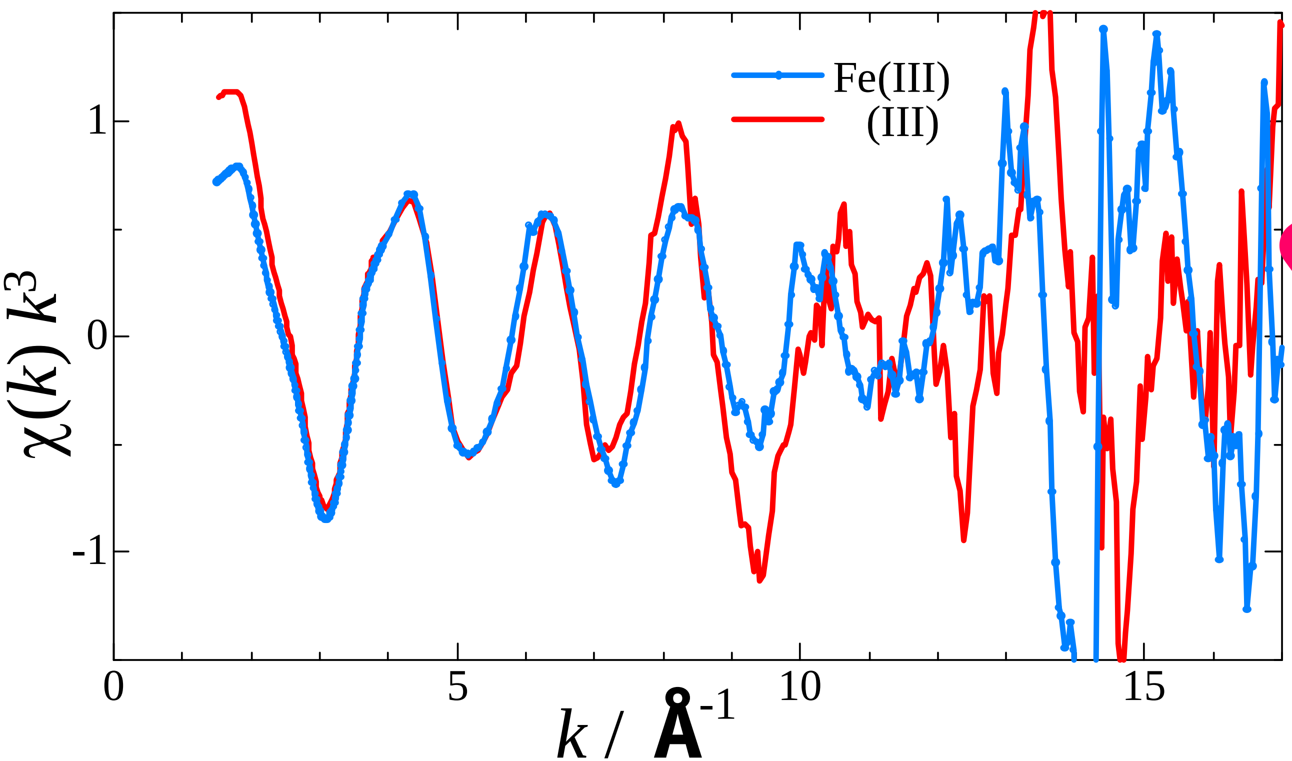
Transmission method

Problem !

Sample: Ge-Si powder



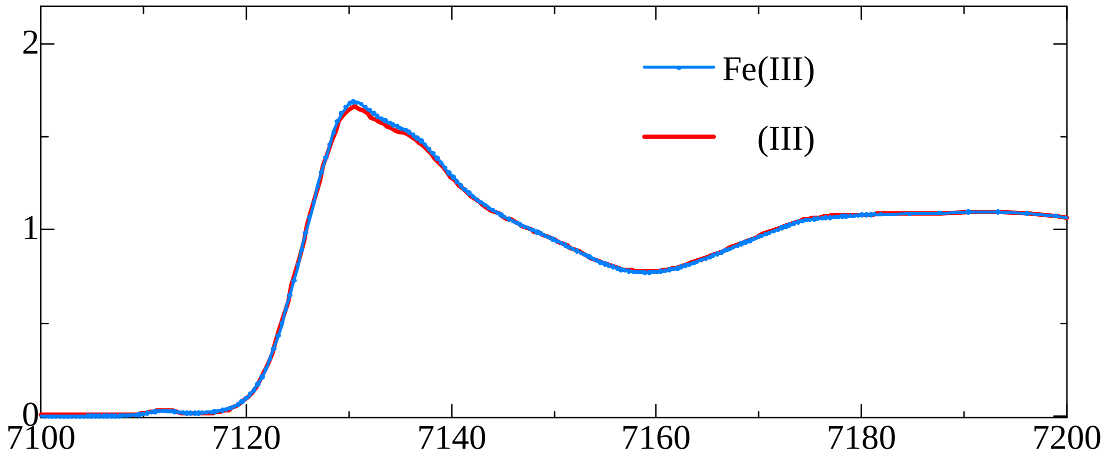
By Masaharu Nomura,
Photon Factory, KEK



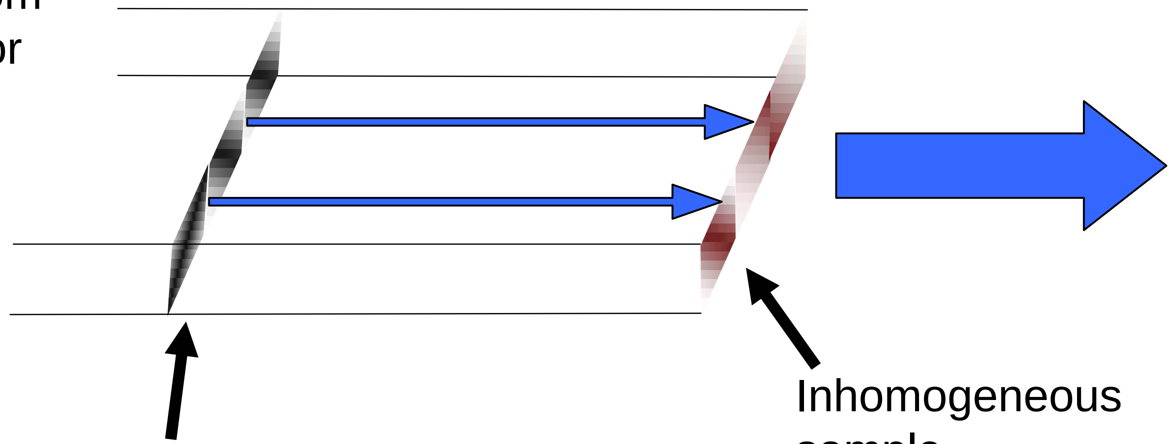
Problem !

Fe(III) ions in aqueous solution

possibly, inhomogeneous sample thickness



X-ray beam from monochromator

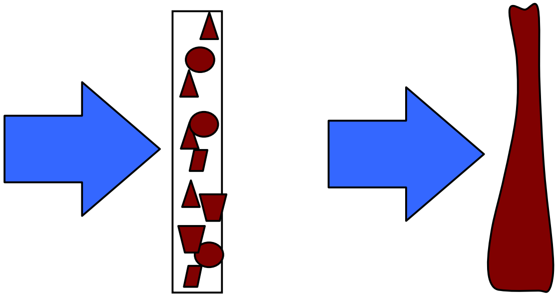


Inhomogeneous sample

X-ray flux is not homogeneous and the density pattern moves and changes along with the monochromator angle scan

solid powder

liquid or film



Leads to weaker EXAFS oscillation amplitude and noisy spectrum

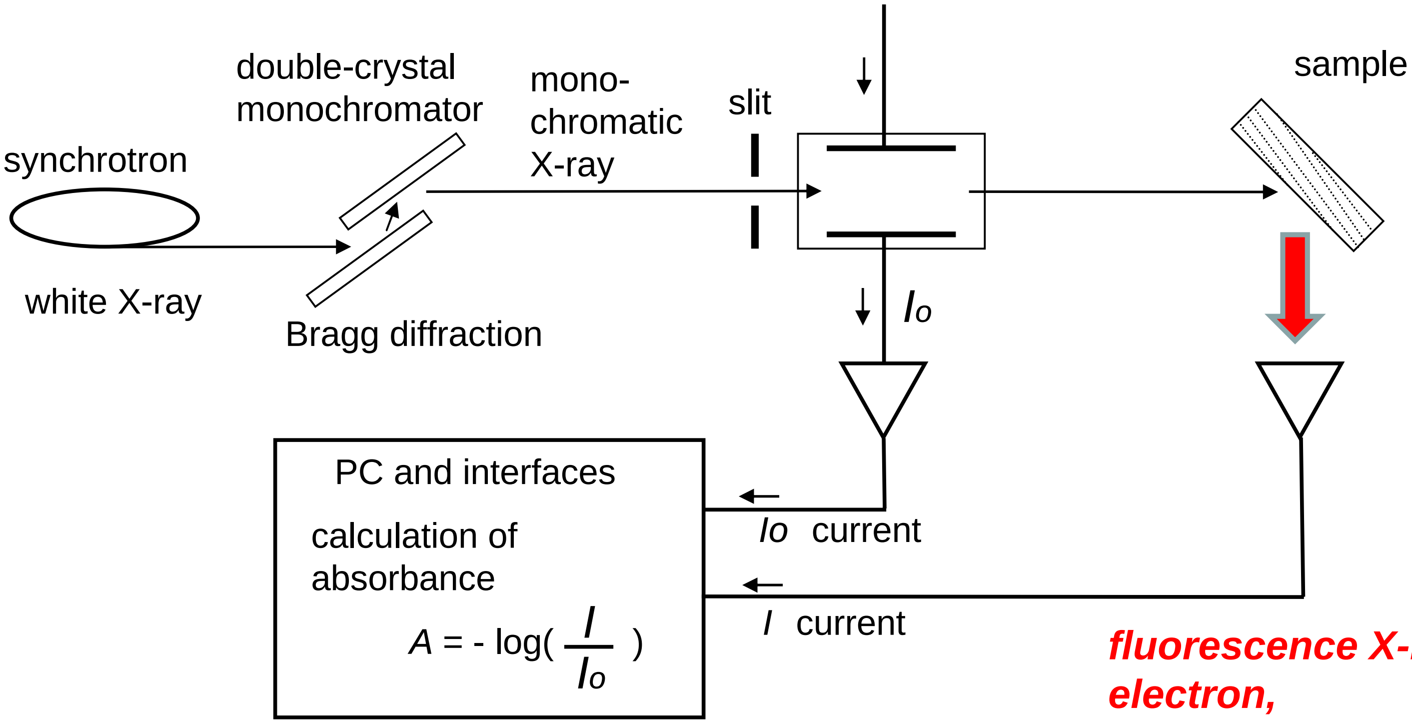
Yield methods:

Fluorescence yield

and

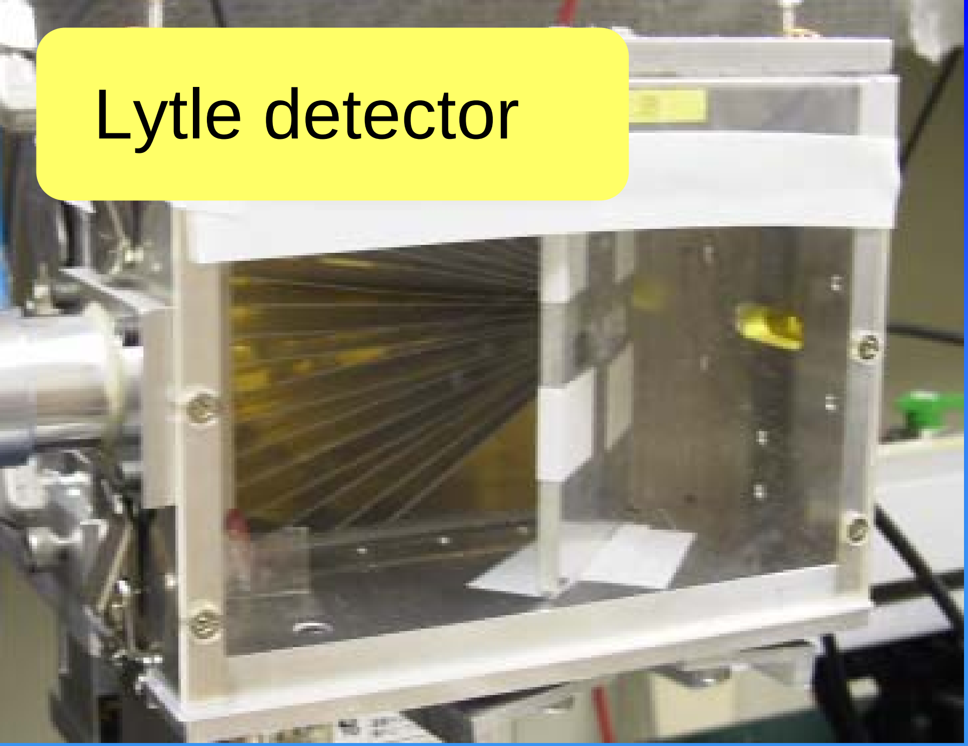
Total-conversion-electron-yield

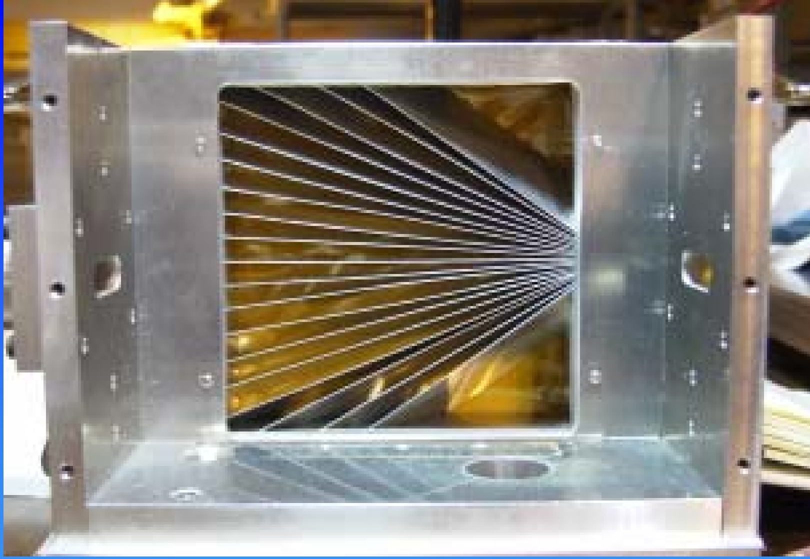
X-ray absorption measurement by yield methods



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

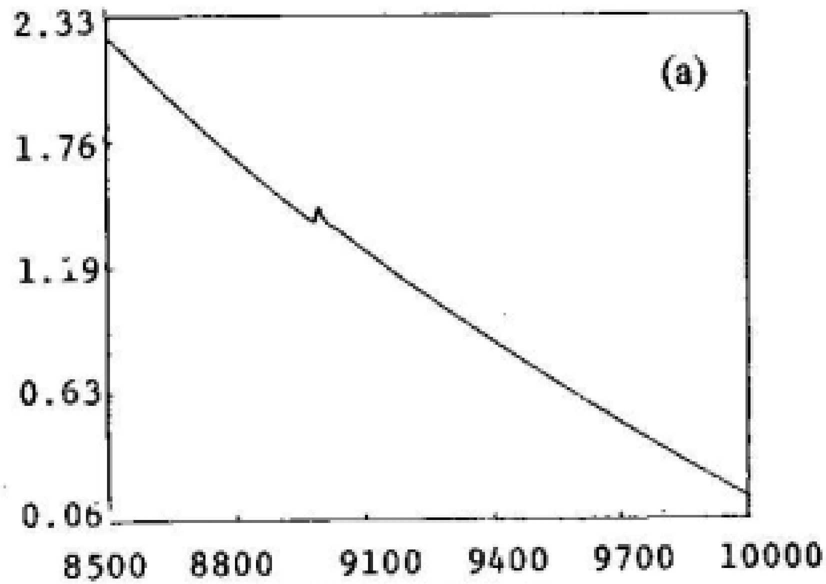
Lytle detector



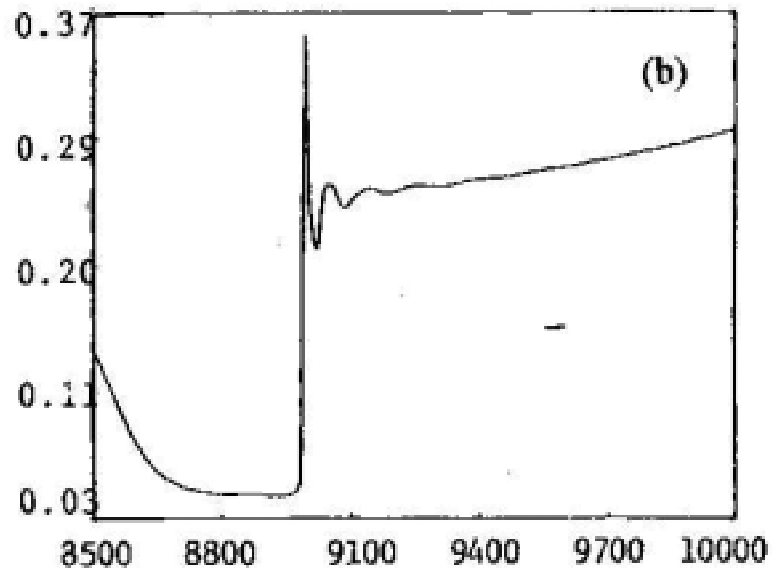


Sample: 0.01 mol dm^{-3} Cu(II) solution

transmittance



fluorescence



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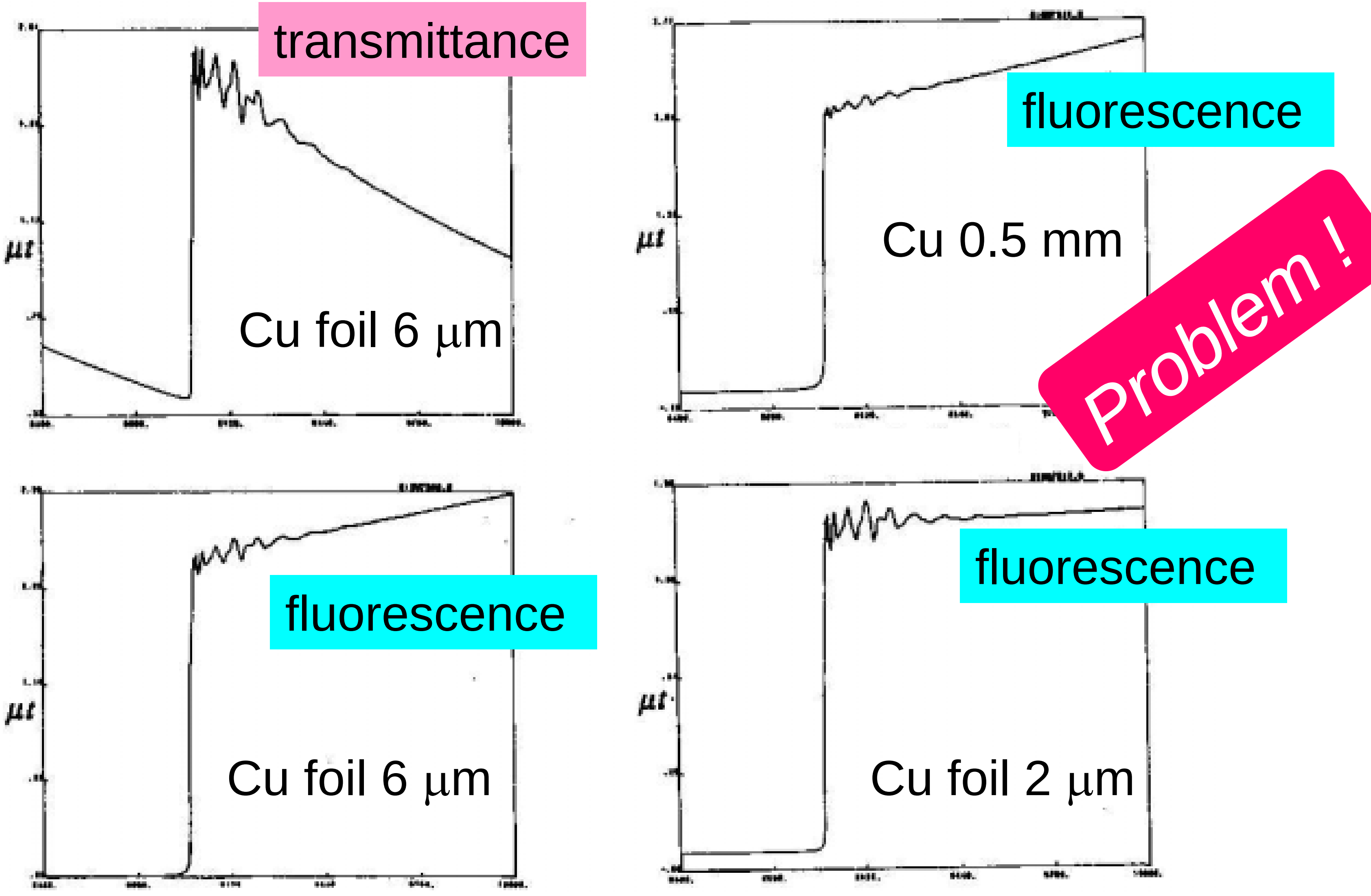

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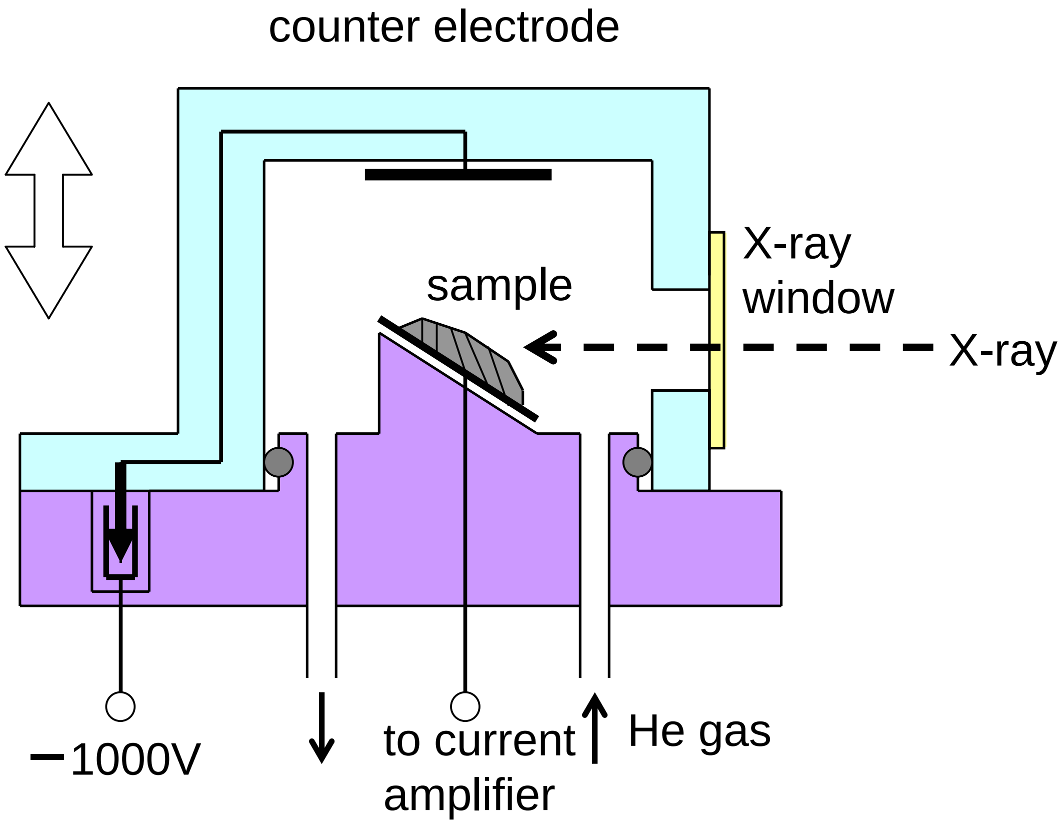
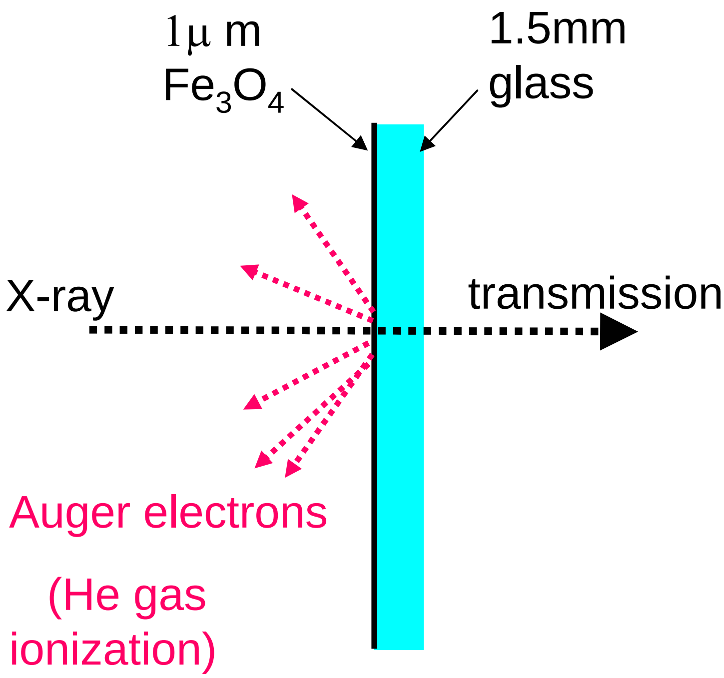
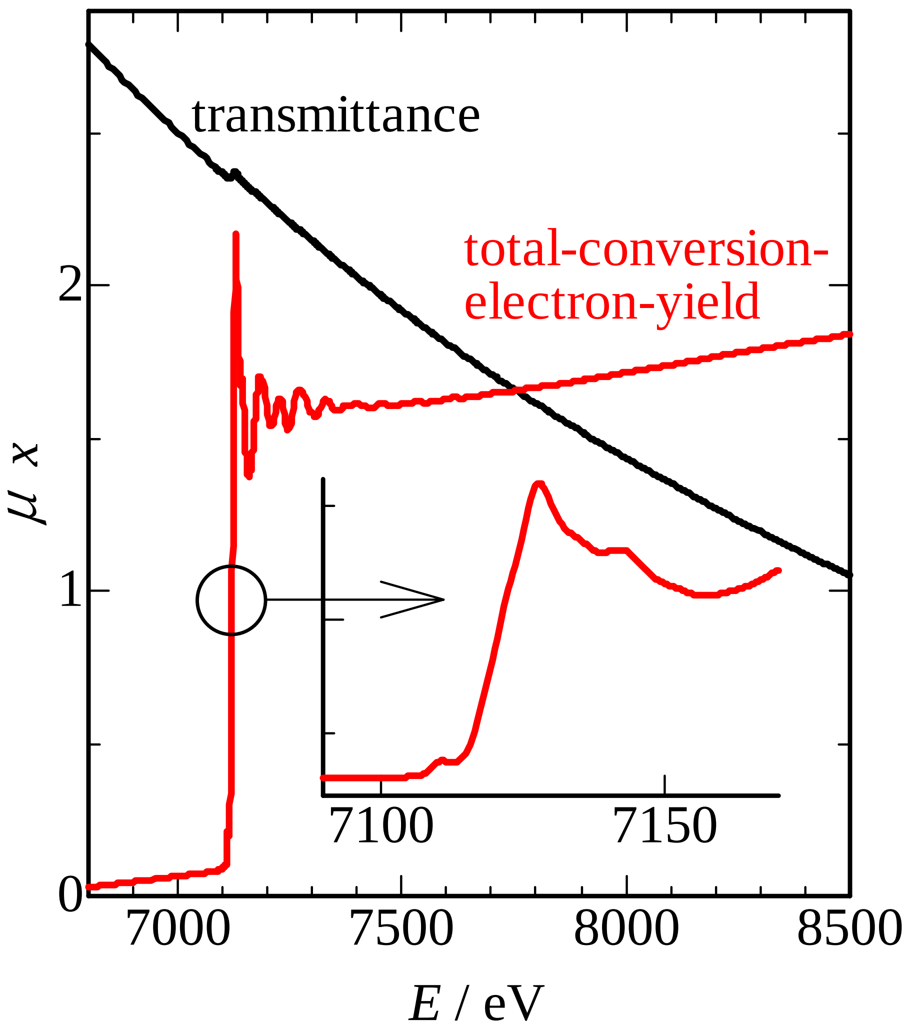
Self-absorption effect → incorrect *N*

Total-Conversion-Electron-Yield method

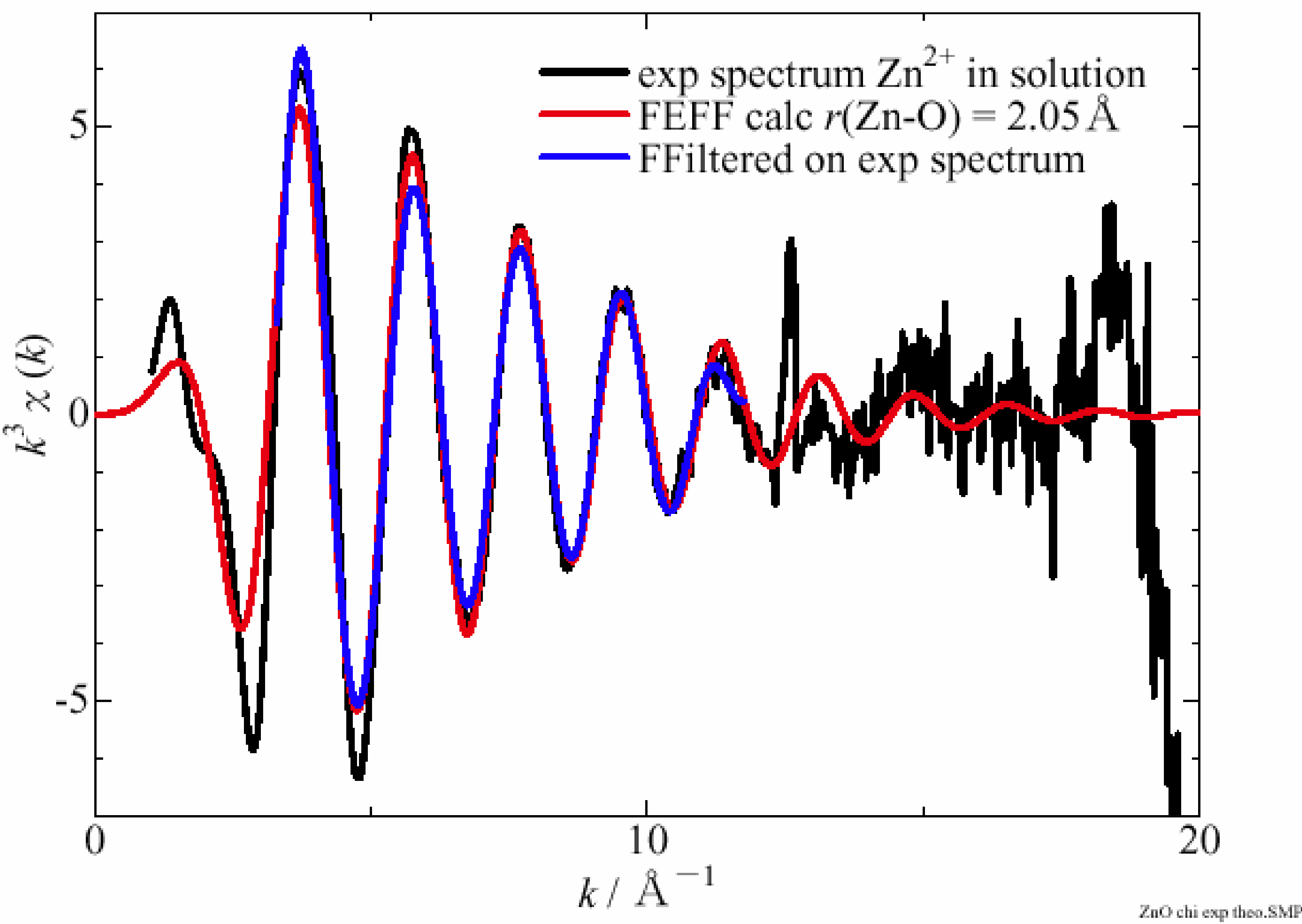




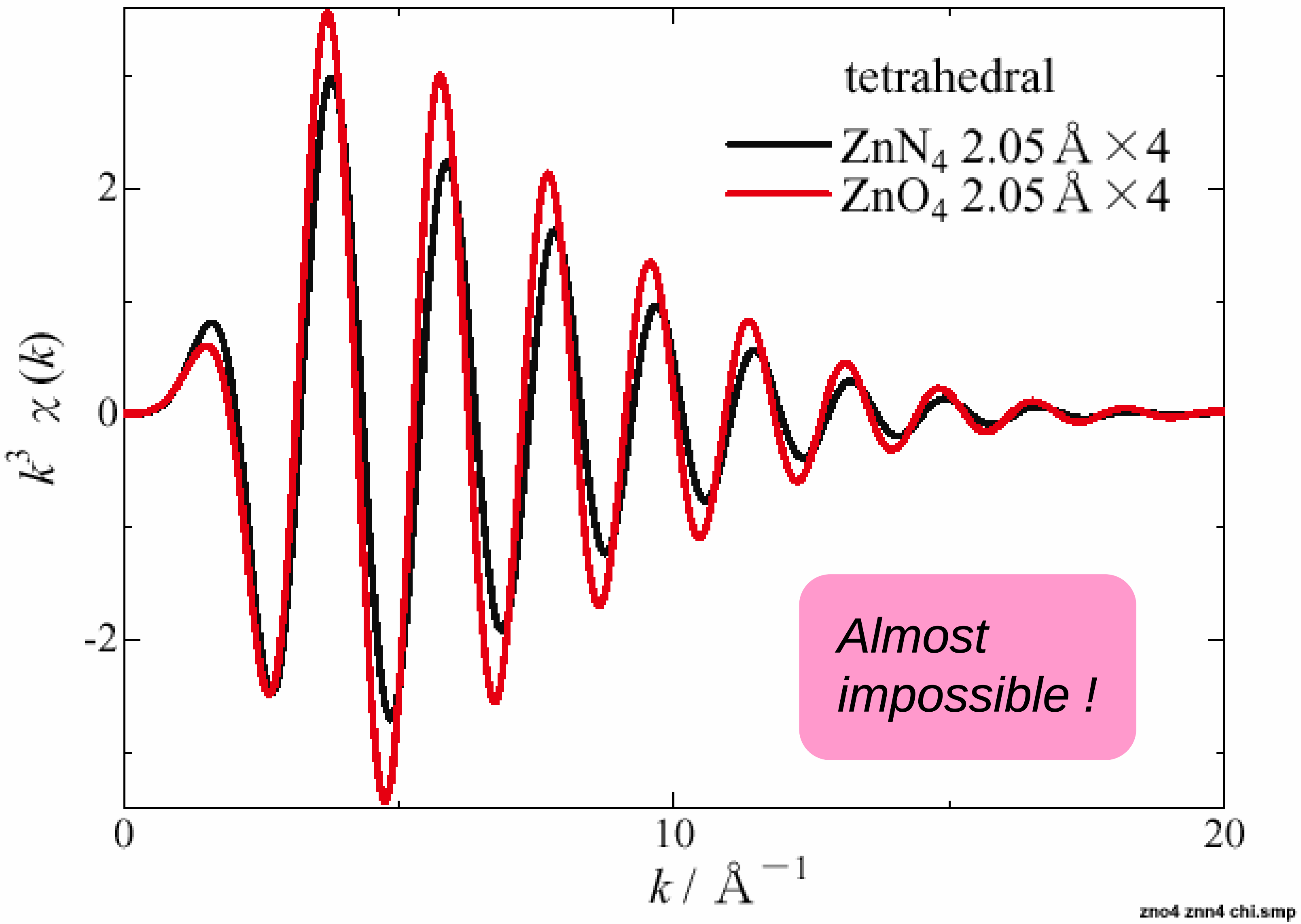


This method can be applied to thick samples owing to the short escape depth of Auger electron.

Can we distinguish oxygen from nitrogen by EXAFS?

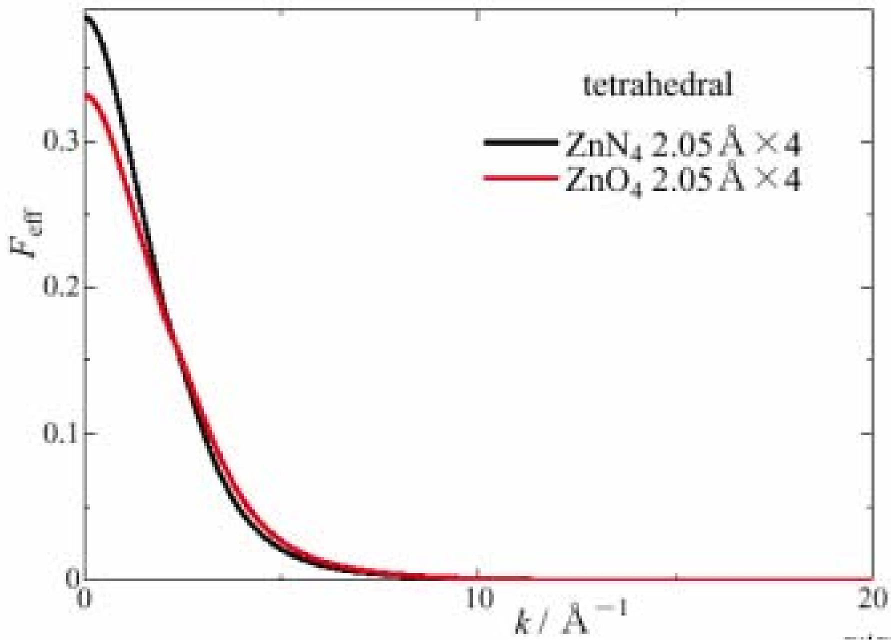


exp spectrum Zn2+ in solution
FEFF calc r(Zn-O) = 2.05 Å
FFiltered on exp spectrum
5
0
-5
k3 χ (k)
0
10
20
k / Å −1
ZnO chi exp theo.SMP

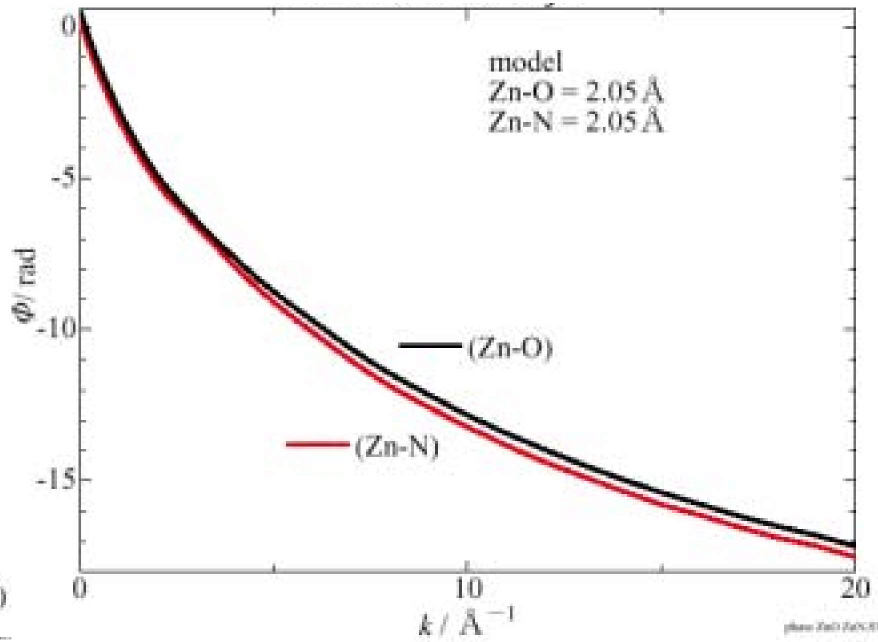


tetrahedral
ZnN_4 2.05 Å ×4
ZnO_4 2.05 Å ×4
Almost impossible !
$k^3\ \chi(k)$
2
0
-2
0
10
20
k / $Å^{-1}$
zno4 znn4 chi.smp

Scattering amplitude



Scattering phase shift



$$\chi(k) = -\sum_{\mathrm{i}} \frac{N_{\mathrm{i}}}{k\, r_{\mathrm{i}}^2} f_{\mathrm{i}}(k) \exp(-2\sigma_{\mathrm{i}}^2 k^2 - 2r_{\mathrm{i}}/\lambda) \mathrm{S}_0^2(k) \sin(2kr_{\mathrm{i}} + \phi_{\mathrm{i}}(k))$$

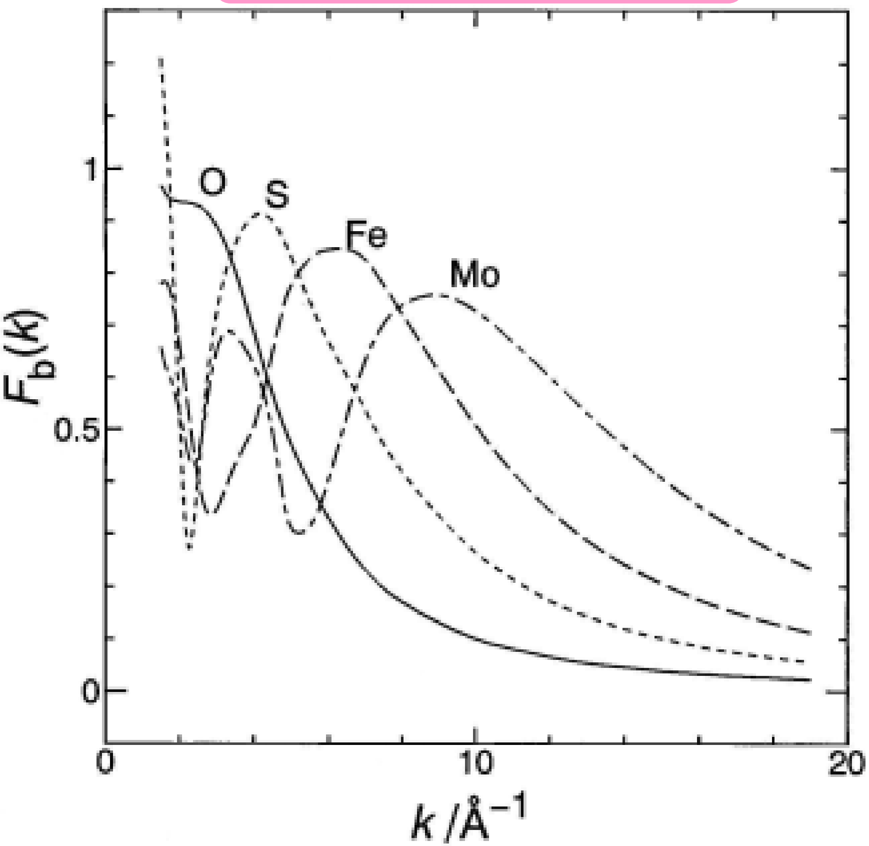
$$\chi(k) = -\sum_{i} \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

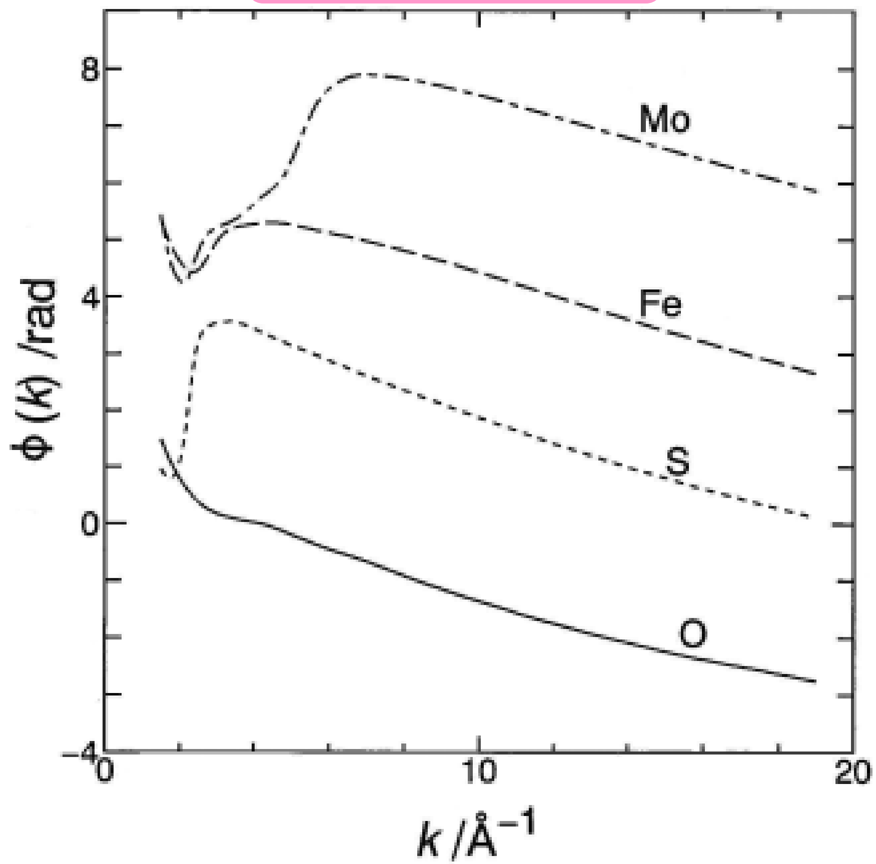
amplitude part

oscillation part

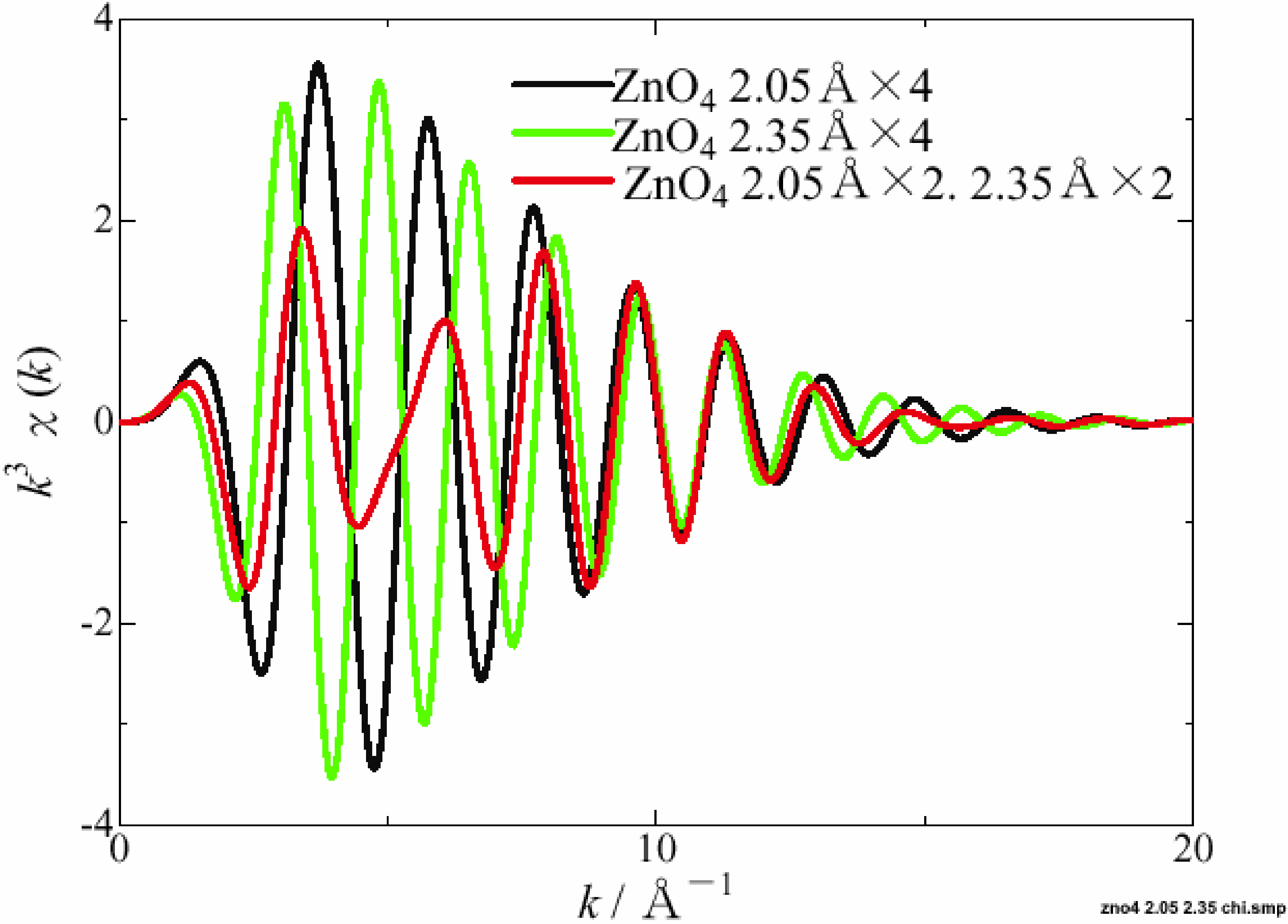
f scattering amplitude

ϕ phase shift



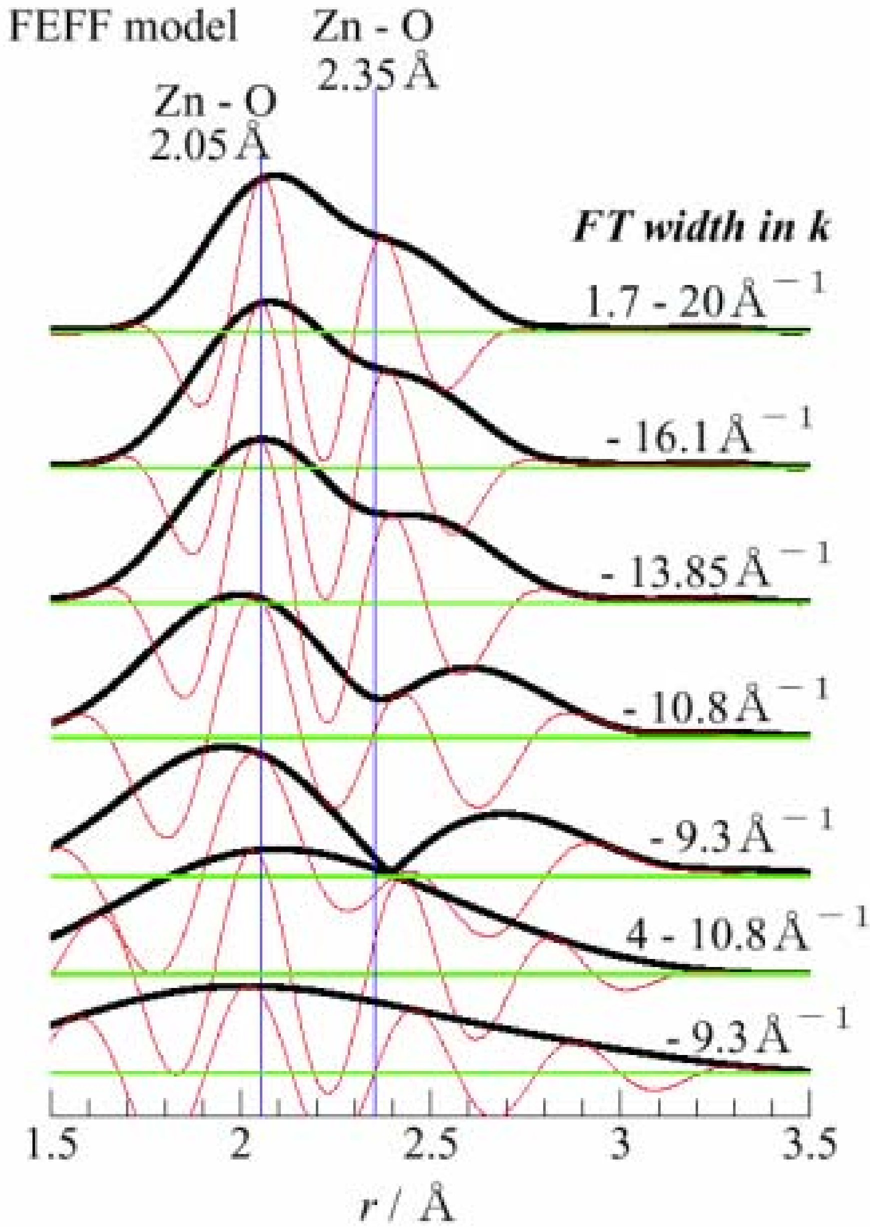


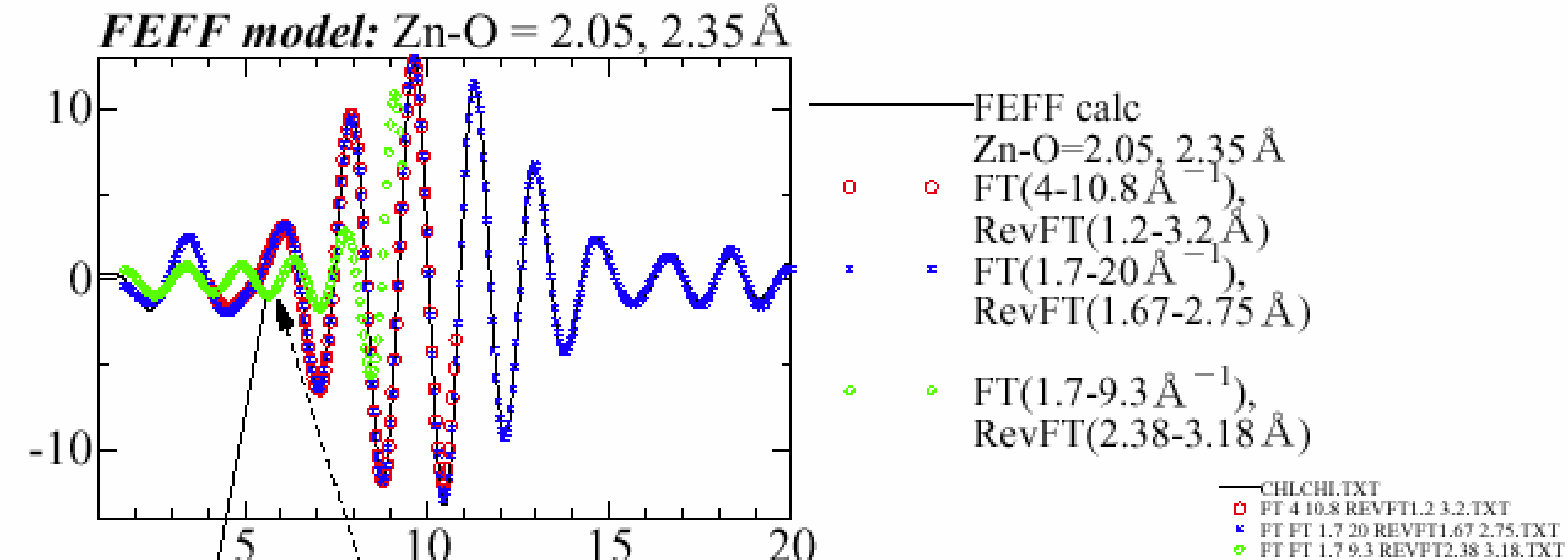
Can we distinguish oxygen atoms 15% distant from others by EXAFS?

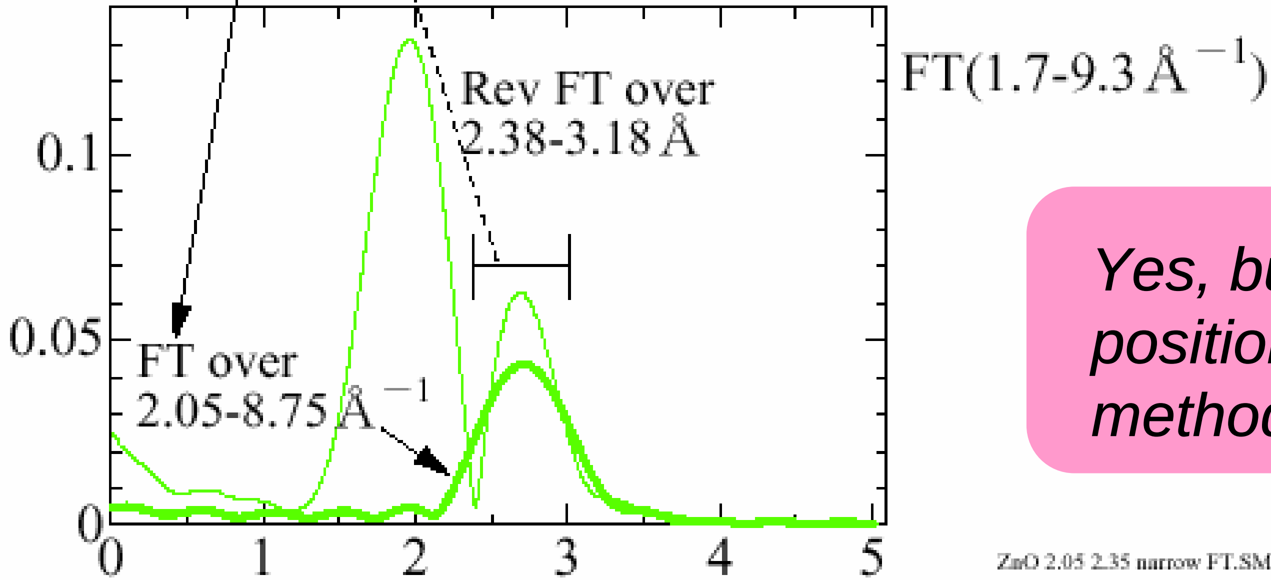


ZnO4 2.05 Å ×4
ZnO4 2.35 Å ×4
ZnO4 2.05 Å ×2. 2.35 Å ×2
4
2
0
-2
-4
0
10
20
k3 χ (k)
k / Å−1
zno4 2.05 2.35 chi.smp

Parameters used for Fourier Trans: O



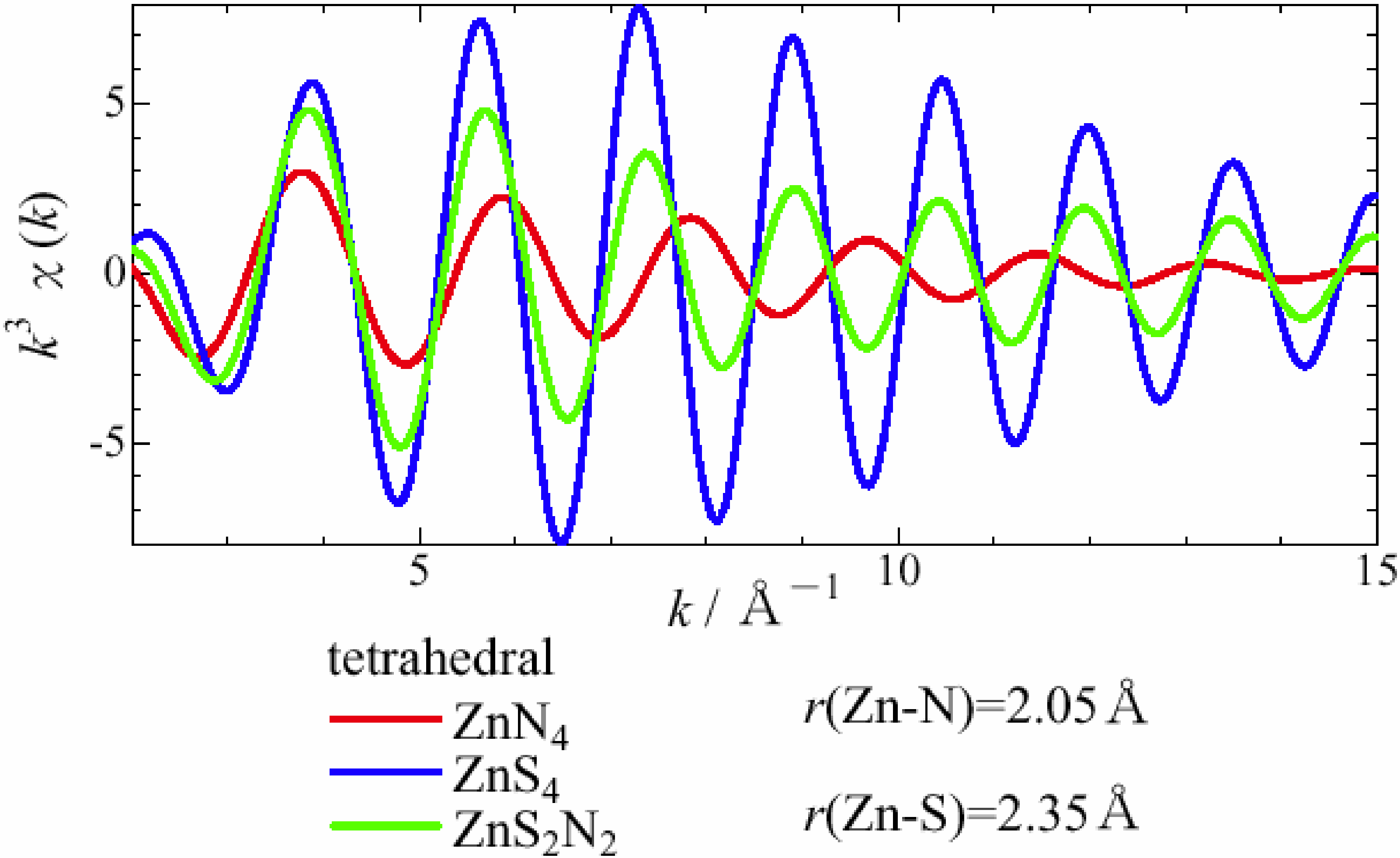




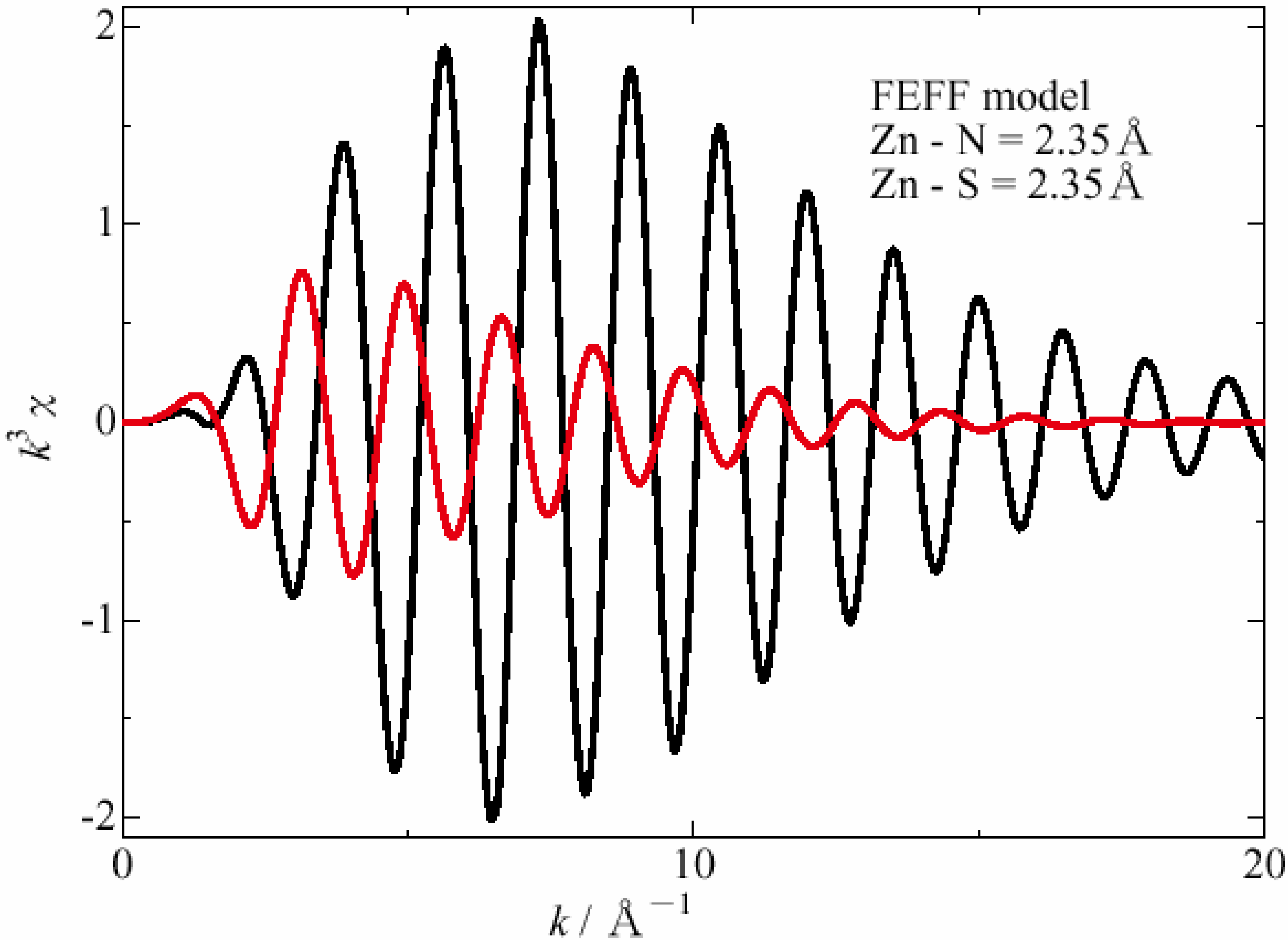
Yes, but at incorrect position by using FT method !

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

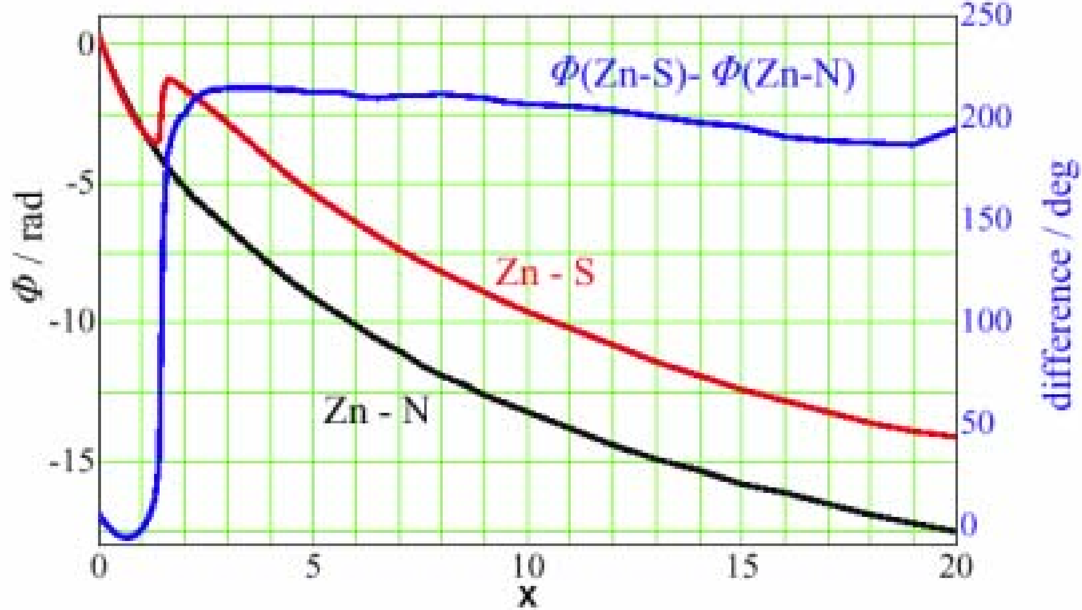
Can we distinguish sulfur from nitrogen (or oxygen) by EXAFS?

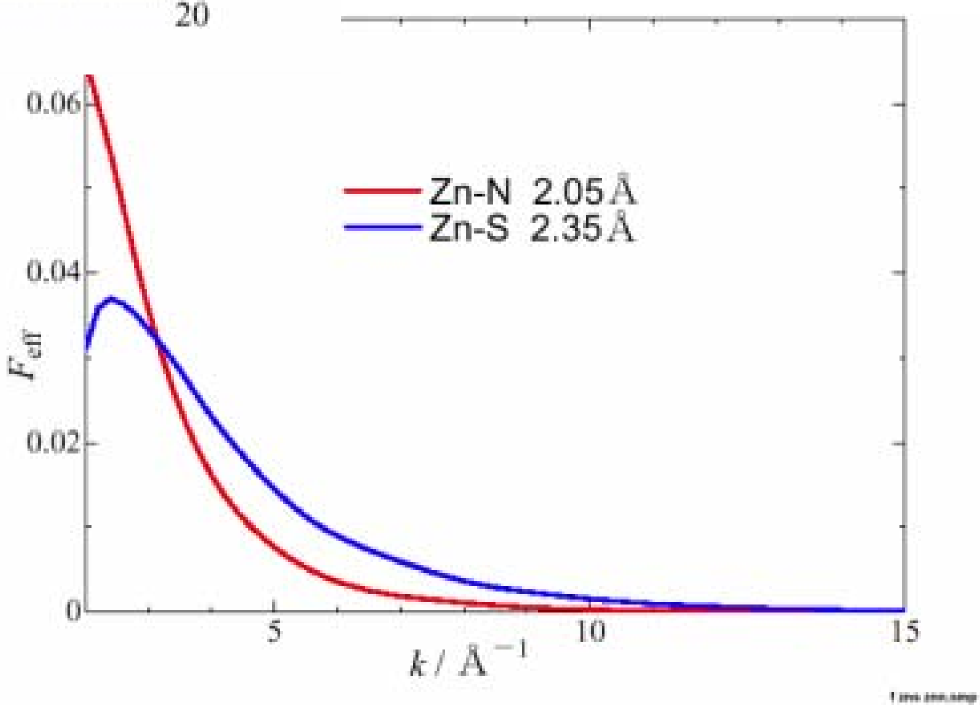


5
0
-5
$k^3\ \chi\ (k)$
5
10
15
k / Å^{-1}
tetrahedral
ZnN_4
ZnS_4
ZnS_2N_2
r(Zn-N)=2.05 Å
r(Zn-S)=2.35 Å

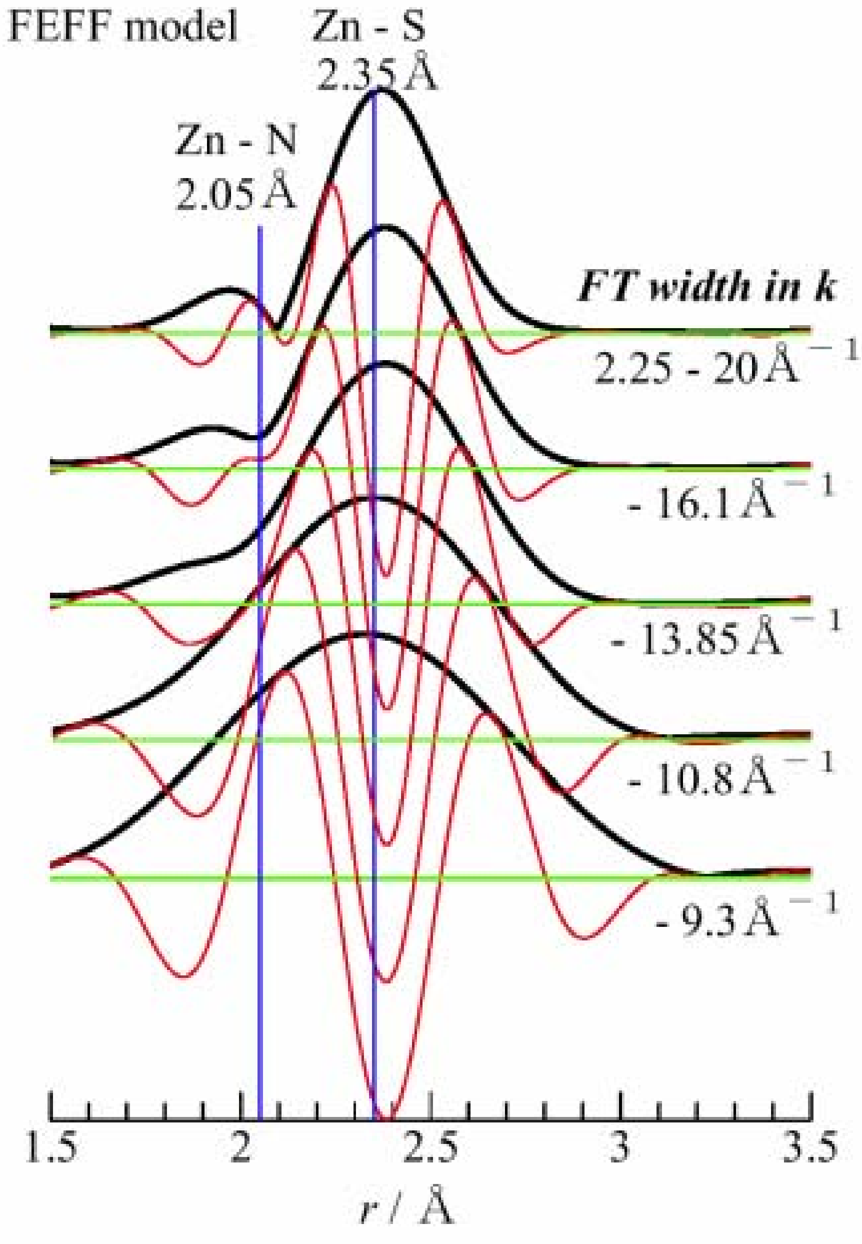


zns 2.35 znn 2.35.smp

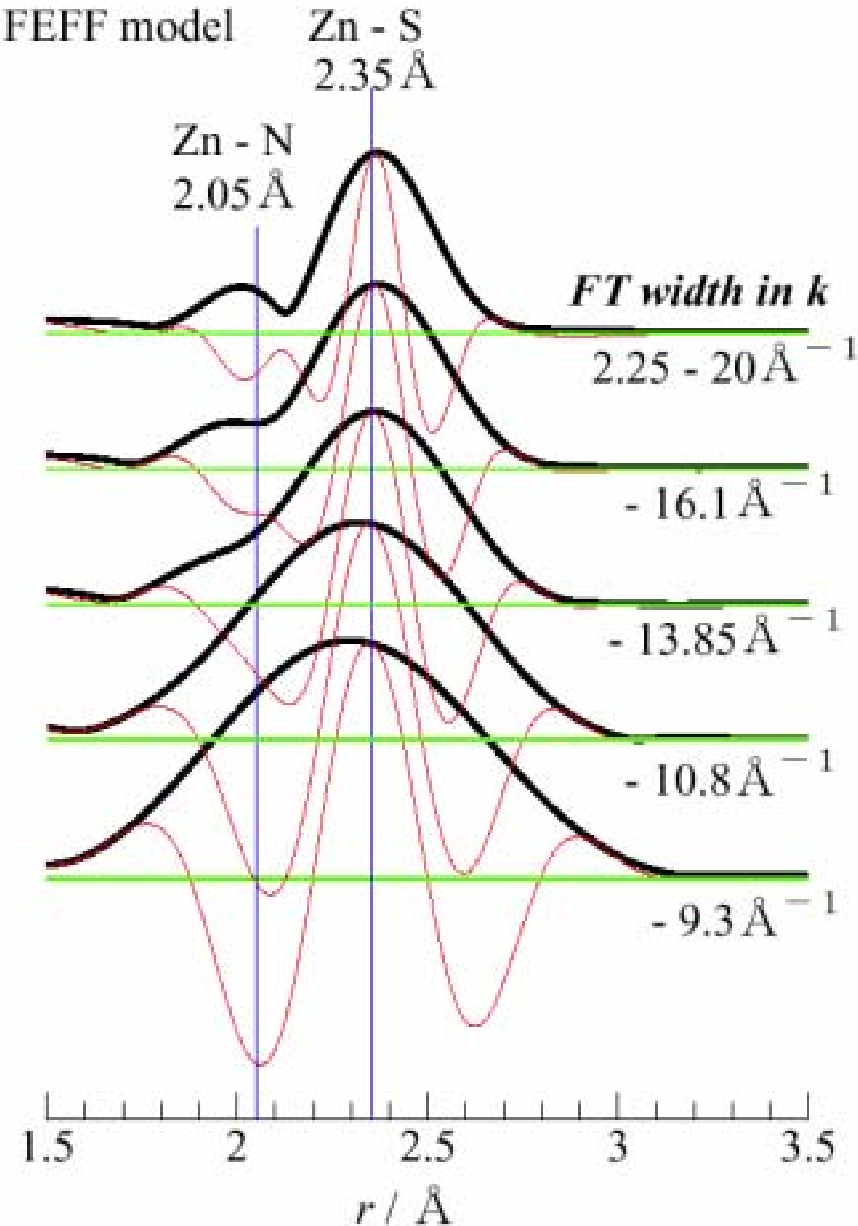

Φ(Zn-S)- Φ(Zn-N)
Zn - S
Zn - N
Φ / rad
difference / deg
0
-5
-10
-15
250
200
150
100
50
0
0
5
10
15
20
x


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

Parameters used for Fourier Trans: N



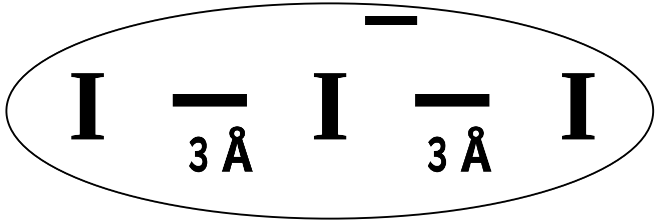
Parameters used for Fourier Trans: S

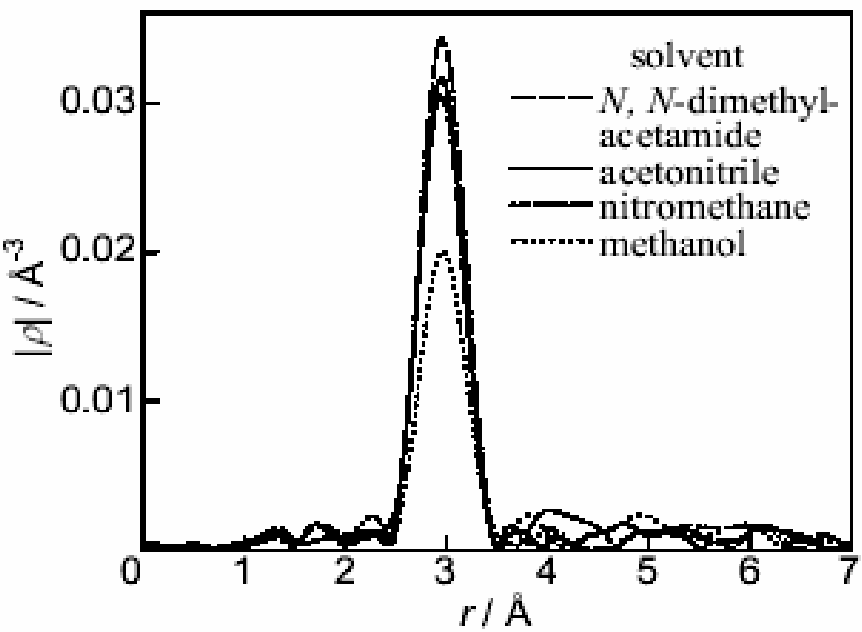


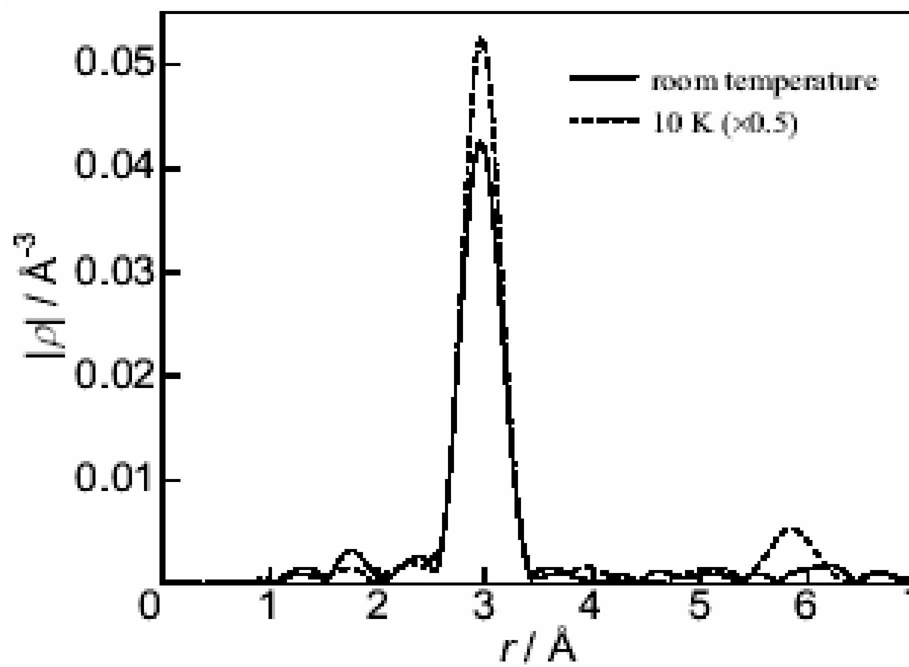
Almost impossible !

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



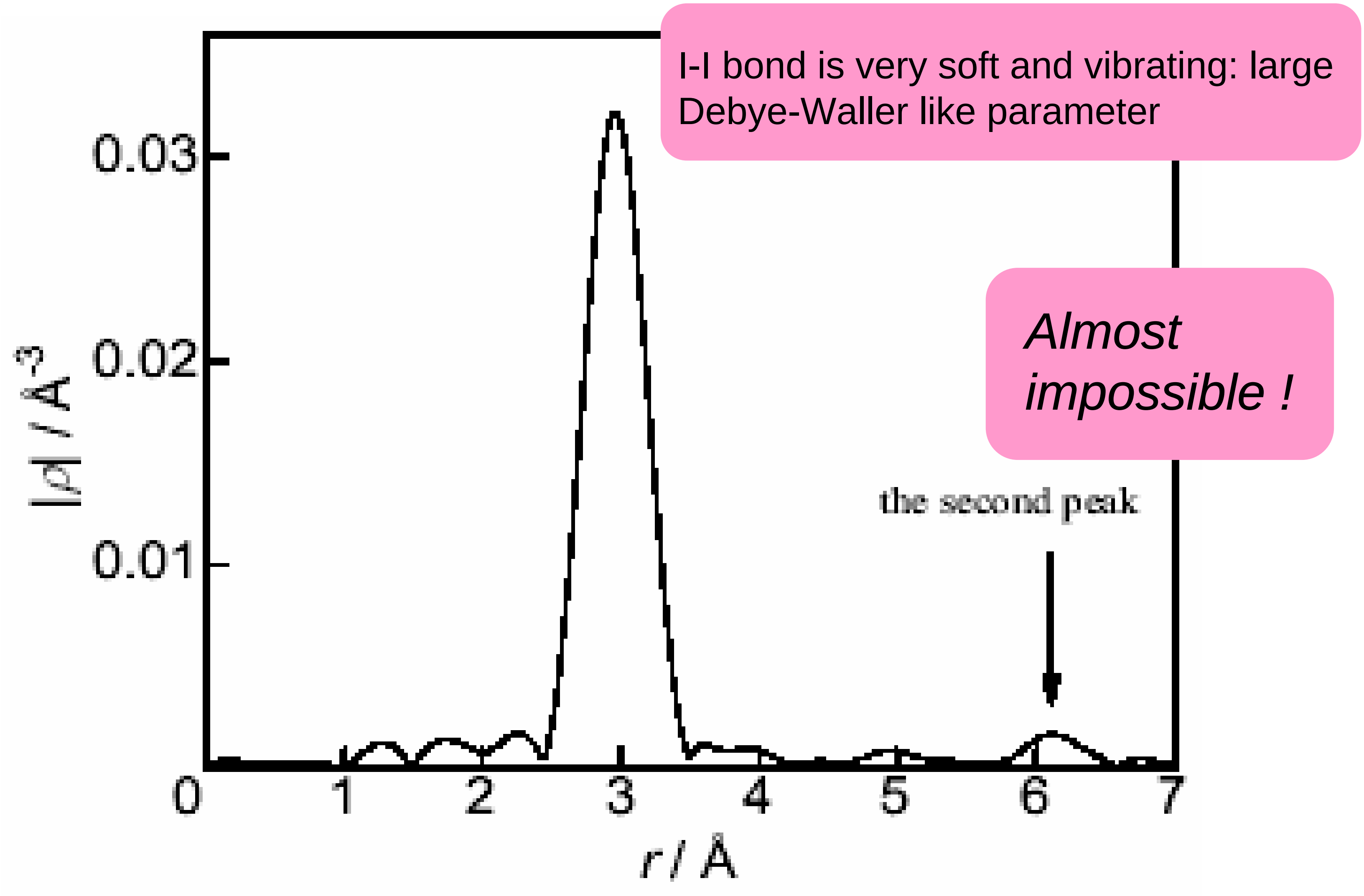




Dissolved in organic solvents

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

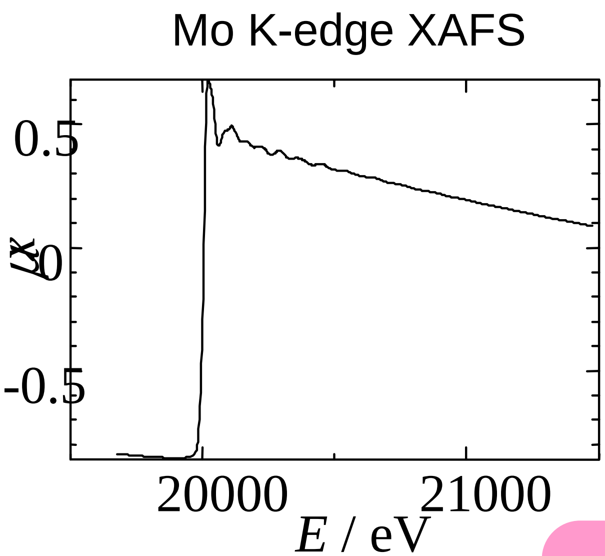
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

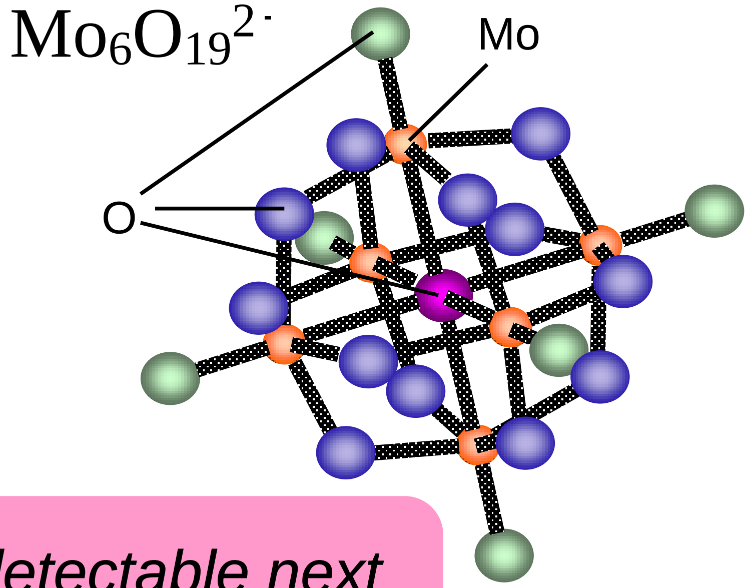


Iodine K-edge EXAFS Fourier transform for the compound spectrum made up from 12 independent spectra for organic solvent solutions.

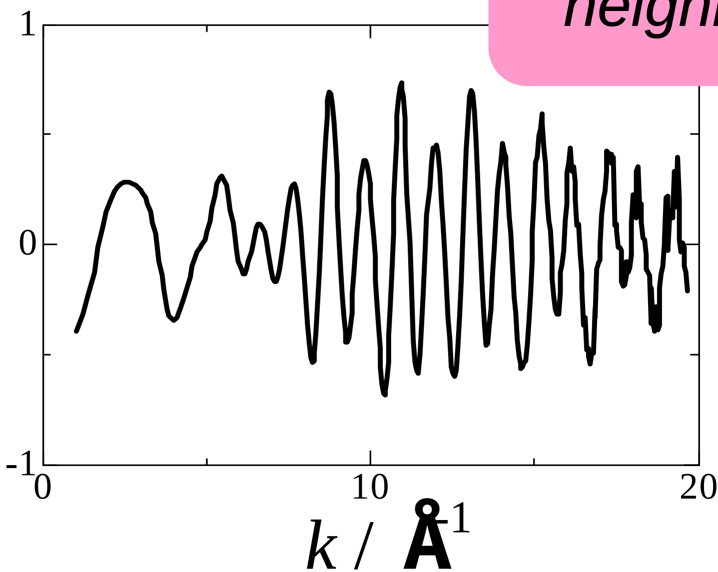
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

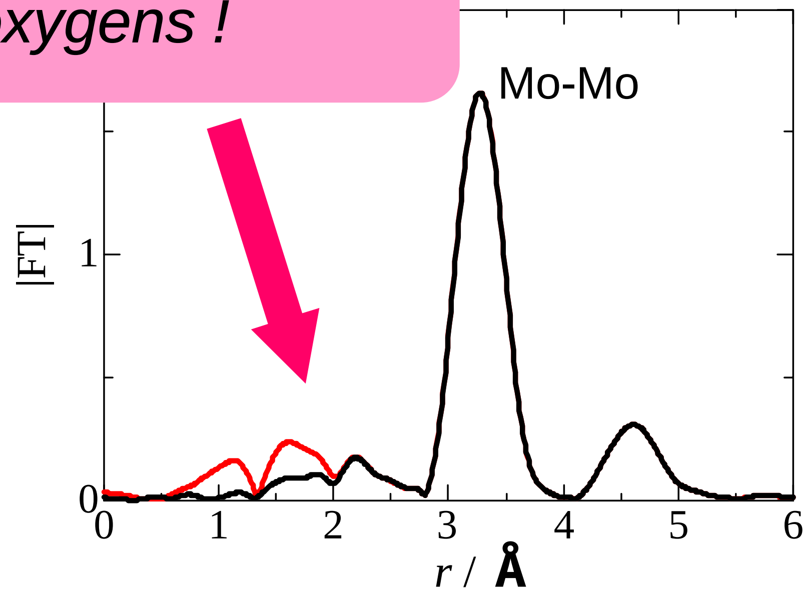
Large symmetrical cluster of molybdenum oxide complex

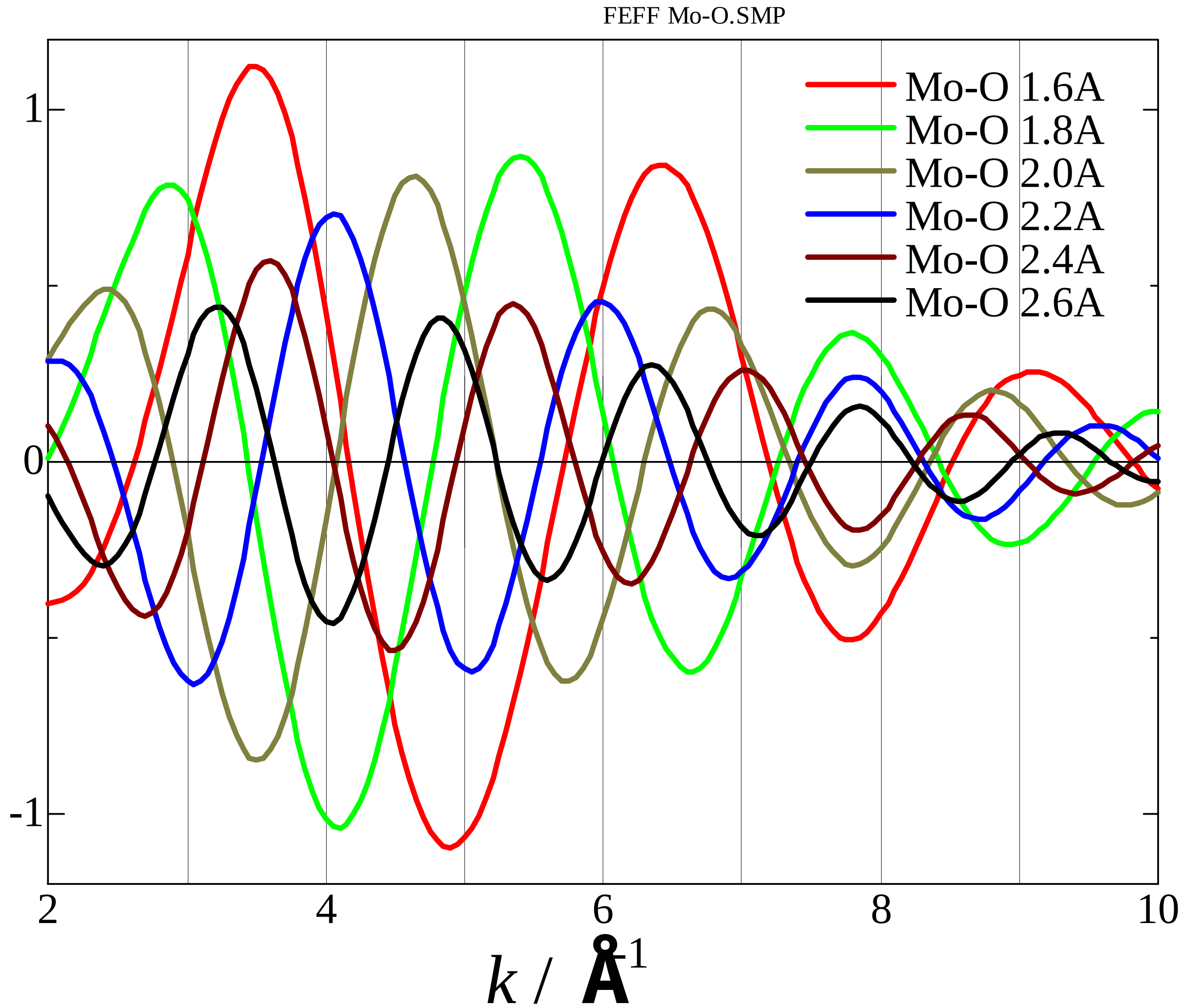




Almost undetectable next neighbor oxygens !






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/~ravel/software/

free software

XAS Analysis Software Using IFEFFIT

ATHENA
EXAFS DATA PROCESSING

Current release: 0.8.056
Release date: 26 July, 2008

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.

ARTEMIS
EXAFS DATA ANALYSIS

Current release: 0.8.012
Release date: 26 July, 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**.