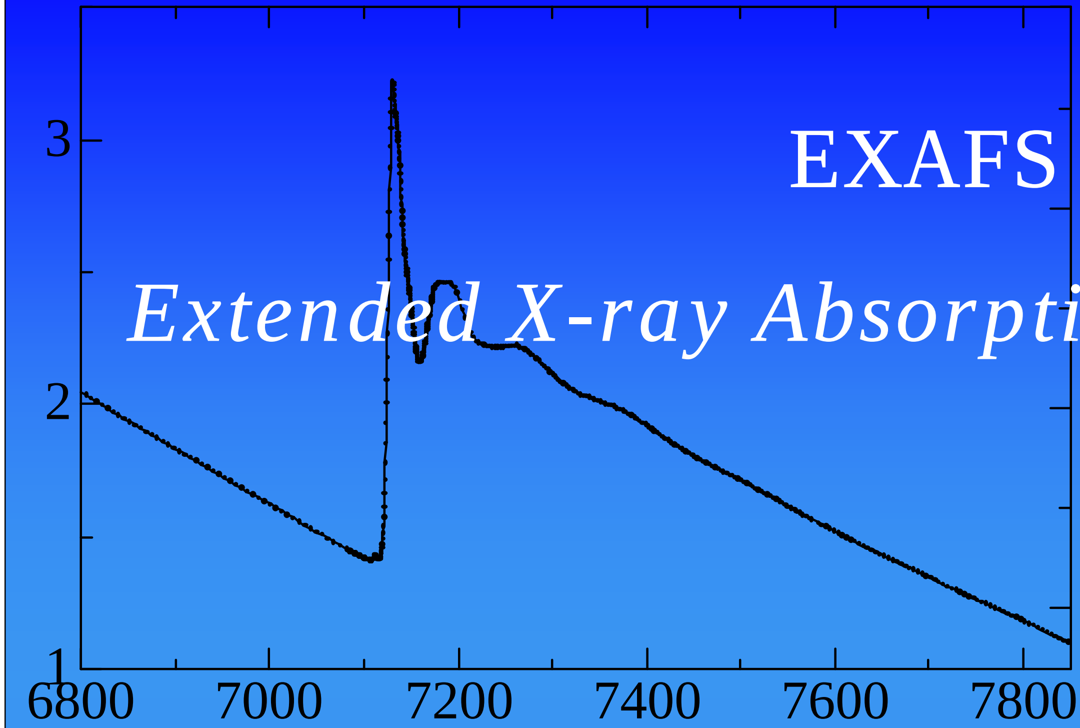
The 1st AOFSRR Summer School
- Cheiron School 2007 –
SPring-8
Sept. 17th, 2007



EXAFS

Extended X-ray Absorption Fine Structure

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Ritsumeikan University

EXAFS

Theory

- Quantum Mechanics
- Models
- Approximations

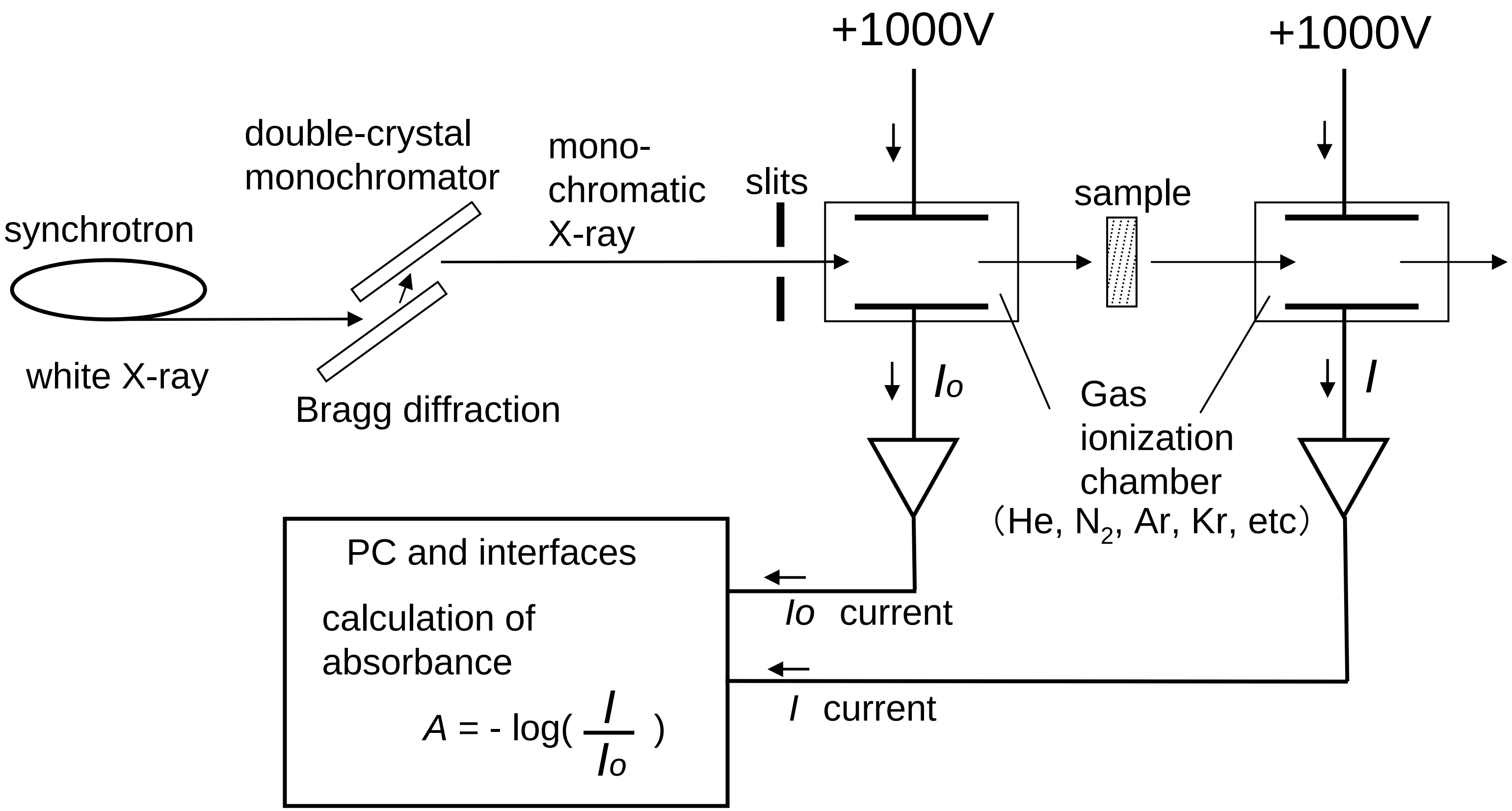
Experiment

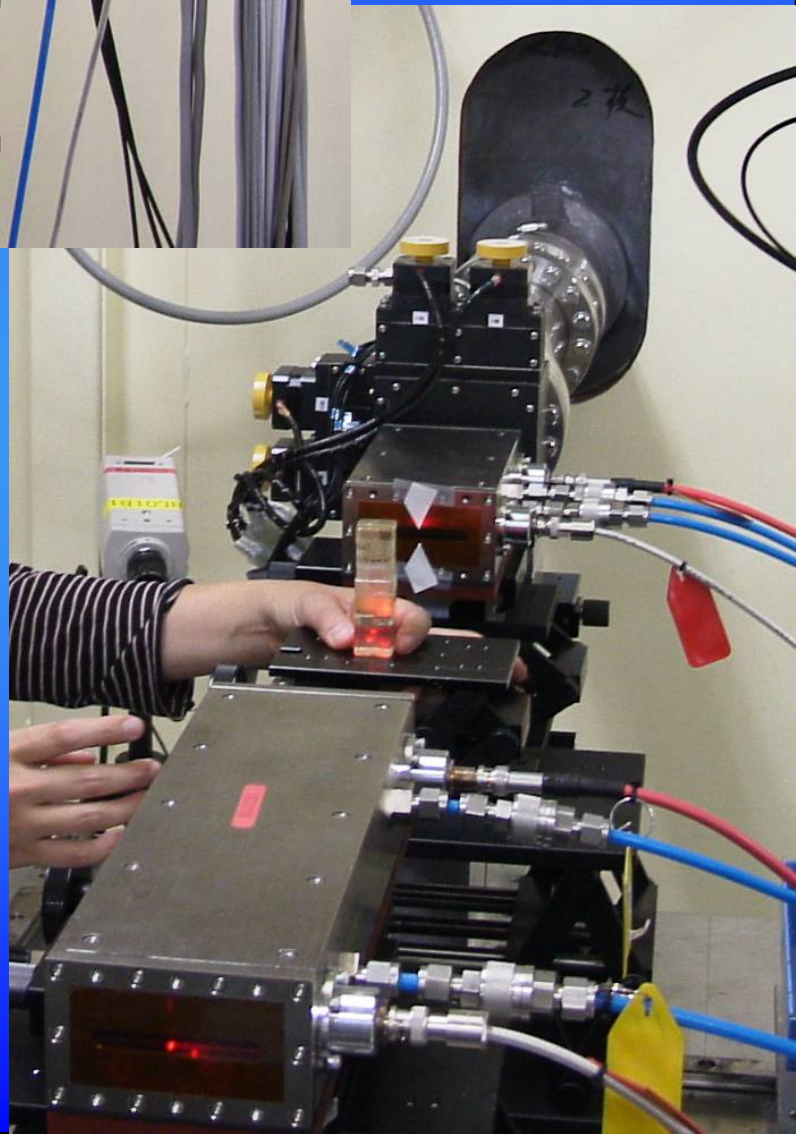
- Light Source
- Monochromator
- Higher Harmonics Rejection
- Sample Preparation
- Detection Methods
- Polarization XAFS

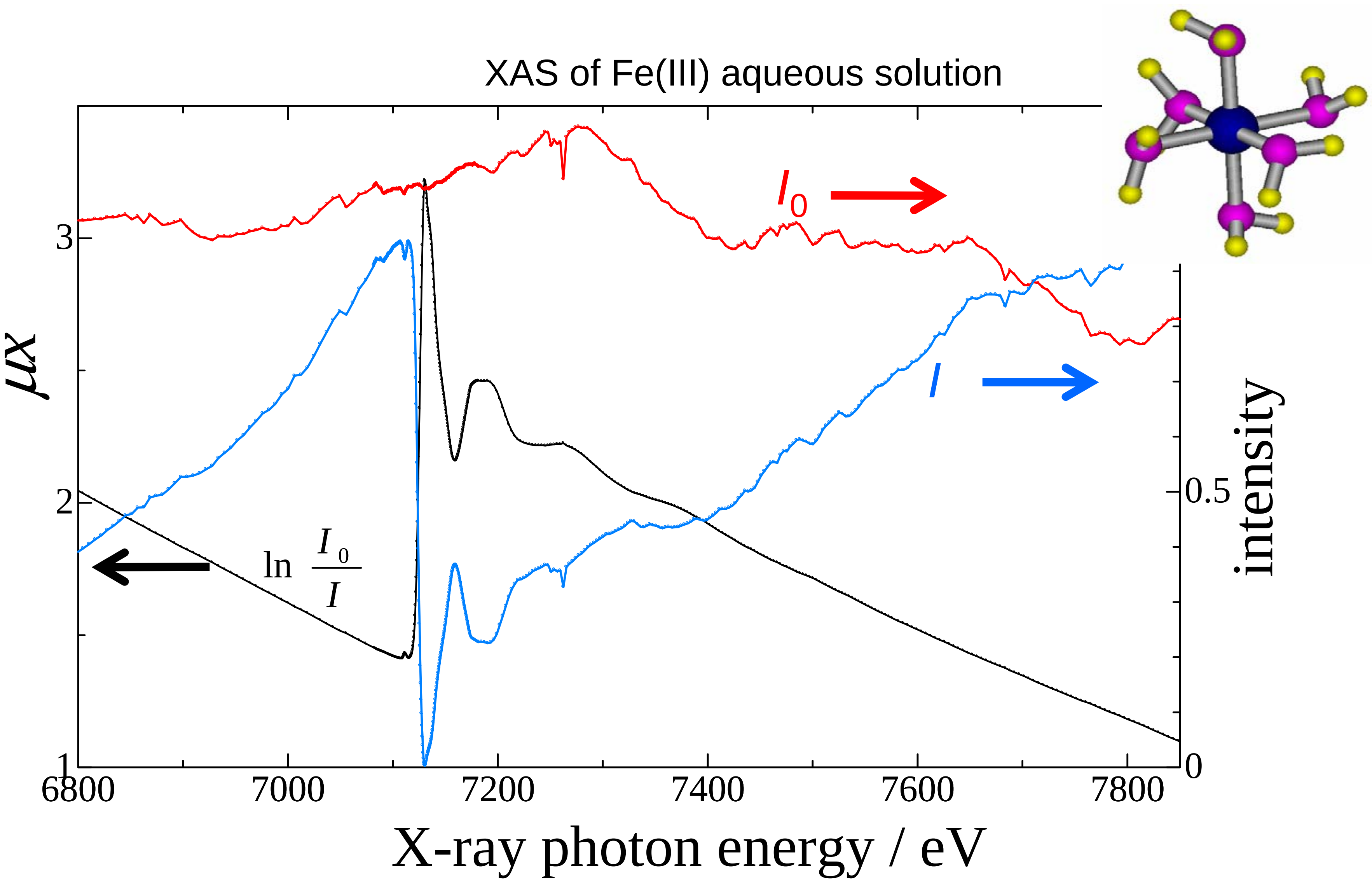
Data Analysis

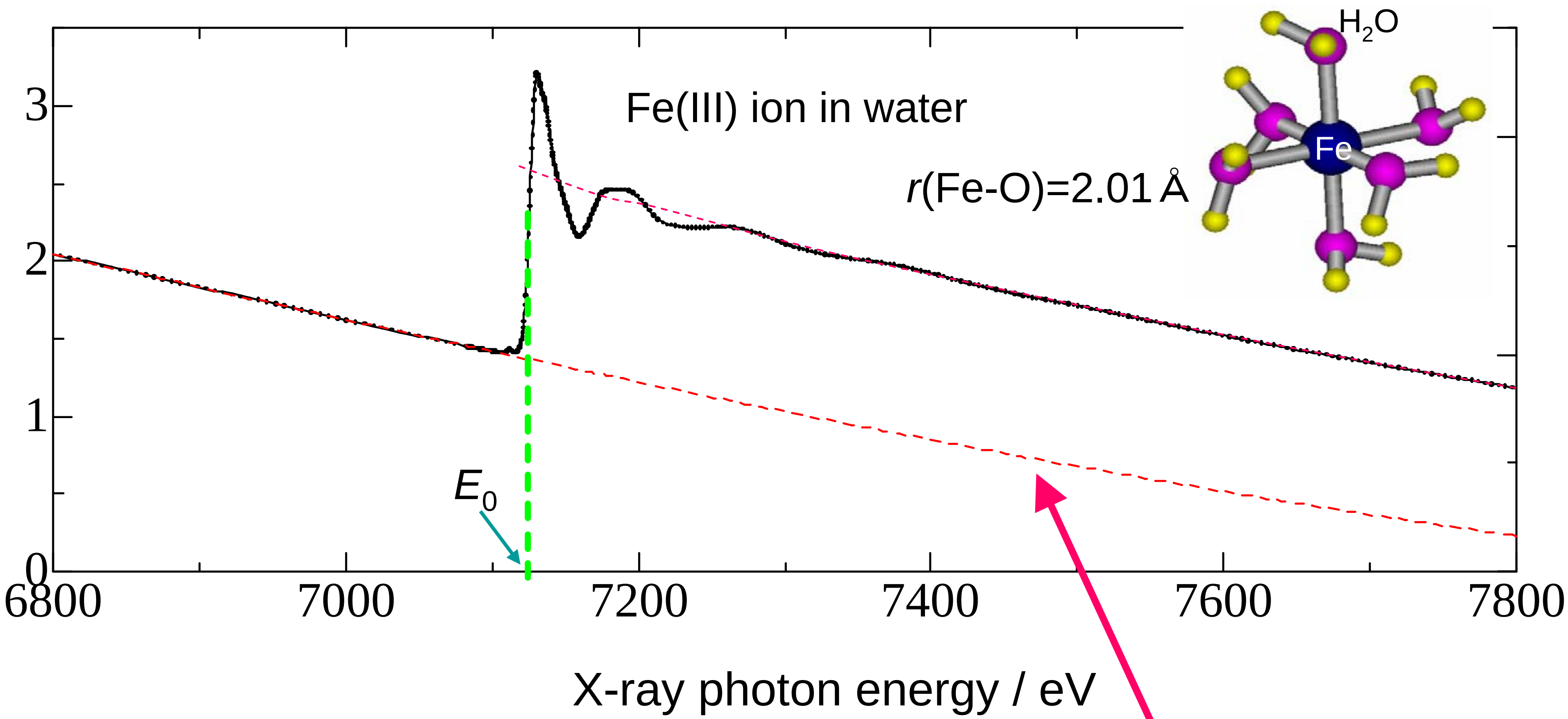
- Limited Usable Range in Experimental Data
- Estimation of Background Curves
- Fourier Transform
- Multi-Scattering
- Curve Fitting Procedure
- Phase Problems
- Debye-Waller-Like Parameter
- Anharmonicity in Potential

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






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

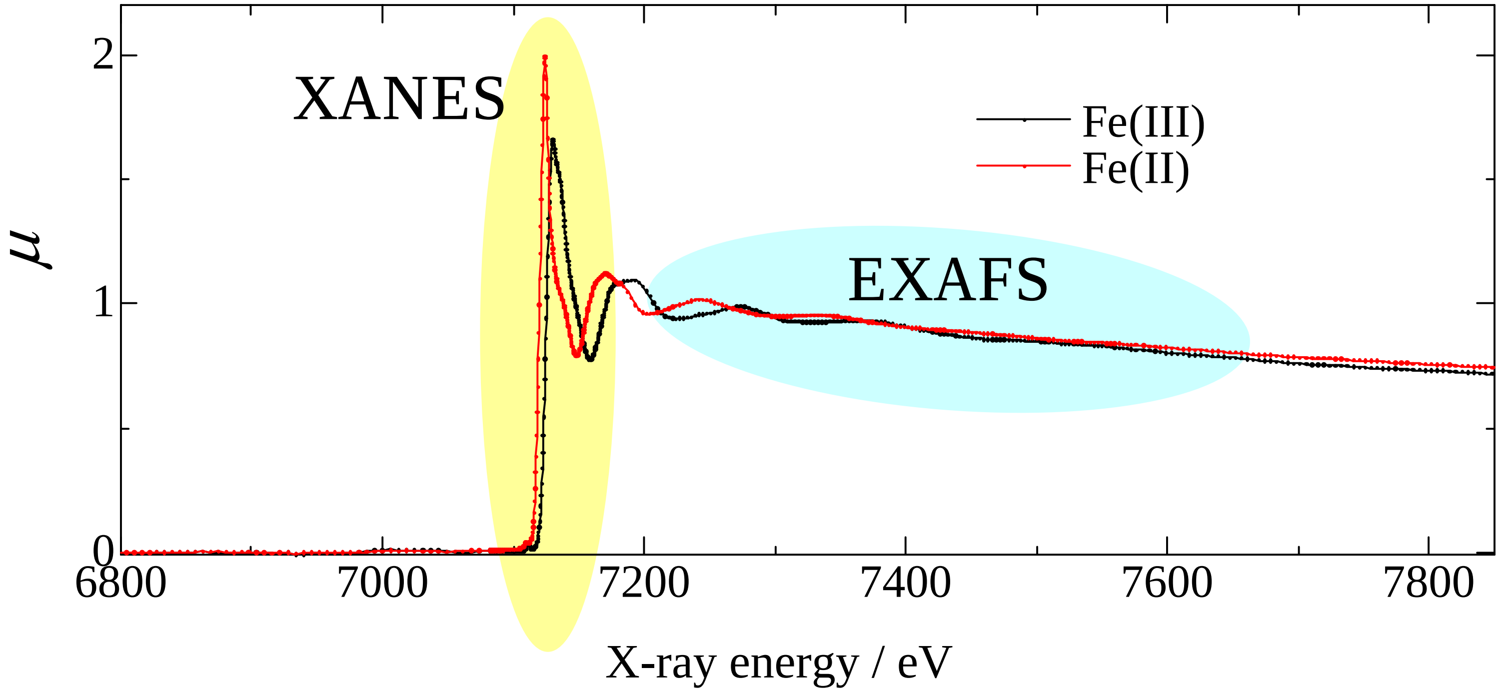


Focusing on K shell (1s electron) excitation

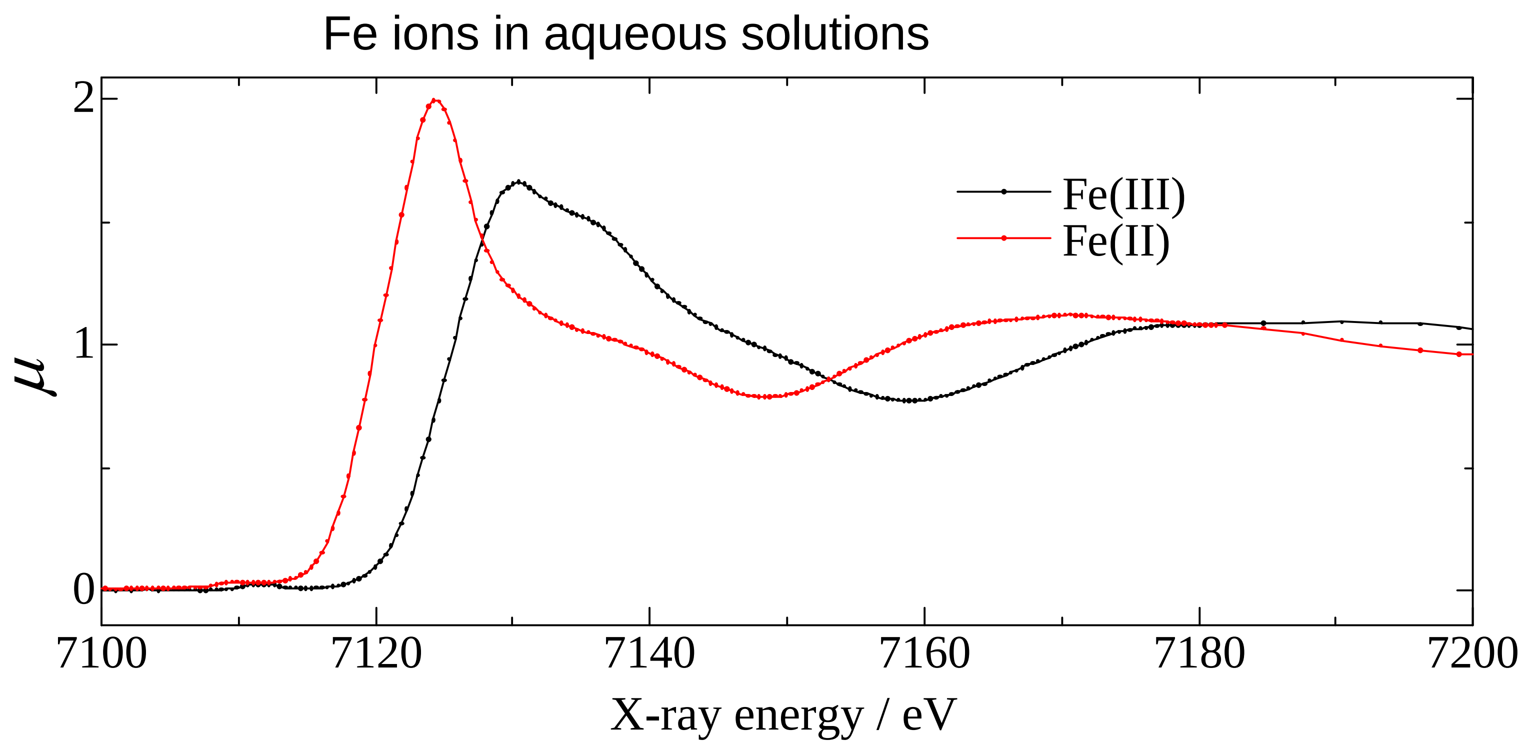
Background absorption due to other atoms and other shell electrons

XAFS: X-ray Absorption Fine Structure

Fe ions in aqueous solutions

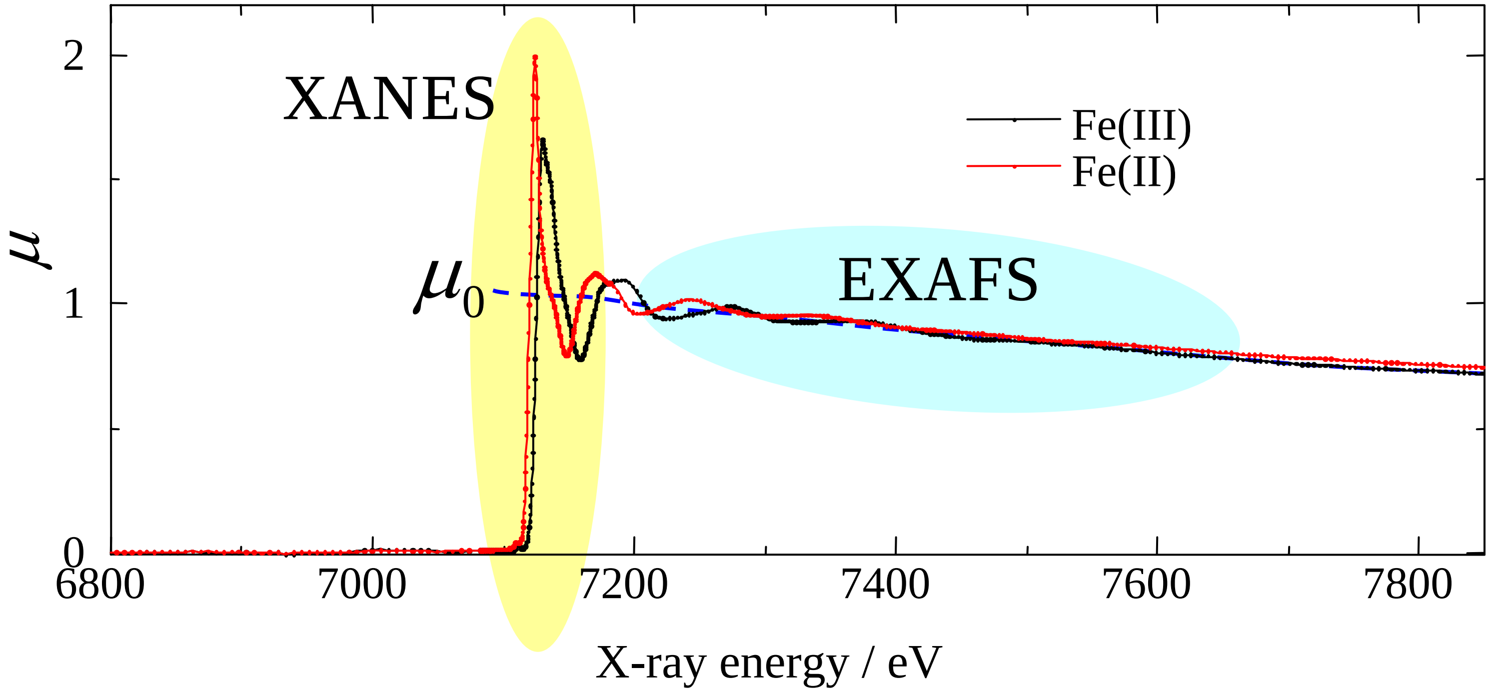


XANES: X-ray Absorption Near Edge Structure



EXAFS: Extended X-ray Absorption Fine Structure

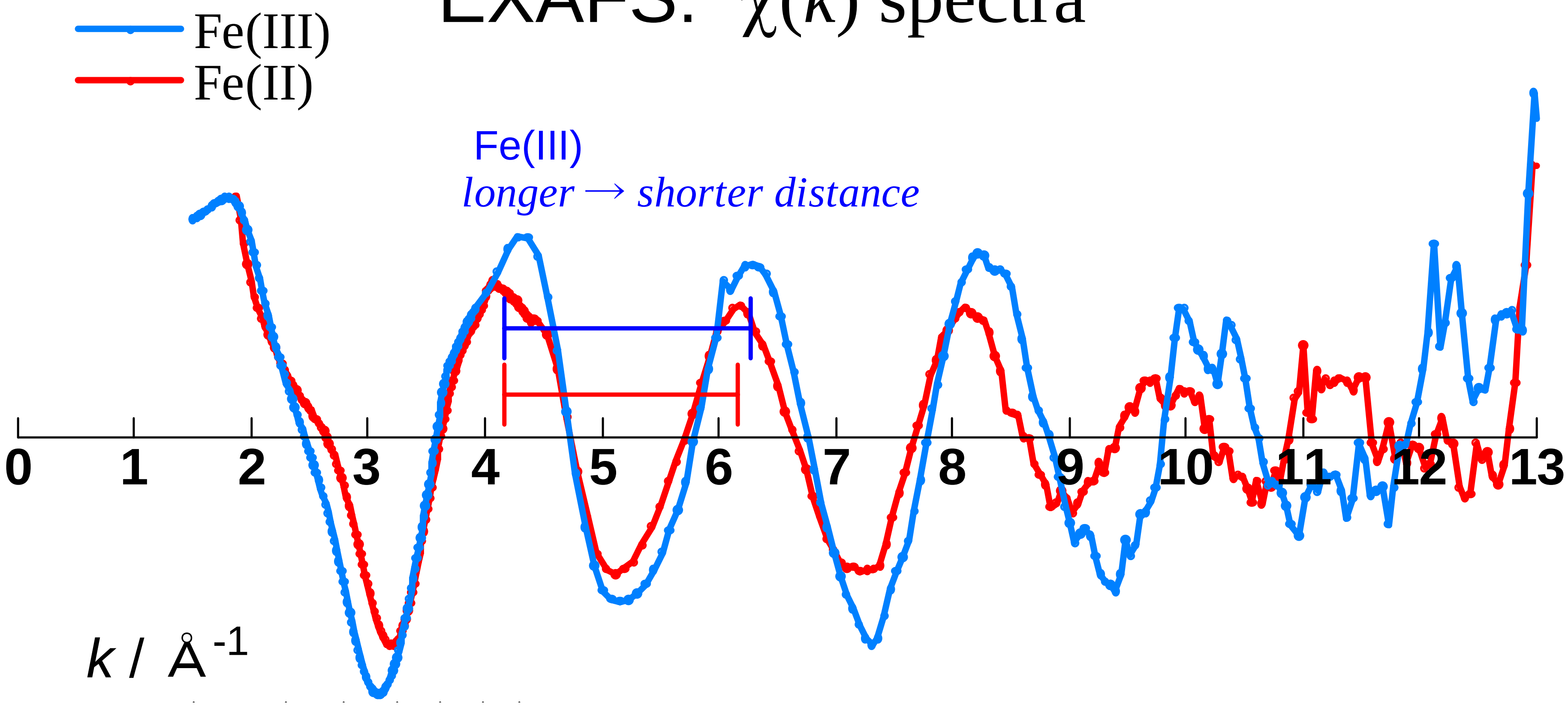
Fe ions in aqueous solutions



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

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

EXAFS: $\chi(k)$ spectra



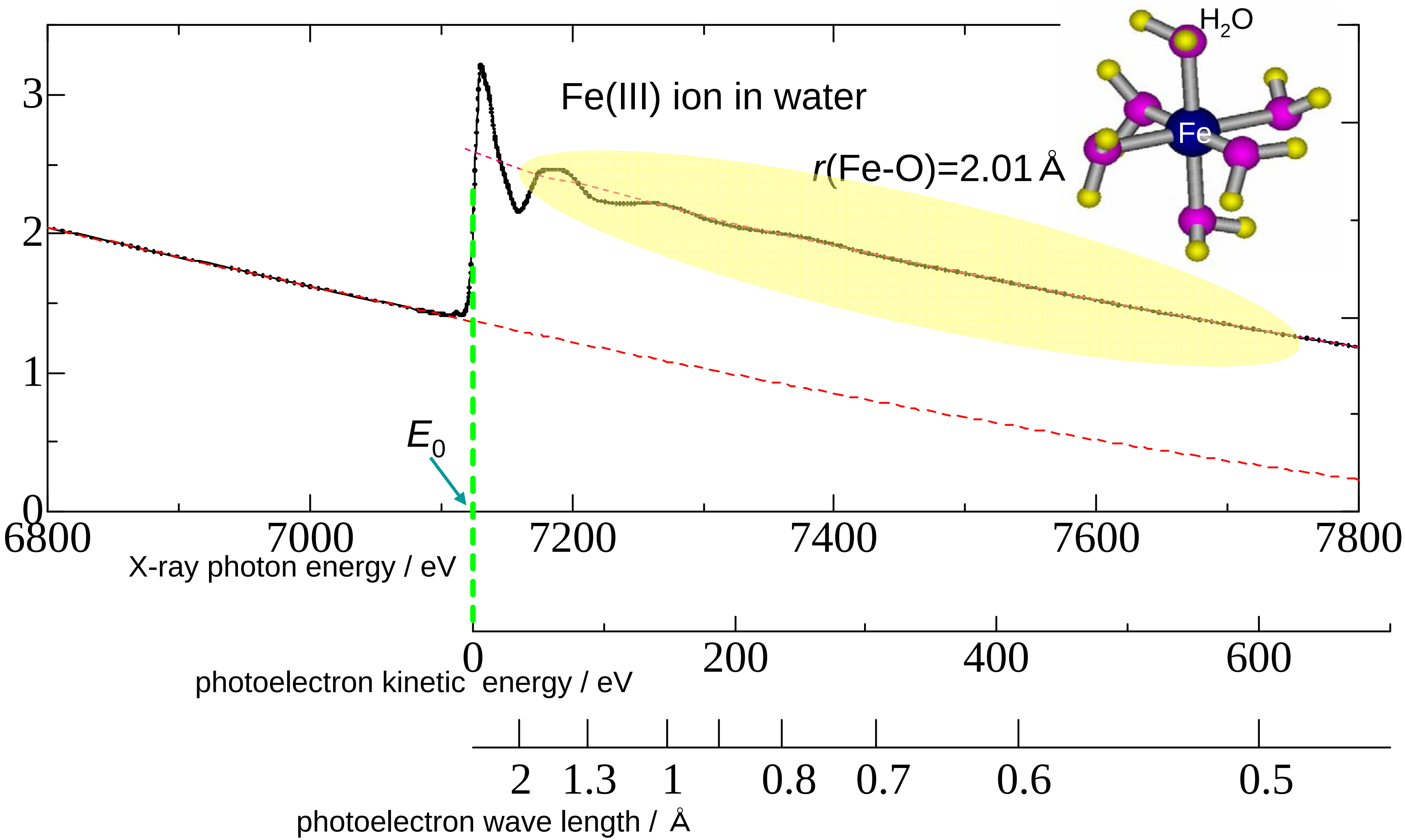
k : wave number, wave vector

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

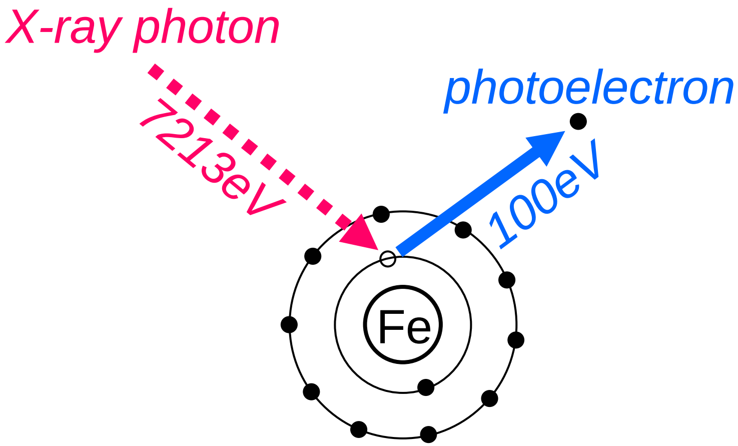
$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

$(E - E_0)$
kinetic energy of photoelectron

Simplest model to explain how the EXAFS oscillation occurs



Fe(III) ion in water
r(Fe-O)=2.01 Å
H2O
Fe
E0
0
1
2
3
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

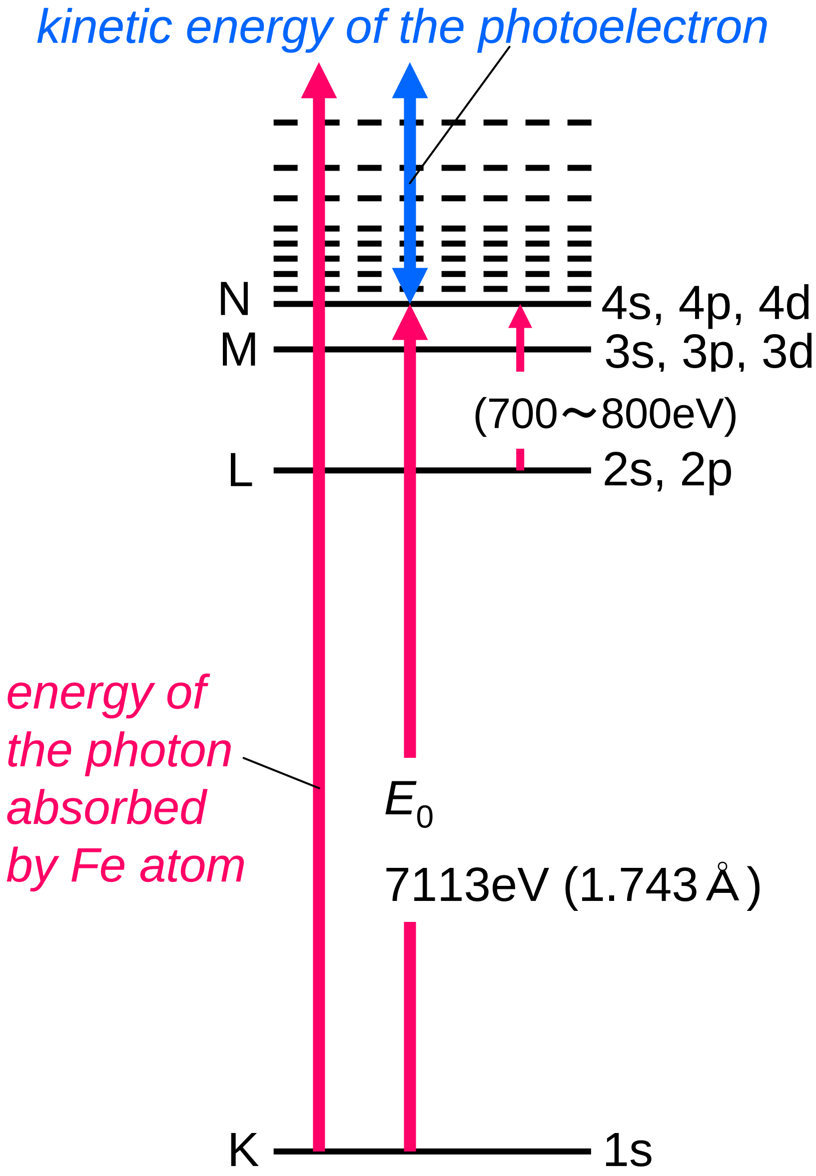


an electron with E_k=100eV behaves
as a wave with λ =1.2 Å

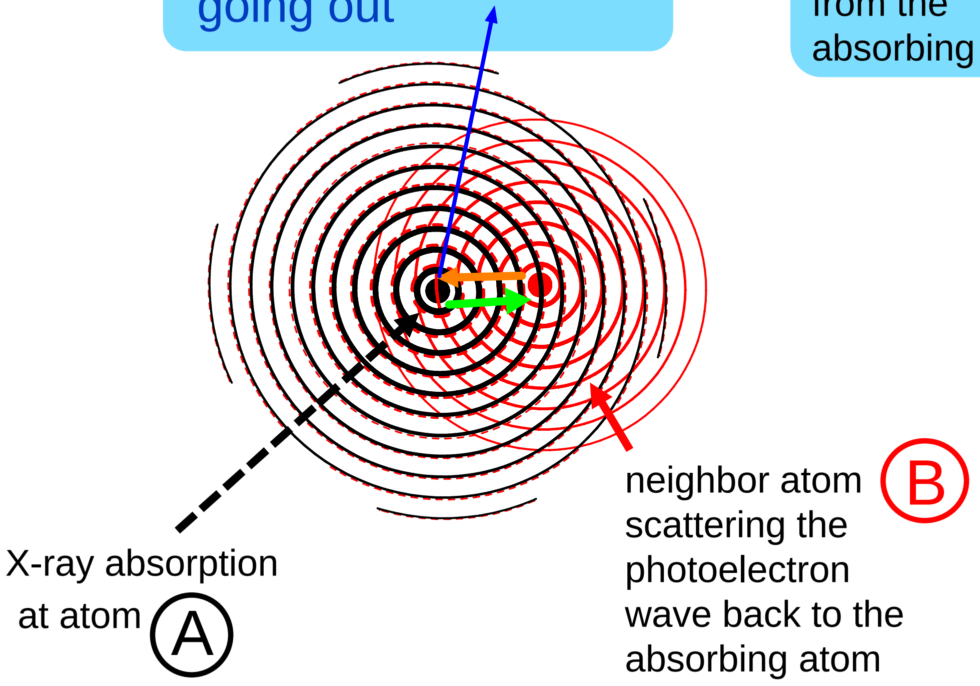
$$\lambda = \frac{h}{p}$$: *de Broglie*

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

The cause for EXAFS appearance !!!



photoelectron (wave) going out = black wave: directly emitted from the absorbing atom + red broken wave: doubly scattered at B and A

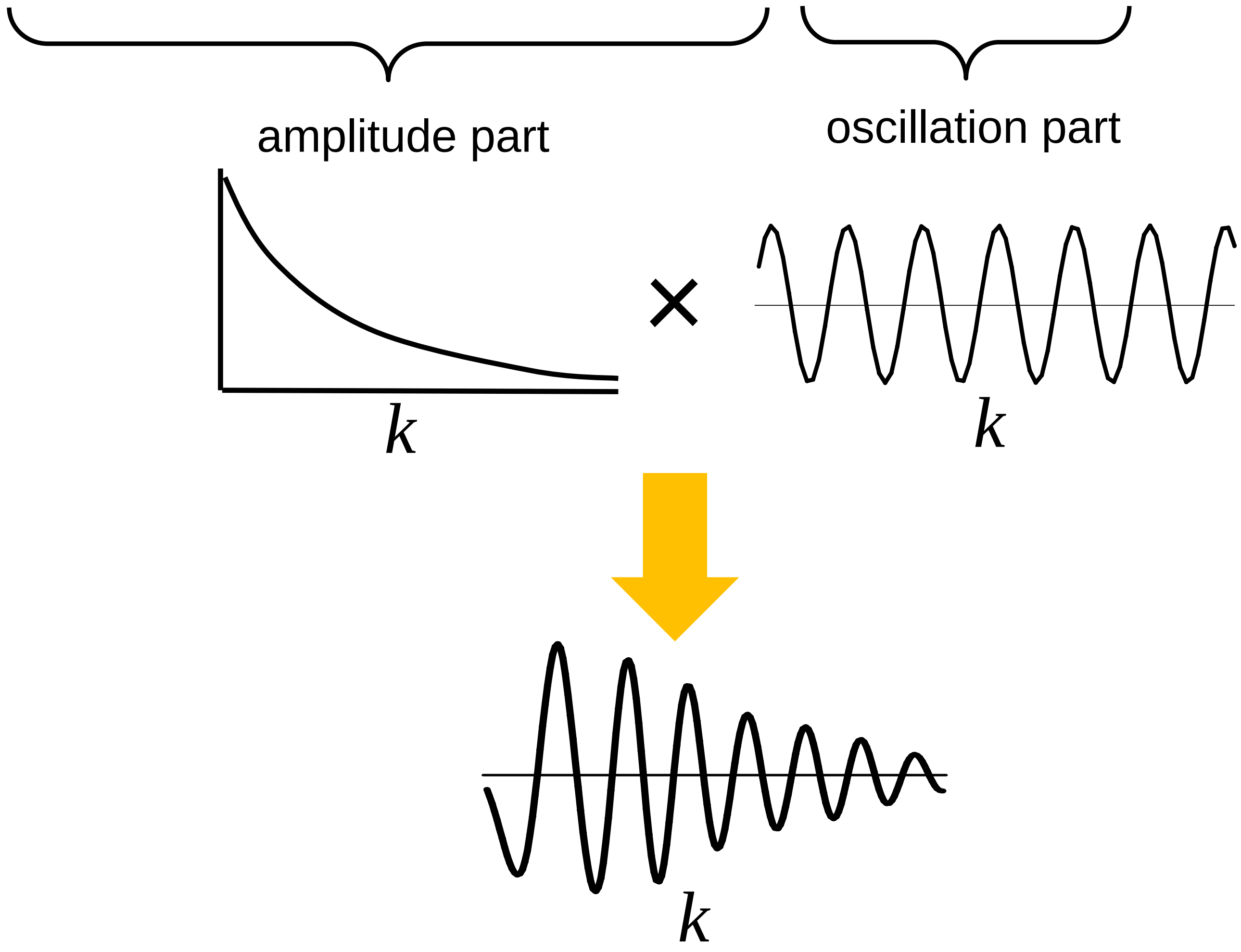


BASIC EXAFS equation

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

BASIC EXAFS equation

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



BASIC EXAFS equation

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

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)

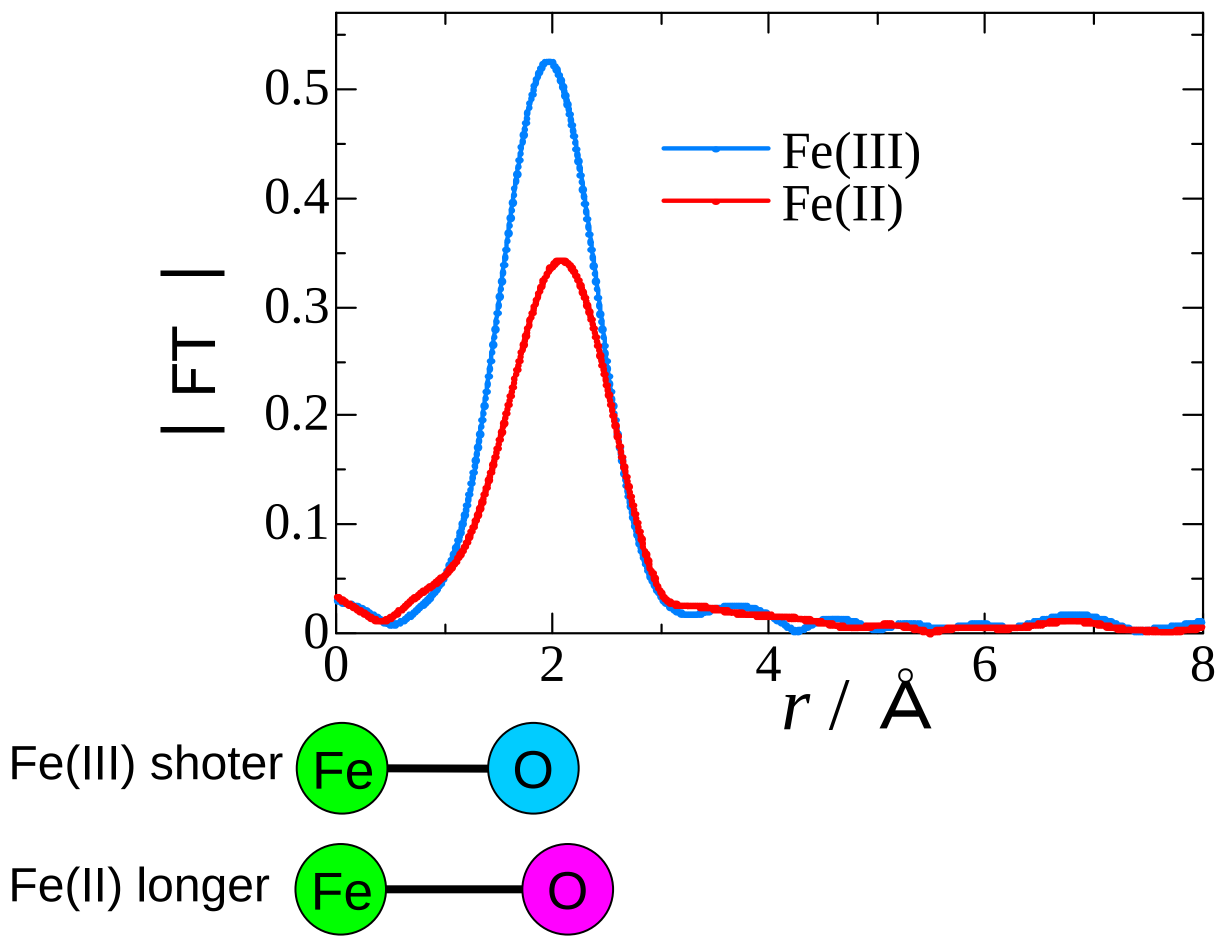
λ photoelectron mean path length

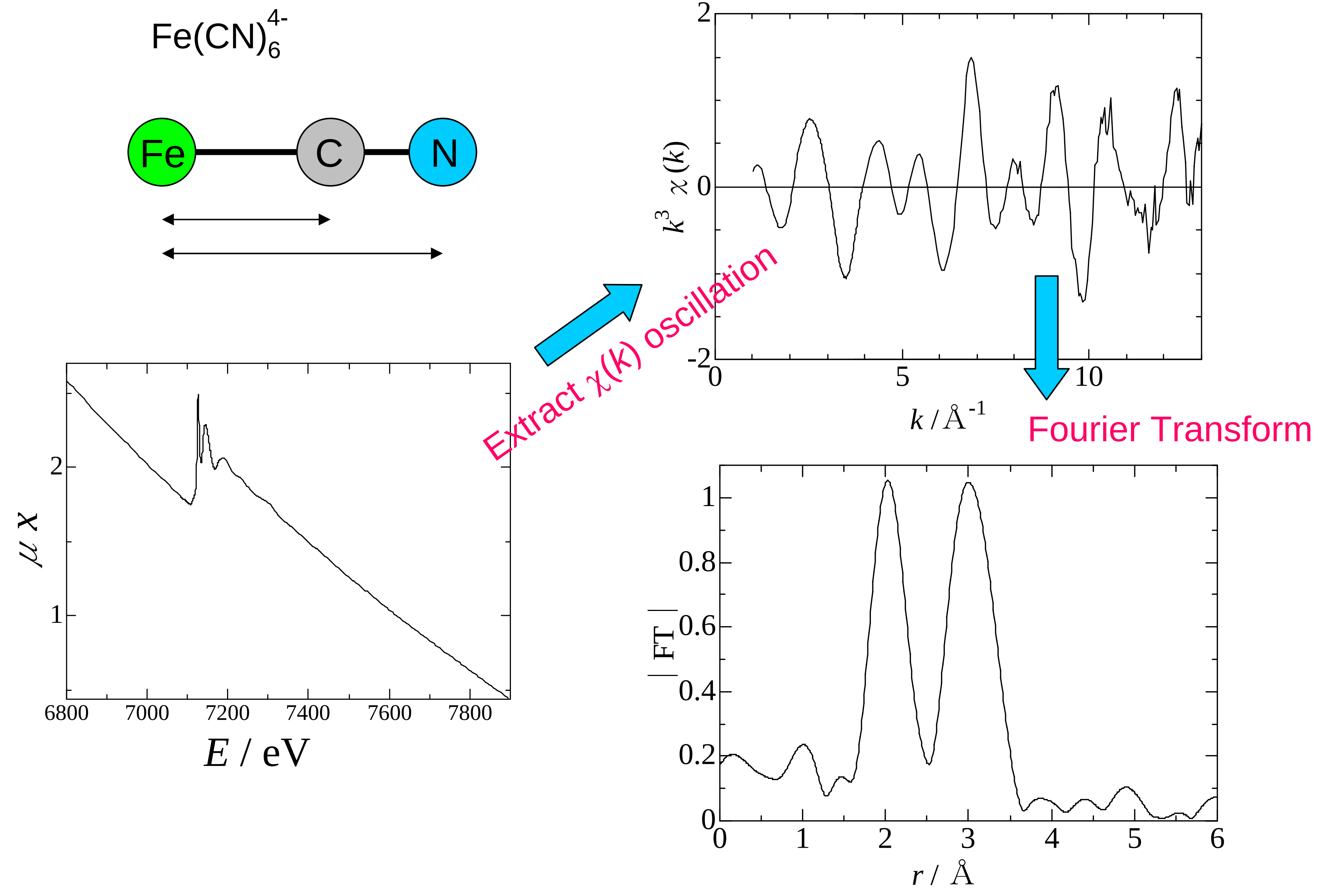
S_0^2 reduction factor

ϕ phase shift

Fourier Transform: Simplest way to analyze the EXAFS oscillation

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

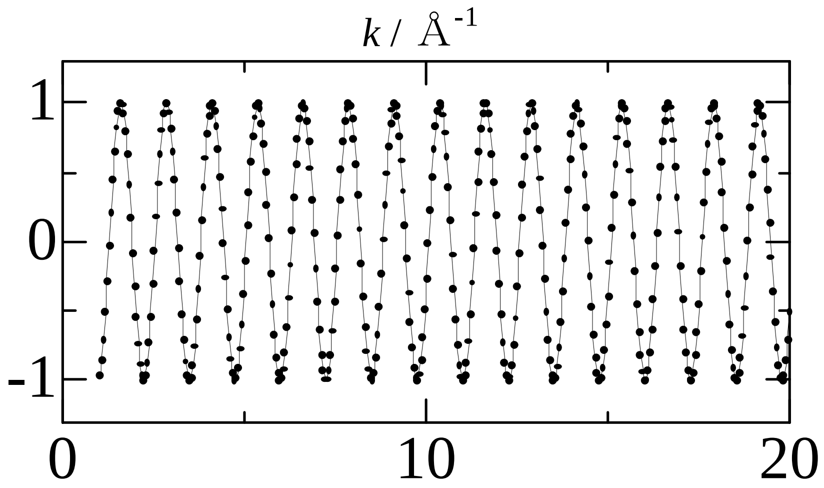


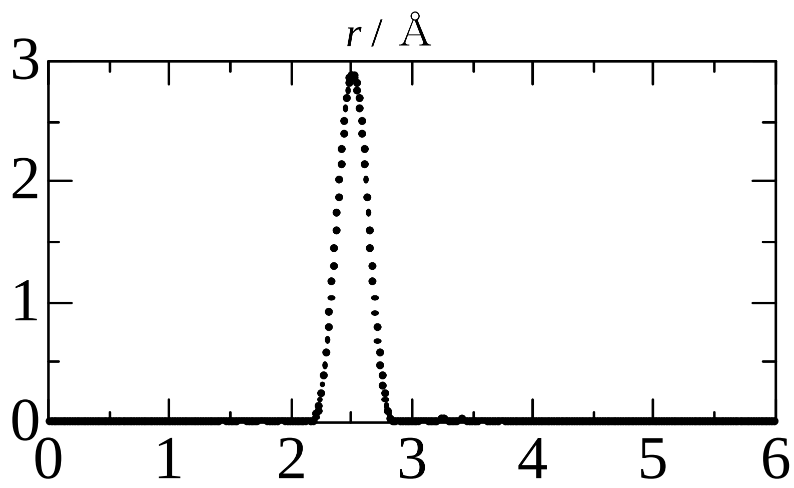


Fe(CN)$_6^{4-}$
Fe
C
N
Extract χ(k) oscillation
Fourier Transform
$k^3\ \chi(k)$
k / Å^{-1}
|FT|
r / Å
μx
E / eV

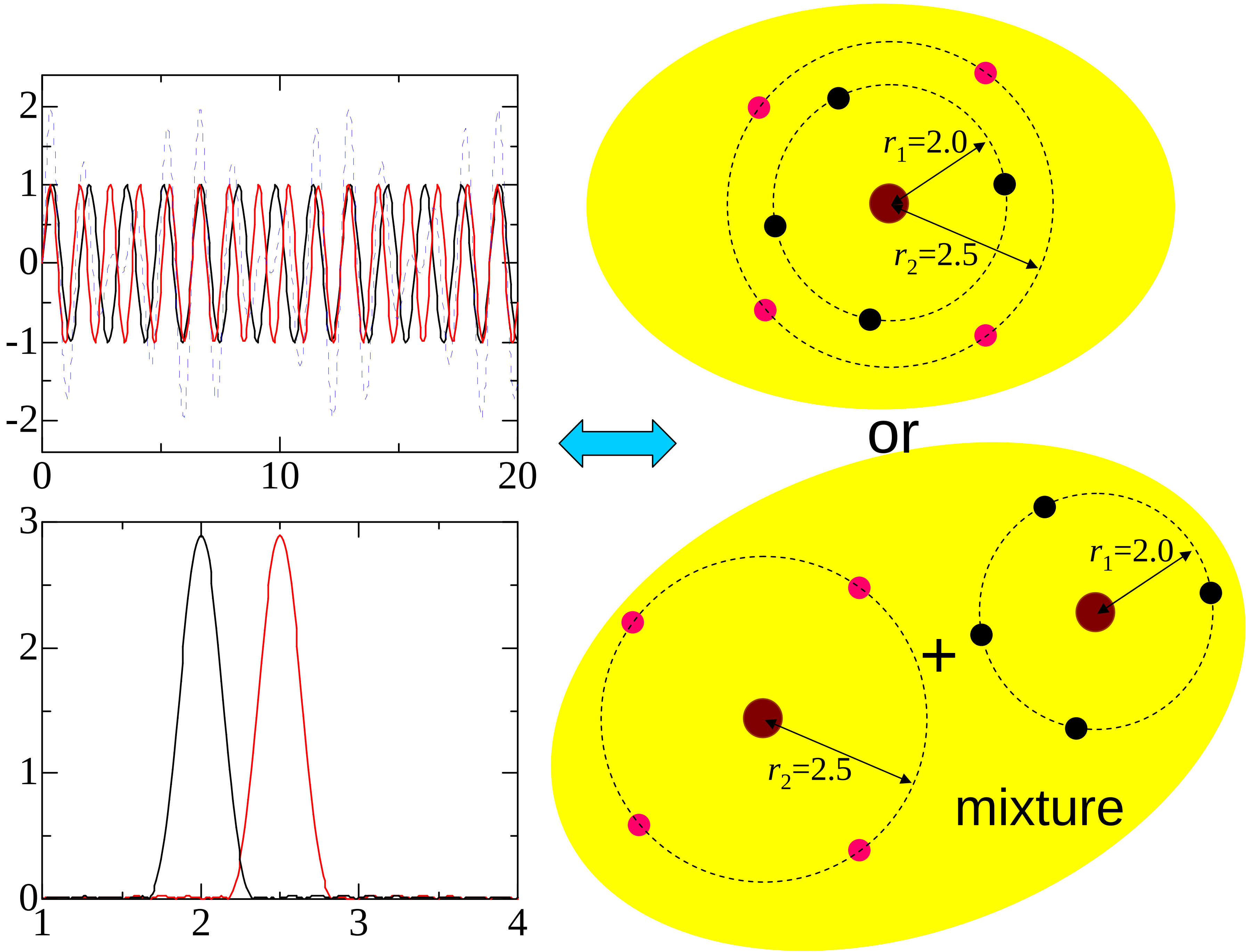
Fourier Transform (Frequency Filter)

will let you know the frequencies of the waves



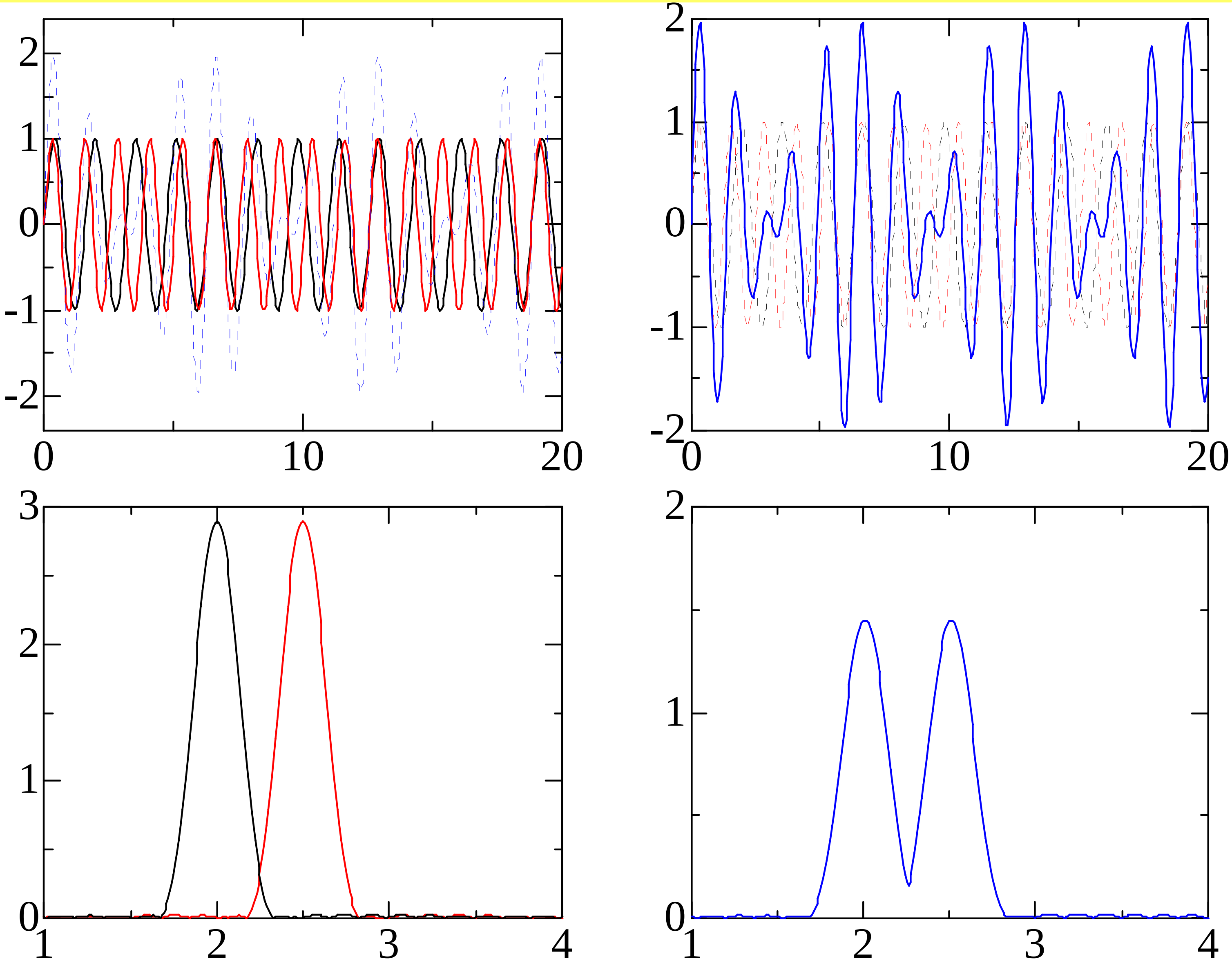


$$\sin(kr)$$

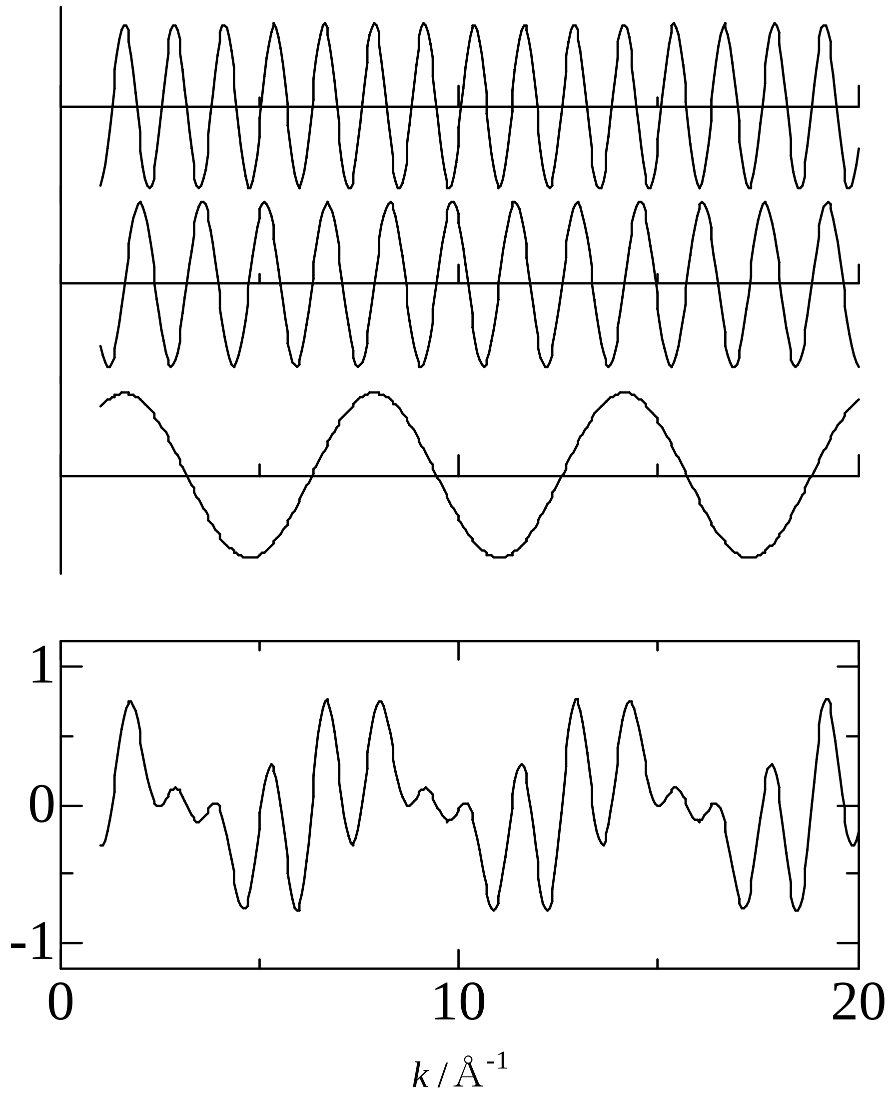


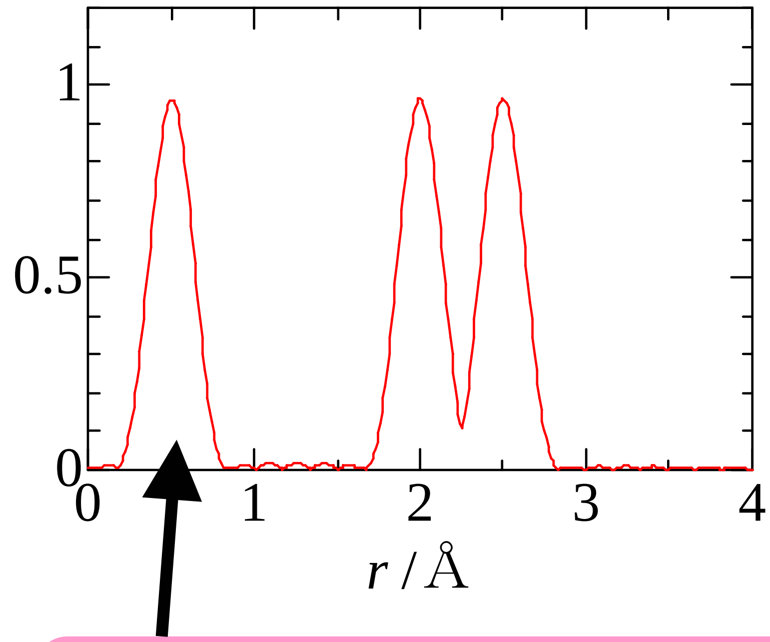
2
1
0
-1
-2
0
10
20
3
2
1
0
1
2
3
4
r_1=2.0
r_2=2.5
or
r_1=2.0
+
r_2=2.5
mixture

Fourier Transform for two-shell model

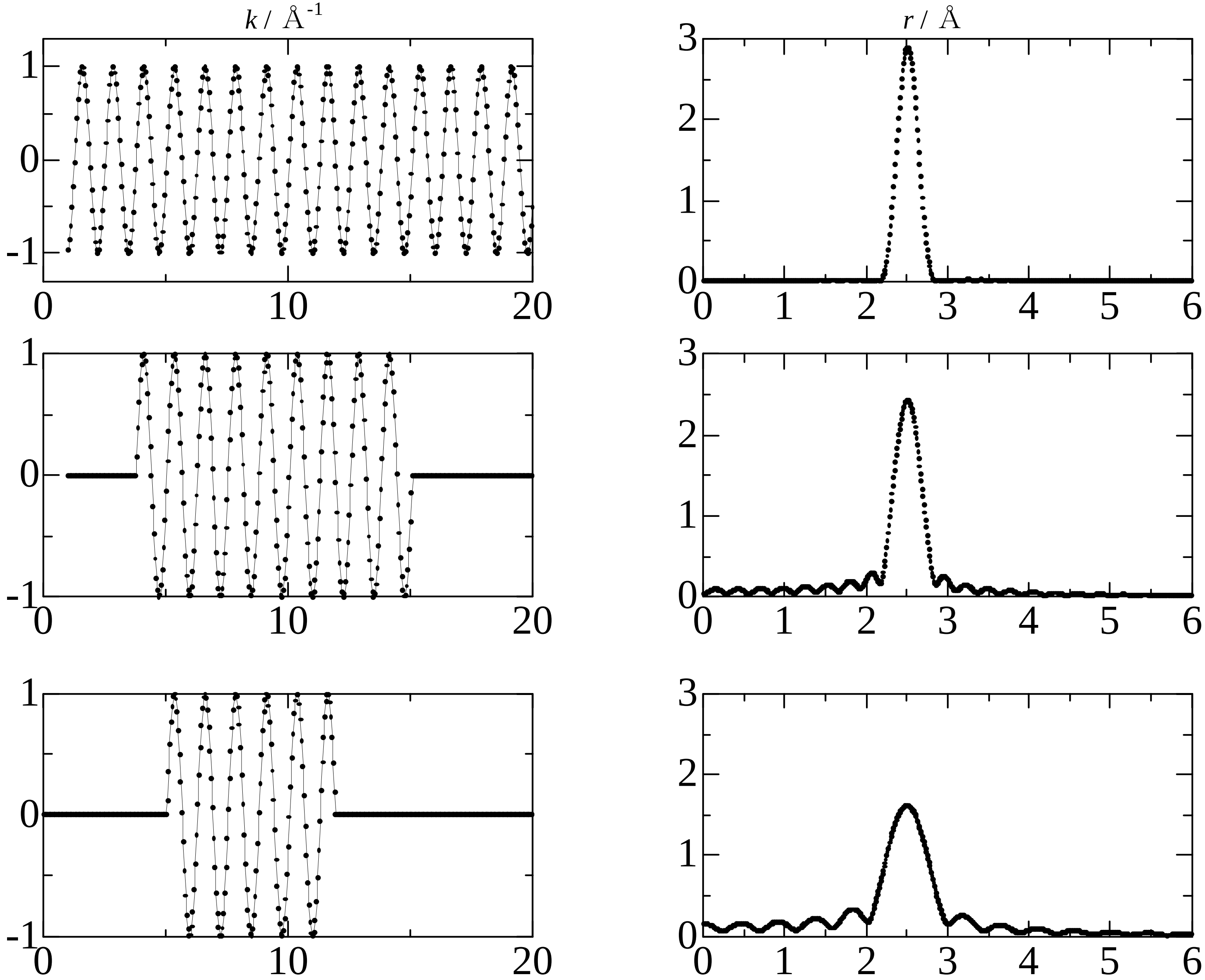


Fourier Transform for a three-shell model

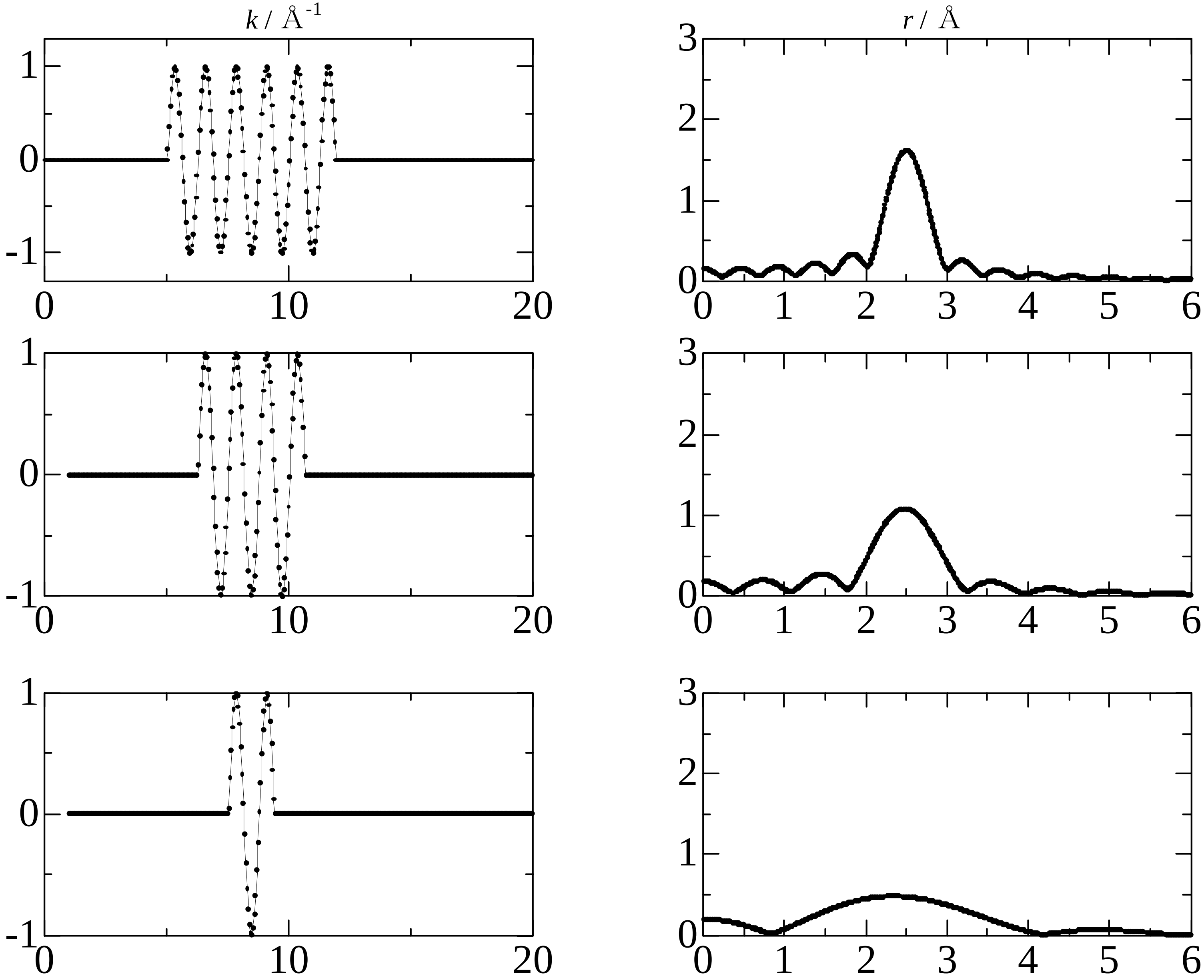




This must be a BACKGROUND structure, not corresponding to a real atom-atom distance.

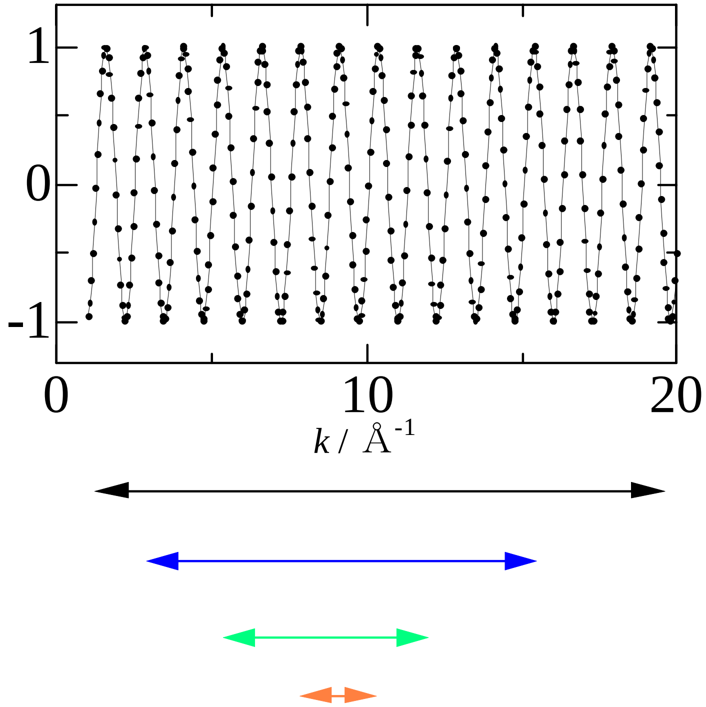


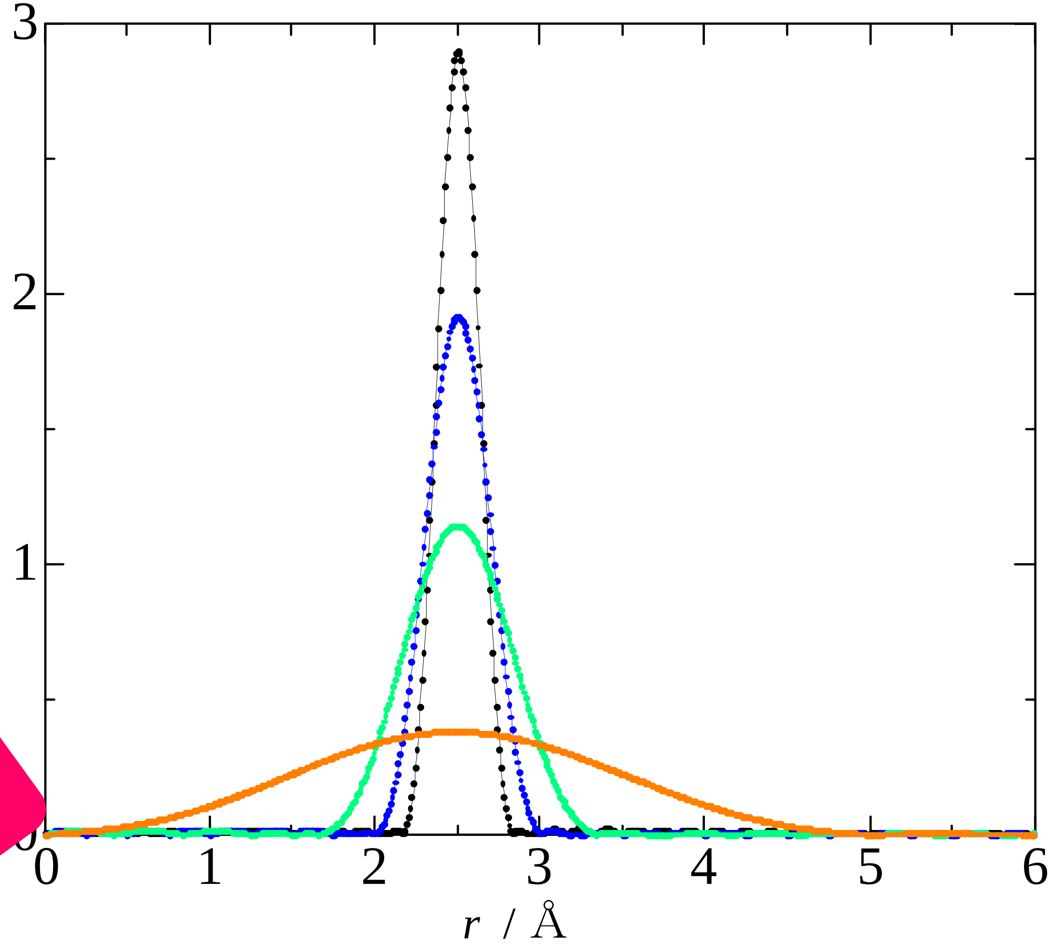
k / Å-1
r / Å



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

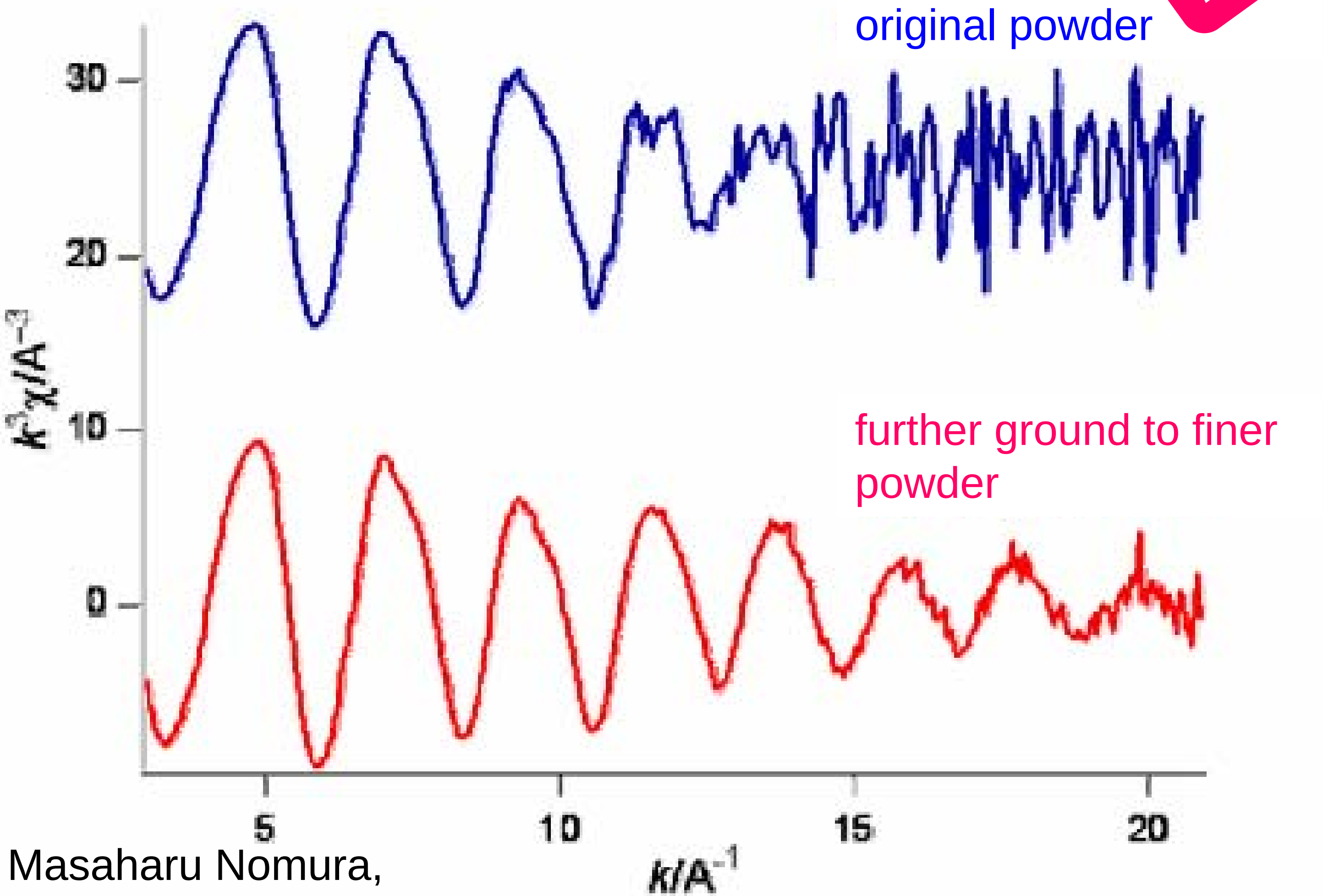
By comparing the theoretical EXAFS $\chi(k)$ and experimental $\chi(k)$, you can determine;

- *N* coordination number
- *r* bond length
- atomic type of coordination

Transmission method

Sample: Ge-Si powder

Problem !



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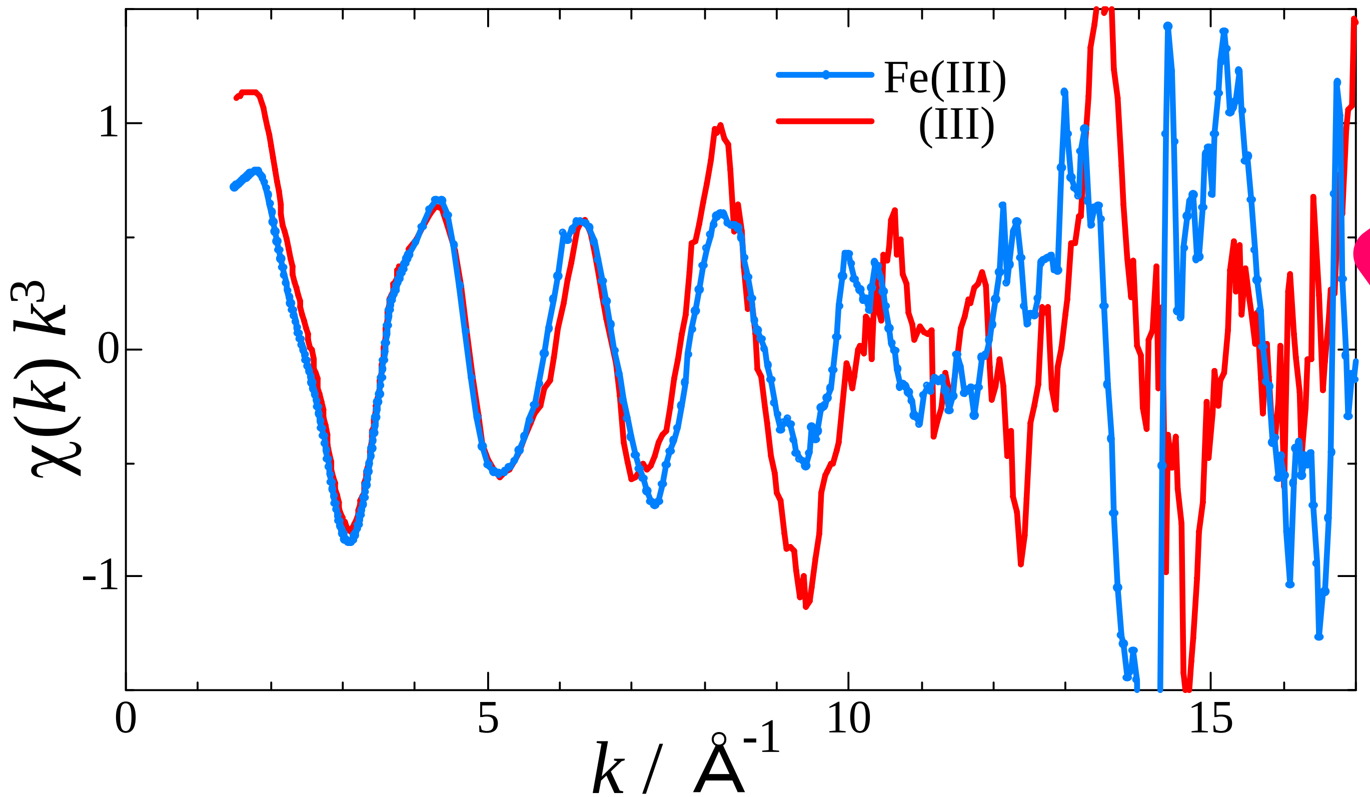
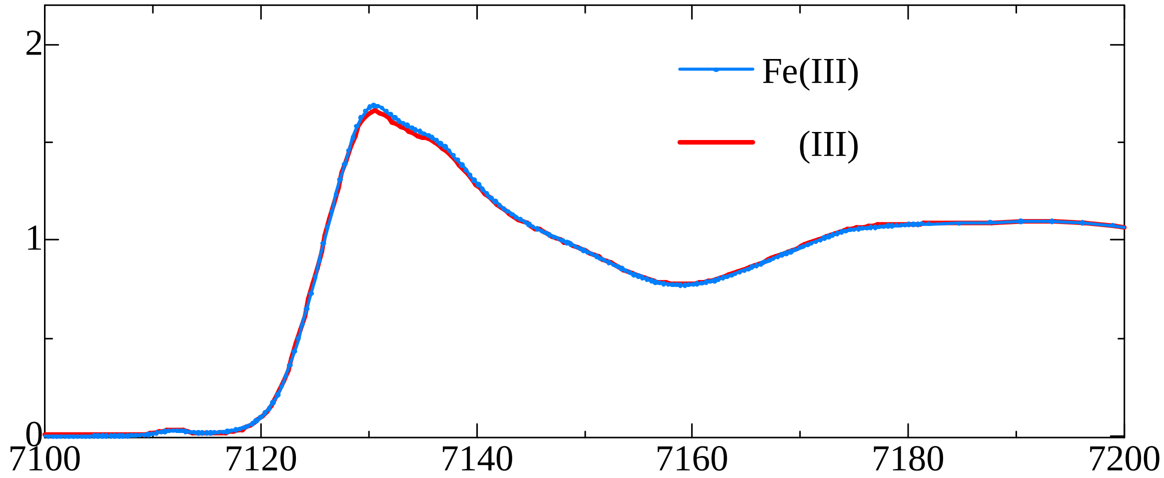
Photon Factory, KEK

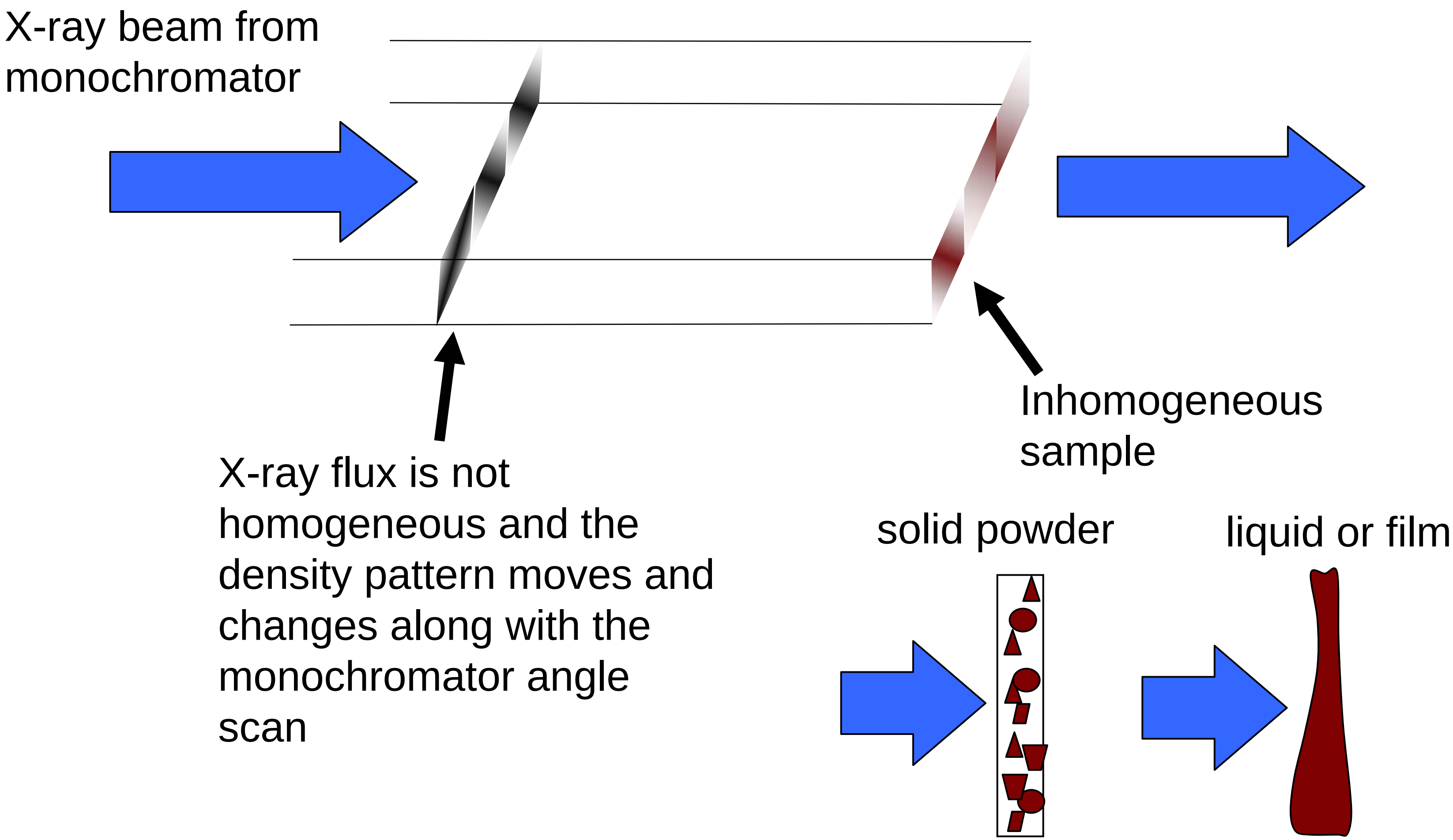


Problem !

Fe(III) ions in aqueous solution

possibly, inhomogeneous sample thickness



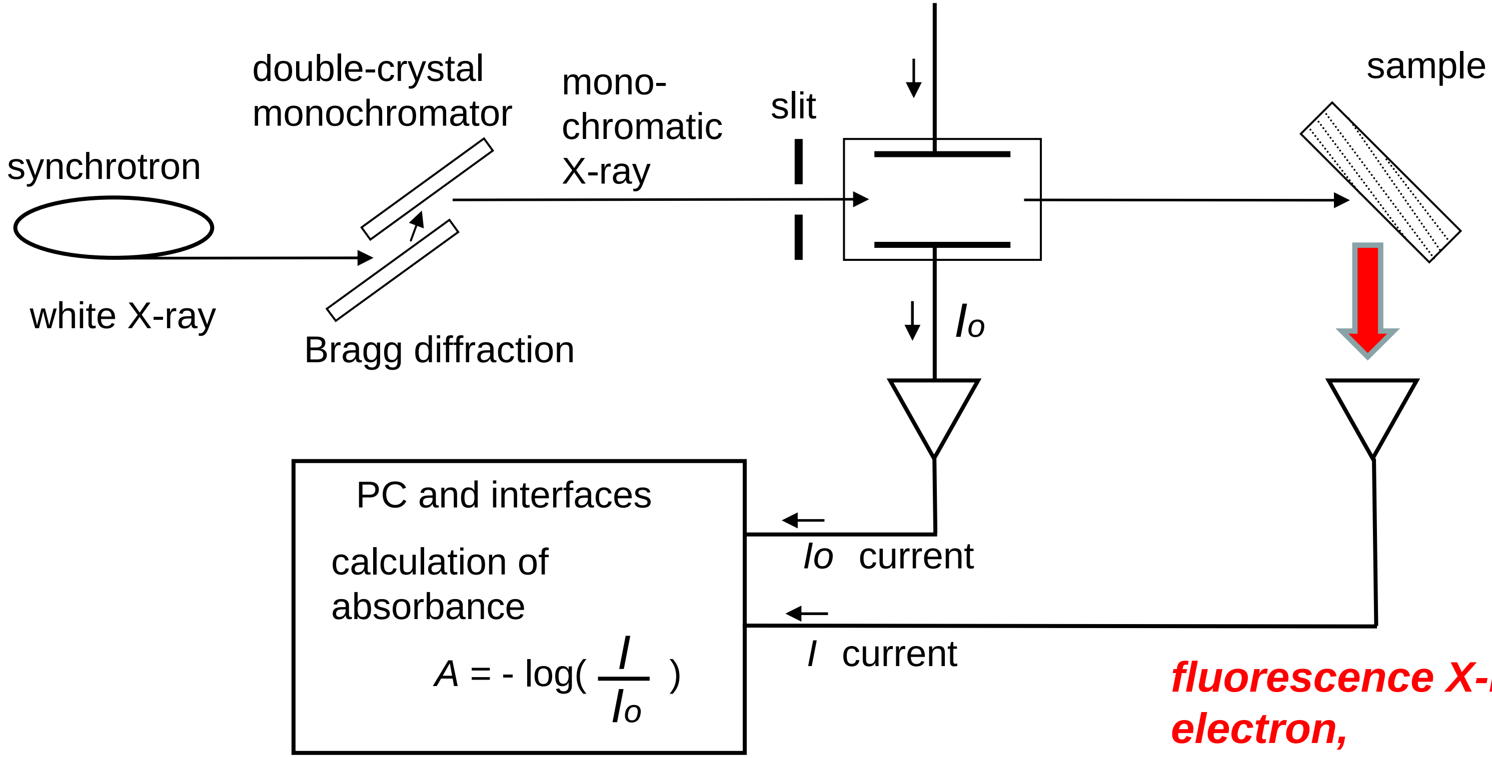


Leads to weaker EXAFS oscillation amplitude and noisy spectrum

Yield methods:

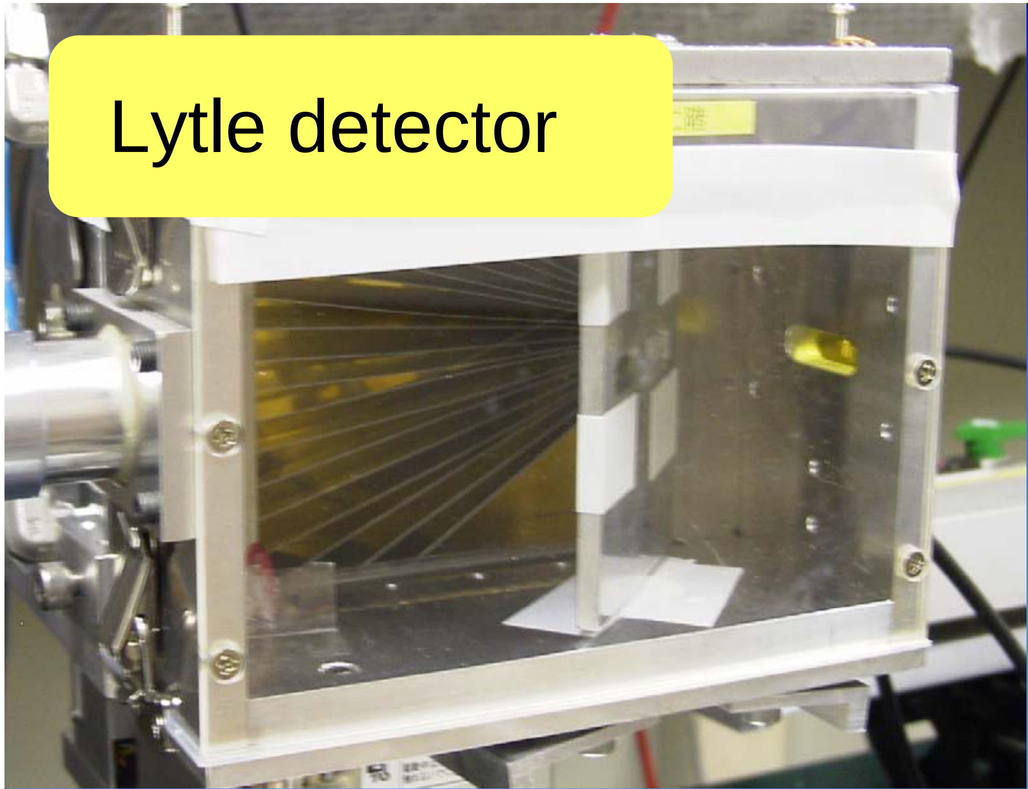
Fluorescence yield
and
Total-conversion-electron-yield

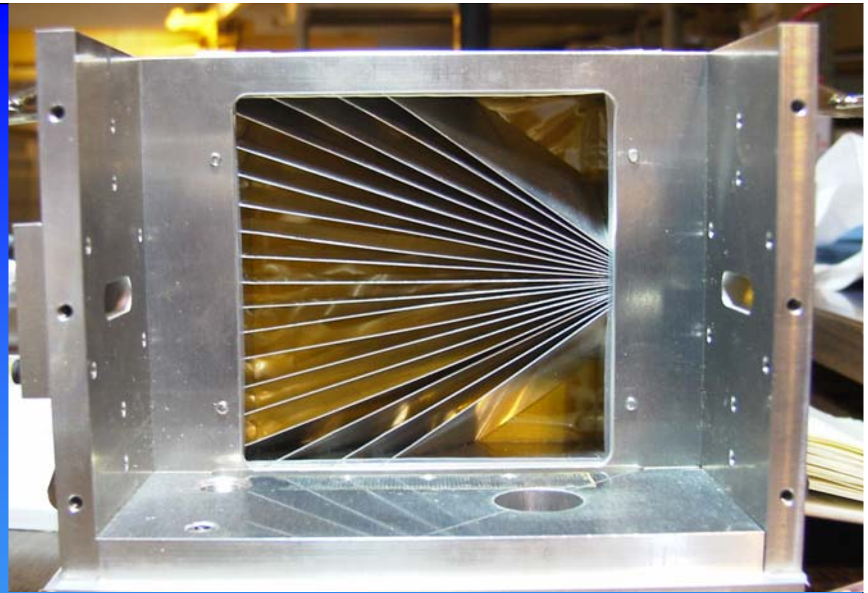
X-ray absorption measurement by yield methods

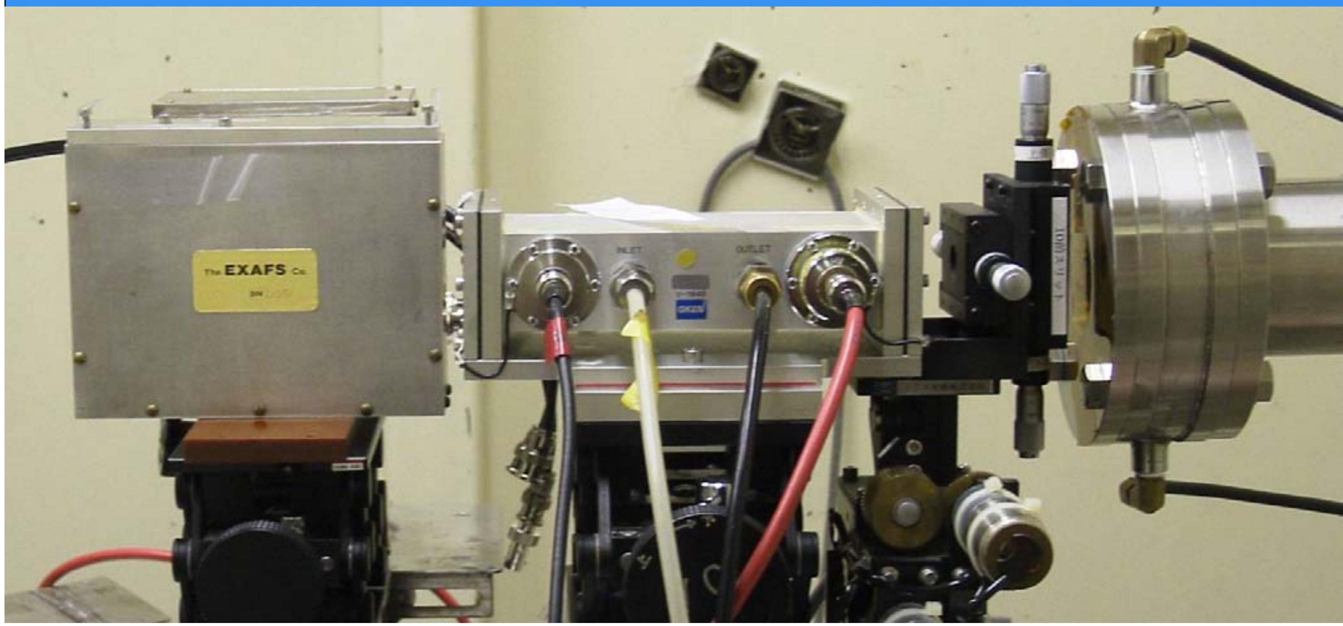


fluorescence X-ray,
electron,
luminescence,
heat, etc;
anything proportional to the X-ray absorption

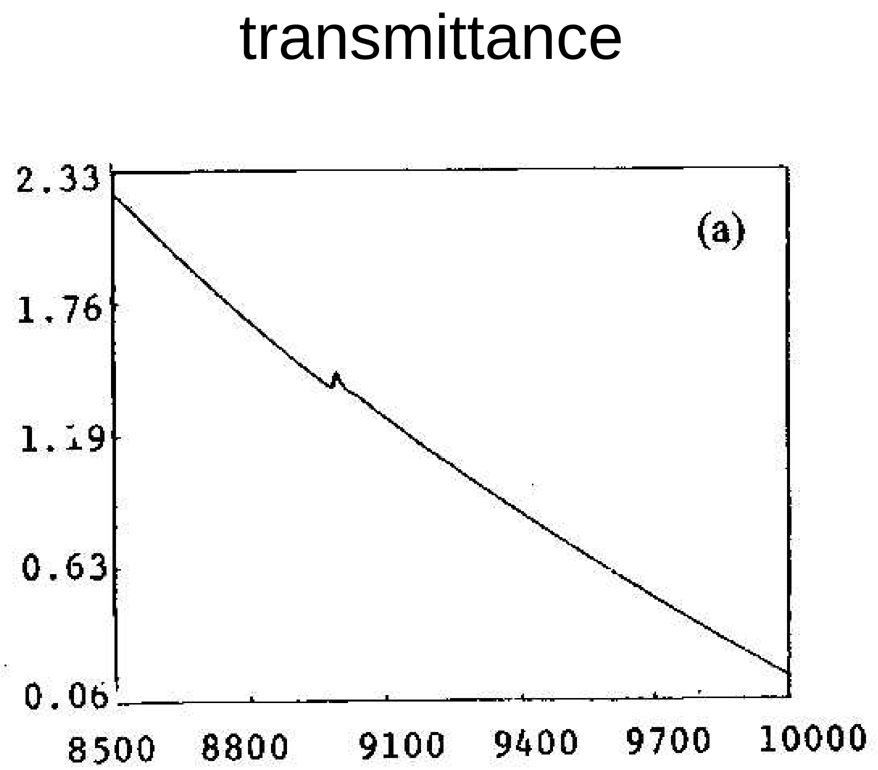
Lytle detector







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



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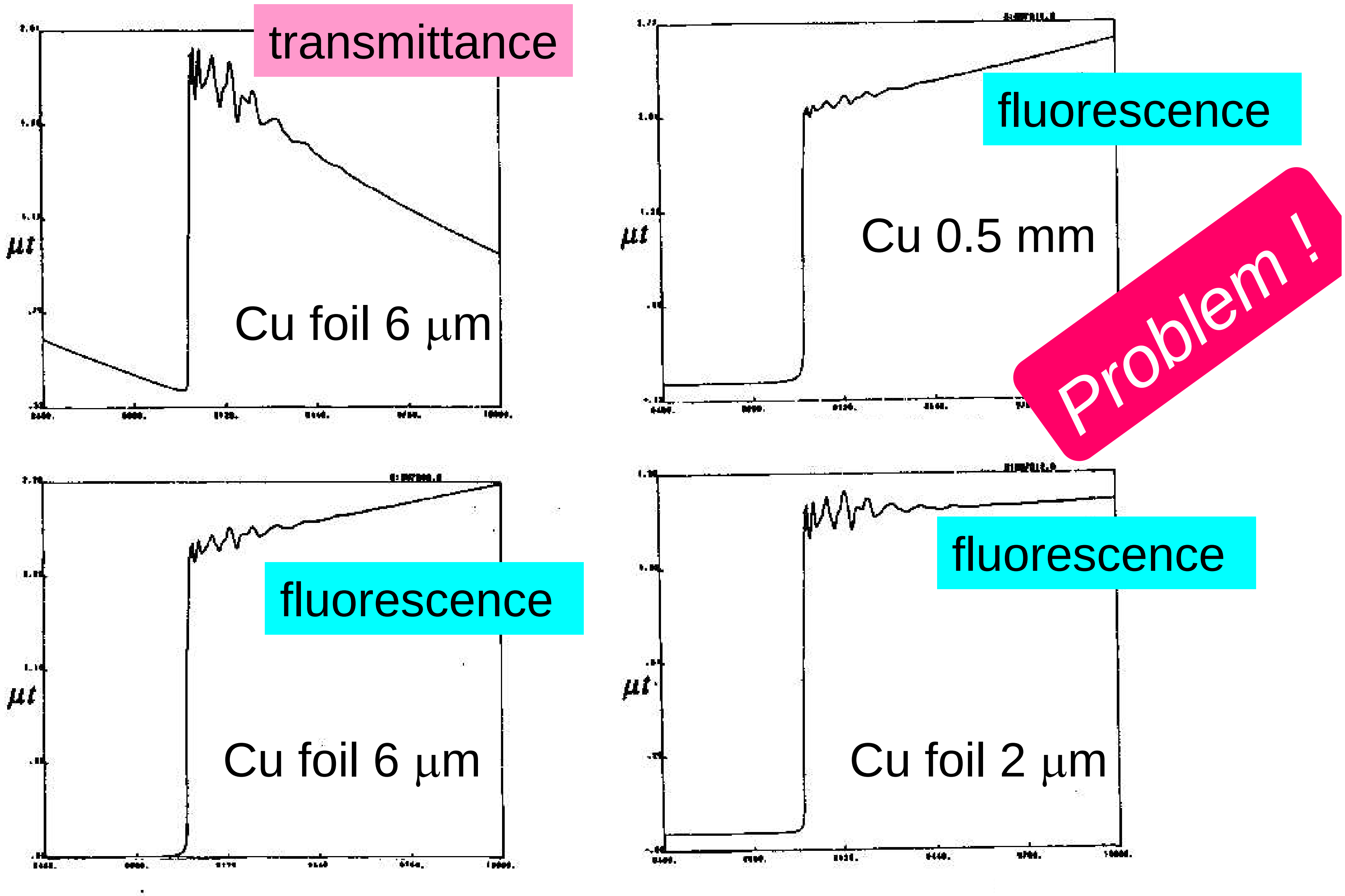
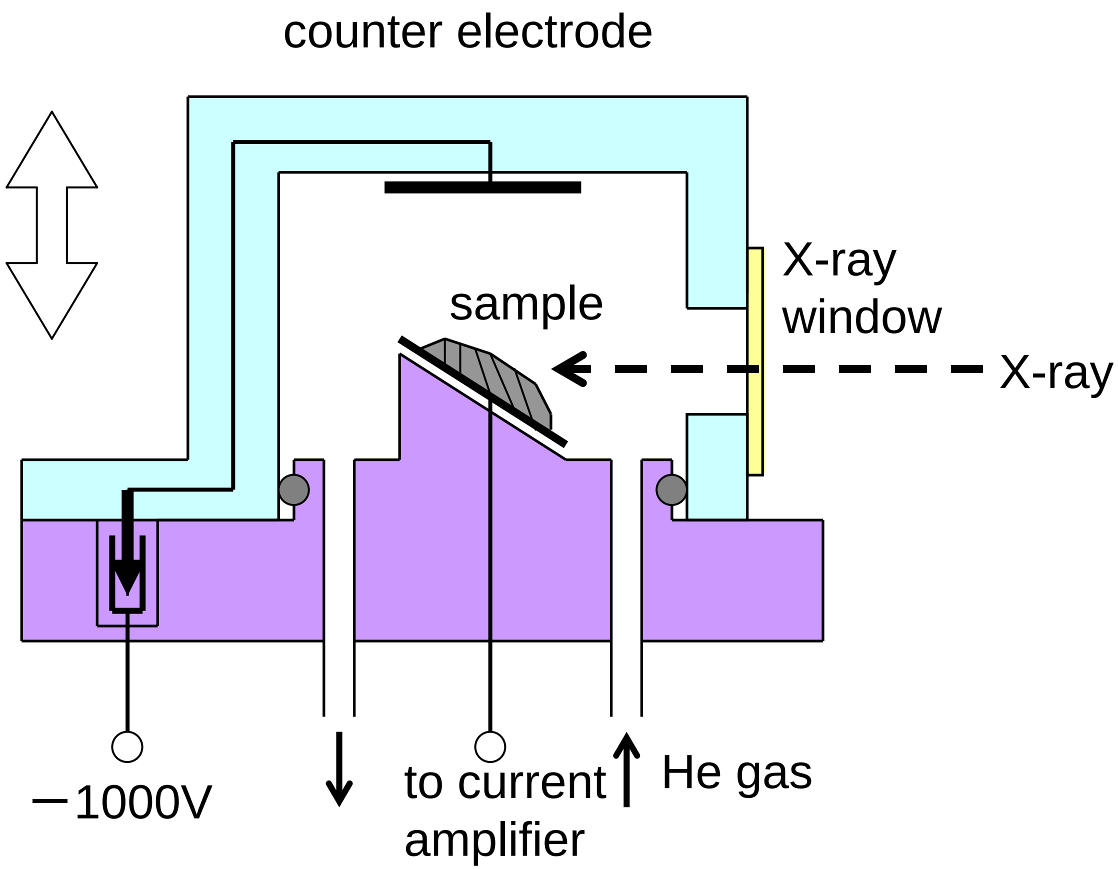
Photon Factory, KEK

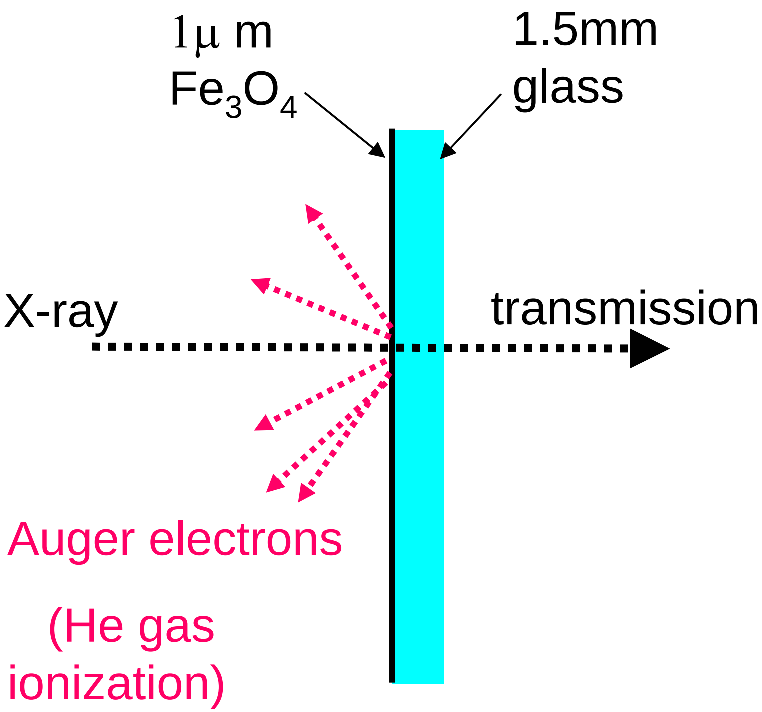


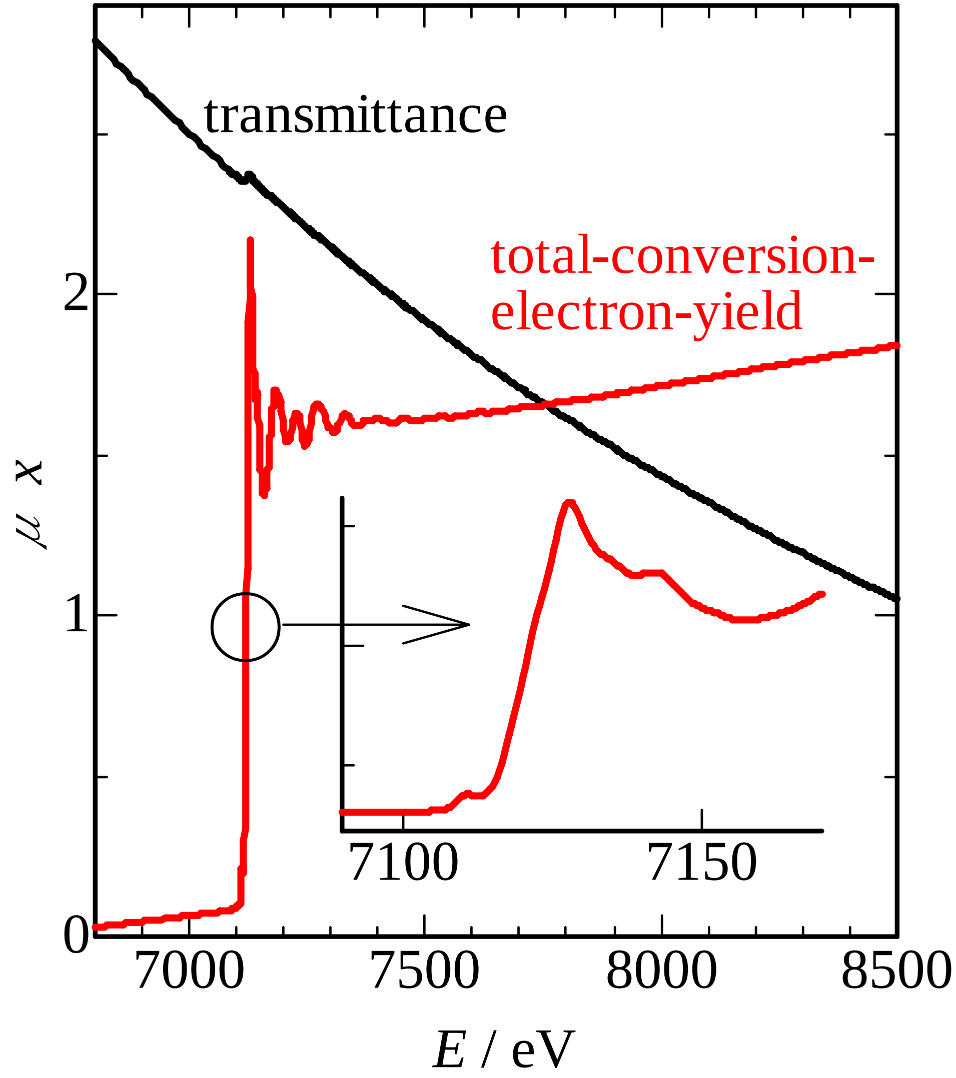
By Masaharu Nomura,
Photon Factory, KEK

Self-absorption effect → incorrect *N*

Total-Conversion-Electron-Yield method

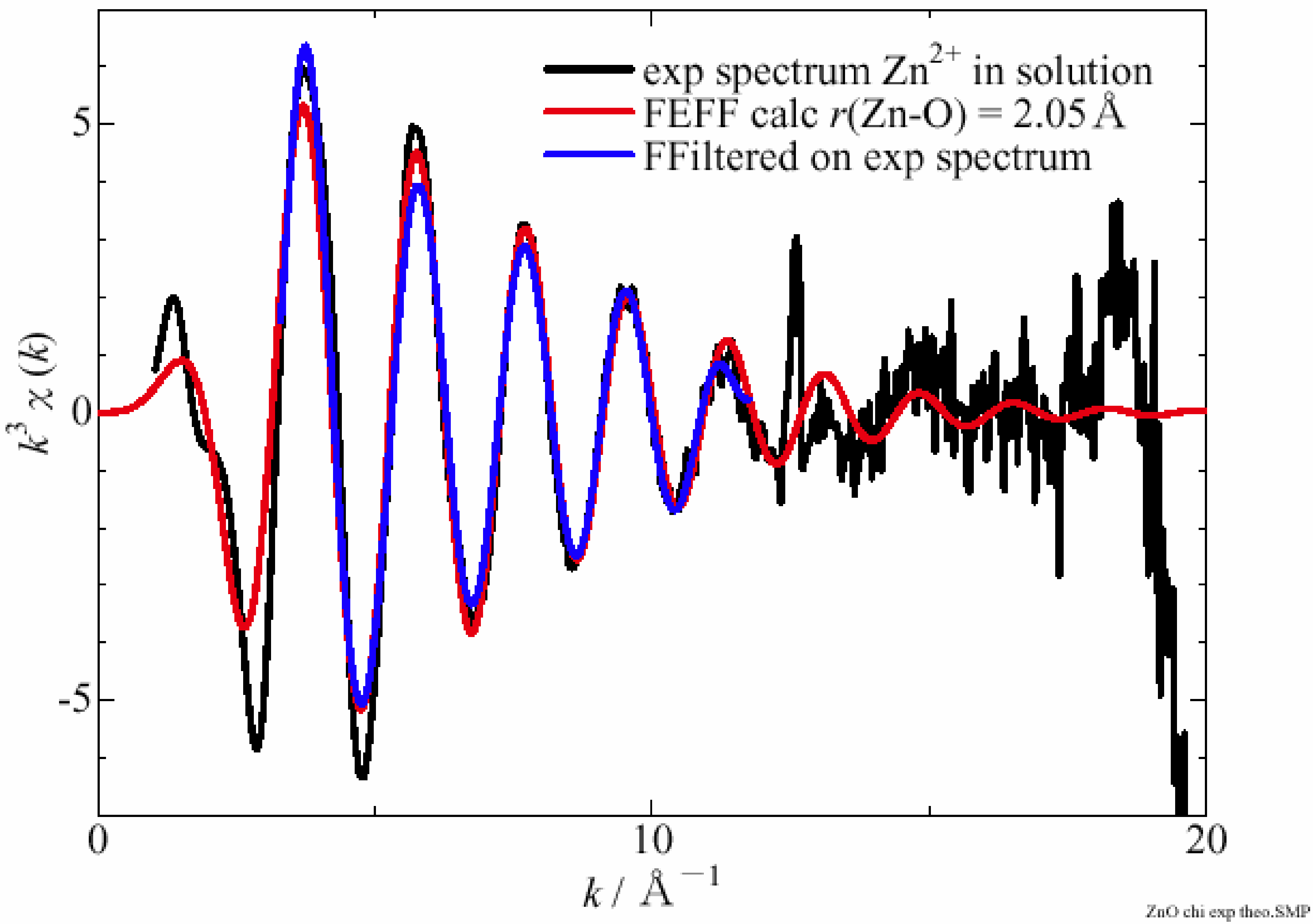




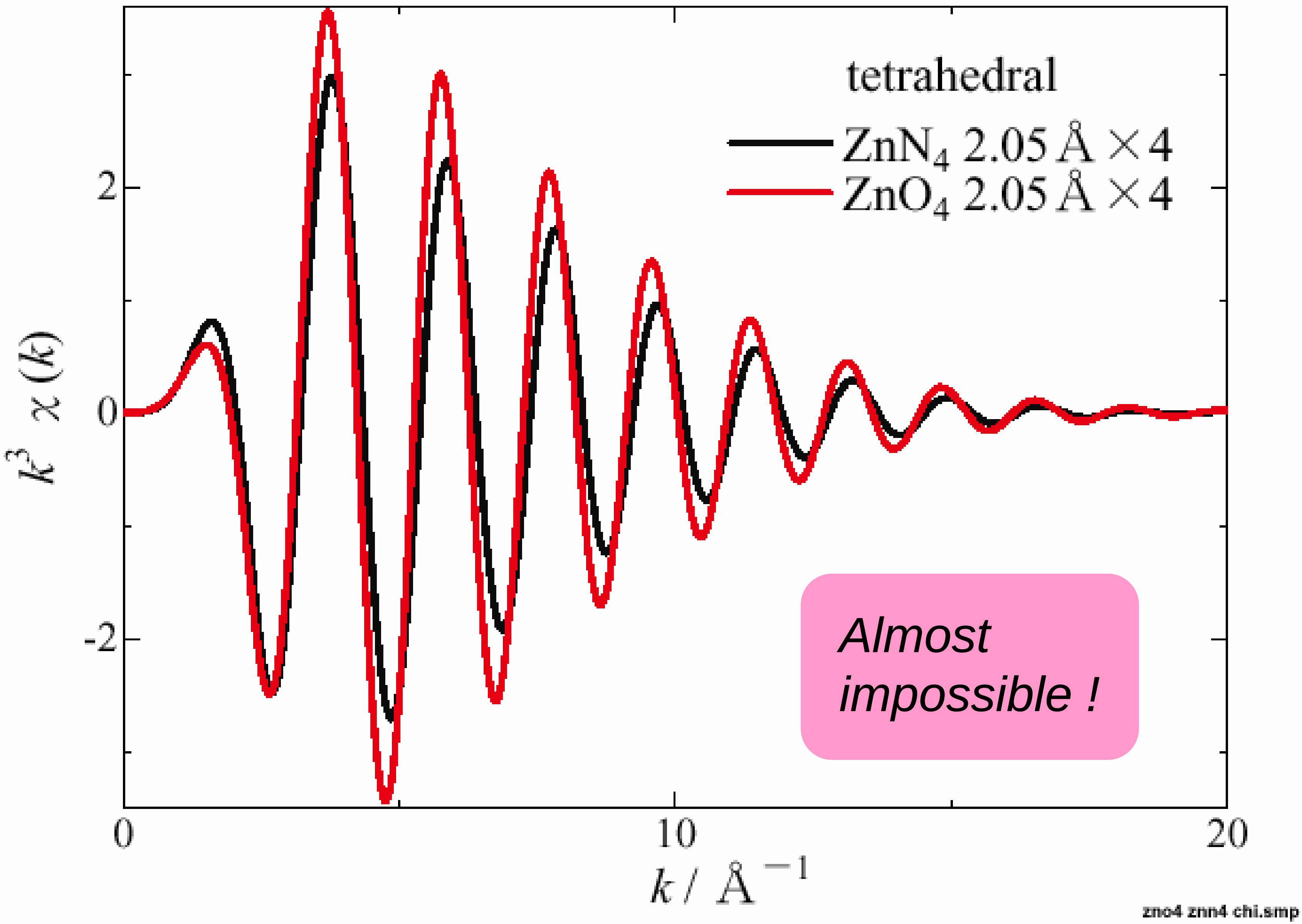


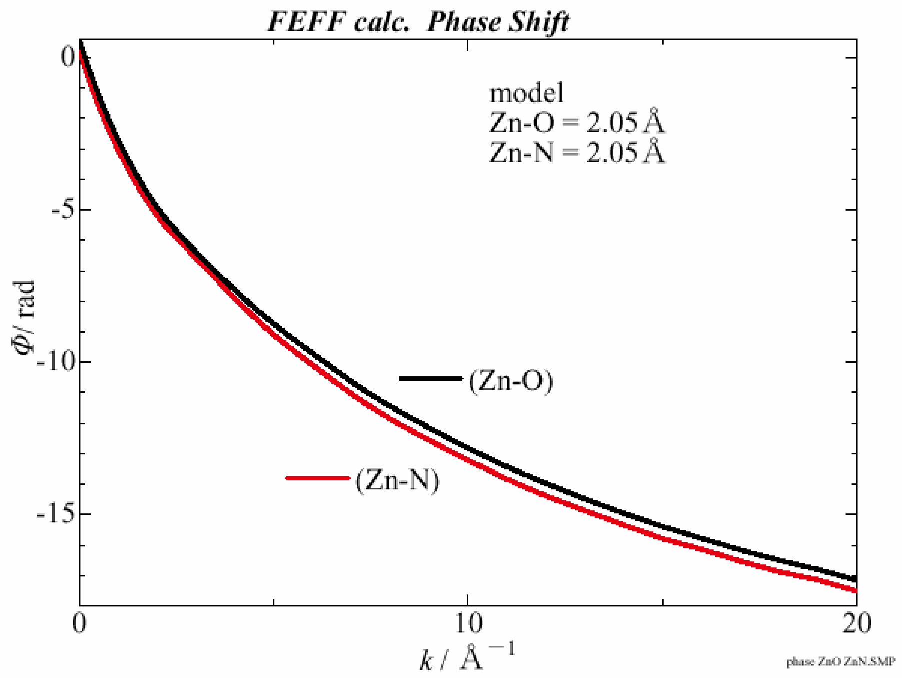
This method can be applied to thick samples owing to the short escape depth of Auger electron.

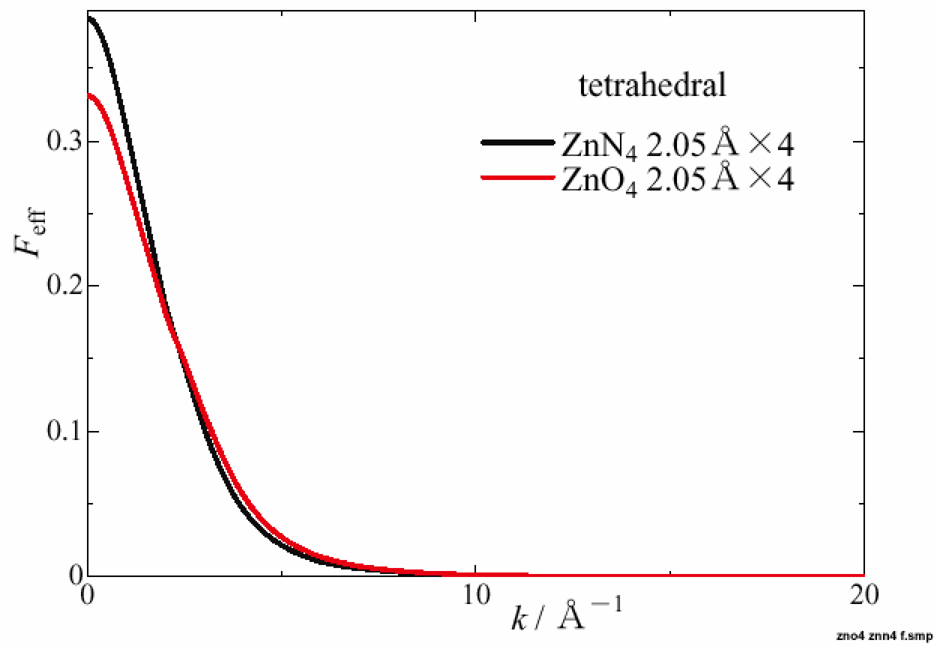
Can we distinguish oxygen from nitrogen by EXAFS?



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


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


FEFF calc. Phase Shift
model
Zn-O = 2.05 Å
Zn-N = 2.05 Å
(Zn-O)
(Zn-N)
Φ / rad
0
-5
-10
-15
0
10
20
k / Å⁻¹
phase ZnO ZnN.SMP


tetrahedral
ZnN4 2.05 Å ×4
ZnO4 2.05 Å ×4
Feff
0.3
0.2
0.1
0
0
10
20
k / Å⁻¹
zno4 znn4 f.smp

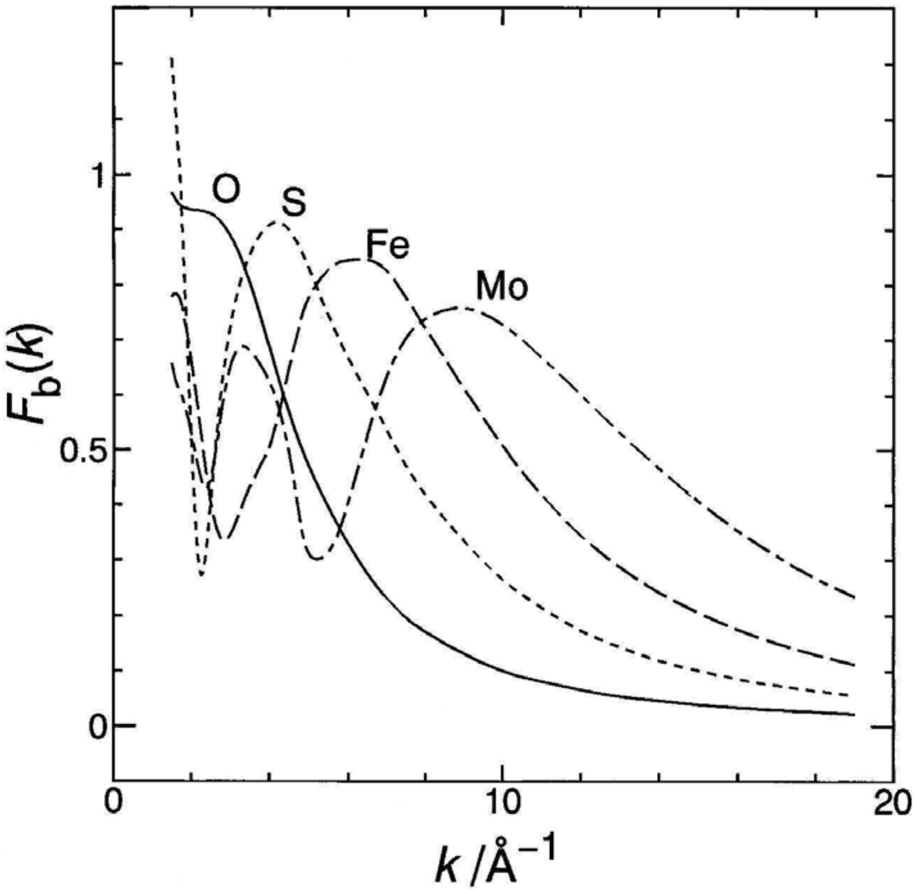
$$\chi(k) = -\sum_{i} \frac{N_i}{k r_i^2} f_i(k) \exp(-2\sigma_i^2 k^2 - 2r_i/\lambda) S_0^2(k) \sin(2kr_i + \phi_i(k))$$

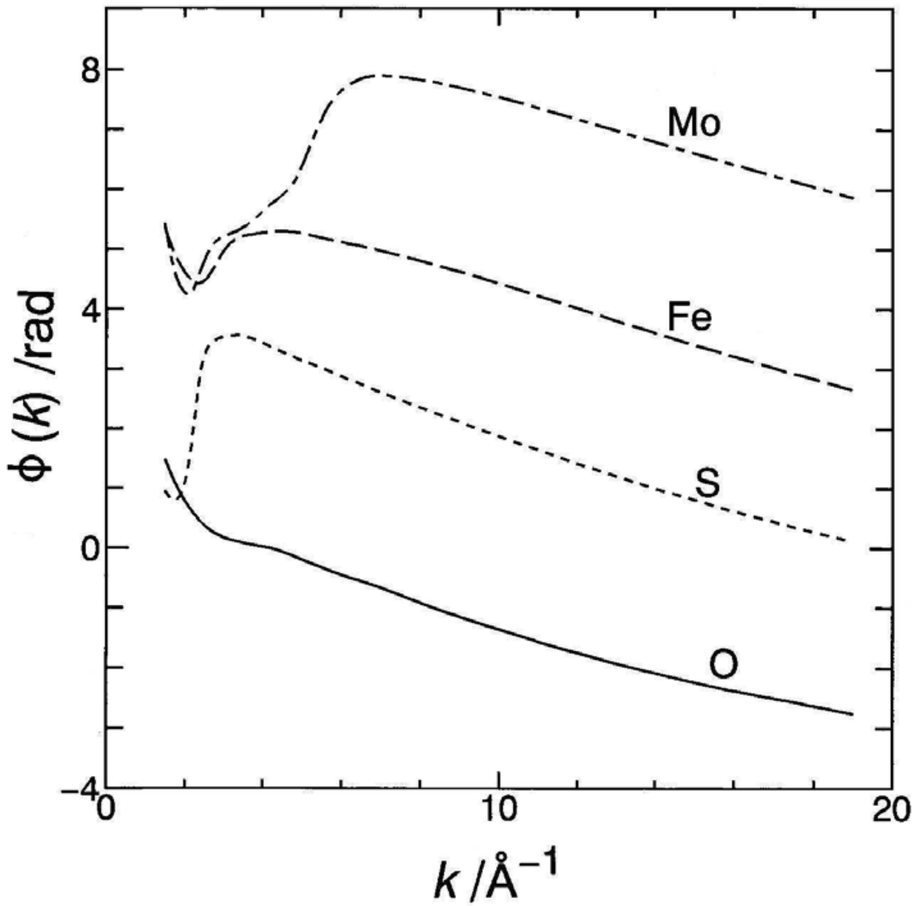
amplitude part

oscillation part

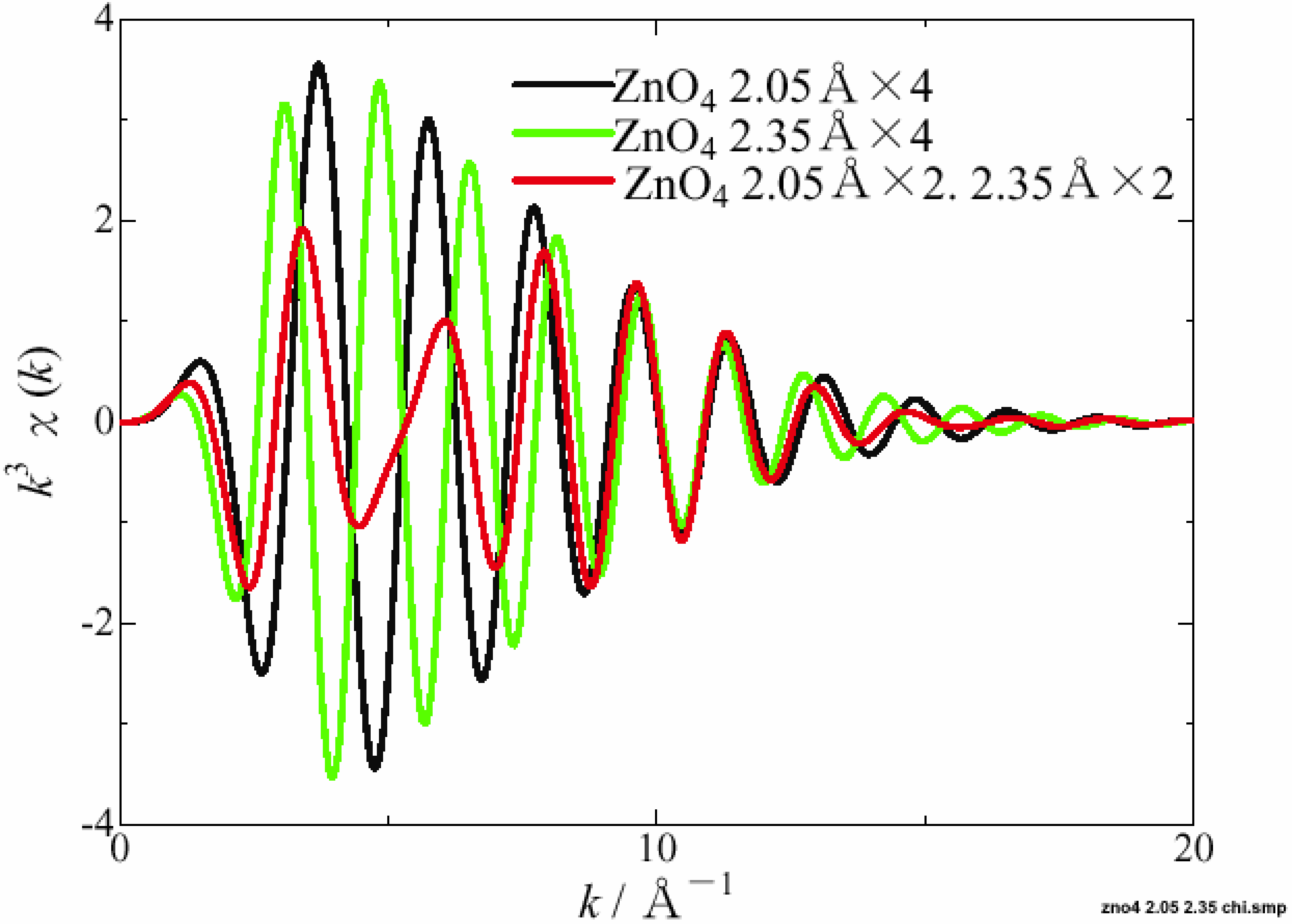
f scattering amplitude

ϕ phase shift

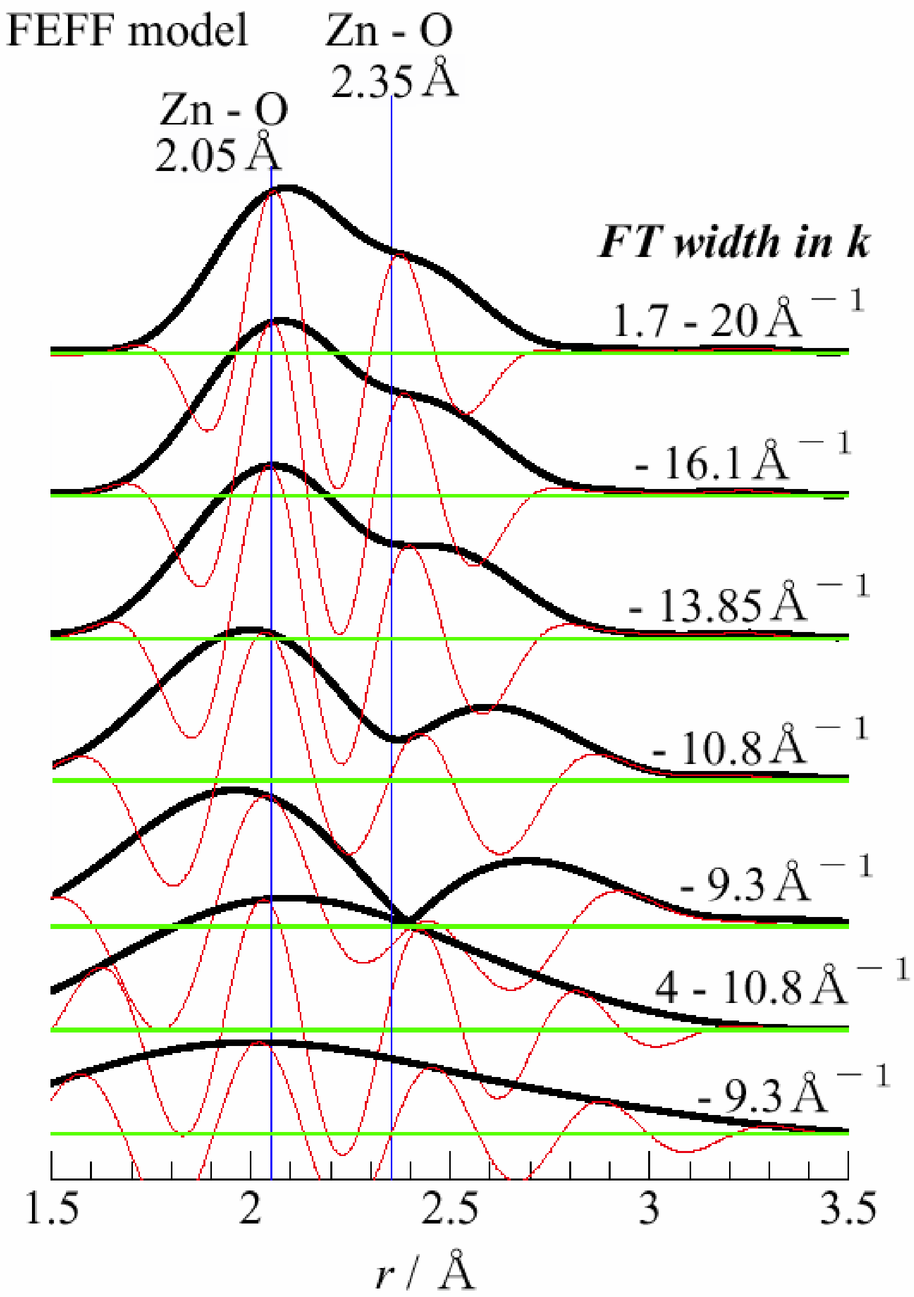


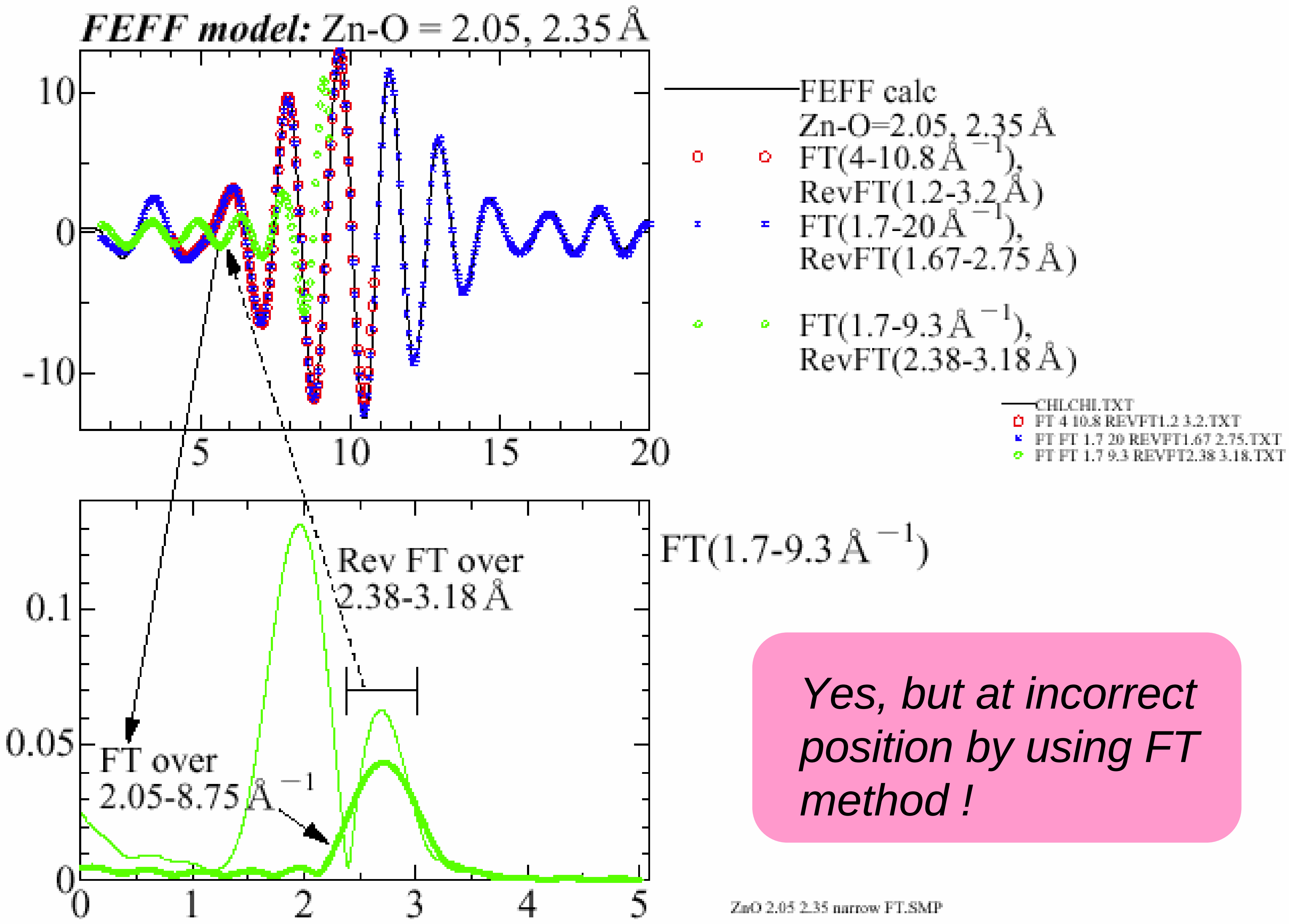


Can we distinguish oxygen atoms 15% distant from others by EXAFS?


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

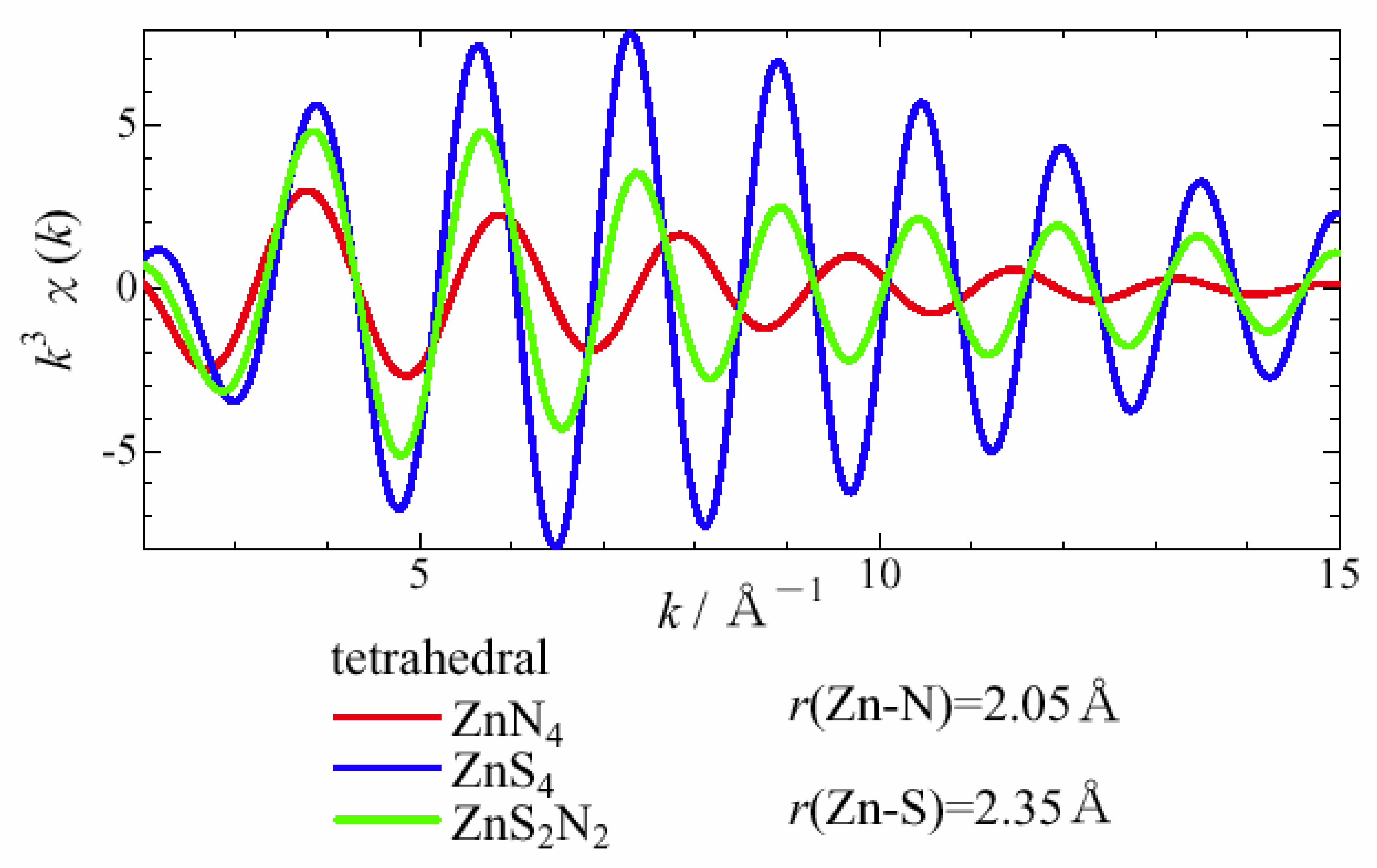
Parameters used for Fourier Trans: O



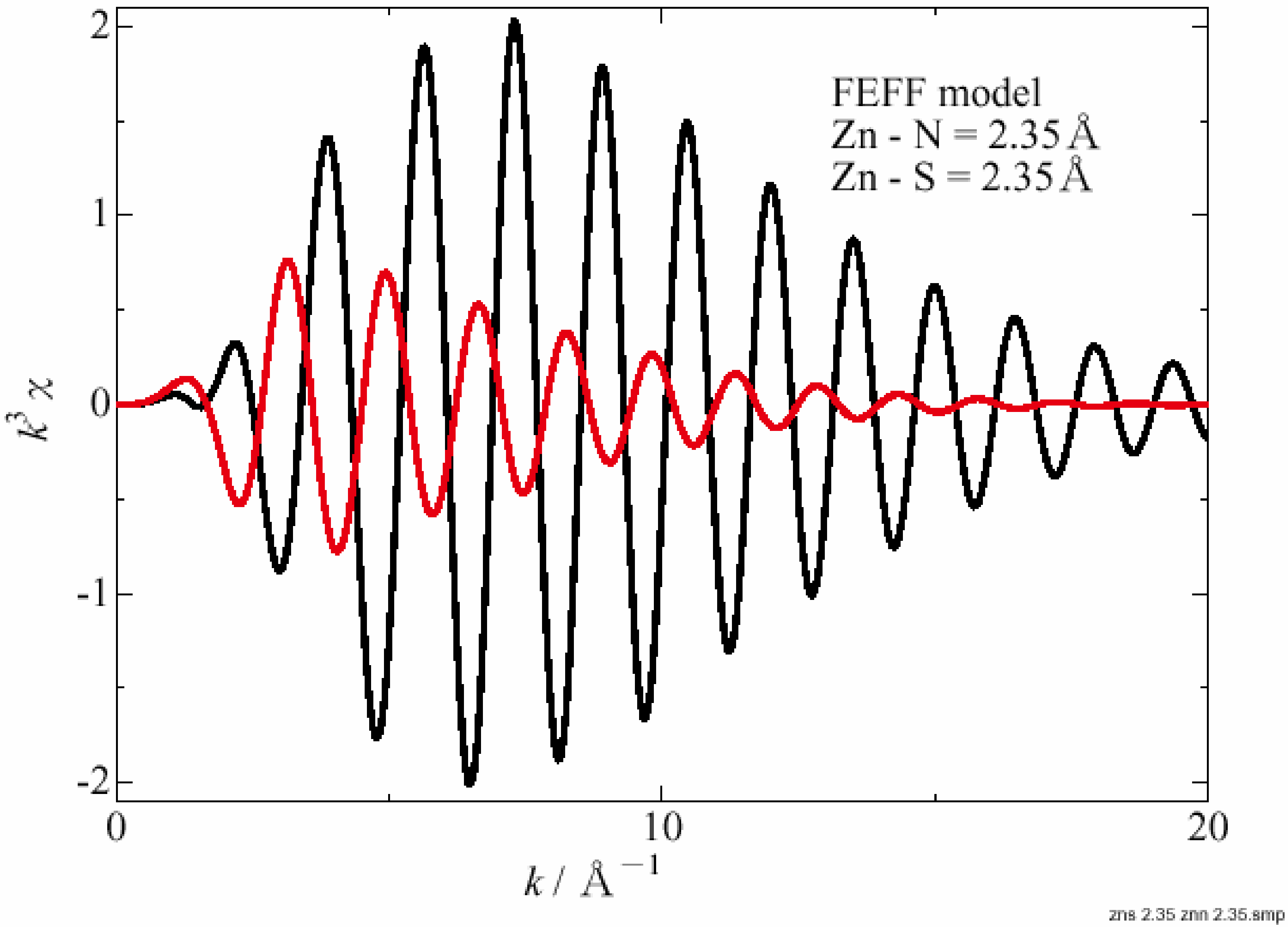

FEFF model: Zn-O = 2.05, 2.35 Å
10
0
-10
5
10
15
20
FEFF calc
Zn-O=2.05, 2.35 Å
FT(4-10.8 Å^{-1}),
RevFT(1.2-3.2 Å)
FT(1.7-20 Å^{-1}),
RevFT(1.67-2.75 Å)
FT(1.7-9.3 Å^{-1}),
RevFT(2.38-3.18 Å)
CHI.CHI.TXT
FT 4 10.8 REVFT1.2 3.2.TXT
FT FT 1.7 20 REVFT1.67 2.75.TXT
FT FT 1.7 9.3 REVFT2.38 3.18.TXT
FT(1.7-9.3 Å^{-1})
Rev FT over
2.38-3.18 Å
FT over
2.05-8.75 Å^{-1}
0.1
0.05
0
0
1
2
3
4
5
ZnO 2.05 2.35 narrow FT.SMP
Yes, but at incorrect position by using FT method !

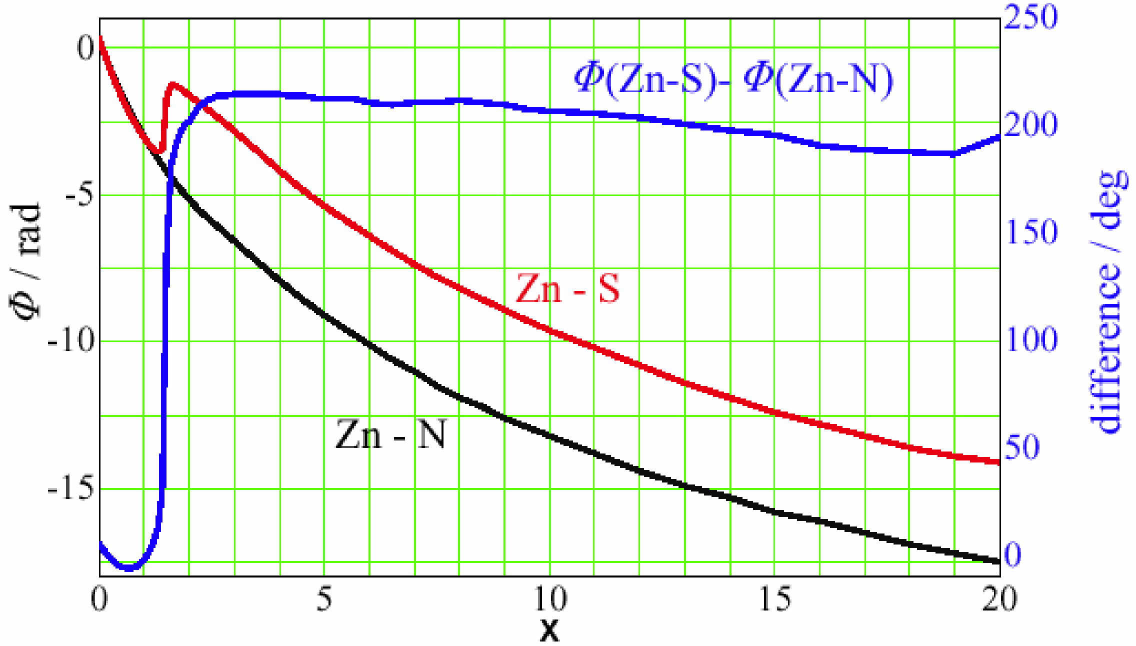
James E. Penner-Hahn *J. Am. Chem. Soc.* 1998,**120**,8401

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

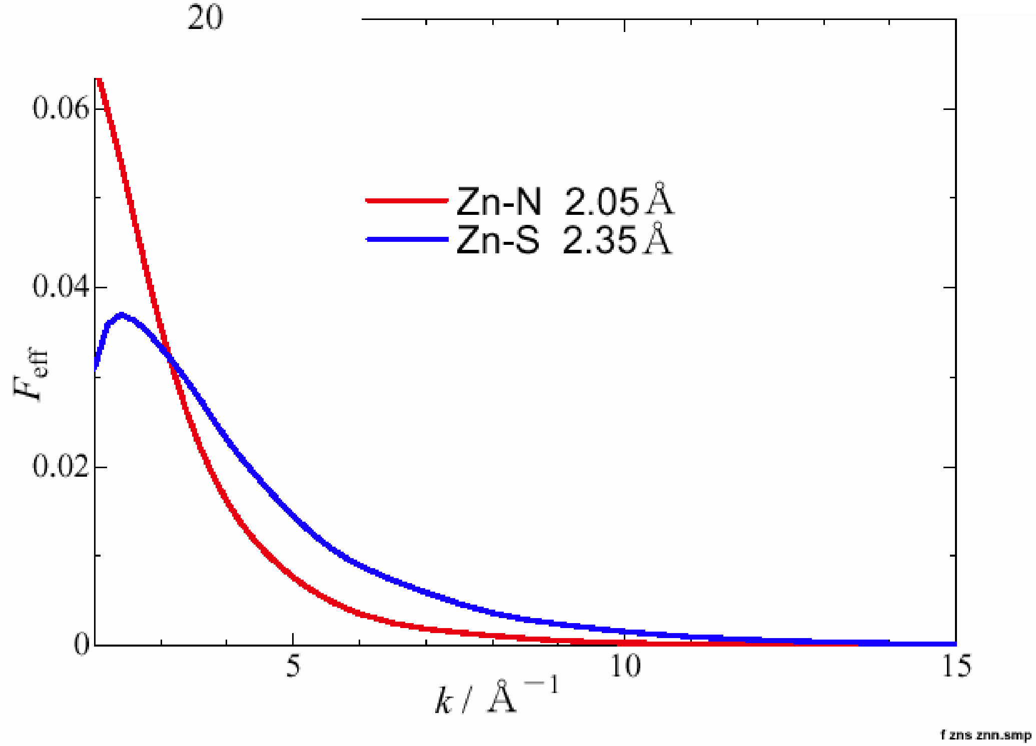


5
0
-5
5
10
15
k / Å −1
k3 χ (k)
tetrahedral
ZnN4
ZnS4
ZnS2N2
r(Zn-N)=2.05 Å
r(Zn-S)=2.35 Å

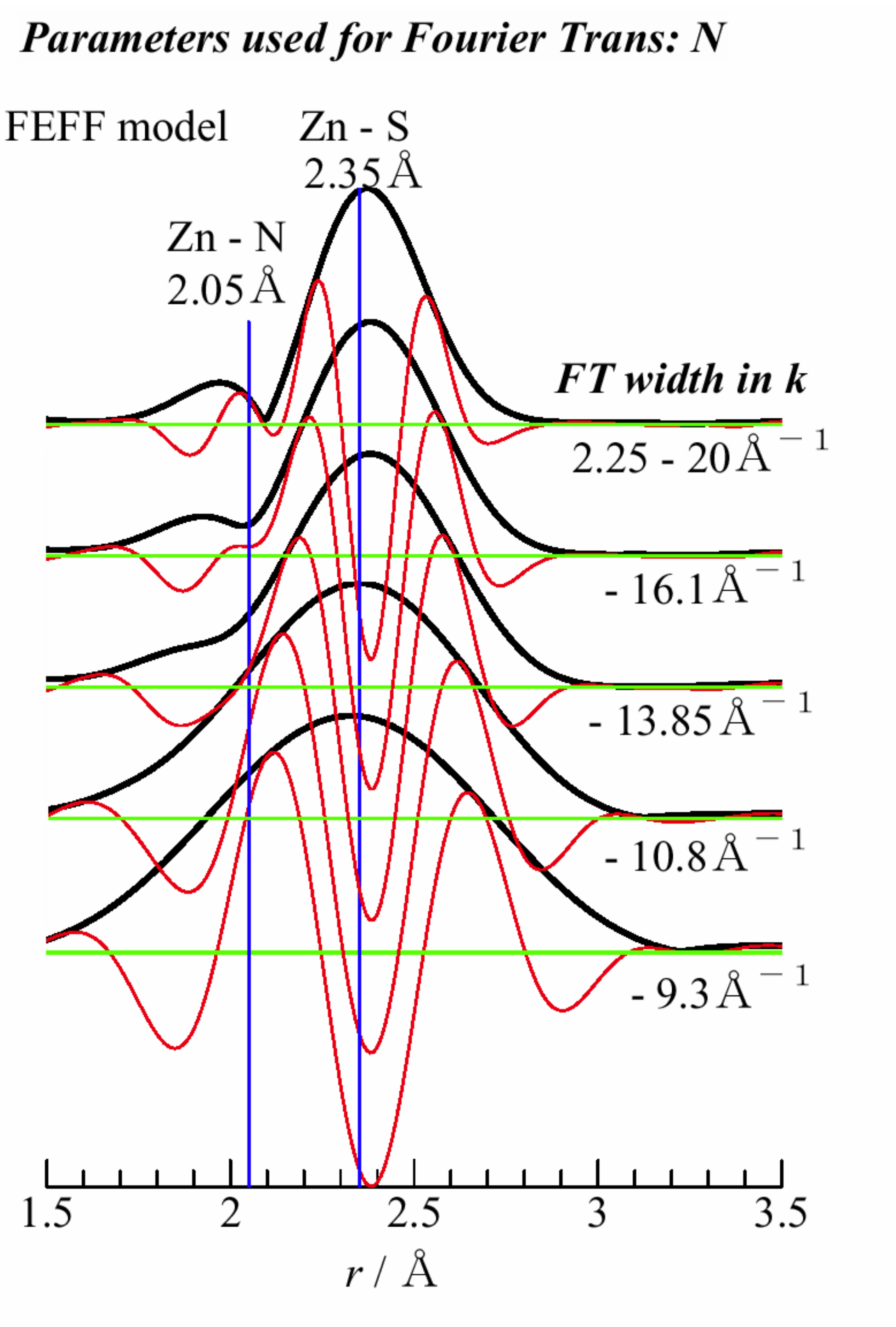

FEFF model
Zn - N = 2.35 Å
Zn - S = 2.35 Å
$k^3\chi$
k / Å^{-1}
2
1
0
-1
-2
0
10
20
zns 2.35 znn 2.35.smp



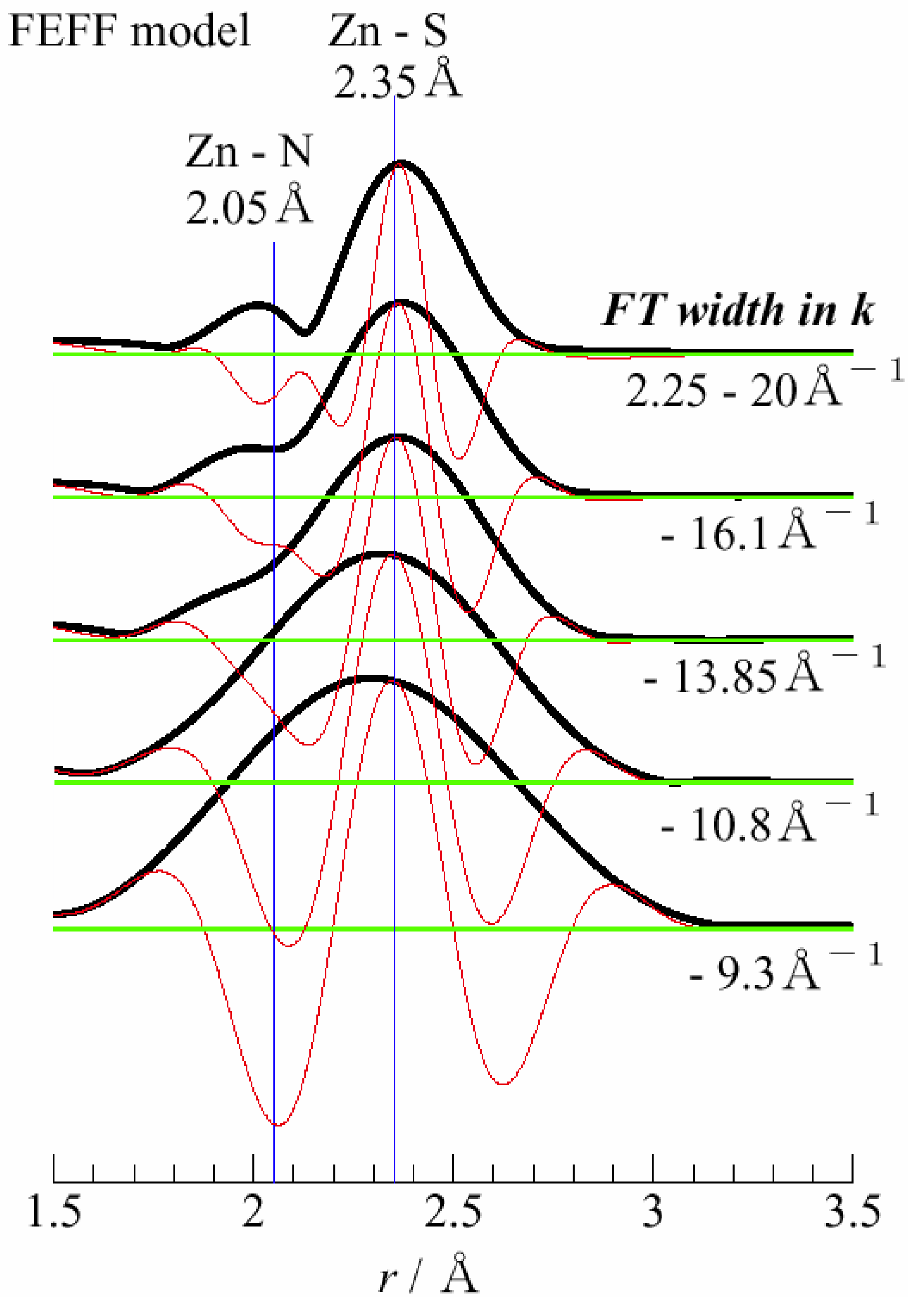
Φ(Zn-S)- Φ(Zn-N)
Zn - S
Zn - N
Φ / rad
difference / deg
X
0
-5
-10
-15
0
5
10
15
20
250
200
150
100
50
0



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


Parameters used for Fourier Trans: N
FEFF model
Zn - S
2.35 Å
Zn - N
2.05 Å
FT width in k
2.25 - 20 Å⁻¹
- 16.1 Å⁻¹
- 13.85 Å⁻¹
- 10.8 Å⁻¹
- 9.3 Å⁻¹
1.5
2
2.5
3
3.5
r / Å

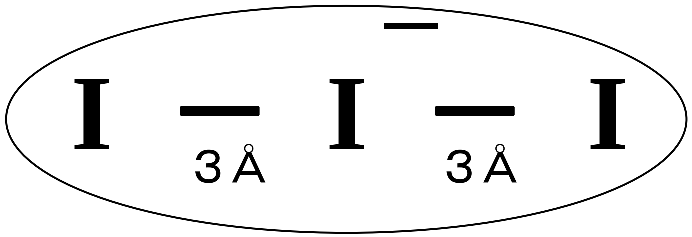
Parameters used for Fourier Trans: S

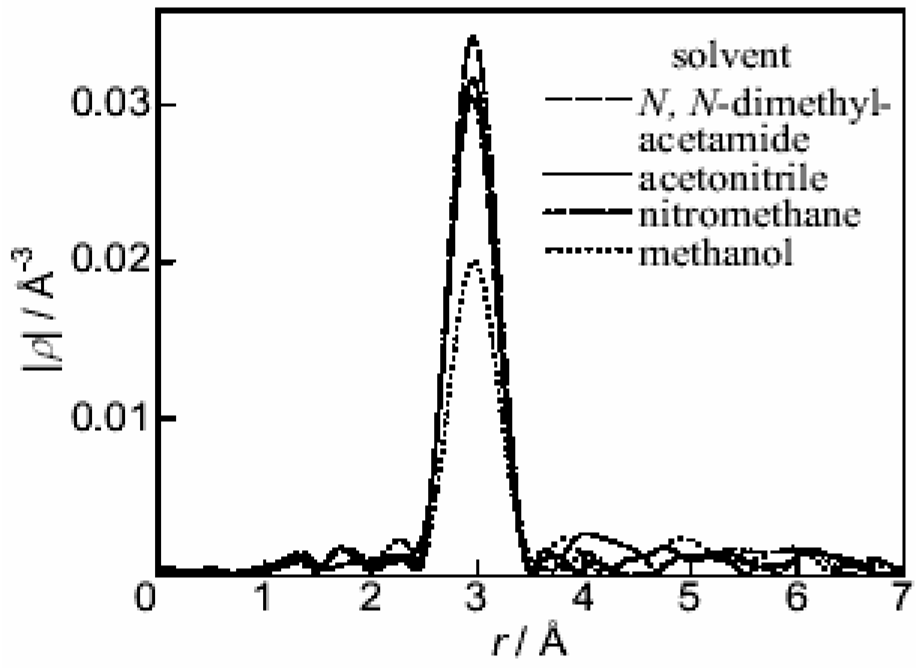


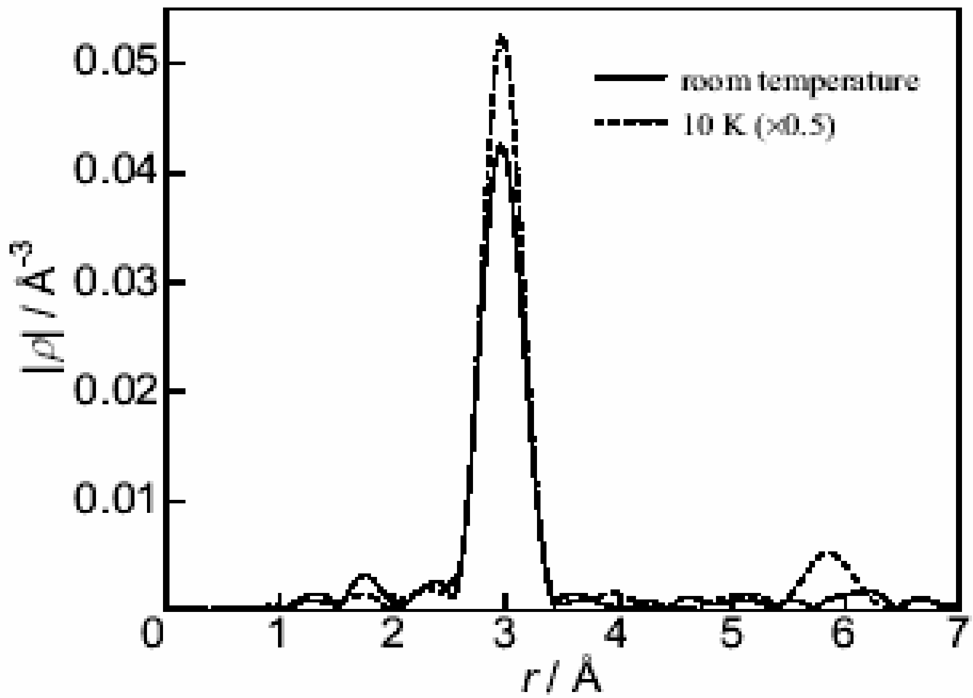
Almost impossible !

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



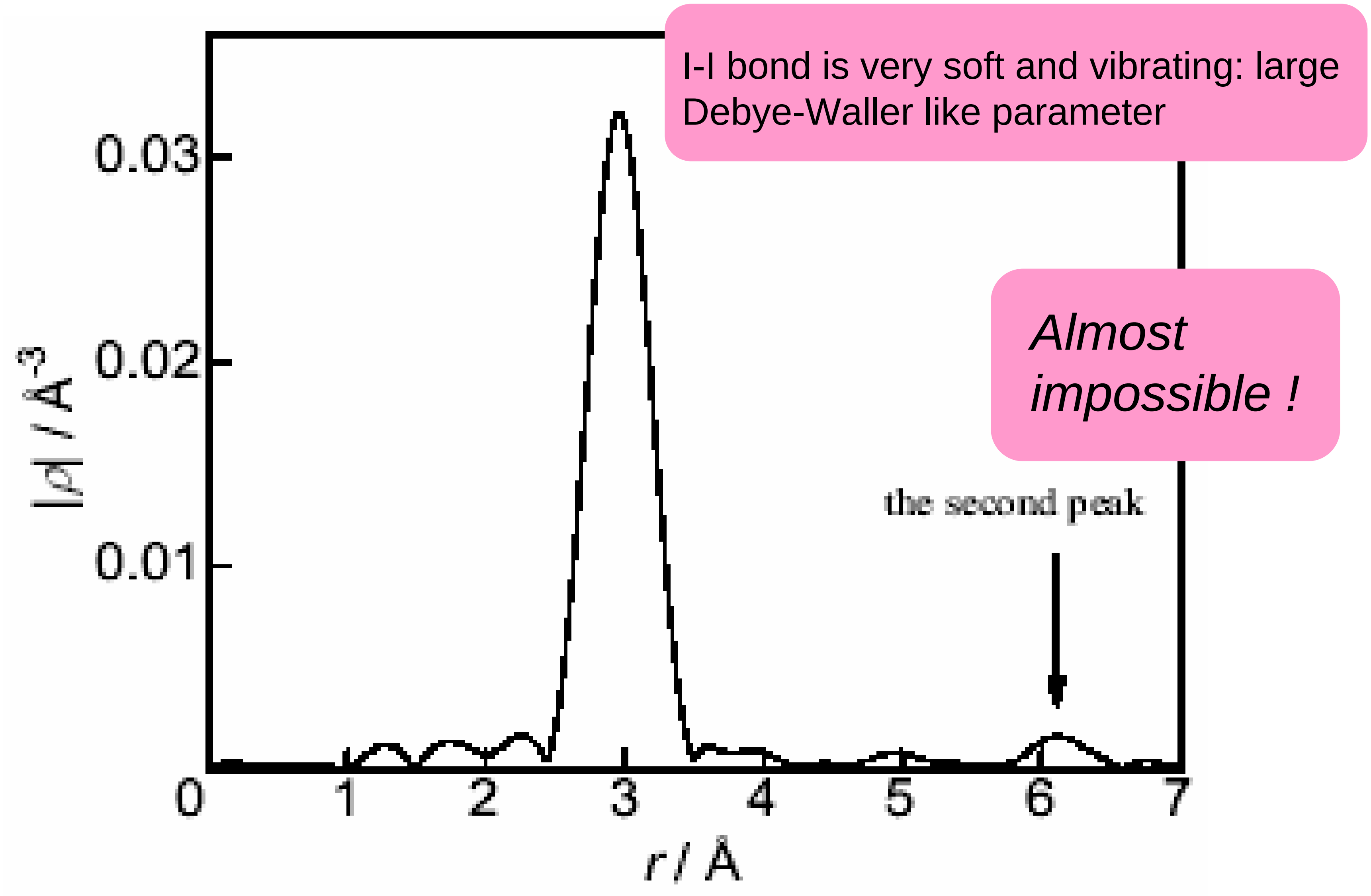




Dissolved in organic solvents

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

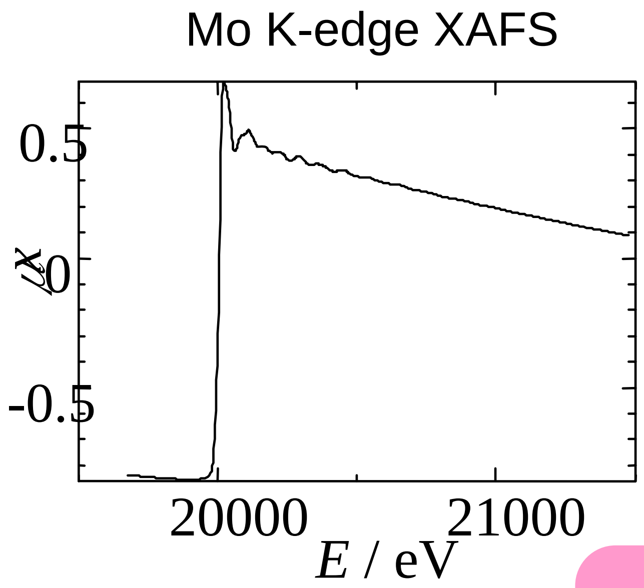
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

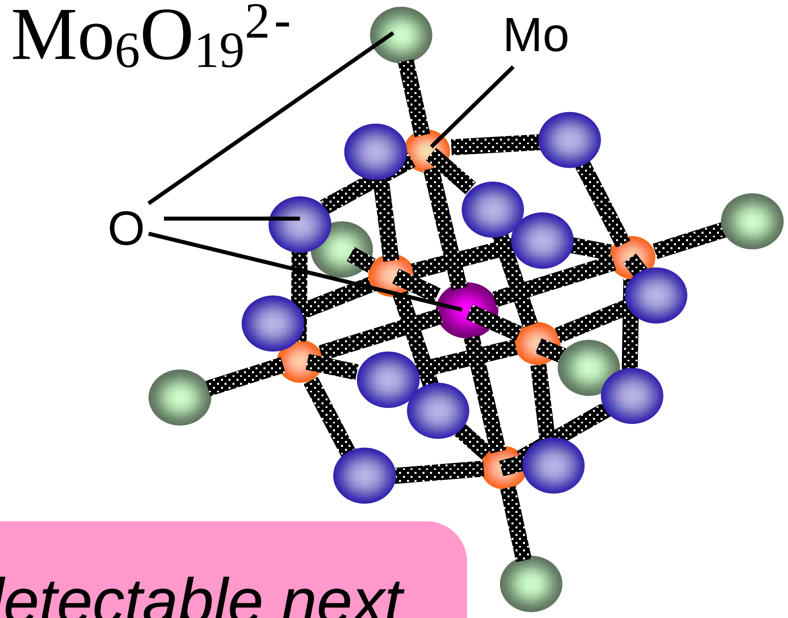


Iodine K-edge EXAFS Fourier transform for the compound spectrum made up from 12 independent spectra for organic solvent solutions.

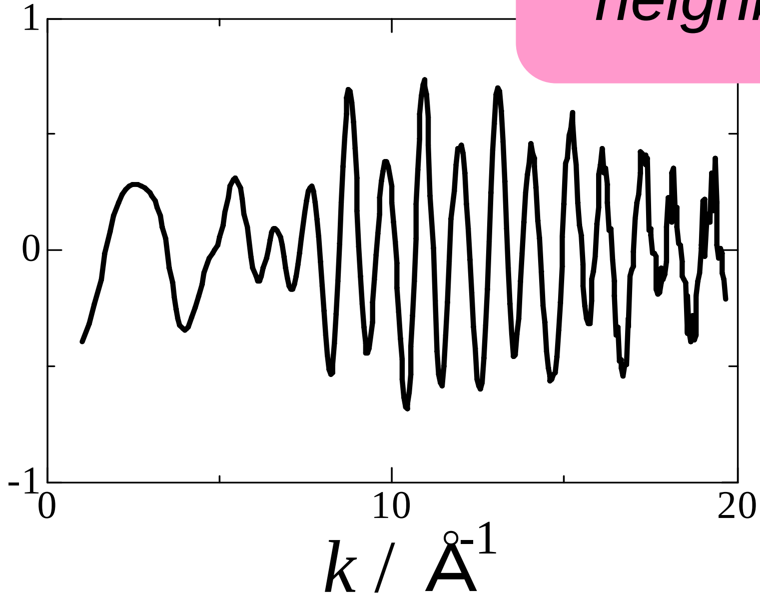
H. Sakane, T. Mitsui, H. Tanida, I. Watanabe. J. Synchrotron Rad. 8, 674 (2001).

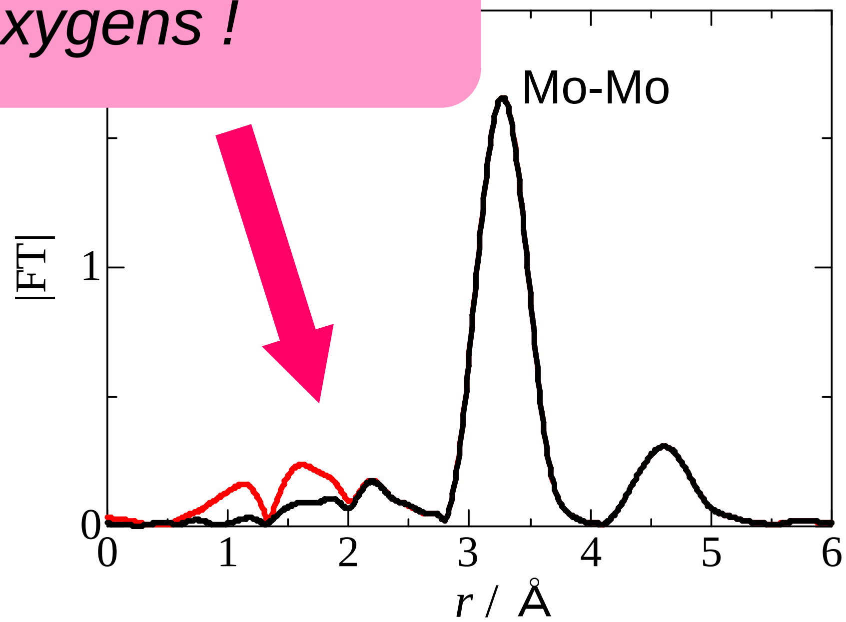
Large symmetrical cluster of molybdenum oxide complex

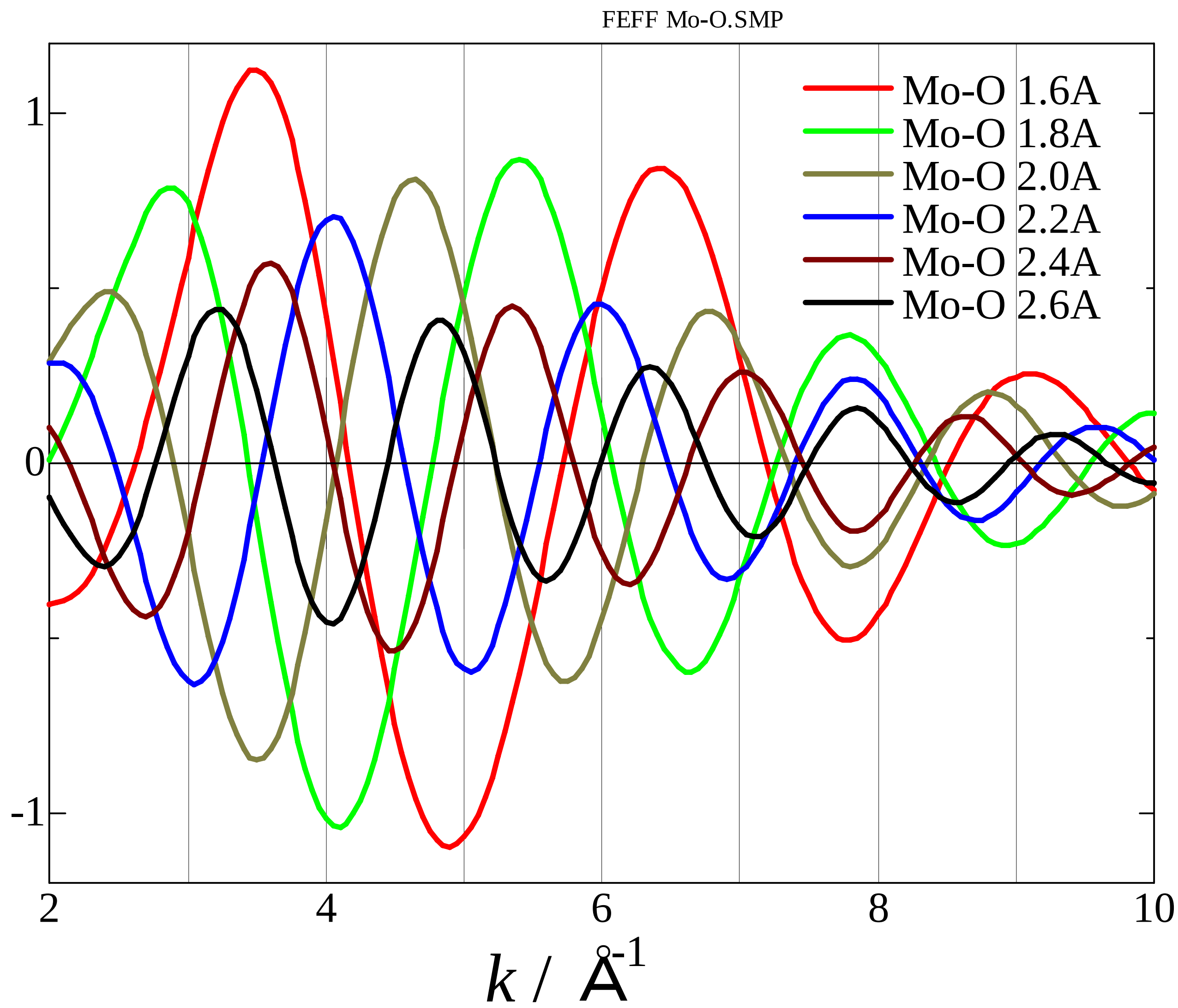




Almost undetectable next neighbor oxygens !






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.