XAFS: Study of the local structure around an X-ray absorbing atom

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(1) Principle of XAFS
(2) Instrumentation
(3) XAFS spectral analysis
(4) XAFS applications
(5) New directions of XAFS
(1) Principle of XAFS
Phenomena caused by X-ray irradiation

- Diffracted X-rays
- Fluorescent X-rays
- Scattered X-rays
- Photoelectrons
- Desorbed ions

X-ray
X-ray absorption spectrum from Pt foil

wavelength
XAFS

X-ray Absorption Fine Structure:
Local electronic and geometric structures around
the x-ray absorbing atom

Absorption Coefficient

Photon Energy

NEXAFS
30-50 eV

EXAFS
50 - 1000 eV

Threshold
XAFS spectrum from an atom
XAFS spectrum from a diatomic molecule
X-ray absorption: Fermi’s Golden Rule

\[
\mu = \frac{4\pi^2 \omega_e^2}{c} N_a |\langle f|e \cdot r|i \rangle|^2 \rho(E_f)
\]

- \(i\): wave function of the initial state \(1s\)
- \(f\): wave function of the final state
- \(\rho(E_f)\): superposition of the ejected wave and back-scattered waves

\[
\chi(k) = \frac{\mu - \mu_0}{\mu_0} \text{ EXAFS function}
\]

Point atom, plane wave, and single scattering approximations

\[
\chi(k) = \sum_j A_j(k) \sin[2kr_j + 2\delta_j(k)]
\]

\[
A_j(k) = \frac{N_j |f(k,\pi)|}{kr_j^2} \exp(-2r_j/\lambda) \exp(-2\sigma^2 k^2)
\]
EXAFS oscillation

\[ \chi(k) = \sum_i A_i(k) \sin(2kR_i + \phi_i) \]

\[ k = \frac{p}{\hbar} = \frac{\sqrt{2m(E - E_0)}}{\hbar} \]

Ri: bond distance

\[ \phi_i \] Phase shift
\[ \chi(k) = \sum_i A_i(k) \sin(2kR_i + \phi_i) \]
Phase shift of the X-ray absorbing atom

$k/A^{-1}$
EXAFS amplitude

\[ A_i(k) = \frac{N_i^*}{kR_i^2} |F_i(k)| \exp\left(-2\sigma_i^2 k^2\right) \exp\left(-2 \frac{R_i}{\lambda}\right) \]

- Effective Coordination number
- Debye-Waller factor
- Back scattering amplitude
- Electron mean free path
Backscattering Amplitude $F(k)$
EXAFS amplitude

High coordination number

Effective Coordination number

Low temperature

Debye-Waller factor

Back scattering amplitude

Electron mean free path

High Z scatterer

Short distance

\[
A_i(k) = \frac{N_i^*}{kR_i^2} |F_i(k)| \exp \left( -2\sigma_i^2 k^2 \right) \exp \left( -2 \frac{R_i}{\lambda} \right)
\]
Au K-EXAFS of Au foil

Absorption Coefficient (arb. units)

Photon Energy (eV)
EXAFS oscillation of Au K-edge

EXAFS function $k^2 \chi(k)$ ($\text{Å}^{-3}$)

Wavenumber $k$ ($\text{Å}^{-1}$)

77K

278K
If the coordination number decreases,
If the bond distance increases,
(2) Instrumentation
Experimental method of XAFS

transmission method

X-rays

monochromator

Io

I

sample

Ion chamber

Data processing
Electron escape depth \(<50\) Å

Secondary electron

Fluorescent X-rays

X-ray escape depth \(>1000\) Å

Auger electron

photoelectron
Filter and solar slit

X-ray

Ionization chamber

sample
Cu K-XAFS of CuSO$_4$ 10mMol aq. solution
0.5 mm film

Transmission

6µm film

Fluorescence
Partial electron yield $\rightarrow$ x-ray absorption of surface atoms

cryostat (liq. $N_2$ or liq. He)

hv
$E$

sample

partial $e^-$ yield detector

$\Lambda$
(3) XAF S spectral analysis
EXAFS function

Fourier transform

Amplitude

$R$, $\phi$
Back Fourier Transformation

EXAFS function

Amplitude

Envelope

Polarization

Temperature

Direction of Bond, Adsorption site

Coordination number

Bond stiffness

Kind of scatterer
Polarization Dependent EXAFS
K-absorption (1s $\rightarrow$ p-like continuum)
Polarization Dependent EXAFS
K-absorption (1s → p-like continuum)
Temperature dependence

\[ \chi(k) = \sum_j A_j(k) \sin[2kr_j + 2\delta_j(k)] \]

\[ A_j(k) = \frac{N_j |f(k, \pi)|}{kr_j^2} \exp(-2r_j/\lambda) \exp(-2\sigma^2k^2) \]

\[ \ln \frac{A(k, T_2)}{A(k, T_1)} \approx 2k^2 \left[ \sigma^2(T_1) - \sigma^2(T_2) \right] \]
Determination of $\sigma^2(T)$

c-As

$$\ln \frac{A(k, T_2)}{A(k, T_1)} \approx 2k^2 \left[ \sigma^2(T_1) - \sigma^2(T_2) \right]$$
What can we get from $\sigma^2(T)$

\[ \sigma_i^2 = \langle [(u_i - u_0) \cdot \bar{R_i}]^2 \rangle \]

\[ = \langle (u_i \cdot \bar{R}_i)^2 \rangle + \langle (u_0 \cdot \bar{R}_i)^2 \rangle + 2\langle (u_0 \cdot \bar{R}_i) \cdot (u_i \cdot \bar{R}_i) \rangle \]

\[ \bar{R}_i = \frac{R_i - R_0}{|R_i - R_0|} \]

Einstein model

\[ \sigma_i^2(T) = \frac{\hbar}{2\mu\omega_E} \coth \left[ \frac{\hbar\omega}{2kT} \right] \]

Einstein frequency

\[ f_E = c^2 \mu\omega_E^2 \]

\[ \sigma_i^2 = \frac{\hbar}{2\mu\omega_E} \left[ \coth \left( \frac{\hbar\omega}{2kT_2} \right) - \coth \left( \frac{\hbar\omega}{2kT_1} \right) \right] \]
c-As
As-As: 216 cm$^{-1}$

a-As
As-As: 234 cm$^{-1}$

c-As$_2$S$_3$
As-S: 332 cm$^{-1}$

g-As$_2$S$_3$
As-S: 330 cm$^{-1}$

c-As$_4$S$_4$
As-As: 222 cm$^{-1}$
As-S: 342 cm$^{-1}$
Data acquisition

Determine $E_0$, Convert from eV to $k$

Background subtraction and normalization

Multiply $k^n$

Fourier transformation

Fourier filtering

Back Fourier transformation

Curve fitting in real space

Model structure
X-ray energy (eV)

EXAFS $\chi(k)$

Atomic distance (Å)

EXAFS $\gamma(k)$
EXAFS analysis-1

\[ \chi(k) = \sum_i A_i(k) \sin(2kr_i + \phi_i) \]

EXAFS \( \chi \) vs. wave number \( k \)

Fourier transformation

Amplitude vs. Distance

1st nearest

2nd nearest

3rd nearest

Amplitude vs. Distance \( r = n + \phi_i \)

Atomic distance

Phase shift

Amplitude

1st nearest

2nd nearest

3rd nearest
EXAFS analysis-2

EXAFS $\chi$ vs. $k$ (wave number)

- Effective Coordination Number
- Debye-Waller factor
- Back scattering amplitude
- Direction of chemical bond
- Pair Potential Function
- Kind of scattering atom
Limitation and Improvement of XAFS theory

- Multiple scattering effect
  which is enhanced at XANES region and also at longer distance above 3 Å.

→ FEFF program developed by J. Rehr can be used for spectral simulation.

![Diagram](attachment:diagram.png)

- Shadowing effect
  - negligible
  - Non-negligible

Shading effect
Limitation and Improvement of XAFS theory

• **Vibrational anharmonicity**
  
  The formula assumes a Gaussian distribution.
  
  ➔ Cumulant expansion method has been developed to take into the anharmonicity, which gives the information of real bond distance, thermal expansion coefficients, radial distribution curve.

\[
\chi(k) = \frac{N}{kR^2} \text{Im} \left[ f_{\text{eff}}(k, kR) \exp \left( 2ikR + \sum_{n=2}^{\infty} \frac{(2ik)^n}{n!} C_n \right) \right]
\]

\[
= \frac{N}{kR^2} F_{\text{eff}}(k, kR) \exp \left[ -2C_2 k^2 + \frac{2}{3} C_4 k^4 - \cdots \right] \sin \left[ 2kR + \phi_{\text{eff}}(k, kR) - \frac{4}{3} C_3 k^3 + \cdots \right]
\]

\[
C_2 = \langle (r - R)^2 \rangle \quad C_3 = \langle (r - R)^3 \rangle \quad C_4 = \langle (r - R)^4 \rangle - 3C_2^2
\]

where \( R = \langle r \rangle \)
(4) XAFS applications

• Catalysis
• Amorphous systems
• Material physics (High Tc, CMR, ....)
• Magnetic materials ⇐ XMCD
• Thin films and Surface science
• Environmental science
• Biological materials
(5) Challenge of XAFS

• Time-resolved XAFS spectroscopy

• Micro XAFS or Nano XAFS
Summary--Features of XAFS

• Applicable to any phase (amorphous, liquid, gas), surface/interface and biomaterials
• Measurable under various conditions
  → under high pressure, gaseous atmosphere, for real catalysis
• Polarization dependence → direction of the bond
• Temperature dependence → strength of any specific bond
• Combined with microbeam → local structure of a local area
• Pump-probe experiment → dynamics of local structure