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Principles of X-ray Absorption Spectroscopy and Applications to Environmental Science

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1st PART

Principles of x-ray absorption spectroscopy

EXAFS and XANES

2nd PART

XAS applied to environmental science

1st PART

Principles of x-ray absorption spectroscopy

EXAFS and XANES

Material from

• <u>S. Pascarelli</u>: EXAFS lecture at the HERCULES school 2010

<u>http://xafs.org/Tutorials</u>, in particular from <u>Matt Neuville</u>'s Tutorial

• <u>P. Fornasini</u>: "An introduction to X-ray absorption spectroscopy"

Outline

- 1. X-ray Absorption
- 2.X-ray Absorption Fine Structure
- 3. Simple theoretical description
- 4.XANES

Outline

X-ray Absorption
 X-ray Absorption Fine Structure
 Simple theoretical description
 XANES

Main X-ray-Matter interactions

Photoelectric absorption

one photon is absorbed and the atom is ionized or excited

Scattering

one photon is deflected from the original trajectory by collision with an electron

coherent (Thomson scattering) the photon wavelength is unmodified by the scattering process (scattering from bound electrons)
incoherent (Compton scattering) the photon wavelength is modified

For an aggregate of atoms:

• elastic scattering: the photon energy is conserved

• inelastic scattering the photon energy is not conserved

Pair creation

the photon annihilates, giving rise to a pair e+ e- (for energies > 1 MeV)

Main X-ray experimental techniques

Spectroscopy

- electronic structure of matter
 - absorption
 - emission
 - photoelectron spectroscopy

(electrons emitted after X-ray absorption are collected and analized)

Scattering

• elastic

Microscopic geometrical structure of condensed systems ((non)crystalline, liquids) Diffraction: elastic scattering from crystalline solids

• inelastic

Collective excitations

• Imaging

macroscopic pictures of a sample, based on the different absorption of X-rays by different parts of the sample (medical radiography and X-ray microscopy)

Cross section quantifies the strength of the X-ray - matter interaction

For photon energies between 1 and 30 keV the photoelectric absorption is the leading interaction with matter



Absorption coefficient and absorbance



 $\alpha = \mu t = \ln (I_0/I)$

Photoelectric absorption

An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core-level electron (*K*, *L*, or *M* shell) which is ejected from the atom.

The atom is left in an *excited state* with an empty electronic level (a *core hole*).

Any excess energy from the X-ray is given to the ejected *photoelectron*.



µ vs E and µ vs Z



In addition, µ has sharp *absorption edges* corresponding to the characteristic core-level energy of the atom which originate when the photon energy becomes high enough to extract an electron from a deeper level



 $\mu pprox rac{
ho Z^4}{AE^3}$

Absorption edge energies



The energies of the K absorption edges go roughly as $E_K \sim Z^2$





All elements with Z > 16 have either a K-, or L- edge between 2 and 35 keV, which can be accessed at many synchrotron sources

De-excitation processes



X-ray Fluorescence

An x-ray with energy = the difference of the core-levels is emitted



 $K_{\alpha}: L \rightarrow K, K_{\beta}: M \rightarrow K.$

Auger Effect

An electron is promoted to the continuum from another core-level



X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom. 14

Core hole lifetime $(T_h \sim 10^{-15} - 10^{-16} s)$

Total de-excitation probability per unit time



 τ_h is un upper limit to the time allowed to the photoelectron for probing the local structure surrounding the absorbing atom

From the time-energy uncertainty relation: $\Gamma_h \simeq \hbar/\tau_h$ the core hole lifetime is associated to the energy width of the excited state Γ_h (core hole broadening) which contributes to the resolution of the X-ray absorption experimental spectra

K-edge core hole broadening as a function of Z



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XAS measurements in real life



Transmission:

The absorption is measured directly by measuring what is transmitted through the sample:

I = I₀
$$e^{-\mu (E)^{\dagger}}$$

 $\mu(E)^{\dagger} = -\ln (I/I_0)^{\dagger}$

Fluorescence:

The re-filling of the deep core hole is detected. Typically the fluorescent X-ray is measured.



Fnerav (keV)

What? Oscillatory behaviour of the of the X-ray absorption as a function of photon energy beyond an absorption edge When? Non isolated atoms

Why? Proximity of neighboring atoms strongly modulates the absorption coefficient

A little history...

- 1895 Discovery of X-rays (Röngten) (high penetration depth)
- 1912 First X-ray diffraction experiments (Laue, Bragg)
- 1913 Bohr's atom electron energy levels
- 1920 First experimental observation of fine structure
- 1931 First attempt to explain XAFS in condensed matter (Krönig)

1970 Availability of synchrotron radiation sources for XAFS

1971 XAFS becomes a quantitative tool for structure determination

VOLUME 27, NUMBER 18 PHYSICAL REVIEW LETTERS 1 NOVEMBER 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray-Absorption Fine Structure*

> Dale E. Sayerst and Edward A. Sternt‡ Department of Physics, University of Washington, Seattle, Washington 98105

> > and

Farrel W. Lytle Boeing Scientific Research Laboratories, Seattle, Washington 98124 (Received 16 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).

XANES and EXAFS



XANES and EXAFS







transitions to unfilled bound states, nearly bound states, continuum

- Oxidation state
- Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
- Orbital occupancy

transitions to the continuum

 Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)

EXAFS qualitatively - isolated atom



X-ray photon with enough energy ejects one core (photo)electron (photoelectric effect)

 $E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$ Kinetic energy of the p.e.

 $k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$ wavevector of the p.e. $\lambda = 2\pi/k$ wavelength of the p.e.

The photoelectron can be described by a wave function approximated by a spherical wave

 $\Lambda \sim 1/(E-E_0)^{1/2}$

EXAFS qualitatively - condensed matter



- The photoelectron can scatter from a neighbouring atom giving rise to an incoming spherical wave coming back to the absorbing atom
- The outgoing and ingoing waves may interfere.

$\lambda \sim 1/(E-E_0)^{1/2}$

Origin of the fine structure (oscillations)

The interference between the outgoing and the scattering part of the photoelectron at the absorbing atom changes the probability for an absorption of X-rays i.e. alters the absorption coefficient $\mu(E)$ that is no longer smooth as in isolated atoms, but oscillates.

The phase relationship between outgoing and incoming waves depends on photoelectron wavelength (and so on the energy of X-rays) and interatomic distance R.

The amplitude is determined by the number and type of neighbours since they determine how strongly the photoelectron will be scattered



The EXAFS signal $\chi(k)$

The EXAFS signal is generally espressed as a function of the wavevector of the photoelectron

$$k = \sqrt{\left[2m(E_{h\nu} - E_0)/\hbar^2\right]}$$

The oscillatory part of the spectrum contains the structural information

We define the EXAFS function as

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



µ₀(E) Smooth function representing the bare atomic background

 $\Delta \mu_0$ Edge step at the absorption edge normalized to one absorption event

$EXAFS : \chi(k)$

XAFS originates from an *interference effect*, and depends on the wave-nature of the photoelectron.

 $\chi(k)$ is often shown weighted by k^2 or k^3 to amplify the oscillations at high-k



$\chi(k)$: sum of damped waves

 $\chi(k)$

 $\mathbf{x}(\mathbf{k})$ is the sum of contributions $\mathbf{x}_{\mathbf{j}}(\mathbf{k})$ from backscattered wavelets:

$$\chi(k) = \sum_j \mathbf{x} \ \chi_j(k)$$

Each $x_j(k)$ can be approximated by a *damped* sine wave of the type:

The larger the number of neighbours, the larger $N_j f_j e^{-1}$ the signal -1

The stronger the scattering amplitude, the larger the signal

Damping of the amplitude at large k, due to static and thermal disorder Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance

 $2kR_j + \delta_j(k)$

EXAFS formula

$$\chi(\mathbf{k}) = \sum_{\mathbf{j}} \frac{\mathbf{N_j S_0^2 f_j(\mathbf{k}) e^{-2\mathbf{R_j}/\lambda(\mathbf{k})} e^{-2\mathbf{k}^2 \sigma_j^2}}}{\mathbf{k} \mathbf{R_j}^2} \mathrm{sin}[2\mathbf{k} \mathbf{R_j} + \boldsymbol{\delta_j(\mathbf{k})}]$$



 $\begin{array}{c|c} f(k) & \begin{array}{c} \text{scattering} \\ \text{amplitude} \\ \hline \delta_j(k) & \begin{array}{c} \text{phase-shift} \end{array} \end{array} \end{array} \text{scattering properties of the atoms} \\ \text{scattering properties of the atoms} \\ \text{neighbouring the photoabsorber (depend on the atomic number)} \end{array}$

- RDistance to the neighbouring atom
- NCoordination number of the neighbouring atom
 - Disorder in the neighbour distance

Amplitudes

The shape of the envelope of each wave is indicative

of the nature of backscatterer atom

AgF (rocksalt structure)





Frequencies

The **frequency** of the single wave, for the same atomic pair, is indicative of the distance of the backscatterer atom (the lower the frequency the

closer the neighbour)

AgF (rocksalt structure)







Multiple scattering

Multiple scattering events may occur. The photoelectron scatter from more than one atom before returning to the central atom



Through multiple scattering EXAFS can give information on the n-body distribution functions $g_n(r)$

Qualitative picture of local coordination in R space

The frequencies contained in the EXAFS signal depend on the distance between the absorbing atom and the neighbouring atoms (i.e. the length of the scattering path).

A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.



Quantitative structural determination

Structural determinations depend on the feasibility of resolving the data into individual waves corresponding to the different types of neighbours (SS) and bonding configurations (MS) around the absorbing atom



XAFS vs. Diffraction Methods

- Diffraction Methods (X-rays, Neutrons)
- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
- Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D RDF containing interatomic distances due to all atomic pairs in the sample

• XAFS

- 1D radial distribution function (centered at the absorber)
- Element selectivity
- Higher sensitivity to local distortions (i.e. within the unit cell)
- Charge state sensitivity (XANES)
- Structural information on the environment of each type of atom:
 - distance, number, kind, static and thermal disorder
 - 3-body correlations
- Investigation of matter in the solid (crystalline or amorphous), liquid, solution or gaseous state with same degree of accuracy.

EXAFS: typical applications

Element selectivity

Local structure sensitivity

- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure

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4.XANES







Edge position: oxidation state



Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

Edge position: oxidation state



The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

Edge position: oxidation state



XANES can be used simply as a fingerprint of phases and oxidation state.

XANES analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components

XANES transitions

• Dipole selection rules apply:

$\Delta \ell - \pm 1$			
$\Delta c = \pm 1$	EDGE	INITIAL STATE	FINAL STATE
$\Delta s = 0$ $\Delta i = \pm 1.0$	K , L ₁	s ({=0)	p (१=1)
$\Delta j = \pm 1, 0$ $\Delta m = 0$	L_2, L_3	p ({=1)	s (l=0), d (l=2)
$\Delta m = 0$			

•The final state is usually not atomic-like and may have mixing (hybridization) with other orbitals.

This is often the interesting part of the XANES!

Transition metals K pre-edge peaks

Transition with a quadrupolar character

Pure octahedron

Centro-symmetry: no p-d mixing allowed only (weak) quadrupolar transitions No, or very low intensity prepeak

Distorted octahedron

Centro-symmetry broken: p-d mixing allowed dipole transition in the edge moderate intensity prepeak





Tetrahedron

No Centro-symmetry : p-d mixing allowed dipole transition in the edge high intensity prepeak



Pre-peak: local coordination environment



Ti K-edge XANES shows dramatic dependence on the local coordination chemistry

White line intensity of L_3 -edge XANES of 4d metals

Transition from $2p_{3/2}$ to 4d states



Linear correlation between white line area and number of 4d-holes for Mo to Ag

Increasing d states occupancy

White line intensity: oxidation state

Re L_3 edge: transition from $2p_{3/2}$ to 5d states



XANES interpretation

The EXAFS equation breaks down at low-k, and the mean-free-path goes up. This complicates XANES interpretation:

A simple equation for XANES does not exist!

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of

coordination chemistry molecular orbitals band-structure multiple-scattering regular, distorted octahedral, tetrahedral, ... p-d orbital hybridization, crystal-field theory, ... the density of available electronic states multiple bounces of the photoelectron

XANES calculations are becoming reasonably accurate and simple. These can help explain what *bonding orbitals* and/or *structural characteristics* give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are also possible

XANES: Conclusions

XANES is a much larger signal than EXAFS

XANES can be done at lower concentrations, and less-than-perfect sample conditions

XANES is easier to crudely interpret than EXAFS

For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient

XANES is harder to fully interpret than EXAFS

The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

This situation is improving, so stay tuned to the progress in XANES calculations ...



XAS applied to environmental science

The case of Chromium

Pre-peaks in Cr compounds have a quadrupolar character (1s->3d bound states)



Fig. 1. Schematic illustration of octahedral crystal field splitting, Δ_6 , of Cr(III)O₆ with d³ electronic configuration, and tetrahedral crystal field splitting, Δ_t , of Cr(VI)O₄ which has an empty d orbital.

Cr(III)

- octahedral symmetry
- centrosymmetric geometry
- no p-d mixing allowed
- d³ electronic configuration

Cr(VI)

- tetrahedral symmetry
- non centrosymmetric geometry
- p-d mixing allowed
- d⁰ electronic configuration

Peterson et al., Geochimica et Cosmochimica Acta 61, 3399 (1997)







The problem of Cr(III) and Cr(VI)

• The size of the prepeak can be used to quantify the proportion of Cr(VI) in a sample if the Cr(VI) fraction is > 5-6 % of the total Cr.

• Prepeak calibration: peak area or height, EXAFS analysis



Role in magnetite in soils for Cr(VI) reduction



- - Cr associated with the magnetite fraction of the soil
 - ___ Cr not associated with
 - the magnetite fraction of the soil

Fe(II) in magnetite may act as an electron source for Heterogeneous Cr(VI)-to-Cr(III) reduction

The case of Arsenic



The case of Arsenic

Model compounds

As(III) As₂O₃ E₀=11870 eV As-OCN 6 at 1.8 Ang As(V) As₂O₅ E₀=11873.5 eV As-O CN 5 at 1.69 Ang



Model compounds



A linear relation between the edge shift and the valence state can be established for a given type of ligand

Importance to know the mineralogy of natural samples

Arcon et al., X-ray spectrometry 34, 453 (2005)



- (Non crystalline) scorodite (FeAsO₄·2H₂O): principal As carrier
- Presence of Al/Si suggests that arsenate is partially adsorbed on Al (hydr)oxide or aluminosilicates (clay)

Arcon et al., X-ray spectrometry 34, 453 (2005)

Road dust particles

- Samples from Traforo del San Bernardo highway tunnel
- Speciation of Fe and Mn

Ideal sample area:

i) average emission from different vehicles using different fuels
ii) comes only from vehicular emission
iii) no temperature fluctuation
iv) no photo-induced effects



Data analysis method

PCA (principal component analysis) + LCF (linear combination fitting)

PCA

- Determination of the minimum number of components necessary to reconstruct the experimental spectrum
- Identification of the best candidates

LCF

• Estimation of the relative concentration of the candidates selected by PCA

Bardelli et al., J. Phys.: Conf. Series 190, 012192 (2009)