Absorption Techniques in X-ray Spectrometry

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Absorption Techniques in X-ray Spectrometry

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1 INTRODUCTION

X-rays are absorbed in matter and the energy of the X-rays is converted into the kinetic energy of photoelectrons, Auger electrons, secondary electrons, or fluorescent X-rays. The incident X-ray energy finally becomes the thermal energy of the absorber.

The amount of energy absorbed by a matter is usually estimated by a transmission method, but can also be estimated by measuring these secondary phenomena, such as photoelectrons, Auger electrons, secondary electrons, fluorescent X-rays, thermal radiation, and drain electric currents. The X-ray intensity of wavelength $\lambda$ before ($I_0$) and after ($I$) the transmission of a thin film of thickness $d$ is expressed by $I(\lambda) = I_0(\lambda) \exp[-\mu(\lambda)\rho_d d]$, where $\mu(\lambda)$ and $\rho$ are the mass absorption coefficient and mass density, respectively, of the $i$th element in the thin film and their dimensions are [cm$^2$ g$^{-1}$] and [g cm$^{-3}$], respectively.$^{(1-7)}$ The mass absorption coefficient $\mu$ of a specimen which contains $n$ kinds of elements is expressed by $\mu = \mu_1(\lambda)W_1 + \mu_2(\lambda)W_2 + \cdots + \mu_n(\lambda)W_n$, where $W_1, W_2, \ldots, W_n$ are the weight fractions of element 1, 2, $\ldots$, $n$ in the specimen. The wavelength dependence of the absorption coefficient $\mu(\lambda)$ is clarified when log $\mu(\lambda)$ is plotted against log $\lambda$ as shown in Figure 1; $\mu(\lambda)$ values are taken from Henke et al.$^{(6)}$ in this plot. Henke et al.$^{(6)}$ tabulated $\mu(\lambda)$ from $Z = 1$ to 92 at energy from 50 eV to 30 keV.

The plot of the mass absorption coefficients of matter against the incident X-ray energy or wavelength is called an X-ray absorption spectrum (XAS), where we find some jumps at particular X-ray energy, corresponding to K, L$_{\alpha}$, L$_{\beta}$, L$_{\gamma}$, and L$_{\delta}$ electron shell binding energies as shown in Figure 1.

$X$-ray absorbance depends on the wavelength of the $X$-rays, atomic number, chemical environment, and concentration of analyte. X-ray absorption spectrometry is a technique for analyzing the chemical environment of an element in an unknown material. This method is closely related to photoelectron spectroscopy, Auger electron spectroscopy, and X-ray fluorescence spectroscopy.

Chemical information in the chemical shift and line shape of XANES (X-ray absorption near-edge structure) spectra is described. The history and theory of EXAFS (extended X-ray absorption fine structure) are discussed in relation to other experimental techniques. Data analysis methods, databases, software packages, instrumentation, and synchrotron radiation facilities for X-ray absorption analysis are overviewed. Alternative methods such as electron energy loss spectroscopy (EELS), self-absorption effect, extended X-ray emission fine structure (EXEFS), X-ray Raman scattering, diffraction anomalous fine structure (DAFS), $\beta$-environment fine structure (BEFS), and inverse photoemission spectroscopy (IPES) are also described.

References

1. Meyers, R. A. (Ed.) Copyright © John Wiley & Sons Ltd.
X-RAY SPECTROMETRY

Figure 1 Mass absorption coefficients of V, Fe, and Zn plotted against wavelength. Both axes are on a logarithmic scale.

Figure 2 Platinum powder XAS. (Reproduced by permission from Udagawa.9)

Figure 2.9 K, L_I, L_II, and L_III denote electron deficiency states from 1s, 2s, 2p_{1/2}, and 2p_{3/2} orbitals, respectively. Arabic numerals 1, 2, 3, . . . have more recently been used in the subscript rather than Roman numerals I, II, III, . . . . The electron configuration of one electron deficiency from the 2p orbital is expressed as 1s^22s^22p_5^23s^23p_6^0 for an Ar atom. This state has two energy levels corresponding to \( j = \frac{1}{2} \) and \( \frac{3}{2} \) states, where \( j \) is the eigenvalue of vector sum \( s + l \), where \( s \) and \( l \) are called spin and angular momentum vectors, respectively, and the vector \( j \) is called the total angular momentum. These two states are written as \( 2p_{1/2} \) and \( 2p_{3/2} \), or \( [2p_{1/2}] \) and \( [2p_{3/2}] \).

The relation between the electron deficiency state and the electron configuration is listed in Table 1. The \( s^{-1} \) hole state has a total angular momentum \( \frac{1}{2} \), and the subscript \( \frac{1}{2} \) is usually omitted. The multiplicity of the state, which is crudely proportional to the spectral intensity, is \( 2j + 1 \).

The jump is called the absorption edge, and the wavelength is highly correlated with the atomic number similarly to Moseley’s law11 in X-ray emission spectra. Moseley’s law in emission spectra is expressed as Equation (1):

\[
\frac{1}{\sqrt{\lambda}} = K(Z - s)
\]

where \( \lambda \) is the X-ray wavelength, \( Z \) is the atomic number, and \( K \) and \( s \) are constants for a spectral series. The absorption coefficient is crudely proportional to \( Z^4 \lambda^3 \) except for the edge jumps. The energy at which the jump is observed is called the threshold energy, but the definition of the threshold is not exact, because it corresponds to the transition from a core orbital to the lowest unoccupied orbital. The ionization limit is a few or a few tens of electron-volts higher than the edge energy.

The mass per unit area is given by \( \rho d \), where \( \rho \) is the mass density. The linear absorption coefficient \( \mu \) is defined by \( \mu = \frac{\rho d}{\rho} \), and its dimension is [cm\(^{-1}\)]. The X-ray attenuation length \( 1/\mu \) is the length at which the X-ray intensity becomes 1/e after traveling in matter. The attenuation length of Cu Kα X-rays (8047.8 eV) is 79 \( \mu \)m in aluminum, 4.2 \( \mu \)m in iron, 24 \( \mu \)m in copper, and 3.9 \( \mu \)m in lead. The attenuation length of Al Kα X-rays (1486.7 eV) is 9.2 \( \mu \)m in aluminum and 0.4 \( \mu \)m in iron. The intensity of X-rays emitted by a copper target X-ray tube is, however, attenuated by only half after transmission through 2-mm-thick aluminum, but depends on the applied power on the X-ray tube, because the X-rays emitted from an X-ray tube are not monochromatic. Thus it should be noted that the X-ray shielding thickness for safety cannot be determined only from the monochromatic X-ray attenuation length.

The linear absorption coefficient can otherwise be expressed as \( \mu = 4\pi\beta/\lambda \), where \( \lambda \) is the X-ray wavelength and \( \beta \) the imaginary part of the complex refractive index.

### Table 1 Relation between the hole state and the electron configuration

<table>
<thead>
<tr>
<th>Hole state</th>
<th>Electron configuration</th>
</tr>
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<tbody>
<tr>
<td>K</td>
<td>[1s]</td>
</tr>
<tr>
<td>L₁</td>
<td>[2s]</td>
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<tr>
<td>L₂</td>
<td>[2p_{1/2}]</td>
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<tr>
<td>L₃</td>
<td>[2p_{3/2}]</td>
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<tr>
<td>M₁</td>
<td>[3s]</td>
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<tr>
<td>M₂</td>
<td>[3p_{1/2}]</td>
</tr>
<tr>
<td>M₃</td>
<td>[3p_{3/2}]</td>
</tr>
<tr>
<td>M₄</td>
<td>[3d_{3/2}]</td>
</tr>
<tr>
<td>M₅</td>
<td>[3d_{5/2}]</td>
</tr>
</tbody>
</table>

1/ in X-ray emission spectra.
(n = 1 − δ − iβ).\(^{7}\) The atomic form factor, \(f = f_1 + if_2\), which is used in the analysis of X-ray diffraction, is related to the refractive index (Equations 2 and 3):

\[
\delta = \frac{N r_0 \lambda^2 f_1}{2\pi} \tag{2}
\]

\[
\beta = \frac{N r_0 \lambda^2 f_2}{2\pi} \tag{3}
\]

where \(N\) is the number of atoms in unit volume and \(r_0 = e^2/(mc^2) = 2.818 \times 10^{-13}\) cm is the classical electron radius (\(e\) the electron charge, \(m\) the mass, and \(c\) the speed of light). The real part \(f_1\) is the Fourier transform of the electron density distribution in an atom. The relation between the absorption coefficient and atomic form factor is used in DAFS described below.

The mass absorption coefficient is the sum of two effects: photoelectric absorption and scattering of X-rays. The photoelectric absorption is the ionization of an inner-shell electron. Therefore, the absorption coefficient due to the photoelectric part can be calculated by the photoionization cross-section.\(^{8}\) The scattering part is due to the Rayleigh (coherent) and Compton (inelastic) scattering of X-rays, but X-ray absorption spectra are often taken as if they represent only the photoelectric absorption effect, although the experimental spectra contain both effects.

The mass absorption coefficients or physically equivalent parameters\(^{9,10,11,12,13}\) and the absorption edge energy or wavelength\(^{14,15}\) can be found in the literature. The value of the absorption edge energy is close to the electron binding energy, which is used in electron spectroscopy, ESCA (electron spectroscopy for chemical analysis) or XPS (X-ray photoelectron (photoemission) spectroscopy).\(^{16,17}\)

The absorption edge jump is not exactly the same as the electron binding energy, because the absorption edge energy corresponds to the excitation of core electrons into the lowest unoccupied molecular orbital (LUMO) in the molecular orbital picture, or Rydberg state in the atomic orbital picture. The Rydberg state and continuum state threshold are clearly seen in rare gas X-ray absorption spectra but are not clear for condensed matter. The difference between the vacuum level and Fermi energy, which defines the highest energy of electrons in a conduction band, is called the work function, \(\Phi\). This is another source of the difference between the electron binding energy observed in XPS and the absorption edge. The photoionization cross-sections\(^{18,19}\) and the electron binding energies\(^{20,21}\) can be found in the literature. The relation between the electron photoionization cross-section (barns) and mass absorption coefficient is simple when the angular dependence is averaged.\(^{22}\)

Absorption techniques in X-ray spectrometry are used to measure the X-ray absorption spectra using various methods described below, and to analyze the obtained spectral line shapes to obtain information on the element, oxidation state, concentration, atomic distance, coordination number, surface geometry, and reaction on solid surfaces, catalysts, or electrodes.

### 2 ACRONYMS AND A BRIEF HISTORY

The mass absorption coefficient plotted against the X-ray energy is called the XAS. The X-ray absorption spectra of condensed matter near the threshold energy have fine structures as shown in Figure 2. Fine structures are sometimes observable at energies less than the threshold energy, and are called the pre-edge structure (Figure 3).\(^{22}\) These fine structures are called the XANES, usually pronounced as “zaenz”. The absorption fine structure will extend up to 1000 eV above the threshold energy, and thus it is called the EXAFS,\(^{23-26}\) pronounced “eksafs”. XANES is restricted from the threshold to ca. 50 eV above (this energy approximately corresponds to \(KR = 2\pi\), where \(k\) is the ejected photoelectron momentum and \(R\) the nearest-neighbor atomic

![Figure 3 Mn K edge XANES spectra of MnO (octahedral, \(O_h\) symmetry) and KMnO\(_4\) (tetrahedral, \(T_d\) symmetry). Pre-edge peak is found in the KMnO\(_4\) spectrum. Chemical shift of the edge is found; the edge of KMnO\(_4\) is higher than that of MnO. (Reproduced by permission from Pandya et al.\(^{22}\))](image-url)
distance as shown in Figure 4(9,26). The momentum of the photoelectron is 
\[ k = \left[ 2m(E - E_0) \right]^{1/2}/h, \]
where \( E \) is the photoelectron kinetic energy, \( E_0 \) the threshold energy, \( m \)
the electron mass, and \( h \) Planck’s constant. The photoelectron matter wave in a condensed system propagates as a spherical wave and forms a standing wave as shown in Figure 5.\(^9\) Recently, XANES has come to be called near-edge X-ray absorption fine structure (NEXAFS),\(^{27}\) pronounced “neksafs”. All the fine structures including NEXAFS and EXAFS are grouped into the term X-ray absorption fine structure (XAFS), pronounced “zafs”.

The history of the development of the understanding and application of XAFS has an interesting feature, as stated by Lytle et al.\(^{28}\) Shiraiwa,\(^{29}\) Stern,\(^{30}\) and Lytle.\(^{31}\) Barkla (after Stern\(^{30}\)) or de Broglie (after Lytle\(^{31}\)) firstly found the X-ray absorption edge. Although XANES was found for both solids and gases, EXAFS was found only for condensed matter such as molecules, solids and liquids. EXAFS was first reported by Fricke in 1920\(^{32}\) and was theoretically interpreted by Kossel.\(^{33}\) He explained that the fine structure was due to the excitation of inner-shell electrons to an unoccupied level. This theory was valid for XANES, and thus XANES was called the Kossel structure. The Kossel theory was called short-range order (SRO) theory, because the electronic structures of unoccupied levels are mostly determined by orbital hybridization between the center atom and the nearest-neighbor atoms. On the other hand, Kronig\(^{34}\) explained that fine structure was the result of the diffraction of photoelectrons as a matter wave when moving in a conduction band of a solid. The electron matter wave travels in a solid when the wavelength of an electron \( \lambda_e \) does not satisfy the Bragg condition, \( 2d \sin \theta = n \lambda_e \). When the Bragg condition is satisfied, then the electrons are scattered and leave the solid. His theory explained EXAFS and thus EXAFS was called the Kronig structure. His theory was called the long-range order (LRO) theory because the band structure is determined by the long-range periodic boundary conditions. Hayasi\(^{35}\) considered that the electron waves that satisfied the Bragg condition form a standing wave in a solid, and thus the electron transition from an inner orbital to a standing wave state yields a maximum of X-ray absorption. Shiraiwa et al.\(^{36}\) and Kozlenkov\(^{37}\) improved the SRO theory to explain the EXAFS, but their method needed to solve a Schrödinger equation to obtain the EXAFS. Sayers et al.\(^{38}\) proposed a Fourier transform method to obtain local structural information on condensed systems. Owing to their Fourier analysis, we do not need to solve the Schrödinger equation directly to obtain the local structure of matter. EXAFS had at that time great potential to be developed as a powerful method of analyzing the local structure of matter. The inelastic mean free path (IMFP) of a photoelectron is usually 2 nm. When the photoelectron is scattered inelastically, the coherence is forgotten. The coherent length, i.e. the length within which the electron matter waves emitted from a single source can interfere with each other, is an important length to apply in the EXAFS method to analyze a condensed system. When the IMFP is included in the LRO theory, it is equivalent to the SRO theory.
The XAFS represents the unoccupied electron density of states for atoms, molecules, solids, or liquids. One of the inner shell electrons, say a 1s electron, is excited into a discrete or continuum unoccupied state by the incident X-ray photon. The transition probability from the 1s to the unoccupied state equals the X-ray absorption intensity (only the photoelectric part is considered here), and thus the plot of the intensity against the incident X-ray energy is the XAS of a specimen. XANES is chiefly due to the transition from the inner shell to the unoccupied discrete level (Figure 6), and EXAFS is to the unoccupied continuum level.

3 X-RAY ABSORPTION NEAR-EDGE STRUCTURE

3.1 Chemical Shift and Line Shape

The XANES spectra show both the line shape modification and chemical shift of the absorption edge or peak. Figure 7 shows typical examples for the S K edge for Na$_2$SO$_4$, Na$_2$SO$_3$, and Na$_2$S$_2$O$_3$. The sharp and prominent absorption peak shown in Figure 7 is called the “white line”. This is because in the early days of X-ray experiments a white line developed on the X-ray film was observed. The white line for insulators is usually sharper than that for metals, because it corresponds to a 1s $\rightarrow$ $\pi^*$ electron transition, where the asterisk denotes an unoccupied antibonding orbital. The $\pi^*$ state is usually a sharply localized state. The metal has a broad conduction band, and thus the absorption spectra show an edge jump but not a white line.

The white line energy plotted against the oxidation number of sulfur is shown in Figure 8. The source of the chemical shift is both the unoccupied level shift and core level shift. The range of the unoccupied level shift ranges from the Fermi level (=0 eV) to the band gap energy (=a few electron-volts). The core level shift is due to the screening of core electrons by valence electrons; if the atom is negatively charged then the core level is shifted to a shallower binding energy, and if an atom is positively charged then it is shifted to a deeper energy. The source of the core level shift is the same as that of an ESCA chemical shift.

In Figure 9 is shown another example of a chemical shift of the absorption edge for Al compounds: Al metal, AlN, and four- and six-fold coordinated oxides. The Al–O distance of four-fold coordinated aluminum oxide (0.17 nm) is shorter than that of six-fold coordinated oxide (0.19 nm), because the oxygen ions interfere with each other and cannot be close to the Al atom for six-fold coordinated oxide. Thus the orbital hybridization of four-fold coordinated oxide is stronger than that of six-fold coordinated oxide, and consequently the six-fold form is...
ionic and the four-fold form is covalent. The effective positive charge of six-fold coordinated Al$^{3+}$ is larger than that of four-fold coordinated oxide. The chemical shift of six-fold coordinated oxide is larger than that of four-fold coordinated oxide. The shift is strongly correlated to Pauling’s electronegativity$^{[43]}$ of the neighboring atom, because the electronegativity determines the effective charge of the ion.

The unoccupied discrete level is composed of Rydberg states in the atomic picture, $\pi^*$ and $\sigma^*$ orbitals in the molecular-orbital picture (the asterisk denotes an antibonding molecular orbital), or conduction bands in crystals. The $\sigma^*$ transition, which is formed in a potential well of neighboring atomic potentials, is called the shape resonance (Figure 4).

While the $1s \rightarrow \pi^*$ transition is a sharp white line, the $1s \rightarrow \sigma^*$ transition usually results in a broad and weak hump at higher energy$^{[44]}$ which is called the shape resonance. The term shape resonance is used in the field of atomic spectra. The excited state or ionized state is bound in a potential well, because of the centrifugal force potential of a high angular momentum orbital such as an f orbital, or surrounding potential such as F in SF$_6$. However, as shown schematically in Figure 4, such a surrounding potential does not have sufficient height to enclose the electron, but a weak resonance is observable. This is the origin of the term shape resonance.

The pre-edge structure shown in Figure 3 above is observed for the K edge of transition metal compounds whose local symmetry around the X-ray absorbing atom is $T_d$ (tetrahedral). On the other hand, it is not observable for locally $O_h$ (octahedral) symmetry solids. This pre-edge is sometimes said to be an electric quadrupole transition from 1s to 3d, whereas ordinary optical absorption is the electric dipole transition (1s $\rightarrow$ 2p or 2p $\rightarrow$ 3s, 3d). The quadrupole transition probability is, however, very weak, as shown in Table 2, where the probability is calculated by the Dirac–Fock method$^{[45]}$. The origin of such a strong absorption as shown in Figure 3 is due to the electric dipole transition. The unoccupied p orbitals strongly hybridize with the d band for tetrahedral symmetry compounds based on the group theory as shown in Table 3$^{[46]}$, where both p and d orbitals belong to the $t_2$ orbital. Thus the electric dipole transition is strongly observed at the energy of an empty d band. On the other hand.

\[
\begin{array}{c|c}
\hline
\text{Transition} & \text{Probability} \\
\hline
K–L_1 & 0.00000038 \\
K–L_2 & 0.19 \\
K–L_3 & 0.37 \\
K–M_1 & 0.00000072 \\
K–M_2 & 0.022 \\
K–M_3 & 0.043 \\
K–M_4 & 0.000025 \\
K–M_5 & 0.000036 \\
\hline
\end{array}
\]

\[
\begin{array}{c|c|c}
\hline
\text{Character} & \text{p} & \text{d} \\
\hline
a_1 & x^2 + y^2 + z^2 & \\
a_2 & (2z^2 - x^2 - y^2, x^2 - y^2) & \\
e & (x, y, z) & (xy, xz, yz) \\
t_1 & & \\
t_2 & & \\
\hline
\end{array}
\]
Table 4 Part of the character table of Oh

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<tbody>
<tr>
<td>a1g</td>
<td>$x^2 + y^2 + z^2$</td>
<td></td>
</tr>
<tr>
<td>a2g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e_g</td>
<td>$(2z^2 - x^2 - y^2, x^2 - y^2)$</td>
<td></td>
</tr>
<tr>
<td>t1g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t2g</td>
<td>$(xy, xz, yz)$</td>
<td></td>
</tr>
<tr>
<td>a1u</td>
<td></td>
<td></td>
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<tr>
<td>a2u</td>
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<td>e_u</td>
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</tr>
<tr>
<td>t1u</td>
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<td></td>
</tr>
<tr>
<td>t2u</td>
<td>$(x, y, z)$</td>
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</table>

The chemical shifts of reference samples are measured and plotted against the electronegativity, and then the neighboring atom type is estimated for an unknown material from the chemical shift of the absorption edge.

After the discovery of high-temperature superconductors, the understanding of the electron correlation effect of transition metal compounds and rare earth compounds has been greatly improved by the study of XPS. Consequently, the understanding of the correlation effect, i.e. how the hole left in the final state of photoionization interacts with d holes in transition metal compounds, has developed substantially. Many reports have been published concerning the electron correlation effect on the XANES line shape of complicated materials.

Mixed-valence rare earth compounds are clearly observed by the measurement of XANES, as shown in Figure 11, but the intensity ratio sometimes does not directly represent the mixed-valence components because of a dynamic electron transfer, i.e. correlation effect, due to the core hole screening. The peak decomposition of XANES spectra into Eu$^{2+}$ and Eu$^{3+}$, as shown in Figure 11, yields a rough estimate of the mixed-valence state. However, the core hole created by the X-ray absorption rearranges the valence electrons and thus the peak intensity does not always represent the exact

![Figure 10 Co K edge spectra of [Co(NH$_3$)$_6$]X$_3$ (X = Cl, Br, and I). The vertical bars show calculated spectra for [Co(NH$_3$)$_6$]$^{3+}$. Peak A is due to the electric quadrupole transition but still mixed with the p orbital owing to the skewing of the molecular structure from exact octahedral symmetry. (Reproduced by permission from Sano. @ 1988 The American Chemical Society.)](image)

![Figure 11 XANES spectra of EuNi$_2$Si$_5$Ge$_{1.5}$ at 19 and 273 K. The dashed-dotted and the dashed spectra indicate the Eu$^{2+}$ and Eu$^{3+}$ final state components, respectively. (Reproduced by permission from Wortmann et al. @ 1991 The American Physical Society.)](image)
portion of the Eu$^{2+}$ and Eu$^{3+}$ states before the X-ray is absorbed.

3.2 Calculation Method for X-ray Absorption

Near-edge Structure Spectra

The electronic states of photoelectrons whose kinetic energy is from a few electron-volts to a few tens of electron-volts are treated as conduction electrons in a conduction band. Thus a multiple scattering (MS) method or Green’s function method, which has been used to calculate the electronic structure of conduction electrons near the Fermi energy in metals, is applicable to calculate the XANES of materials. The line shape of a XANES spectrum represents the partial and local electron density of states of the X-ray absorbing atom.$^{(54)}$ Hence any kinds of electronic structure calculations other than the MS theory, such as the LCAO-MO (molecular orbital derived from a linear combination of atomic orbitals) method or the APW (augmented plane wave) method, are also applicable to interpret the near-edge fine structure. One of the most popular methods for calculating XANES spectra is the MS theory.

In the MS theory, a sphere of radius $r_i$ centered at the $i$th atom is considered, and the solid is divided by spheres. A spherically symmetric atomic potential $V(r)$ is put inside each sphere and the potential equals zero or constant outside the spheres. This is called the muffin-tin (MT) potential. The wave function in the solid is expressed as the overlap of spherical Bessel functions (radial part of the wave function) multiplied by the spherical harmonic functions (angular part of the wave function).

The wave function $\psi (r)$ of a photoionized electron is scattered by an atomic potential $V(r)$ near the ionized atom, and finally it becomes itself after being scattered many times (Equation 4)

$$\psi (r) = -\frac{1}{4\pi} \int \frac{\exp (ik|r-r'|)}{|r-r'|} V(r')\psi (r') \, dr'$$  \hspace{1cm} (4)

where $k^2 = \varepsilon$ is the kinetic energy of a photoelectron and $k$ is real for $\varepsilon > 0$ (photoionized electron), $\exp (ik|r-r'|)/(|r-r'|)$ represents a spherically expanding wave, and $V(r)$ is the MT potential. This method is called the MS method, Green’s function method, or Korringa–Kohn–Rostker (KKR) method.$^{(55)}$ The KKR method is only exact for solids that have translational symmetry, or periodic boundary conditions. Small clusters, molecules, amorphous or surface adsorbates have a lower symmetry, and it is difficult to apply directly the KKR method. Thus the cluster calculation method was proposed by Johnson$^{(56)}$ and was called the multiple scattering X$\alpha$ (MS-X$\alpha$) method, because Slater’s X$\alpha$ exchange potential$^{(57)}$ is used in place of the Hartree–Fock (HF) exchange integral. The X$\alpha$ method is also called the Hartree–Fock–Slater (HFS) method, and recently it has been developed as a local density approximation (LDA) theory. The calculation method for XANES spectra is a modified MS-X$\alpha$ method.$^{(58)}$ In another way, the MS method is the expansion of the wave function of positive energy by an infinite sum of the spherically outgoing and incoming scattering waves. The electrons excited into the continuum level have a wave function of a standing wave formed by the infinite number of incoming and outgoing spherically traveling waves. That is to say, a wave whose intensity is $V(r')\psi (r')$ coming from every point $r'$ in space is synthesized and forms a wave $\psi (r)$ at point $r$. This method produces a wave function similar to the APW method, which is an appropriate method to calculate a metallic band structure, but APW requires a greater number of basis functions than the MS method.

The wave function at point $r$ is the sum of all the scattered waves multiplied by the phase factor. The LCAO-MO method is another choice for calculating the electronic structures of solid or molecules, and is thus applicable to the calculation of XANES spectra.$^{(59)}$

An atomic calculation yields a satisfactory agreement between experiment and theory, as shown in Figure 12,$^{(60)}$ after the inclusion of the perturbation of crystal field splittings. Bragg reflection of electrons in a crystal reproduces a rough XANES spectrum.$^{(61)}$

4 THEORY OF EXTENDED X-RAY ABSORPTION FINE STRUCTURE

4.1 Single Scattering Theory

Whereas MS of photoelectrons in a solid is a good approximation to treat XANES, because the electron kinetic energy of the EXAFS region is very high, single scattering is a good approximation to EXAFS except for
special cases. The wave function $\phi_b(r)$ of a photoelectron scattered by a single atom is asymptotically expressed by Equation (5):

$$
\phi_b(r) \rightarrow \exp(ikz) + \frac{f(\vartheta)}{r} \exp(ikr)
$$

where $f(\vartheta)$ is the scattering amplitude and $\vartheta$ is the scattering angle ($\vartheta = 0^\circ$ for forward scattering and $\vartheta = 180^\circ$ for backscattering). The scattering amplitude of an electron of velocity $v$ scattered by an atom of atomic number $Z$ is expressed by the first Born approximation (Equation 6):

$$
f(\vartheta) = \frac{e^2}{2mv^2}[Z - A(\vartheta)] \frac{1}{\sin^2(\vartheta/2)}
$$

where $e$ and $m$ are the charge and the mass of an electron, respectively, and $A(\vartheta)$ is the atomic structure factor for X-rays, given by Equation (7):

$$
A(\vartheta) = 4\pi \int_0^\infty \sin \frac{kr}{r} \rho(r)^2 dr
$$

where $k = (4\pi mv/\hbar)\sin(\vartheta/2)$ is the change in electron momentum before and after the scattering and $\rho(r)$ is the charge distribution in an atom. The forward scattering amplitude crudely depends on the atomic number in a way such that (Equation 8)

$$
f(0^\circ) = \frac{1}{3} \int_0^\infty 4\pi \rho(r)r^4 dr = \frac{1}{3}Z(r^2)
$$

in atomic units, because (Equation 9)\(^{62}\)

$$
Z = \int_0^\infty 4\pi r^2 \rho(r) dr
$$

where $\langle \rangle$ denotes an average. The calculated scattering amplitude is shown in Figure 13.\(^{63}\)

The EXAFS is expressed by Equation (10):\(^{64}\)

$$
\chi(k) = -\sum_j \frac{N_j}{2kr_j} |f_j(k, \pi)| \exp(-2\sigma_j^2 k^2) \sin[2kR_j + \phi_j(k)]
$$

where $k = \sqrt{2m(E_0 - E)/\hbar}$ is the photoelectron wave vector, $N_j$ is the number of nearest neighbors, $|f_j(k, \pi)|$ is the backscattering amplitude, and $R_j$ is the distance from the center atom. The exponential term contains the Debye–Waller-like vibrational effect and damping. The dumping due to the finite coherent length of the photoelectron, $\exp[-2R_j/\lambda(k)]$, is multiplied for a more exact expression. The Debye–Waller factor contains both effects of thermal vibration and geometric randomness. The oscillating part of the EXAFS equation, $-\sin 2kR_j/(kR_j)^2$, if plotted as a function of $kR$, is the EXAFS oscillation.

The EXAFS oscillation amplitude is larger when the atomic number of neighboring elements is higher. For example, the Si K edge EXAFS oscillation amplitude of Si is stronger than that of SiO\(_2\), because the atomic number of Si is higher than that of O. The white line of SiO\(_2\) is sharper and stronger than that of Si. Hence the EXAFS oscillation and the white line intensity do not directly indicate the concentration of the atom in the analyte. However, the edge jump is a good measure of concentration, and the measurement of edge jump could determine the concentration without a working curve, as shown in Table 5.\(^{65}\)

The effect of thermal vibration on the line shape of X-ray absorption spectra is shown schematically in Figure 14.\(^{44}\) This is the line in the XANES region. Similarly, the EXAFS oscillation becomes unclear owing to thermal vibration. As the atomic number becomes

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**Figure 13** Calculated plane-wave scattering factor amplitude $|f|$ of nickel as a function of both the scattering angle $\theta_{Ni}$ and the photoelectron kinetic energy. (Reproduced from M. Sagurton et al., ‘Derivation of Surface Structures from Fourier Transforms of Photoelectron Diffraction Data’, Phys. Rev. B, 30, 7332–7335, © 1984, with permission from Elsevier.)

**Table 5** Results of copper–zinc solution to test the trace element analysis

<table>
<thead>
<tr>
<th>Zn ($\mu$g mg(^{-1}) Cu solution)</th>
<th>Edge jump</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.092</td>
<td>0.0059</td>
</tr>
<tr>
<td>0.049</td>
<td>0.0035</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0021</td>
</tr>
<tr>
<td>0.000</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

Reproduced by permission from Nomura\(^{65}\), © 1992 The American Chemical Society.
higher, the core hole lifetime becomes shorter. A shorter lifetime of the inner shell level indicates that the energy of the inner shell becomes vague because of Heisenberg’s uncertainty principle. Consequently, the EXAFS oscillation of the K spectrum for higher atomic number elements is not clear compared with that of the L edge spectrum of the same element.

The IMFP of photoelectrons is a function of kinetic energy for a particular material, as shown in Figure 15. It is 1–2 nm for the usual EXAFS experiments. Hence the photoelectron is only coherent within a few nanometers, and it probes the local structure within the IMFP. Thus 1–2 nm regularity, usually up to the next-nearest neighbors, in the structure is sufficient for the EXAFS oscillation to emerge.

4.2 Relation to Other Techniques (X-ray Photoelectron Diffraction, Low-energy Electron Diffraction, X-ray Fluorescence Holography)

X-ray photoelectron diffraction (XPD) is used to study the local structure of surfaces. The photoelectron intensity as a function of detected polar and azimuthal angles is measured in this technique. The photoelectron intensity is anisotropic in its detection angle. This effect is due to photoelectron diffraction, but roughly speaking it is due to the photoelectron’s forward scattering by the nearest-neighbor atoms around the photoelectron-emitting atom. XPD uses forward scattering of photoelectrons; EXAFS uses backscattering of photoelectrons.

Recently XPD has been treated as photoelectron holography (PEH). The intensity distribution of the photoelectrons of a single crystal is measured and Fourier transformed, and then a local atomic structure of the single crystal near the photoelectron-emitting atom can be constructed. The phase shift of electron waves scattered by a neighboring atom makes the analysis of the Fourier transform for PEH complicated. The angular distribution of the X-ray fluorescence intensity is measured and the Fourier transform of the angular distribution reconstructs the crystal image. This is called X-ray fluorescence holography (XFH). XFH is free from the phase shift problem, but this method is bulk sensitive, whereas XPD and PEH are surface sensitive.

Low-energy electron diffraction (LEED) is a surface crystallography experimental method where electrons of a few hundred electron-volts impinge on a single crystal and a diffracted electron pattern is observed. The penetration depth of these energy electrons is a few nanometers, hence this method is surface sensitive. Electron diffraction requires a periodic structure of at least 10 nm on the surface, hence the LEED method cannot probe the structure clusters of a few nanometers on a surface.

5 DATA ANALYSIS AND SOFTWARE PACKAGES FOR X-RAY ABSORPTION FINE STRUCTURE

The measured (Figure 16a) X-ray absorption spectral energy is converted into photoelectron momentum. The smooth background $\mu_0(E)$, which means an isolated atom absorption coefficient, is subtracted from the observed
value $\mu(E)$ and normalized according to Equation (11):

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


This is the EXAFS oscillation. If we want to enlarge the oscillation for a larger $k$ region, we sometimes plot $k^2\chi(k)$ or $k^3\chi(k)$ in place of $\chi(k)$ as shown in Figure 16(b).
Then this is Fourier transformed as shown in Figure 16(c), and a radial distribution function is obtained. To obtain the coordination geometry, measurement of the polarization-dependent EXAFS oscillation is important, as shown in Figure 17(a) and (b).\(^{(70)}\) An example of S K edge spectra of CS\(_2\) on a Cu(111) surface is shown in Figure 18.\(^{(71)}\)

A spline function or higher order polynomial determines the smooth background. Theoretically, the smooth background has a shape of \(\tan^{-1} \theta\) at the threshold, because the discrete absorption line shape is a Lorentzian function and its sum in a Rydberg series becomes \(\tan^{-1} \theta\) as shown in Figure 18.

An incident X-ray beam forms a standing wave in a large-sized single crystal. In this case, additional fine structure, the 1985-eV structure in Figure 19,\(^{(72)}\) for example, depending on the incident angle of X-rays, is observable. The standing wave profile is sensitive to the location of impurity atoms in a crystal, i.e. which site in the lattice. The use of standing waves is one of the surface analysis methods, but sometimes interferes with obtaining \(\chi(k)\), as shown in Figure 19.

Another effect interfering with the observation of \(\chi(k)\) is the multiple ionization effect. The effect of an additional one or two electrons ionized from outer shell(s) is not negligibly small.\(^{(73)}\) The double ionization probability is sometimes more than 30% of single K shell ionization. This is a source of error in EXAFS analysis.

EXAFS Fourier analysis is sometimes not easy when additional peaks such as multiple ionization, standing wave structure, and impurity peaks originating from the analyte, X-ray source, or X-ray optics emerge.

Data analysis methods have been developed and several standard computer programs are now available.

![Figure 18](image1.png)  
**Figure 18** Experimentally obtained S K-edge XANES spectra (dots) of a CS\(_2\) multilayer (30 L) at an X-ray incident angle of 55°, and submonolayer (0.02 L) at 15°, 55°, and 90°. (Reproduced from S. Yagi et al., ‘Structural and Electronic Properties of Molecularly Adsorbed CS\(_2\) on Cu(III) Studied by X-ray Absorption and Photoelectron Spectroscopies’, Surf. Sci., 311, 172–180, © 1994, with permission from Elsevier Science.)

![Figure 19](image2.png)  
FEFF is the most popular program that is used by EXAFS users. The EXAFS analysis program is not difficult to code, and a laboratory that studies EXAFS may have its own program, but not always published. Some of the programs listed in Table 6 can be downloaded from Web sites.

6 INSTRUMENTATION

6.1 Laboratory Extended X-ray Absorption Fine Structure

To measure the X-ray absorption spectra, a strong X-ray source of continuous energy is required, such as white radiation from an X-ray tube or synchrotron radiation (SR). A metallic wheel is rotated in vacuum and a high electric potential is applied between the wheel and a filament. Thermal electrons are emitted from the filament and bombard the wheel target. Water flows inside the wheel to cool it against heating by the electron bombardment. To eliminate the heating, the wheel is rotated. Therefore, this type of rotating anode X-ray tube produces one order of magnitude stronger X-rays than the ordinary sealed X-ray tubes. The electron deceleration at the metal target converts the electron kinetic energy into X-ray energy. The X-rays thus produced are continuum X-rays in addition to characteristic X-rays and the maximum energy is the acceleration electric potential applied. The X-rays from the X-ray tube are then monochromated by a crystal monochromator using the Bragg diffraction condition. Then the monochromatic X-rays are incident on the specimen as shown in Figure 20. Sometimes, to compensate for the weak source intensity, a position-sensitive proportional counter is used as shown in Figure 21. However, the very simple experimental set-up shown in Figure 22 is sometimes used.

Recently, SR has frequently been used as an X-ray source. Synchrotron is the name of an electron (or positron) accelerator made of an ultrahigh vacuum (UHV) ring and electrons rotating inside the ring. High voltage is applied to the rotating electrons using variable-frequency radio waves and the frequency is synchronized with the electron rotation during the acceleration of the electrons in the ring. When the electron speed reaches close to the speed of light, a very sharp X-ray beam is emitted in a tangential direction because of the relativistic effect. This X-ray beam is called the SR. Usually SR from a storage ring is used. A ring in which electrons (or positrons) are rotated at a certain constant speed is called the storage ring. Usually electrons accelerated to a sufficient speed by a synchrotron or a linear accelerator are injected into the storage ring, and the tangential radiation when a magnet bends the electron beam is used as an X-ray source. The SR thus produced from a bending magnet is continuous over a wide range (more than 1000 eV) of X-ray energy and a few orders of magnitude stronger than the rotating
anode X-ray tube. The smaller emittance indicates the electron orbit stored in a storage ring being sharpened, but practically it indicates a smaller X-ray beam size and higher photon density. The emittance is measured in meter \( \cdot \) radians (m \( \cdot \) rad). The emittance is a measure of beam quality. The smaller the emittance, the more the beam becomes parallel. The SR is monochromated by a single crystal.

Continuous X-rays from a bending magnet are most convenient for X-ray absorption spectroscopic experiments. The rotating axis of monochromator crystals is parallel to the electric vector of the SR X-rays to make good use of the X-rays. To obtain stronger X-rays, SR from an undulator or wiggler beam line is used. The undulator and wiggler are insertion devices in the storage ring, and made of many strong permanent magnets. The electron beam in the storage ring is undulating when it goes through an undulator, and a coherent quasi-monochromatic X-ray beam is produced. It consists of many harmonics and each harmonic has a narrow (say 100 eV) bandwidth. By changing the magnet gap width, the peak energy of the X-rays from the undulator is controlled; the wider the gap, the lower is the energy. Thus, to scan the energy over 1000 eV continuously using an undulator, both the undulator gap and monochromator crystal rotation should be controlled simultaneously. This is a difficult task but now routinely done in some SR undulator beam lines. An undulator can produce a few orders of magnitude stronger X-rays than a bending magnet beam line. If the X-rays produced by undulating by magnets are not coherently interfered, such an insertion device is called a wiggler. X-rays from a wiggler are not strong compared with those from an undulator but are continuous in energy, and thus much easier to use in X-ray absorption experiments than those from an undulator. An example of the experimental set-up of a wiggler is shown in Figure 23.\(^{(78)}\)

SR facilities are classified into first-, second-, and third-generation sources. The first-generation synchrotrons were particle accelerators, and spectroscopists parasitically used the SR. Such SR was unstable. The second-generation synchrotrons use a storage ring to obtain SR but the emittance is still not small enough, i.e. \(10^{-7}\) mrad. The emittance of the third-generation synchrotrons have emittance as small as \(10^{-9}\) m \( \cdot \) rad. Such a small-emittance storage ring requires a large-radius electron orbit because a large number of magnets are required to keep the electron beam cross-section small. The fourth generation of synchrotron has not yet been constructed and not defined, but may be a free electron laser facility using an electron accelerator. The third-generation SR facilities are tabulated in Table 7, and the second-generation SR facilities can be reached via the links of the Web pages listed.

The first crystal in the monochromator used in an SR beam line experiences a high heat load, and the lattice constant is slightly different from the second crystal. The crystal optics should be cooled by flowing water. To adjust the difference in the lattice constant between the first and the second crystals, usually one of the two crystals is independently finely moved by a piezoelectric

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**Table 7** Third-generation SR facilities and Web sites

<table>
<thead>
<tr>
<th>Facility</th>
<th>Web Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALS</td>
<td><a href="http://www-als.lbl.gov/als/">http://www-als.lbl.gov/als/</a></td>
</tr>
<tr>
<td>APS</td>
<td><a href="http://epicsaps.anl.gov/welcome.html">http://epicsaps.anl.gov/welcome.html</a></td>
</tr>
<tr>
<td>ESRF</td>
<td><a href="http://www.esrf.fr/">http://www.esrf.fr/</a></td>
</tr>
<tr>
<td>SPring-8</td>
<td><a href="http://www.spring8.or.jp/">http://www.spring8.or.jp/</a></td>
</tr>
</tbody>
</table>

---
mechanism. The adjustment of the two crystals should always be monitored for the measurement of EXAFS for the 1000-eV range. The monitoring of the adjustment is done by measuring the incident X-ray intensity, which is maximized at every energy point scanned.

6.3 Secondary Yield Techniques and Applications

The intensity of the monochromated X-rays is monitored by an ionization chamber. X-rays pass through the ionization chamber \( I_0 \) and are then incident on a specimen, and the transmitted X-ray intensity is measured by another ionization chamber. The XAS is the plot of \(-\log(I/I_0)\) against the X-ray energy. The absorption spectra are usually measured by this transmission method as shown in Figure 24(a).\(^{79}\) When the X-rays are absorbed strongly by the sample, the secondary responses such as photoelectron intensity, sample electric current intensity, secondary electron intensity (electrons whose kinetic energy < 50 eV is mostly the secondary electrons), Auger electron intensity, and X-ray fluorescence intensity become strong. Therefore, equivalent spectra to the absorption spectra are measurable by these secondary phenomena such as photoelectron intensity, secondary electron intensity, Auger electron intensity (Figure 24b), sample drain current (Figure 24c and d), X-ray fluorescence intensity (Figure 24e), ion intensity due to photostimulated desorption, and other secondary techniques.

The photoelectron intensity for a single crystal has an anisotropy with respect to the observed direction because of the photoelectron diffraction. The angular average of the photoelectron intensity measured as the change in incident X-ray energy is the XAS. This method is called the photoelectron yield method. If Auger electrons are detected, this is the Auger electron yield method. The intensity of Auger electrons from a single crystal also has an angular anisotropy. The detection angle is therefore important for interpreting the observed data for these electron yield methods. Many kinds of electrons are detected, such as secondary electrons, core photoelectrons, valence photoelectrons, and Auger electrons, as shown in Figure 25(a–c).\(^{80}\) The different kinetic energy electrons correspond to the different probing depths. Thus the electron yield spectra are a mixture of various depth spectra as well as a mixture of various processes of electron production. The relation between the X-ray absorption process and the electron emission process is neither direct nor clear.

The electric drain current is of the order of \(10^{-9} \) A when using a bending magnet SR beam line. The electric drain current is a measure of X-ray absorption, and this method is called the TEY method. This is because the drain current represents the sum of all the electrons emitted from the sample. The electrons produced in a solid are scattered in the solid as shown in Figure 26,\(^{81}\) and only electrons produced near the surface contribute to the electric drain current. When we detect ions desorbed from the surface due to X-ray absorption, the ion intensity represents the surface top layer.

These methods of detecting electrons (or electric current) or ions are surface sensitive and therefore are called surface extended X-ray absorption fine structure (SEXAFS). If the sample current is measured in an air or helium atmosphere, then the ejected electrons are converted into \(O_2^+\) or other ions and a positive or negative current is observable depending on the sample electric potential with respect to the ground. This method is called the conversion electron yield (CEY) method.

The XFY method is not surface sensitive, because the fluorescent X-rays originate from as deep a location as the X-ray attenuation length. However, if XFY is combined with the grazing-incidence X-ray technique (Figure 27),\(^{82}\) where the total reflection X-ray technique is combined with the TEY and CEY methods, it becomes more surface sensitive than normal-incidence TEY or
Figure 25 Schematic photoelectron spectra for (a) the excitation energy below the excitation threshold of core level A, (b) just above the absorption threshold but below the photoionization threshold, and (c) far above the threshold. The contributions to the photoelectron intensity from different level photoelectrons and Auger electrons are indicated. At the bottom the window settings for various electron yield X-ray absorption techniques are shown. (Reproduced by permission from Stöhr et al.© 1984 The American Physical Society.)

CEY. The X-rays are totally reflected on the surface and the evanescent X-ray wave penetrates only a few nanometers from the surface. X-ray reflectivity is also a measure of XAFS.

The grazing exit angle method is also possible, as shown in Figure 28, because of the reciprocal theorem of optical beams. The XFY method has atomic selectivity because an X-ray detector usually has energy resolution, hence the signal-to-noise ratio is better than in the TEY method, and minor elements adsorbed on the surface can be detected by the XFY method. X-ray absorption spectra of very dilute analytes can be detected using the XFY method; the detection limit is $<10^{12}$ atoms cm$^{-2}$. The X-rays emitted from a deep location in a specimen suffer from the self-absorption effect and the spectral shape is different from that of an absorption-free spectrum. The XFY method combined with the grazing incidence method does not suffer heavily from the self-absorption effect compared with the normal-incidence method.

Some materials emit luminescence in the visible wavelength range when irradiated with X-rays. This optical luminescence signal intensity corresponds to the
amount of X-rays absorbed by the specimen. Various processes of optical luminescence de-excitation are shown in Figure 29. Optical luminescence is usually strong for rare earth compounds, but some crystals which have defects in their crystal structure emit stronger luminescence, although a perfect single crystal of the same material does not emit optical luminescence.

The photoacoustic (PA) effect produces sound on irradiating a sample surface by a chopped photon beam. This effect was discovered by Alexander Graham Bell. Heat is produced while the sample is irradiated by an optical beam and it diffuses during the beam chopping. The chopping frequency usually ranges from a few to a few hundred hertz. The sound wave is detected by a microphone or a piezoelectric device. When the chopping frequency is low, the heat diffuses into deeper location in the sample compared with when it is high. Thus the probing depth is variable by changing the chopping frequency. All the incident photon energy is finally converted into thermal energy through nonradiative transition processes in the solid. The PA process in the visible wavelength range is used for the very sensitive absorption spectrometry of thick bulk samples, which are not transparent to an optical beam. This method has been applied to the measurement of the X-ray absorption, where the incident X-ray beam should be chopped to produce acoustic waves in the sample. This method is a thermal yield method.
Figure 29 Schematic diagram of X-ray absorption and optical luminescence processes. Three different excitation processes, from the 1s orbital to a continuum state (absorption coefficient $\mu_1$) and to a bound state ($\mu_2$), and from the 2s orbital to a continuum state ($\mu_3$), give rise to a single luminescence with luminescence yields $\eta_1$, $\eta_2$, and $\eta_3$, respectively. X-ray fluorescence, KLL Auger, electron multiscattering, nonradiative decay, and radiative decay processes are schematically shown.

Figure 30 Schematic illustration of a liquid cell. (Reproduced by permission from Emura et al. (85) © 1993 The American Physical Society.)

Liquid samples are inserted into a cell shown in Figure 30 (87) and an electrode is used to measure the photoconductive spectra; electrical conductivity is induced by the incident X-rays. Spectra thus measured are sometimes the inverse of the transmission spectra and sometimes similar to the transmission spectra, depending on the concentration. (88) Electrode surface reaction processes can be measured using X-ray absorption in combination with the total reflection X-ray technique.

X-ray submicrometer beams are now available in major SR facilities, and using these beam lines micro- or nanobeam techniques are now applicable, as shown in Figure 31. (89) Where the XFY is measured by a solid-state detector (SSD). The energy resolution of an SSD is of the order of 100 eV, while the energy shift of an absorption edge is a few electron-volts. If the incident X-ray energy is between the edge energies of two chemical states (say FeO and Fe$_2$O$_3$), then only one kind of chemical state (FeO) can emit the X-ray fluorescence. Using this technique, chemical state mapping is possible.

Using a bent crystal monochromator as shown in Figure 32, (90) multiple-energy X-rays can be focused on a sample and the transmitted X-rays are detected by a position-sensitive detector, which is made of a photodiode array (PDA). Using such a kind of energy-dispersive optics, one spectrum can be measured within a few milliseconds. (91) This method is called quick X-ray absorption fine structure (Q-XAFS).

Circularly polarized X-rays can be produced by linearly polarized X-rays transmitted through a diamond single crystal at a special angle depending on its wavelength, which is called the phase retarder, as shown in Figure 33. (92) The vertical and horizontal components, the ratio of which is called helicity, of the X-ray electric vector can be controlled by the small rotation and tilting of the diamond crystal. Absorption spectra of a magnetic sample can be measured. This is X-ray magnetic circular dichroism (XMCD) X-ray absorption. The magnetic S and N poles applying the magnetic field to the sample are inverted.
or the circularly rotating direction of the X-ray electric field is inverted and the difference in the absorbance is measured. The former is usually used to measure the dichroism. Magnetic thin multilayers have recently become important for information mass storage devices, and these materials are characterized with microbeam XMCD X-rays. The difference in the absorption coefficients for the left and right circularly polarized X-rays is illustrated schematically in Figure 34. The details of MCD are described in several books.

High-resolution X-ray fluorescence spectra of transition metal compounds show multiplet splitting due to the exchange interaction between the unoccupied 3d level and the core X-ray hole. Thus the XFY absorption spectrum of each multiplet line provides spin-selective absorption spectra, as shown in Figure 35. This method can measure spin-selective X-ray absorption spectra without applying a magnetic field to the sample. This method is useful for characterizing mixed-valence protein compounds.

The phase transition due to the temperature change is observable, as shown in Figure 36. The phase transition is a small change in bond distance and bond angle, and consequently the electronic structure of the sample changes. Thus both XANES and EXAFS region spectra change their line shapes.

The surface of water, where a liquid monolayer is present, could be analyzed by grazing incidence X-ray reflection XAFS. When the monolayer absorbs metal...
ions from the water solution, the concentration of the metal ion on the surface is slightly higher than that in the water. The coordination structure around the metal ion is analyzed by the EXAFS method.

When a powder is measured by the XFY and TEY methods on a substrate, then the depth-selective chemical state analysis of a fine particle can be performed. Fly ash is a powder of micrometer-sized particles, which are a source of acid rain when they are dispersed in the air. The particles are put on an aluminum foil and irradiated by monochromated X-rays, and XANES spectra are measured by TEY and XFY methods. The TEY method is sensitive to the surface chemical state of the powder particle, and XFY is sensitive to deep parts of the particle (micrometers). The chemical shift of the white line in the absorption spectra is a measure of the oxidation state of an element in the particle.

The surface catalyst process could be elucidated by the analysis of EXAFS spectra. The incident X-ray polarization dependence is an important parameter for the determination of the geometry of a reactant and the surface. X-ray detectors in the XFY method have been developed for X-ray absorption experiments, such as a 19-element Ge detector array; a schematic illustration of a seven-element detector is shown in Figure 23; a 100-element detector array can be used for more efficient detection of X-rays.

Transition metals are usually a target of XAFS analysis, the energy range of which is from 5 to 20 keV. The beamline for X-rays of this energy range uses Be and polymer films as windows to separate the vacuum system from the atmosphere. Both lower and higher energy XAFS experiments require different techniques.

Soft X-ray XAFS experiments, ranging from 0.1 to 5 keV, require UHV techniques. This is because any windows between the SR storage ring and the sample heavily absorb X-rays, hence a windowless beamline is required. Consequently, the sample chamber is made of UHV components and must be baked out up to 200°C. The contaminants in X-ray windows and other X-ray optics are carbon and oxygen, which are in the soft X-ray region (250–600 eV). Hence a windowless system is appropriate for the analysis of these elements. The shortcoming of the soft X-ray region experiment is the UHV system, because samples requiring X-ray absorption analysis could not always be inserted into the UHV system because they would emit gas into the clean system. A vacuum of 10⁻² Pa is sufficient to avoid the absorption of X-rays in the X-ray path. The XAFS spectra of this soft X-ray region are surface sensitive and the profile changes of the spectra due to chemical state are very large. The spectra measured can be used for the same purpose (chemical state analysis) as XPS or ESCA. The detection limit of XAFS is usually lower than that of ESCA, hence XAFS has an advantage over ESCA if SR is available.

XAFS experiments higher than 20 keV require different experimental techniques. The number of application examples is not large, mainly because high-energy X-ray sources are limited without using third-generation SR facilities. In place of measuring this energy range K-edge XAFS, the L-edge XAFS, the energy of which usually falls in the range 5–20 keV, is measured. The L XAFS spectra are composed of L₁, L₂ and L₃ edge jumps, which interfere with each other. To avoid this, the K edge is useful for the analysis. The lifetime of the K hole state of high-energy K-edge XAFS of higher atomic number elements is, however, shorter than the long-wavelength region. Because of the Heisenberg uncertainty principle,
the line widths of the absorption spectral components are as large as 100 eV. Both the EXAFS oscillation and XANES lose fine structure owing to this lifetime broadening. High-energy XAFS has recently been measured with the development of third-generation SR facilities, because the numerical analysis overcomes the short lifetime effect.

7 SOURCES AND DATABASES

Academic societies and E-mail lists discuss the standardization of X-ray absorption spectrometry. As XAFS is used in many areas of research, standardization has been required. To achieve standardization, the International XAFS Society (IXS) was established in the 1990s. The purpose of the IXS is stated as follows:

The International XAFS Society represents all those working on the fine structure associated with inner-shell excitation (near-edge and extended) by various probes (e.g. X-rays and electrons), and related techniques for which the data are interpreted on the same physical basis. The purpose of the IXS is to oversee activities which benefit the community as a whole, to establish operational committees, to provide for education in the field, to disseminate relevant information, to work with other related regional, national and professional organizations in promoting and developing XAS and related disciplines, and to act as representative for the community to other professional organizations.

This society has a close relation to the International Union of Crystallography (IUCr). The WWW home page of the IXS is at Illinois Institute of Technology, http://ixs.iit.edu/, where a large number of XAFS databases are presented. This WWW page links to other related WWW home pages. National society and working groups are active in many countries. All the information concerning these activities is obtainable at the international conferences on XAFS. The first XAFS international conference was held at Daresbury, UK, in 1981, and subsequent conferences are listed in Table 8.

Many kinds of activity reports published by SR facilities are useful sources of experimental methods and standard spectra. Journal sources are listed in Table 9. Fundamental reviews in Analytical Chemistry published in even years refer to X-ray absorption spectrometry. In a book by Meisel et al., references are classified by atomic number and spectral series. Recently several books which treat newer X-ray techniques and concerning X-ray absorption have been published. The Materials Research Society has held symposia on applications of SR in materials science.

The Denver X-ray analysis conference and international conferences on electron spectroscopy, on X-ray and inner-shell processes and on vacuum ultraviolet physics are sources of X-ray absorption spectroscopy and spectrometry.

8 ALTERNATIVE METHODS

8.1 Electron Energy Loss Spectroscopy

An electron beam, with an energy from a few hundred electron-volts to a few hundred kiloelectron-volts, impinges on a sample and loses its kinetic energy. When the sample is a bulk material, reflected electron energy is measured. Usually the loss of transmitted electron energy is measured for thin-film samples less than a few micrometers or a few tens of nanometers thick. This is called EELS. EELS is usually combined with transmission electron microscopy (TEM). The electron energy loss structure is similar to the XAFS. The EXAFS region in EELS is called the extended electron energy loss fine structure (EXELFS). Forward-scattered (0°) electron energy loss spectra, formed when electrons are transmitted in a thin film, are approximately equivalent to the optical spectra; the selection rule is the electric dipole. Energy loss spectra of electrons scattered at a large angle are not treated by the electric dipole transition, and sometimes include optically forbidden transitions. The transmission method used in TEM has a very high spatial...
resolution, hence chemical state imaging by the chemical shift of the absorption edge is possible.\(^{133,134}\) High energy resolution and high spatial resolution are not always achieved by a single instrument. The EELS spectra are sensitive for low atomic number elements such as boron and carbon. It is not easy to measure the XAFS spectra of these long wavelengths using an SR facility.

### 8.2 Self-absorption

Although the characteristic X-ray wavelength of an element is usually separated from the absorption edge wavelength of the same element for hard X-rays, they are very close to each other for the soft X-ray region. These close lines are, for example, transition metal L\(\alpha,\beta\) X-ray emission lines and L\(2,3\) absorption edges. The L\(\alpha\) and L\(\beta\) X-ray emission lines emitted in a deep location in a solid are absorbed during the travel in the solid. Hence the X-ray emission spectra have dips due to the X-ray absorption spectra. The profiles of the L\(\alpha,\beta\) X-ray emission lines of transition metals excited by different electron energies (3 and 16 keV) change because of the self-absorption effect.\(^{135}\) If the electron energy is high (16 keV), then the penetration depth of the electron is deeper. Hence the X-ray emission spectrum suffers heavily from the self-absorption effect. In contrast, if the electron energy is low (3 keV), then the penetration depth is shallow, and the X-ray emission spectrum is free from the self-absorption effect. The comparison of these two spectra yields an X-ray absorption. Similarly, one set of X-ray emission spectra is obtainable by tilting the sample to the X-ray detector or to the incident electron beam, when the electron energy is fixed.

### 8.3 Extended X-ray Emission Fine Structure

The radiative Auger effect (RAE) is always associated with the X-ray characteristic lines and this effect is an energy loss structure in characteristic X-ray emission, as shown in Figure 37.\(^{136}\) The second electron shaken up into an unoccupied orbital has similar information to the XAFS. This is called EXEFS.\(^{137}\) This method is used to measure low atomic number elements such as Na, Mg, Al, and Si, because the RAE satellite intensity is strong for these elements. If wavelength-dispersive electron probe microanalysis (EPMA) is available, XAFS spectra of 1 \(\mu\)m diameter area are measurable using this method.

### 8.4 X-ray Raman Scattering

X-ray Raman scattering is the effect of energy loss on X-ray scattering. Raman scattering is a similar physical process to Compton scattering. The difference is that Raman scattering involves scattering by core electrons whereas Compton scattering involves scattering by conduction band electrons. X-ray Raman scattering is a method for measuring soft X-ray absorption spectra (say of carbon) with a hard X-ray spectrometer (a few kiloelectron-volts). Hard X-rays can be measured in air; soft X-ray absorption spectroscopy, which usually requires UHV, is possible in air by this method. Hard X-rays (8265 eV) impinge on a carbon-containing sample, and the X-rays lose energy by the carbon K edge due to the Raman scattering (ca. 300 eV), as shown in Figure 38.\(^{138}\)
The X-ray that should be detected is at ca. 8 keV, which still falls in the hard X-ray region. The XAFS study of catalysts during reaction with gases is possible using the Raman effect.

8.5 Diffraction Anomalous Fine Structure

DAFS was proposed by Stragier et al.\(^{(139)}\). XAFS usually measures the wavelength dependence of \(f_2\), the imaginary part of the atomic structure factor; DAFS measures \(f_1\). The wavelength dependence of \(f_1\) and \(f_2\) has a close relation through the Kramers–Kronig transformation. In the DAFS experiment, the intensity of a diffraction peak of a specimen is measured by the change in the incident X-ray energy. The sample and detector angles \((\theta - 2\theta)\) are measured by the change in the incident X-ray energy, or powder X-ray diffraction patterns are measured by the change in incident X-ray energy. This method can measure site-selective XAFS of the same element, because the diffraction peak corresponds to a different site in the crystal. If the diffraction peaks which originate from the surface and bulk phases are separated, space-selective EXAFS-like spectra are obtainable by this method.

8.6 \(\beta\)-Environment Fine Structure

The \(\beta\)-electron emission process in a nuclear conversion process suffers interference by the crystal structure for the same reason as EXAFS. This method is called BEFS.\(^{(140)}\)

8.7 Inverse Photoemission Spectroscopy

IPES is an alternative method to measure the unoccupied electronic structure by irradiating electrons and detecting photons.\(^{(141)}\) This method is otherwise called bremsstrahlung isochromat spectroscopy (BIS). The extended structure like EXAFS is also observable in BIS and this is called the extended X-ray bremsstrahlung isochromat fine structure (EXBIFS).\(^{(142)}\) The BIS is usually combined with an ESCA instrument, and thus occupied and unoccupied electronic structures (similar to XANES) are measurable.\(^{(143)}\)

9 CONCLUSION

X-ray absorption spectroscopy is chiefly used in the area of electronic structure study and structural analysis for the study of new materials, surfaces, and catalysts. The spectra measured are surface sensitive or bulk sensitive depending on the detection method. Chemical shift and profile changes are observable. Thus the spectral analysis is useful for materials characterization. This method is also powerful for analyzing mixed chemical states in industrial, environmental, and biological analytes. The development of SR facilities will make it possible to measure nanometer-sized samples in less than a few milliseconds.

ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>APW</td>
<td>Augmented Plane Wave</td>
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<tr>
<td>BEFS</td>
<td>(\beta)-Environment Fine Structure</td>
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<tr>
<td>BIS</td>
<td>Bremsstrahlung Isochromat Spectroscopy</td>
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<tr>
<td>CEY</td>
<td>Conversion Electron Yield</td>
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<tr>
<td>DAFS</td>
<td>Diffraction Anomalous Fine Structure</td>
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<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
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<tr>
<td>EPMA</td>
<td>Electron Probe Microanalysis</td>
<td></td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
<td></td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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</tr>
<tr>
<td>EXBIFS</td>
<td>Extended X-ray Bremsstrahlung Isochromat Fine Structure</td>
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<td>EXEFS</td>
<td>Extended X-ray Emission Fine Structure</td>
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<td>EXELFS</td>
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<tr>
<td>HF</td>
<td>Hartree–Fock</td>
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<tr>
<td>HFS</td>
<td>Hartree–Fock–Slater</td>
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<tr>
<td>IMFP</td>
<td>Inelastic Mean Free Path</td>
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<tr>
<td>IPES</td>
<td>Inverse Photoemission Spectroscopy</td>
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<tr>
<td>IUCr</td>
<td>International Union of Crystallography</td>
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<tr>
<td>IXS</td>
<td>International XAFS Society</td>
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<tr>
<td>KKR</td>
<td>Korringa–Kohn–Rostker</td>
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<tr>
<td>LCAO-MO</td>
<td>Linear Combination of Atomic Orbitals-Molecular Orbital</td>
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<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
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<tr>
<td>LEED</td>
<td>Low-energy Electron Diffraction</td>
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<tr>
<td>LRO</td>
<td>Long-range Order</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>MS</td>
<td>Multiple Scattering</td>
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<tr>
<td>MS-X(\alpha)</td>
<td>Multiple Scattering X(\alpha)</td>
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<tr>
<td>MT</td>
<td>Muffin-tin</td>
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<tr>
<td>NEXAFS</td>
<td>Near-edge X-ray Absorption Fine Structure</td>
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<td>PA</td>
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<tr>
<td>PDA</td>
<td>Photodiode Array</td>
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<td>PEH</td>
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<td>Q-XAFS</td>
<td>Quick X-ray Absorption Fine Structure</td>
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<tr>
<td>RAE</td>
<td>Radiative Auger Effect</td>
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<td>SEXAFS</td>
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<tr>
<td>SR</td>
<td>Synchrotron Radiation</td>
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</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>SRO</td>
<td>Short-range Order</td>
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<tr>
<td>SSD</td>
<td>Solid-state Detector</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>TEY</td>
<td>Total Electron Yield</td>
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<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
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<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure</td>
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<td>XANES</td>
<td>X-ray Absorption Near-edge Structure</td>
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<td>XAS</td>
<td>X-ray Absorption Spectrum</td>
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<td>XFH</td>
<td>X-ray Fluorescence Holography</td>
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<td>XFY</td>
<td>X-ray Fluorescence Yield</td>
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<tr>
<td>XMCD</td>
<td>X-ray Magnetic Circular Dichroism</td>
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<tr>
<td>XPD</td>
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### RELATED ARTICLES

**Environment: Water and Waste (Volume 4)**
- X-ray Fluorescence Spectroscopic Analysis of Liquid Environmental Samples

**Surfaces (Volume 10)**
- Auger Electron Spectroscopy in Analysis of Surfaces
- Soft X-ray Photoelectron Spectroscopy in Analysis of Surfaces
- X-ray Photoelectron Spectroscopy in Analysis of Surfaces

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- Energy Dispersive, X-ray Fluorescence Analysis
- Structure Determination, X-ray Diffraction
- Total Reflection X-ray Fluorescence
- X-ray Fluorescence Analysis
- X-ray Techniques: Overview

### REFERENCES

ABSORPTION TECHNIQUES IN X-RAY SPECTROMETRY


45. T. Mukoyama, unpublished work.


