I. Introduction

Since X-rays have wavelengths on the order of atomic dimensions, these highly energetic photons can be used to sample the molecular structure of materials. One example of this use is X-ray diffraction from crystalline samples resulting in a complete three-dimensional (3D) crystal structure. X-ray absorption spectroscopy (XAS) can also yield limited molecular structural information on non-crystalline (amorphous) samples. Since an X-ray absorption spectrum is a mea-
An X-ray absorption spectrum plotted as absorption coefficient versus photon energy. 
(a) Expanded view of the edge region. (b) Full spectrum showing the pre-edge, edge, and extended X-ray absorption fine structure (EXAFS) regions.

Figure 1

Measurement of the energy-dependent absorption coefficient of a material, a tunable X-ray source is required. The advent of synchrotron radiation as a high-intensity, tunable source of X-rays has been responsible for the emergence of XAS within the last three decades as an important new structural and spectroscopic technique.

A typical X-ray absorption spectrum is shown in Figure 1. At a well-defined X-ray photon energy, a sharp rise in absorption coefficient is observed. This rise is called an X-ray absorption edge and is due to electron dissociation from a core level of one type of atom (the absorbing atom) in the sample (see below). Spectral features in the edge region are sensitive to the electronic structure of the absorbing atom and can often be used to identify the geometric arrangement of atoms around the absorbing atom. Above the edge, the quasiperiodic modulations in the X-ray absorption coefficient are referred to as EXAFS. The EXAFS may be analyzed to give direct structural information about the local environment around the absorbing atom.

In the literature, a bewildering array of (often redundant) acronyms have been used to describe techniques for extracting the structural and spectroscopic information from the X-ray absorption spectrum. X-ray absorption spectroscopy (XAS) is the generic term that refers to all the techniques. Recently, X-ray absorption fine structure (XAFS) has gained some popularity as another generic reference to analysis of "fine structure" in both edge and EXAFS regions of the spectrum (Fig. 1). The spectral features in the edge region (and their analysis) are
most often given the acronym XANES (X-ray absorption near-edge structure), but are sometimes referred to as NEXAFS (near-edge X-ray absorption fine structure). The acronym EXAFS refers to both the modulations in the absorption coefficient above the edge (Fig. 1) and also to the techniques used to analyze them in terms of molecular structure. Other acronyms are sometimes used to describe EXAFS techniques applied to particular types of samples. For example, surface extended X-ray absorption fine structure (SEXAFS) is a technique used to measure the EXAFS of surface species. To avoid confusion, only XAS and EXAFS will be used in this chapter. Any discussion of analysis of the spectral features in the X-ray absorption edge region will simply refer to the edge region.

As will be discussed in some detail below, the utility of XAS as a structural technique stems from its ability to give direct structural information about a local region around specific elements in amorphous samples. The technique is element specific since each element in the periodic table exhibits an X-ray absorption edge at a different energy (see Fig. 3). Thus, in a sample with several different elements, the structure around each element may be probed independently. The EXAFS technique yields radial structural information within a 4–5 Å radius around the absorbing atom. Specifically, the question to be answered is How many of what type of atom are at what distance from the absorbing atom? Since EXAFS only gives radial distance information, orientation of the absorbing atom sites within a sample is not important. Amorphous samples (e.g., powders, solutions, frozen solutions, and gases) are amenable to study by this technique. The chemical environment of the absorbing element has only a small (yet measurable) effect on the energy of the edge, causing the EXAFS from all occurrences of that element in the sample to overlap. A heterogeneous population of site structures therefore gives rise to an average structural environment making EXAFS a poor technique for identifying such structural heterogeneity. The technique is best suited for samples in which all sites of the absorbing atom are structurally identical. In contrast to the simple radial structural information available from EXAFS, the spectral features in the edge region can yield geometrical structural information (e.g., distinguishing tetrahedral from octahedral coordination), making these two spectral regions complementary for structural determinations.

II. Theory of X-Ray Absorption Spectroscopy

In this section, a brief look at the theoretical basis of the X-ray absorption spectroscopic technique will be given. For a more in-depth look at the basic principles, data collection techniques, and applications of XAS, two books are helpful (see Koningsber and Prins¹ and Teo².)

A. Edges

The X-ray absorption spectrum of a given sample will exhibit an edge at a photon energy equal to the ionization potential of a bound electron in the constituent atoms of the sample. As illustrated in Figure 2, scanning the photon energy
causes every atom in the sample to give rise to several absorption edges as the photon energy matches the ionization potential of each bound electron \( 1s, 2s, 2p_{1/2}, 2p_{3/2}, \ldots \). These X-ray absorption edges are named for the shells of the Bohr atom (K edges for \( n = 1 \), L edges for \( n = 2 \), M edges for \( n = 3 \), etc.) as indicated in Figure 2. Current synchrotron sources can deliver high-intensity X-ray beams with photon energies \( (hv) \) up to about 30 keV. The low-energy limit is dictated by window material and atmospheric absorption. Thus, unless samples can be handled in ultrahigh vacuum on a windowless beamline, it is difficult to use photon energies below about 2 keV. The approximate K and L\_III edge energies of a few representative elements are listed in Figure 2. These edge energies are a monotonic function of atomic number (Fig. 3), so the accessible X-ray photon energy region \( (\sim 2\text{–}30\text{ keV}) \) defines the range of accessible K edges to extend from approximately P to Sn. However, since the same type of structural infor-
The K, L₁, and L₃ X-ray absorption edge energies for elements as a function of their atomic numbers. Elements with K-edge energies above the available source photon energies can be studied by examining their L edges.

Information may be obtained from L edges, the rest of the elements in the periodic table are also amenable to the XAS technique. (Accessible L₃ edges range from \( \sim 2.1 \text{ keV} \) for Y to \( \sim 22 \text{ keV} \) for Lr.)

X-ray absorption edges are not simple discontinuities in the absorption coefficient as suggested by the atomic energy level diagram in Figure 2. For example, the spectrum shown in Figure 1 exhibits spectral features at or just before the edge and understanding the origin of these features can yield information about the electronic structure of the absorbing atom site in the sample. The peaks (shoulders) just before the edge arise from electronic transitions from the core level (1s for K edges) to valence levels just below the continuum. Using appropriate selection rules, the intensities of these transitions may be related to the symmetry of the absorbing atom site. Also, the exact energy of the edge is dependent on the charge density at the absorbing atom, which is influenced by the chemical environment (e.g., valence or oxidation state). In general, the higher the oxidation state of the absorbing atom, the higher the energy of the X-ray absorption edge. A simple electrostatic explanation is that it is more difficult to dissociate an electron from an atom with higher positive charge. Some examples of these effects will be discussed in detail later.
B. EXAFS

The information content of the EXAFS technique arises from the physical interaction of the photoelectron (the photoelectron) with electron density surrounding neighboring atoms. It is the influence of this photoelectron electron scattering on the absorption coefficient for the X-ray photon that gives rise to the EXAFS modulations (see Fig. 5). For this reason, structural information about the neighboring electron density responsible for photoelectron scattering is "encoded" into these absorption coefficient modulations. This section will describe the quantitative details of this photoelectron scattering that allow this structural information to be "decoded" from the EXAFS data.

In the EXAFS region, the X-ray photons absorbed have a higher energy than that necessary to ionize the absorbing atom. Since energy must be conserved, all the energy delivered by the X-ray photon must be accounted for. Defining the X-ray absorption edge energy as $E_0$ (the threshold energy, equivalent to the ionization potential) and assuming a photon energy of $E$ ($E > E_0$), where did the extra energy ($E - E_0$) delivered by the X-ray photon go? It is transferred into kinetic energy of the photoelectron, which can be considered as a wave. The wavelength of the photoelectron wave (referred to as the de Broglie wavelength) is dependent on its kinetic energy, so that as the photon energy is scanned throughout the EXAFS region, the wavelength of this photoelectron is also "scanned". A photoelectron wave with kinetic energy ($E - E_0$) can be considered to be propagating through-space from the absorbing atom origin at a velocity, $v$, where $(E - E_0) = m_e v^2/2$ ($m_e =$ electron mass). The de Broglie wavelength of the photoelectron is inversely proportional to its momentum ($m_e v$) : $\lambda = h/m_e v$. When discussing EXAFS data, it is convenient to use the photoelectron wave vector, $k$, as the independent variable, rather than the energy, $E$. The parameter $k$ is proportional to momentum.

$$ k = \frac{2\pi m_e v}{h} = \frac{2\pi}{\lambda} = \left[ \frac{8\pi^2 m_e}{h^2} (E - E_0) \right]^{1/2} = 0.262449 (E - E_0)^{1/2} \quad (1) $$

The final numerical expression holds for $E$ and $E_0$ expressed in units of electron-volts and $k$ in units of reciprocal angstroms.

One early observation that aided understanding of the origin of the EXAFS modulations was the complete absence of these modulations in X-ray absorption spectra of monoatomic gases such as Kr (Fig. 4). In contrast, EXAFS is always observed in condensed media (liquids and solids) or polyatomic gases in which an
absorbing atom is surrounded by other atoms in a regular arrangement. To understand the origin of EXAFS, we must consider the scattering of the photoelectron wave from electron density surrounding neighboring atoms. In this context, the neighboring atoms are often referred to as "scattering atoms" or "scatterers". Consider the simplest possible arrangement of atoms, a diatomic molecule with an absorbing atom $a$ and a scattering atom $s$. Figure 5(a) shows the photoelectron wave propagating from atom $a$ (solid arcs) and scattering from the electron density around atom $s$ (dashed arcs). In fact, the photoelectron scatters from $s$ in all directions; only the backscattered wave is shown in Figure 5. Mathematically, we

\[ E = E_1 \]

\[ E = E_2 \]

\[ \text{Absorption Coeff. (}\mu\text{)} \]

\[ \text{Energy (eV)} \]

\[ E_1 \quad E_2 \]

Figure 5
Diagram of photoelectron waves generated by X-ray photon absorption at two different energies. Parts (a) and (b) indicate the photoelectron scattering for energies $E_1$ and $E_2$, respectively, as indicated in the spectrum in (c). In (a), the scattered photoelectron has a maximum amplitude at the absorbing atom $a$ and in (b), the scattered photoelectron has a minimum amplitude at atom $a$. This interference leads to a maximum and minimum, respectively, in the EXAFS shown in (c). In (d), the scattering observed at energy $E_1$ is displayed with a more realistic phase shift (dashed arcs) compared to the simplified diagram of (a) (dotted arcs). As the photoelectron wave "passes through" atom $s$, the scattered wave is phase shifted with respect to the outgoing wave (solid arcs).
can write the scattering amplitude as a function of both $\theta$, the angle of scattering, and $k : f_s(\theta, k)$. Then, the backscattering ($\theta = \pi$) amplitude is $f_s(\pi, k)$.

To relate the photoelectron scattering event, which we normally cannot directly observe, to the X-ray absorption coefficient, $\mu$, which we can observe, we must consider the electric dipole transition moment that is equal to the square of the integral $\langle \hat{\epsilon} \rangle$, where $\hat{\epsilon}$ and $\hat{i}$ represent wave functions for the final state and the initial state, respectively, and $\hat{\epsilon}$ is the electric dipole operator. For the purposes of this discussion, it suffices to consider only the overlap of initial and final state wave functions. For K edges, the initial state is a $1s$ wave function centered on atom a. (For other edges, the initial state wave function is still centered on atom a.) For an X-ray photon in the EXAFS region, the final state wave function is a combination of the electronic wave function of the relaxed ionized absorbing atom a and the photoelectron wave (both "outgoing" and back-scattered). Since it is only the energy ($k$) dependence of $\mu$ in which we are interested (the EXAFS is just the energy-dependent modulation of $\mu$ above the edge), we can ignore the contribution from the ionized atom a and concentrate on the photoelectron wave.

Given the localization of the initial state wave function on atom a, only the amplitude of the backscattered photoelectron wave at the absorbing atom contributes to the transition moment. Figure 5(a) shows that, for energy $E_1$, this amplitude is a maximum (illustrated by the dashed arc through atom a), thus giving rise to a maximum in the modulation of $\mu$ [Fig. 5(c)].

Increasing the photon energy to $E_2$ generates a photoelectron with a shorter wavelength (larger kinetic energy), the scattering of which is illustrated in Figure 5(b). At this energy, the backscattered photoelectron wave has a minimum amplitude at atom a, generating a minimum in the $\mu$ modulation [Fig. 5(c)]. Extending this analysis to energies in the rest of the EXAFS region generates the periodic modulation of $\mu$ as the photoelectron wavelength is scanned and the backscattered photoelectron wave periodically goes in and out of phase with the outgoing photoelectron wave (an interference effect). Thus, the $\mu$ modulation (i.e., the EXAFS) generated by a single scattering atom resembles a sine wave. [The damping of these sinusoidal components that is evident in Figure 5(c) is caused by static and dynamic variations in absorber-scatterer distances. This damping is termed the Debye-Waller effect and will be discussed in detail later.]

This description implies a dependence of the EXAFS modulation on the nature and location of the scattering atom s. Thus, proper analysis of the EXAFS can extract this information, elucidating the local structure around the absorbing atom a. In particular, EXAFS can determine how many of what type of atom are at what distance from atom a. Before detailing the mathematical analysis of the EXAFS data to extract this information, a less precise physical picture is useful. Each scattering atom contributes a (damped) sine wave to the overall EXAFS spectrum of a typical coordination site (e.g., in a discrete molecule or a solid lattice). Each of these sine waves can be described by three measurable quantities: frequency, amplitude, and phase. Each of these observables contains structural information about the nature and location of the scattering atom(s) giving rise to that EXAFS component sine wave. As the chart below summarizes, the frequency of the sine wave is a measure of the distance between atoms a and s, the
amplitude of the sine wave is a measure of the number of atoms (of that type) at that distance, and the phase of the sine wave helps define the element doing the scattering (i.e., the identity of atom s).

<table>
<thead>
<tr>
<th>Observable</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>Distance</td>
</tr>
<tr>
<td>Amplitude</td>
<td>(Coordination) number</td>
</tr>
<tr>
<td>Phase</td>
<td>Atom type</td>
</tr>
</tbody>
</table>

The frequency–distance relationship can be seen by examining Figure 5(a) again. At a given photon energy (i.e., a given photoelectron wavelength), a longer a–s distance implies that more periods of the photoelectron wave are required to cover the distance from a to s and back. (The reader should note that the concept of the photoelectron wave traveling from a to s and back is a classical description and has limitations.) Thus, for a longer distance, it takes less of a change in photoelectron wavelength (less of a change in photon energy) to go through one period of the interference. The absorption coefficient is therefore modulated at a higher frequency in \( E \) (or \( k \)).

The relationship of EXAFS sine wave amplitude to the number of atoms s is straightforward. In a coordination site with two identical atoms s (e.g., two oxygen or two sulfur atoms) at the same distance from a, each will contribute identical sine waves to the EXAFS that simply add together to give a sine wave with twice the amplitude. One inherent limitation of the EXAFS technique is that it yields only radial (no angular) structural information. Thus, it does not matter how the two s atoms are arranged around atom a, only that they are at the same distance. This radial dependence gives rise to the concept of “shells” of atoms, which are defined as a collection of atoms (of the same type) all residing at the same distance from the absorbing atom. One shell of atoms gives rise to one (damped) sine wave in the EXAFS.

The phase/atom type relationship is somewhat more difficult to visualize. A subtle effect of the photoelectron scattering illustrated in Figure 5 is the phase shift introduced into the photoelectron wave during the scattering process. For clarity, Figure 5(a) was drawn with no phase shift of the photoelectron wave upon backscattering from atom s. Figure 5(d) illustrates a more realistic phase shift; the backscattered photoelectron wavelength and EXAFS sine wave frequency remain unaffected. Since the size of this phase shift depends on the electron density at atom s (and at atom a), for a given absorbing atom, different scattering atom types introduce different phase shifts, yielding EXAFS components with different phases. The cross relationship (diagonal arrow on the chart) between amplitude and atom type refers to the fact that heavier scattering atoms (elements with higher atomic number) are better scatterers, yielding EXAFS components with larger amplitudes (for a given number of atoms).
Figure 6
One possible multiple-scattering pathway for a photoelectron generated by X-ray absorption by atom a in the presence of two scattering atoms, s₁ and s₂. The scattering pathway indicated is a–s₁–s₂–a. The multiple-scattering contribution to the EXAFS depends on the distances involved and on the angles θ₁ and θ₂.

So far, only single-scattering EXAFS theory has been discussed. In other words, we have only considered the photoelectron backscattering to atom a directly from a single atom s. This treatment ignores the possibility that the photoelectron might encounter two (or more) scattering atoms in its “round trip” back to atom a (Fig. 6), a possibility that is now known to contribute to the EXAFS in certain cases. Although this multiple-scattering phenomenon has been thoroughly treated, it is beyond the scope of this text to include the detailed theoretical treatment here. The EXAFS expression to be discussed next only treats single scattering.

The quantitative analysis of EXAFS data in terms of absorber-scatterer (a–s) distances, scatterer numbers, and scatterer types, requires a mathematical expression for the EXAFS quantity, χ, as a function of k. The parameter χ is defined to refer only to the quasiperiodic portion (the modulations) of the EXAFS region of the X-ray absorption coefficient, μ.

\[ \chi \equiv \frac{\mu - \mu_0}{\mu_0} \] (2)

In Eq. (2), μ₀ is the energy-dependent X-ray absorption coefficient that would have been observed if the sample contained only the absorbing atom (at the same concentration) without any neighboring scattering atoms. The parameter μ₀ is referred to as the free-atom absorption coefficient. In theory, this expression isolates the quasiperiodic EXAFS modulations from the smooth background free-atom absorption and normalizes the EXAFS to a “per absorbing atom” basis. Operationally, μ₀ proves impossible to measure and difficult to simulate so that Eq. (2) must be modified as discussed later.

The theoretical single-scattering expression for χ is given by Eq. (3):

\[ \chi(k) = \sum_s \frac{N_s |f_s(\pi, k)|}{k R_{as}^2} \exp(-R_{as}/\lambda_f) \exp(-2\sigma_{as}^2 k^2) \sin[2kR_{as} + \alpha_{as}(k)] \] (3)
The summation is over shells of scattering atoms, \( s \), and each term within the summation consists of an amplitude term, an exponential damping term (the Debye–Waller factor), and a sine function to describe the (quasi-)periodic behavior of the EXAFS. As noted previously, the EXAFS amplitude is directly proportional to the number of scattering atoms \( (N_s) \) and the \( k \)-dependent shape of the EXAFS amplitude (the amplitude envelope) is defined by the backscattering amplitude \( |f_s(\pi, k)| \), which is different for every scattering atom type. The amplitude also shows a \( k^{-1} \) dependence but this is usually compensated (as is the Debye–Waller damping) by working with the quantity \( k^n \chi(k) \) \( (n = 3, \text{ usually}) \) (see below). The \( R_{as}^{-2} \) dependence makes the EXAFS of long-distance shells much weaker than that from nearby atoms. Thus, only atoms within a radius of about 4–5 Å of the absorbing atom contribute significant scattering to the EXAFS. This fall-off of EXAFS amplitude at high \( R_{as} \) also has a contribution from inelastic losses of the photoelectron, which are more serious for longer distances. These inelastic losses are usually treated by defining a mean free path for the photoelectron, \( \lambda_f \), and incorporating the \( \exp(-R_{as}/\lambda_f) \) term in Eq. (3).

Within a shell of scattering atoms, there is some variation in \( R_{as} \), which may be static (a spread in the \( a-s \) distances from structural distortion or site heterogeneity) or dynamic (e.g., due to a stretching vibration in the \( a-s \) bond). This variation leads to a damping of the EXAFS oscillations, which is physically described by \( \sigma_{as}^2 \), a root-mean-square (rms) deviation in the distance, \( R_{as} \). The vibrational portion of \( \sigma_{as}^2 \) has a characteristic temperature dependence.

The quasiperiodic behavior of the EXAFS is described by the sine function of Eq. (3), the argument of which has a frequency, \( 2R_{as} \), and a phase shift, \( \alpha_{as}(k) \). Thus, the measured frequency of each shell's EXAFS contribution is directly proportional to the \( a-s \) distance. The phase shift is dependent on \( k \) and also dependent on the nature of both the absorbing and scattering atom types. There will be more to say about both the backscattering amplitude, \( |f_s(\pi, k)| \), and backscattering phase shift, \( \alpha_{as}(k) \), in the discussion of data analysis.
Equation (3) describes the EXAFS, \( \chi(k) \), as a sum of damped sine waves in \( k \) space, suggesting that a Fourier transform (FT) of \( \chi(k) \) might be a useful analysis technique. (Fourier transformation of a sum of sine waves yields peaks in the appropriate frequency space centered at the frequency of each sine wave.) For EXAFS, the frequency of each component is \( 2R_{as} \), so that a proper FT will yield a set of peaks in distance space, yielding a direct visualization of the shells of scattering atoms at different distances from the absorbing atom.

III. X-Ray Absorption Spectroscopy Data Collection

The spectrometer required to measure an X-ray absorption spectrum contains all the basic components found in a typical ultraviolet–visible (UV–vis) spectrophotometer: a source, a monochromator, and detectors (Fig. 7). Each of these components is specifically adapted for the X-ray region of the spectrum. Two types of data collection will be discussed. Transmission XAS consists of measuring the X-ray photon intensity \( (I_0) \) incident on the sample and an intensity \( (I) \) transmitted through the sample (Fig. 7). Then \( \ln(I_0/I) \) is proportional to the absorption coefficient. The second mode of data collection utilizes fluorescence excitation techniques in which fluorescent X-ray photons are counted (using a fluorescence detector, Fig. 7) as the photon energy is scanned, generating a signal proportional to the absorption coefficient \( (F/I_0) \). The fluorescence technique will be discussed in more detail below after each component of the XAS spectrometer is described.

A. Source

The EXAFS technique is inherently insensitive. At \( k \approx 10 \, \text{Å}^{-1} \), the EXAFS modulations are always less than about 1% of the size of the edge. Since such a small signal must be extracted from a large background, the X-ray source must be powerful. Four main types of X-ray sources are available: fixed-anode sources, offering monochromatic X-rays typically used for X-ray diffraction; rotating...

![Figure 7](image)

Schematic illustration of a typical experimental setup for X-ray absorption (see text for a description of each component).
anodes, emitting a broader range of X-ray energies and more intensity than fixed-
anode sources; plasma sources, offering the possibility of time-resolved measure-
ments; and electron (or positron) storage rings, yielding synchrotron radiation, a
broad-band, high-intensity source. Since an X-ray absorption spectrum requires
scanning the X-ray photon energy, it is obviously important to have a source with
high intensity throughout a range of energies. Fixed-anode sources are thus not
useful for XAS. Rotating anode sources are used for XAS, usually as components
of laboratory XAS spectrometers, which will be discussed later. Synchrotron ra-
diation first became available for spectroscopic uses in the early 1970s and revolu-
tionized the field of X-ray absorption spectroscopy, since the high-brightness
(high intensity in small spot size), tunable synchrotron radiation made XAS fea-
sible for a large range of dilute samples for which other sources were inadequate.
For the purposes of this discussion, we can just consider the synchrotron source
as providing a high-intensity, small cross section (typically $\sim 2 \times 20$ mm or less),
highly collimated beam of X-rays with a spectral range covering the approximate
2–30-keV region necessary for XAS of most elements.

B. Monochromator

Since X-rays penetrate most optical materials, dispersive optical elements (gratings
and prisms) are not available for the hard X-ray region. For this reason, X-ray
monochromators utilize Bragg reflection from single crystals for monochroma-
tization. The wavelength ($\lambda$) of the diffracted beam depends on the angle of inci-
dence ($\theta$) with a Bragg lattice plane of the crystal and upon the d spacing of the
crystal (the separation between the lattice planes).

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (4)

For the fundamental reflection, $n = 1$; higher energy harmonics that satisfy this
Bragg relationship for $n > 1$ are also reflected from the crystal. Usually, two
parallel single crystals (both cut parallel to the same lattice planes) are utilized in
a double-crystal monochromator as illustrated in Figure 7. Simply rotating both
crystals to vary $\theta$ allows tuning of $\lambda$ [Eq. (4)] and thus energy [Eq. (1)] through a
range covering the spectral region of interest. The single-crystal slabs used as
monochromator elements are often several centimeters in each dimension (and
$\sim 1$ cm thick) so that silicon is usually (but not exclusively) the material of choice
(the semiconductor industry has developed methods for growing silicon crystals
large enough for this application) and the Si(111), Si(220), or Si(400) are the most
frequently used reflections. As shown in Figure 7, vertical entrance and exit slits
are usually present for energy resolution and scattered radiation rejection.

C. Detectors

For quantitative measurement of X-ray absorption spectra, detectors are required
to measure the flux (photons s$^{-1}$) of the X-ray beam. Since hard X-rays can ion-
ize gases, a simple detector can be built to measure the amount of ionized gas per
unit time (in a defined volume) which is proportional to X-ray flux. These ion-
ization chambers consist of thin X-ray transparent windows on each end of a chamber holding an inert gas (He, N₂, Ne, or Ar, depending on photon energy range) between two charged plates. Ionized gas molecules (atoms) migrate to the cathode plate and the electrons migrate to the anodic plate, creating a current proportional to the X-ray flux. Ionization chambers work well as transmission detectors since a significant fraction of the X-ray photons are transmitted through the detector (e.g., to the sample and other detectors; see Fig. 7). For concentrated samples (i.e., ones with a high molar ratio of absorbing atoms), the transmission technique works well. However, in cases for which the sample consists mainly of atom types other than the one being investigated (spectroscopically dilute samples, such as metalloenzymes, highly dispersed supported catalysts, ultrathin films, etc.) fluorescence excitation techniques are much more sensitive.

For K X-ray absorption edges, at photon energies above the edge, a fraction of the ionized absorbing atoms relax by emission of a fluorescent X-ray photon [Fig. 8(a)]. This usually occurs by transition of an electron from the n = 2 levels to the 1s level, giving rise to Kα fluorescence. Since the n = 2 levels lie well below the continuum, the energy of these Kα photons is significantly lower than the K-edge energy. (For example, for Cu with a K edge of 8.98 keV, the Kα fluorescence occurs at 8.05 keV.) The fluorescence excitation XAS technique consists of monitoring the Kα emission (by a photon-counting fluorescence detector, Fig. 7) while the incident X-ray photon energy is scanned through the K edge and EXAFS regions. Since the number of emitted Kα photons is directly proportional to the number of photons absorbed (i.e., the absorption coefficient of the absorbing atom), the fluorescence excitation technique gives a spectrum that mimics the X-ray absorption spectrum of the absorbing atom. The fluorescence excitation technique has a distinct advantage for dilute samples. A transmission spectrum of a dilute sample displays background absorption by all other atoms in the sample [Fig. 9(a)], whereas the fluorescence excitation spectrum displays only the absorption by the atom of interest (the absorbing atom, whose Kα emission is being monitored) [Fig. 9(b)]. Since the background absorption in the transmission spectrum contributes no signal (only noise), the fluorescence excitation spectrum (with no background) yields a better signal-to-noise (S/N) ratio.

This ideal situation holds only for fluorescence detectors with very high energy resolution. Fluorescence excitation spectra often have a (small) background contribution from scattered photons [Fig. 9(b)]. As shown in Figure 8(b), most of these scattered photons have energies equal to the energy of the incident X-rays (i.e., they are elastically scattered), so that fluorescence detectors with high-energy resolution, monitoring the Kα fluorescence, will not detect them (this is referred to as scatter rejection). A small amount of Compton scattering may be detected as background near the Kα energy [Fig. 9(b)]. Occasionally, low-energy resolution fluorescence detectors (e.g., scintillation detectors or ionization chambers) are used for fluorescence excitation XAS. These detectors cannot resolve the Kα fluorescence from the scattered photons and can only provide improved sensitivity over the transmission technique if another means of scatter rejection is employed. This scatter rejection is usually accomplished by placing between the sample and the fluorescence detector a low-pass filter with a cut-off energy be-
Figure 8
(a) The relationship between the X-ray absorption edge energy and the energies of the $K\alpha$ fluorescence emission lines used for fluorescence excitation detection of X-ray absorption spectra. The $K\alpha$ emission lines result from relaxation of the atom by transition of an electron from an $n = 2$ level to the 1s level. (b) The use of a low-pass filter to reject the background scatter in a fluorescence excitation experiment. The $K\alpha$ fluorescent photons are not absorbed appreciably by the filter but the elastic- and Compton-scattered photons are.

Figure 9
Comparison of (a) transmission and (b) fluorescence excitation X-ray absorption spectra for a dilute sample. These spectra were collected on a 2-mM aqueous sample of a nickel enzyme. The presence of the Ni edge in the transmission spectrum is indicated by the arrow in the inset of (a). Scatter rejection in (b) was achieved by the use of electronic discrimination with a high-energy resolution solid-state detector.
between the absorption edge and the Kα energies [Fig. 8(b)]. This filter preferentially absorbs background scatter photons, allowing the Kα photons through to the detector. A convenient material for such a filter is a thin layer of the element with atomic number (Z) one less than the element being studied (a “Z-minus-one” filter). The development of this filtering strategy with low-energy resolution detectors and the availability of high-count rate high-energy resolution detectors (e.g., solid-state detector arrays) has made fluorescence excitation XAS a standard tool for examining spectroscopically dilute samples.

D. Laboratory Spectrometers

For X-ray absorption spectroscopic investigations of a concentrated sample (e.g., solids and concentrated solutions), the high brightness of synchrotron sources is often unnecessary. Often a laboratory can acquire a rotating anode source, then purchase one of several commercially available X-ray spectrometers designed for XAS. The most common design of such a laboratory XAS spectrometer is shown in Figure 10. Since the source point is much closer to the monochromator than for synchrotron radiation, this “bent crystal” monochromator proves most efficient for collection of a significant amount of the source radiation. (That is, it allows the collection of a large angular spread of source radiation without excessive degradation of spectral resolution.) The spectrometer arrangement shown in Figure 10 is known as the Johansson geometry, with a single crystal bent to a radius of 2R and polished to a radius of R. At a given arrangement, all the source (so) X-rays impinging on the polished crystal surface have the same incident angle with the lattice planes (stripes on the crystal cross section in Fig. 10) and all the diffracted rays have the same energy and are focused through the sample (sa) onto the detector (d). To move to the next energy in a scan, the crystal is turned through a small angle θ, while the sample and detector are pivoted around the same point by 2θ.

Figure 10
Typical geometry for a laboratory curved-crystal X-ray absorption spectrometer. The curved crystal at the top is shown in cross section with its Bragg planes indicated by the arcs of a circle of radius 2R. (so = source; sa = sample; d = detector).
IV. Data Reduction and Analysis

The X-ray absorption data collected as discussed in Section III consist of a set of discrete data points: detector counts as a function of monochromator angular position. Depending on the data collection method, the output of $I_0$ and $I$ detectors (transmission) or $F$ and $I_0$ detectors (fluorescence) or both were recorded (see Fig. 7). Usually, the angular position of the monochromator crystals [defining the Bragg angle, Eq. (4)] is recorded as a motor position ($m_i$) of the motor controlling the crystal carriage. This position has been crudely calibrated to the correct energy at data collection, but usually must be precisely calibrated during data reduction. The most common calibration procedure is to use an absorption peak or inflection point from the spectrum of a known standard (often a thin foil of the element being examined) that has been recorded under identical conditions as the sample. The “internal” calibration method involves placing a third ionization chamber ($I'$) behind the two in Figure 7 and placing a standard sample between $I$ and $I'$. Then, with every sample spectrum, a transmission spectrum of the standard [ln($I/I'$)] is also recorded. This standard spectrum is analyzed to yield the monochromator angle ($m_c$) at the defined calibration point, which has a known energy ($E_c$) from previous measurements. Given this single-point calibration, and knowing the relationship between the motor position measurements and angle ($\Delta$, in units of motor position deg$^{-1}$), each data point’s motor position ($m_i$) can be converted to a Bragg angle ($\theta_i$) and an absolute energy ($E_i$):

$$\theta_c = \sin^{-1} \left( \frac{hc}{2dE_c} \right)$$  \hspace{1cm} (5)

$$\theta_i = \theta_c + \frac{|m_i - m_c|}{\Delta}$$  \hspace{1cm} (6)

$$E_i = \frac{hc}{2d \sin \theta_i}$$  \hspace{1cm} (7)

The absorption coefficient proportional data ($\delta_i$) to be analyzed are generated by $\delta_i = \ln[I_0(i)/I(i)]$ for transmission or $\delta_i = F(i)/I_0(i)$ for fluorescence detection, yielding the function $\delta(E)$ [e.g., the solid line in Fig. 11(a)]. To calculate the EXAFS quantity $\chi$, we need to know $\mu$ [see Eq. (2), which is the X-ray absorption coefficient for just the absorbing atom site of interest. But the data of Figure 11(a) also contain a background contribution ($\mu_{\text{back}}$) from either absorption by other (lower atomic number) atoms in the sample (in transmission) or scatter from the sample (in fluorescence):

$$\delta = \mu + \mu_{\text{back}}$$  \hspace{1cm} (8)

It is usually very difficult to measure or simulate $\mu_{\text{back}}$, so that polynomial or half-Gaussian fitting procedures are used to mimic it as well as possible. This results in an approximate background function, $\mu_{\text{back}}(E)$ [dashed line in Fig. 11(a)], which does not completely remove the background:

$$\delta_i = \delta - \delta_{\text{back}} = \mu + \Delta \mu$$  \hspace{1cm} (9)
\[ \Delta \mu = \mu_{\text{back}} - \delta_{\text{back}} \]  

(Here, \( \Delta \mu \) is the remaining background absorption.)

If this background-subtraction procedure had worked perfectly (\( \Delta \mu = 0 \)), then we would only have needed to subtract the free-atom X-ray absorption coefficient \( (\mu_0) \) from \( \delta_1 \) and normalize to get \( \chi \) [Eq. (2)]. Unfortunately, one cannot determine the value of \( \Delta \mu \) and subtraction of \( \mu_0 \) generally does not work. Since \( \mu_0 \) would have been the smooth curve underneath the quasiperiodic EXAFS oscillations [Fig. 11(b)], we need a corrected smooth curve \( [\mu_\chi, \text{dashed line in Fig. 11(b)}] \) that does track the absorption coefficient above the edge. This curve is usually calculated by a (cubic or quartic) spline fitting procedure, which generates

\[ \mu_\chi = \mu_0 + \Delta \mu \]  

The true free-atom absorption coefficient \( (\mu_0) \) can be calculated from the Victoreen formula\(^7\) and must be used for normalization (this normalization serves to correct for any pathlength or concentration differences among samples and yields \( \chi \) data normalized to a “per absorbing atom” basis.)

\[ \chi = \frac{\delta_1 - \mu_\chi}{\mu_0} \]  

The resulting EXAFS data \( (\chi) \) are shown in Figure 11(c) for our example.

The EXAFS data, \( \chi \), are normally treated not as a function of energy, \( E \), but as a function of photoelectron wave vector, \( k \). To convert from \( E \) to \( k \), the threshold energy \( (E_0) \) is needed [see Eq. (1)]. The threshold energy is equivalent to the ionization potential for the 1s electron (for K edges), but it is difficult to measure independently. Since there are often features just before the edge corresponding to bound-state transitions, using an inflection point on the observed edge as \( E_0 \) is not quite correct. Assuming \( E_0 \) is the same for every occurrence of a particular element is not correct either, since \( E_0 \) depends slightly on the chemical environment of the absorbing atom. Either method can estimate \( E_0 \) to within a few electron volts (eV) and both are used. For our example, assuming \( E_0 = 9000 \) eV yields the \( k \) scale shown at the top of Figure 11(c). The EXAFS data are replotted as \( \chi(k) \) in Figure 11(d). Although the EXAFS oscillations extend to high \( k \) values, they are “masked” at high \( k \) due to the severe damping from the Debye–Waller term in Eq. (3). For this reason, it is standard practice to work with \( k^n \) weighted \( \chi(k) \) data \( (n = 3 \) usually); \( k^3 \chi(k) \) is plotted in Figure 11(e).

Analysis of the EXAFS data in terms of structural information makes use of Eq. (3) to simulate the EXAFS pattern expected for a given hypothetical arrangement of atoms around the absorbing atom. As discussed above, each damped sine wave in the \( \chi(k) \) data arises from one shell of atoms at a given distance from the absorbing atom. One effective means of visualizing these shells of atoms is to perform a FT on the \( k^3 \chi(k) \) data. Fourier transformation effectively does a frequency analysis of the EXAFS data, yielding a peak at the frequency of each sine wave component in the EXAFS. Since the sine wave frequency is directly proportional to the absorber-scatterer separation distance, \( R_{as} \) [Eq. (3)],
Figure 11
Example of data reduction for EXAFS analysis. (a) Fluorescence excitation XAS data (solid line) are corrected by subtraction of a pre-edge background (dashed line); (b) a smooth curve (dashed line) is fit to the pre-edge-subtracted data (solid line) by a cubic spline procedure to yield (c) the EXAFS data. (d) The EXAFS data displayed as a function of photoelectron wave vector, \( k \), and then (e) weighted by \( k^3 \). (f) The magnitude of the FT of the \( k^3 \chi(k) \) data in (e) displayed as a function of the phase-shifted distance, \( R' \).

The FT generates a set of peaks in radial distance space, each peak representing a particular shell of atoms [Fig. 11(f)]. [These peaks do not occur at the precise distances owing to contributions from the phase shift, \( \alpha_{as}(k) \), in Eq. (3). Therefore a phase-shifted distance, \( R' \), is used as the FT abscissa in Fig. 11(f). Often \( R_{as} \approx R' + 0.4 \text{ Å} \).] Although Fourier transformation is a useful means for visu-
alizing the radial distribution of scattering atoms around the absorbing atom, one must exercise extreme caution in assigning small peaks in the FT to shells of atoms. Small artifactual FT peaks are generated by truncation of the $k^3\chi(k)$ data, by the $k^3$ weighting function itself, which acts as an artificial resolution enhancement function in the FT, and by inadequate background subtraction (usually due to poor choice of the spline function used to generate $\mu_s$).

Since the FT of the EXAFS displays a peak for each shell of atoms, it provides a method for separating out contributions from individual shells. The technique of Fourier filtering consists of constructing a (filter) window [dotted lines in Fig. 12(b)] around the FT peak of interest, which when multiplied by the FT data yields only that FT peak [solid lines in Fig. 12(b)]. Back-transformation of these filtered FT data yields the extracted EXAFS arising solely from that shell of atoms [Fig. 12(c and d)]. [Adding these two "shells" of EXAFS together generates Fig. 12(e), showing that these shells were the main sine wave components of the original EXAFS data in Figure 12(a).] The Fourier filtering technique is a good way of simplifying the initial curve-fitting simulation of individual shells, which is discussed next.

Although Fourier transformation can yield a qualitative visualization of the radial structure of a site, quantitative structural information (How many of what type of atoms are at what distance from the absorbing atom?) can only be obtained by curve-fitting simulation of the $k^3\chi(k)$ data. In general, a hypothetical set of atom shells is generated and Eq. (3) (or some more sophisticated extension of it) is used to calculate the expected EXAFS data. The calculated EXAFS data are compared to the observed data and (a subset of) the parameters in each "shell" of Eq. (3) ($N_s, R_{as}, \sigma_{as}$) are optimized in a least-squares sense. If the fit to the observed data is judged inadequate, additional shells of atoms may be added, or the identity of the atoms in the shells may be changed, and the curve-fitting optimization repeated. Some subjective judgment is required in deciding what constitutes a "good fit". Mathematically, the more shells [terms in the summation of Eq. (3)] that are added, the better the fit should be, but this does not necessarily mean that the added shells are required. The art of EXAFS analysis is in deciding which shells are uniquely required to adequately fit the data. Chemical intuition is also helpful in discarding shells with unreasonable distances or coordination numbers. Depending on previous characterization, other pieces of independent information about the site being studied may be available to guide the choice of acceptable hypothetical structures. If nothing is known, one must rely heavily on statistical analysis of the EXAFS data and chemically reasonable bond distances. The more information that is available, the more detailed the structural questions can be.

In the above discussion, it was assumed that once an a–s (absorbing atom–scattering atom) pair was chosen for a shell of the hypothetical structure, it would be straightforward to generate that shell's expected EXAFS using Eq. (3). This assumption implies that one knows the scattering characteristics of the s atoms, that is, that one knows the backscattering amplitude function $|f_s(\pi,k)|$ and the backscattering phase shift function $\alpha_{as}(k)$ for this a–s pair. Two basic approaches have evolved for obtaining these functions. The empirical approach involves
Figure 12
Example of Fourier filtering of individual shells of EXAFS data. Raw EXAFS data (a) are Fourier transformed to yield (b). In (b), the first-shell FT peak is filtered using the window (dotted line) centered at $R' \approx 1.5 \text{ Å}$ giving rise to the filtered $[k^3 \chi'(k)]$ data in (c). The second-shell FT peak in (b) is filtered using the window (dotted line) centered at $R' \approx 2.6 \text{ Å}$ yielding the filtered data in (d). In (b), the solid lines represent the product of the FT magnitude and the filter windows in each case. The sum of the two filtered EXAFS data sets in (c) and (d) is displayed in (e) and looks very similar to the raw EXAFS data in (a), which indicates that these two shells are the main components of the EXAFS.
measuring EXAFS data for structurally characterized (model) compounds with a symmetric shell of one type of atom. The FT of these EXAFS data will yield a single peak that can be Fourier filtered [e.g., see Fig. 12(c)] to yield $|f_s(\pi, k)|$ and $\alpha_{\alpha\alpha}(k)$ directly. Unfortunately, the empirical method depends on the availability of model compounds with the appropriate $\alpha$–$s$ combination in a shell that can be separated from any other shells by Fourier filtering. The theoretical approach involves ab initio computation of the scattering behavior of any given $\alpha$–$s$ pair and depends on having good wave functions for the atoms involved. These theoretical computations continue to improve and the resulting scattering functions now rival those obtained by the empirical method in accuracy.

Analysis of EXAFS data has advanced to the point that reliable radial structural information can be obtained with relatively simple computational tools. Although the spectral structure in the near-edge region (Fig. 1) is rich and varied, the analysis of this region is more complicated and therefore not as well developed as EXAFS analysis. Conceptually, the near-edge energy region can be divided into the region below and the region above $E_0$ (the threshold energy). In the region below the threshold, bound-state transitions from the $1s$ level (for K edges) to empty or partially filled valence levels just below the continuum may give rise to peaks or shoulders in the absorption coefficient. For example, for K edges of first-row transition metals, $1s \rightarrow 3d$, $1s \rightarrow 4s$, and $1s \rightarrow 4p$ transitions may be observed. Since these are electronic transitions, electric-dipole selection rules are usually sufficient to predict site symmetries from the relative intensities of these transitions. In the region just above $E_0$, the extra photon energy converted to photoelectron kinetic energy is small and low-energy photoelectrons are more prone to multiple scattering. The predominance of multiple-scattering contributions in this low-$k$ region makes it impossible to extend reliably the single-scattering EXAFS analysis to below about 30 eV above $E_0$. Multiple-scattering effects also make the X-ray absorption coefficient just above the edge more sensitive to geometry than the higher $k$ EXAFS region. Thus, the information available from the edge region (molecular symmetry and geometry, as well as electronic structure) is complementary to that from EXAFS (radial molecular structure). Although several attempts at ab initio computation of X-ray absorption edge spectra have been made, they have met with limited success, and analyses of the edge region are often qualitative.

V. Applications of X-Ray Absorption Spectroscopy

With the complementary electronic and molecular structural information available from analysis of X-ray absorption edges and EXAFS, it is not surprising that the technique has been applied to structural investigations of a wide variety of materials. XAS techniques have made a significant impact in fields as diverse as condensed-matter physics, materials science, geology, chemistry, biology, and medicine. In any of these fields, successful application of the technique requires a knowledge of both the strengths and limitations of XAS.
In this section, a selection of applications of XAS are presented as examples of the use of the technique in answering structural questions of interest to inorganic chemists. The XAS technique is most useful when applied to samples with a homogeneous population of sites containing the metal being studied. When used to investigate samples with more than one structural type of site (containing the same metal), EXAFS is inherently incapable of distinguishing whether a shell of ligands belongs to the coordination sphere of one site or the other. Only an average metal environment can be deduced from the EXAFS data.

A. What Is the Molecular Symmetry of the Site?

Extended X-ray absorption fine structure is not capable of giving direct information about the geometric arrangement of ligand atoms around a metal (the molecular symmetry) in amorphous samples. (The technique may yield indirect information in the few cases for which the metal–ligand distance is known to be well correlated with molecular symmetry. For samples with long-range order (e.g., single crystals), polarized EXAFS can be used to sense the arrangement of distinguishable ligand atoms.\(^8\)) On the other hand, the X-ray absorption edge can yield direct information about the molecular symmetry of metal sites in amorphous samples and has been very useful in this regard. In general, the edge is most sensitive to the local molecular symmetry, defined by the atoms directly coordinated to the metal.

Nickel(II) compounds provide an illustrative example of this type of application, which relies on assignment of pre-edge bound-state electronic transitions and a knowledge of the symmetry properties of selection rules for these transitions. Other examples can be found in the literature for Ni,\(^9\) Fe,\(^10\) and Cu.\(^11\) For K X-ray absorption edges of first-row transition metals, bound-state transitions at energies just below the edge have been variously identified as \(1s \rightarrow 3d\), \(1s \rightarrow 4s\), and \(1s \rightarrow 4p\) transitions. Only the \(1s \rightarrow 4p\) transitions are symmetry allowed by electric-dipole selection rules. The others can gain some intensity by orbital mixing or through higher order (e.g., electric quadrupole) transition moments.\(^12\)

A number of representative Ni(II) K X-ray absorption edge spectra are compared in Figure 13. The small pre-edge peak at about 8332 eV in the spectra of approximately tetrahedral (\(T_d\)) Ni(II) sites [Fig. 13(a)] is assignable to the \(1s \rightarrow 3d\) transition. This transition is most prominent for tetrahedral sites due to the increase in 4p orbital character of the 3d final state (p–d mixing is allowed in noncentrosymmetric point groups such as \(T_d\)), which lends some symmetry allowedness to this transition. The \(1s \rightarrow 3d\) transition is much less prominent in centrosymmetric sites [e.g., octahedral sites, Fig. 13(c), or square planar sites, Fig. 13(d)]. Thus, observation of a relatively intense \(1s \rightarrow 3d\) transition signals the absence of a center of symmetry in the site. This intensity relationship has been quantified for Ni\(^9\) and Fe.\(^10\)

The Ni(II) complexes with square planar (\(D_{4h}\)) symmetry give rise to K edge spectra with a large characteristic pre-edge peak about 5 eV below the main edge [Fig. 13(d); \(\sim 8338\) eV for NiN\(_4\) sites, \(\sim 8336\) eV for NiE\(_4\) sites, \(E = S\) or Se]. On
Figure 13
Comparison of Ni K X-ray absorption edge spectra for a series of Ni(II) compounds of varying site symmetry. (a) Approximately tetrahedral compounds Ni(tropocoronand–(CH₂)₆, (CH₂)₆) (solid line)¹³ and [Ni(SPh)₄]²⁻ (dotted line).¹⁴ (b) Approximately square pyramidal compound [Ni(tetramethylcyclam)Br]⁺,¹⁵,¹⁶ (c) Approximately octahedral compounds [Ni(1,4,7-triazacyclononane)]₂²⁺ (solid line)¹⁷,¹⁸ and [Ni(1,4,7-trithiaclyclononane)]₂²⁺ (dotted line).¹⁹ (d) Approximately square planar compounds [Ni(phthalocyanine)] (solid line),²⁰ [Ni(maleonitriledithiolate)]²⁻ (dotted line)²¹,²² and [Ni(Se₂C₂(CF₃)₂)] (dashed line).²³ [This figure was adapted from Scott²⁴; for an expanded analysis of Ni(II) edges, see Colpas et al.⁹]

the basis of comparison with Cu(II) K-edge spectra, this peak has been assigned to a 1s → 4pₓ transition. (The assignment is actually most likely to be “1s → 4pₓ plus shakedown”,²⁵ involving a simultaneous promotion of a 1s electron to the 4pₓ orbital and a ligand–metal charge transfer (LMCT) to a Ni(II) 3d orbital:

\[
1s^2 \ldots 3d^8/L^n \rightarrow 1s^1 \ldots 3d^9 4p_x^1/L^{n-1}
\]

It appears as a resolved peak in the K-edge spectra of square planar Ni(II) complexes owing to the lower energy of the 4pₓ orbital in the absence of ligands along the molecular z axis (perpendicular to the plane of the molecule). Since no discrete peaks are observed at these energies for tetrahedral [Fig. 13(a)] or octahedral [Fig. 13(c)] Ni(II) sites with the same ligand sets, the presence of a resolved peak in this energy region can be used as a signature for a square planar site.
Figure 14
The Ni K X-ray absorption edge spectra of the two isomers of cofactor F₄₃₀ of the methyl reductase enzyme of methanogenic bacteria. The native isomer (solid line) is known to be six coordinate with two axial H₂O ligands and the 12,13-diepimer (dotted line) has a four-coordinate square planar structure. The structure of the unligated native F₄₃₀ cofactor is inset. [This figure was adapted from Shiemke et al.²⁶]

For Ni(II) sites with square pyramidal (C₄v) symmetry, the K-edge spectrum [Fig. 13(b)] exhibits features intermediate between those from square planar and octahedral sites. The 1s → 4p₂ transition has moved to higher energy (relative to the main edge), becoming a shoulder, as expected from interaction with one axial ligand. The 1s → 3d transition is more intense than that observed for octahedral Ni(II) sites, reflecting the absence of a center of symmetry in the square pyramidal Ni(II) site.

These characteristic edge features can be used to obtain structural information that is complementary to the type of information available from EXAFS. For example, the Ni(II) K edge spectra of two isomers of the Ni containing tetrapyrole cofactor F₄₃₀ from the methylreductase enzyme of methanogenic bacteria are shown in Figure 14. (This enzyme catalyzes the final step in the production of CH₄ and the F₄₃₀ Ni is thought to be involved.²⁷) These data indicated that the native F₄₃₀ isomer was six coordinate with two axial H₂O ligands (giving rise to an octahedral-type edge spectrum) while the 12,13-diepimer was square planar with no axial ligands (giving rise to a square planar-type edge spectrum).²⁸

Edge comparisons like the ones discussed above do not always yield a unique
answer. Some of the qualitative edge distinctions are not always obvious (cf. solid lines in Figs. 13(b) and (c). As discussed before for EXAFS analysis, caution is suggested in drawing firm conclusions about site geometry from edge spectra if no other information is available. For example, in F430, it is fairly safe to assume that a NiN4 equatorial ligand environment is present (from the tetrapyrrrole macrocycle) and the question being addressed by edge comparisons is more focused: Does the Ni bind axial ligands?

B. Does a Particular Treatment Generate a Redox Change?

As already mentioned, the position of the X-ray absorption edge is sensitive to the redox state of the metal. The edge energy generally increases with an increase in oxidation of the metal site. However, the presence of pre-edge features arising from bound-state transitions makes the correlation of absolute edge energy with redox state difficult. It is somewhat easier to correlate changes in edge position with changes in redox state, although this is also prone to error, especially when a change in molecular symmetry accompanies a redox change. When examining a particular type of metal in selected oxidation states, one must make sure that the spectral changes observed are reliable indicators of redox change and do not just reflect a structural rearrangement.

For example, characteristic differences between the Cu K X-ray absorption edge spectra of Cu(I) and Cu(II) sites have allowed the development of a difference technique for quantitative determination of Cu(I) content in samples with mixed oxidation state composition. Representative Cu K-edge spectra for Cu(I) and Cu(II) sites are shown in Figure 15(a). The feature at 8983–8984 eV in the Cu(I) edge spectrum is assigned as a 1s → 4p transition and is characteristic of Cu(I). The Cu(I)-minus-Cu(II) difference spectrum gives rise to a peak at this energy, the intensity of which can be correlated with the amount of Cu(I) present in a sample containing a mixture of Cu(II) and Cu(I). [This works well for two- or three-coordinate Cu(I) sites, but tetrahedral Cu(I) does not exhibit the 8984-eV feature.]

This technique was applied to a multi-copper enzyme known as laccase. This polyphenol oxidase contains four copper ions per functional unit, which are spectroscopically distinguishable and are referred to as type 1 (mononuclear), type 2 (mononuclear), and type 3 (dinuclear), the last giving rise to a 330-nm band in the oxidized enzyme. Preparation of a T2D laccase derivative resulted in the absence of a 330-nm UV–vis band. Addition of H2O2 (but not other oxidants) regenerated the 330-nm band, a result first attributed to formation of a type-3 Cu–peroxide (O22−) complex. However, Cu X-ray absorption edge spectra [Fig. 15(b)] unambiguously demonstrated that the type-3 site in T2D laccase remained in the Cu(I) state and could only be reoxidized to Cu(II) by H2O2.

C. What Types of Atoms Are in the First Coordination Sphere? (Edge Analysis)

Aside from being caused by a redox change, a shift in the X-ray absorption edge energy may also be the result of a change in the ligand composition of the site.
Figure 15
(a) Typical Cu(I) (solid line) and Cu(II) (dashed line) K X-ray absorption edge spectra showing the 1s → 4p transition at about 8983 eV in the Cu(I) edge. The Cu(I) complex has CuN₂O ligation and the Cu(II) complex has CuN₄O ligation. [This figure was adapted from Kau et al.¹¹] (b) The Cu K X-ray absorption edge spectra for native (solid line), type-2 depleted (T2D) (dash-dot line), and H₂O₂ treated T2D (dotted line) forms of the copper enzyme laccase. The native enzyme contains all Cu(II) sites and H₂O₂ treatment of T2D enzyme laccase simply reoxidizes a reduced type-3 site (see text). Note that the spectra in (b) are not normalized as described in the text. [This figure was adapted from Lu Bien et al.²⁹]
Figure 16
Comparison of Cu(II) K X-ray absorption edge spectra for a series of Cu(II) compounds with (dashed lines) and without (solid lines) sulfur ligation. (a) Trigonal bipyramidal complexes with CuN4O (solid line) or CuN2S2O (dashed line) ligation. (b) Trigonal bipyramidal complexes with CuN5 (solid line) or CuN3S2 (dashed line) ligation. (c) Square planar complexes with CuN4 (solid line) or CuN2S2 (dashed line) ligation. In each case, the lower energy of the edge for the S-containing complexes indicates an increase in charge density at the Cu(II) due to more covalent bonding.

For the higher oxidation states of transition metals, it is often observed that an increase in the proportion of "soft" ligands (donor atoms of P, S, Se, ...) results in a shift of the edge position to lower energy. One possible explanation for this effect is increased covalency of metal–ligand bonds for soft ligands. This increased covalency would presumably involve a significant amount of ligand–metal charge transfer, resulting in an increase in the effective electron density on the metal, decreasing the observed K-edge energy. This sensitivity of edge position to hard/soft ligand composition must be considered along with redox changes as the explanation for an observed edge energy shift (or an abnormally low edge energy).

The alert reader will have already noted that Ni(II) sites obey the rule of thumb that soft ligands result in lower edge energy [Fig. 13(a), (c), and (d)]. It is also generally true that the overall (normalized) edge height is lower for sites with soft ligands (at least those containing M–S bonds) and this is observed routinely in Ni(II) sites, although the explanation for this trend is unknown. Figure 16 illustrates that these trends apply equally well to Cu(II) sites. In each comparison, the Cu(N₂O₅)ₓS₂ compound displays an edge to lower energy with reduced height compared to that for Cu(N₂O₅)ₓ+2 (x = 2 or 3). These observed trends can often be used in a "fingerprint" mode to suggest the relative hard/soft character of ligand donor atom composition for sites of unknown structure.
D. What Types of Atoms Are in the First Coordination Sphere? 
(EXAFS Analysis)

Although the shape and position of the X-ray absorption edge can yield some clues as to the types of ligands bound to the metal site, quantitative information about the structure of the first coordination sphere depends on analysis of the EXAFS data. Usually some information is available on what possible ligand atoms are bound to the metal and this reduces the number of hypothetical compositions that need to be considered. For example, in a metalloenzyme, only biologically relevant ligand atoms (N, O, S, Se, and Cl?) need be considered. For a transition metal complex of unknown structure, the possible ligands are known from other analytical information. For example, mixing a Cu(II) salt with the potential chelating ligand mercaptopropionylglycine (MPG) generates a complex with the proposed structure\(^{32}\).

![Cu EXAFS](image)

Cu EXAFS can be used to determine whether the thiolate S is in fact bound to the Cu.

The Cu EXAFS data for Na[Cu(MPG)(H\(_2\)O)] are shown in Figure 17(a). Fourier transformation of these data reveals two separate peaks [Fig. 17(b)] originating from two main shells of ligand atoms. Recalling that FT peaks usually appear at distances about 0.4 Å shorter than the true metal–ligand distances, these peaks represent shells with distances of about 1.9 and 2.3 Å. A survey of structures of Cu(II) complexes reveals that typical Cu–(N,O) distances range from about 1.9–2.1 Å, while typical Cu–S distances range from about 2.25–2.35 Å. Thus, the appearance of the FT suggests that the thiolate S is coordinated to the Cu(II). Confirmation of this can be obtained by curve-fitting of the filtered Cu EXAFS data [Fig. 17(c)]. In this example, Cu(II)–N and Cu(II)–S scattering functions were empirically determined by examining the EXAFS of a series of structurally characterized (model) Cu(II) compounds. Then, initial guesses for coordination number (\(N_s\)), metal–ligand distance (\(R_{as}\)), and Debye–Waller \(\sigma_{as}^2\) parameters were made for each shell, and a subset of these parameters were optimized to match the calculated and observed EXAFS data as well as possible. For each shell, \(\sigma_{as}^2\) may be fixed at the value found in model compounds and \(N_s\), \(R_{as}\) optimized; or \(N_s\) may be fixed at selected integer values and \(\sigma_{as}^2\) and \(R_{as}\) optimized. The latter method was used for Na[Cu(MPG)(H\(_2\)O)] and the results...
Figure 17
Curve-fitting analysis of the Cu EXAFS data for Na[Cu(MPG)(H$_2$O)]. The raw EXAFS data in (a) give rise to the FT in (b). Fourier filtering the first two FT peaks [solid line in (b)] gives rise to the filtered data represented by the solid line in (c). The best-fit simulation (Table I, Fit 4) is shown as the dashed line in (c) and the FT of this simulation is compared to the FT of the raw EXAFS data in (d).

shown in Table I. A good fit is one for which the difference between the calculated and observed EXAFS data is minimal (as measured by the $f'$ statistic) and for which the calculated $\sigma_{as}^2$ is close to the $\sigma_{as}^2$ observed for the model compound ($\Delta\sigma_{as}^2 = \sigma_{as}^2(\text{sample}) - \sigma_{as}^2(\text{model}) \approx 0$).

For Na[Cu(MPG)(H$_2$O)], Table I shows that the presence of both a Cu–(N,O) and a Cu–S shell is necessary to get an adequate fit to the EXAFS data. For one Cu–S and one Cu–(N,O) shell (Fit 3), the $\sigma_{as}^2$ value for the Cu–(N,O) shell is quite large, indicating significant static disorder (spread) in the Cu–(N,O) distances. Alternatively, if two Cu–(N,O) and one Cu–S shells are used (Fits 4 and 5), the $\sigma_{as}^2$ values for the two Cu–(N,O) shells more closely approximate the $\sigma_{as}^2$ value for the model compound. This improvement in $\sigma_{as}^2$ agreement and the reduction in $f'$ lend support for the proposed structure. [Fits 4 and 5 of Table I show that EXAFS cannot distinguish between a site with two long and one short Cu–(N,O) bonds and a site with one long and two short Cu–(N,O) bonds.]
Table 1: Curve-Fitting Results for the First Coordination Sphere of Na[Cu(MPG)(H₂O)]₄

<table>
<thead>
<tr>
<th>Fit</th>
<th>Nₛ</th>
<th>Rₘₐₜ (Å)</th>
<th>Δσₘₐₜ (Å²)</th>
<th>Cu-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(4)⁴⁺</td>
<td>2.05</td>
<td>+0.0096</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(3)</td>
<td>1.99</td>
<td>+0.0097</td>
<td>(1)</td>
</tr>
<tr>
<td>4</td>
<td>(1)</td>
<td>2.08</td>
<td>−0.0020</td>
<td>(1)</td>
</tr>
<tr>
<td>4</td>
<td>(2)</td>
<td>1.93</td>
<td>+0.0028</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(2)</td>
<td>2.04</td>
<td>+0.0012</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>(1)</td>
<td>1.89</td>
<td>−0.0005</td>
<td></td>
</tr>
</tbody>
</table>

⁴ The parameter Nₛ is the number of scatterers per copper; Rₘₜ is the copper-scatterer distance; Δσₘₜ is a relative mean-square deviation in Rₘₜ, Δσₘₜ = σₘₜ (sample) − σₘₜ (model), where the model is [Cu- (imidazole)₄]²⁺ at 4 K for Cu-(N₃O) and [Cu(malonitriledithiolate)]²⁻ at 4 K for Cu-S. All fits were over the range k = 3.0–13.0 Å⁻¹.

⁵ The parameter f' is a goodness-of-fit statistic normalized to the overall magnitude of the k²χ(k) data:

\[ f' = \left( \frac{\sum_k k^2 (\chi_{\text{obs}}(k) - \chi_{\text{calc}}(k))^2 / N}{(k^2 \chi)^{\text{max}} - (k^2 \chi)^{\text{min}}} \right)^{1/2} \]

Numbers in parentheses were not varied during optimization.

E. Does a Particular Treatment Result in a Structural Change?

Since both the X-ray absorption edge and the EXAFS are sensitive to the local structural environment of the absorbing metal atom(s), XAS is a good technique for determining whether the structure of a metal site is affected by a given treatment. The position and shape of the edge can give information about electronic structure (e.g., redox state) and molecular geometry, while the EXAFS can be analyzed to yield the detailed nature of the structural change.

As an example, consider the reductive lithiation (lithium intercalation) of the amorphous material, MoS₃. (The lithiated MS₃ compounds have shown some promise as electrode materials for lithium batteries.) Comparison of the Mo K X-ray absorption edge spectra for the parent MoS₃ and the lithiated material of limiting composition, Li₄MoS₃, showed a shift in the edge to lower energy as expected for reduction of Mo upon Li incorporation [Fig. 18(a)]. The Mo EXAFS Fourier transforms indicate that a very significant structural change of the Mo coordination environment accompanies this reduction [Fig. 18(b)]. The initial structure of MoS₃, involving 5–6 Mo–S bonds at 2.42 Å and about 1 Mo–Mo bond at 2.75 Å, changes into one containing more Mo–Mo bonds upon
Figure 18

(a) Comparison of the Mo K-edge spectra for untreated MoS$_3$ (dash-dot line labeled 0) and for Li$_{4.0}$MoS$_3$ (solid line labeled 4). Note the shift of the Mo edge for the lithiated sample, suggesting a reduction in the average Mo oxidation state. (b) Comparison of the Mo EXAFS Fourier transforms for untreated MoS$_3$ (dashed line) and for Li$_{4.0}$MoS$_3$ (solid line). Note the substantial increase in the high $R'$ (2.3–2.4 Å) FT peak in the lithiated material. This indicates an increase in the number of the approximate 2.7-Å Mo–Mo (bonded) interactions upon lithiation, as suggested by the proposed structural change from an extended-chain to a high-nuclearity cluster structure in (c). [These figures were adapted from Scott et al.$^{34}$]

lithiation to Li$_{4.0}$ MoS$_3$ (∼3 Mo–S bonds at 2.50 Å and about 4 Mo–Mo bonds at 2.66 Å). This increase in Mo neighbors indicates a condensation of Mo atoms into higher nuclearity clusters upon lithiation, as indicated in the proposed conversion of a chain structure to an octahedral Mo$_6$ cluster [Fig. 18(c)].

In many cases, the treatment being examined is the addition of a potential ligand and XAS is then used to determine whether this compound actually binds to the metal site of interest. In biochemistry, the site of binding of known inhibitors (or substrate analogues) for a metalloenzyme can be tested. This works best if the inhibitor contains a heavy atom (e.g., S, Br, and As) that can easily be detected by EXAFS in the presence of a number of other light-atom (e.g., N and
0) ligands (e.g., see Scott et al., Clark et al., Scott et al., Holz et al., and Cramer and Hille). Alternatively, inhibitors that generate other unique EXAFS signatures can be used; the most common is cyanide. Figure 19 compares edge, EXAFS, and FT data for two samples of a Cu substituted form of liver alcohol dehydrogenase (LADH), one untreated (solid lines) and the other treated with cyanide (dashed lines). This form of LADH has Cu substituted for Zn in the catalytic sites of each monomer of the dimeric enzyme and is therefore referred to as [Cu₂Zn₂]LADH. The coordination of the Cu(II) in the untreated enzyme is by two cysteine thiolates, one histidine imidazole, and one water. Binding of cyanide to a metal ion usually results in a linear M–C–N arrangement with a fairly short M–C bond distance. The EXAFS scattering amplitude from the remote N is enhanced by a multiple-scattering mechanism (see Fig. 6) through the intervening C, resulting in a large M···N FT peak at about 2.8 Å. This FT peak may be used as a signature for detecting the binding of cyanide to a metal site. Both edge and EXAFS spectra are different for the cyanide-treated [Cu₂Zn₂]LADH compared to the untreated form, suggesting a significant change in the Cu site structure [Fig. 19(a and b)]. More definitively, a large new FT peak appears at about

![Figure 19](image)

(a) The Cu XAS edge, (b) the EXAFS, and (c) FT data for the Cu substituted form of liver alcohol dehydrogenase ([Cu₂Zn₂]LADH). Solid lines are data from the untreated form and dashed lines are data from the cyanide-treated form. The FT data were generated by $k^3$-weighted transform over the $k = 3.0-13.0\text{-Å}^{-1}$ range. [This figure is from unpublished work of Dooley and Scott.]
2.8 Å [arrow in Fig. 19(c)], suggesting that cyanide binds to the Cu. Cyanide binding is also suggested by the splitting of the first-shell FT peak into two peaks, implying a larger separation in first-shell distances in the cyanide-bound enzyme [Cu–C at ~1.9 compared to Cu–(N,O) at ~2.0 and Cu–S at ~2.2 Å]. Detailed curve-fitting confirms this conclusion.

F. Is the Metal Being Studied Part of a Metal Cluster?

Since the scattering power of an atom increases with increasing atomic number, additional metal atoms (M') in the vicinity (~2.5–4.0 Å) of the absorbing metal atom (M) should give rise to characteristic, easily discernible EXAFS contributions. Observation of this M–M' scattering in the EXAFS could then confirm the presence of a metal cluster (M, M')ₙ (n ≥ 2) in a structurally uncharacterized sample. The M–M' scattering stands out when M and M' are directly bonded, when the M–M' distance is relatively short (<3 Å), or when M' is a very heavy metal. Examples like this include the Mo–Mo clusters in Li₅MoS₃ already discussed, the Fe–Fe clusters in iron–sulfur proteins,⁴⁰ and organometallic Mo–Ir clusters.⁴¹

In all of these examples, a separate peak in the FT can be assigned to the M–M' scattering [e.g., see Fig. 18(b)]. However, even in mononuclear sites, FT peaks often occur in a region corresponding to M–X distances of about 3–4 Å [e.g., see Fig. 19(c)]. These usually result from outer-shell scattering atoms that are part of an extended ligand framework (e.g., C and N of imidazole- or pyridine-like rings, C of a porphyrin skeleton). These FT peaks can obscure the presence (or absence) of a M–M' FT peak, making the detection of a metal cluster difficult.⁴² This interference is a frequent problem in metalloenzymes thought to contain dinuclear sites, since histidine imidazole and porphyrin ligation are so common. For example, it has been particularly difficult to measure the Cu··Fe distance in the dinuclear O₂ interaction site of resting state cytochrome c oxidase given the presence of histidine and porphyrin ligation. Studies by two different groups have assigned the Cu··Fe distance as 3.0 or 3.8 Å, depending on which FT peak in the Cu EXAFS contains the Cu··Fe contribution.⁴³ Figure 20 shows the FTs of the Cu and Fe EXAFS of resting state cytochrome c oxidase; the arrows indicate the peaks that have been interpreted as containing Cu··Fe (Fe··Cu) scattering; both peaks also contain M···C scattering from histidine imidazoles (M = Cu) or from the porphyrin ring (M = Fe). It is noteworthy that, even with crystal structures now available for two cytochrome oxidases,⁴⁵ the Cu–Fe₃ distance remains a matter of controversy. Similar difficulties were encountered in the successful analysis of the dinuclear Fe–Fe site of hemerythrin.⁴⁶–⁴⁸

The main problem is that the standard single-scattering EXAFS analysis cannot adequately simulate scattering from outer-shell atoms, since it contains a significant multiple-scattering component. Also, there are often not enough structurally characterized model dinuclear compounds from which to extract empirical M–M' scattering functions. Now with some of the newer EXAFS analytical techniques that properly treat multiple scattering and rely on more exact ab initio computation of scattering functions⁴,⁵ some of these ambiguities are beginning to be overcome.
Figure 20
Fourier transforms of Cu EXAFS (a) and Fe EXAFS (b) for resting state cytochrome c oxidase. The arrows in both FTs indicate the peaks that have been assigned by different researchers to Cu⋯Fe (Fe⋯Cu) scattering. Spectrum (a) was adapted from Li et al.44 Spectrum (b) was adapted from Scott.43

References


21. Davison, A.; Holm, R. H. “Metal Complexes Derived from cis-1,2-Dicyano-1,2-Ethyleneedithiolate and Bis(trifluoromethyl)-1,2-Dithieta” Inorg. Synth. 1967, 10, 8–26.


29. LuBien, C. D.; Winkler, M. E.; Thamann, T. J.; Scott, R. A.; Co, M. S.; Hodgson, K. O.; Solomon, E. I. “Chemical and Spectroscopic Properties of the Binuclear Copper Active Site in Rhus Laccase; Direct Confirmation of a Reduced Binuclear Type 3 Copper Site in Type 2 Depleted Laccase and Intramolecular Coupling of the Type 3 to the Type 1 and Type 2 Copper Sites” J. Am. Chem. Soc. 1981, 103, 7014–7016.


44. Li, P. M.; Gelles, J.; Chan, S. I.; Sullivan, R. J.; Scott, R. A. “Extended X-Ray Absorption Fine Structure of Copper in CuA-Depleted, p-(Hydroxymercu)benzoate-Modified, and Native Cytochrome c Oxidase” Biochemistry 1987, 26, 2091–2095.


General References


A good basic introduction to the background and theory of XAS, but without the modern ab initio theoretical treatment of photoelectron scattering.


An early attempt at providing history, background, theory, and applications of EXAFS to mostly materials research. Some discussion of synchrotron sources of the era is also provided.


A more recent attempt to provide a comprehensive review of the background and theory of both EXAFS and XANES, as well as applications ranging from biology to surface science.


An early, now classic, review of the EXAFS technique and its application to structural determinations, mostly in solid-state materials.

A very recent discussion of the state of the art, including remaining unsolved problems. Most of the examples are from materials science applications.


A chronological series of useful reviews of the biological applications of XAS. Most also have a treatment of the basic theory and methodology of XAS.


Three excellent examples of the use of the edge region of the X-ray absorption spectrum to provide information on the molecular geometry of metal sites.


Recent, in-depth discussions of the importance of multiple scattering and its application to structural applications of EXAFS.