4.2 EXAFS

Extended X-Ray Absorption Fine Structure

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Introduction

The discovery of the phenomenon that is now known as extended X-ray absorption fine structure (EXAFS) was made in the 1920s, however, it wasn't until the 1970s that two developments set the foundation for the theory and practice of EXAFS measurements.[1] The first was the demonstration of mathematical algorithms for the analysis of EXAFS data. The second was the advent of intense synchrotron radiation of X-ray wavelengths that immensely facilitated the acquisition of these data. During the past two decades, the use of EXAFS has become firmly established as a practical and powerful analytical capability for structure determination.[2–8]

EXAFS is a nondestructive, element-specific spectroscopic technique with application to all elements from lithium to uranium. It is employed as a direct probe of the atomic environment of an X-ray absorbing element and provides chemical bonding information. Although EXAFS is primarily used to determine the local structure of bulk solids (e.g., crystalline and amorphous materials), solid surfaces, and interfaces, its use is not limited to the solid state. As a structural tool, EXAFS complements the familiar X-ray diffraction technique, which is applicable only to crystalline solids. EXAFS provides an atomic-scale perspective about the X-ray absorbing element in terms of the numbers, types, and interatomic distances of neighboring atoms.

EXAFS is part of the field of X-ray absorption spectroscopy (XAS), in which a number of acronyms abound. An X-ray absorption spectrum contains EXAFS data as well as the X-ray absorption near-edge structure, XANES (alternatively called the near-edge X-ray absorption fine structure, NEXAFS). The combination of XANES (NEXAFS) and EXAFS is commonly referred to as X-ray absorption fine structure, or XAFS. In applications of EXAFS to surface science, the acronym SEXAFS, for surface-EXAFS, is used. The principles and analysis of EXAFS and SEXAFS are the same. See the article following this one for a discussion of SEXAFS and NEXAFS.

Experimental Aspects

An EXAFS experiment involves the measurement of the X-ray photoabsorption of a selected element as a function of energy above its core-shell electron binding energy. The most direct measurement of EXAFS is the transmission method, wherein the sample is placed in the X-ray beam and the incident and transmitted X-ray intensities, I_0 and I_t, respectively, are recorded (see Figure 1). The measurement of I_0 and I_t is accomplished with two ion chamber proportional counters that are gas filled (typically with nitrogen and argon) to provide about 10–20% absorption of I_0 and 80–90% absorption of I_t. As shown in Figure 1, it is useful to have a third ion chamber for simultaneous measurements of a reference material (e.g., a thin metal foil) to maintain accurate energy calibration throughout the course of experiment. For successful transmission measurements, the ideal sample thickness x is one absorption length, i.e., $x = 1/[(\mu/\rho)\rho]$; here μ/ρ is the total mass absorption coefficient and ρ is the density. Transmission EXAFS data for samples with larger absorption lengths can be seriously distorted and are not suitable for analysis.[9] Transmission EXAFS data are displayed in the form $\ln(I_0/I_t)$ versus incident X-ray energy, as shown in Figure 2.

A wide selection of metal reference foils and powder films of ideal thickness for tranmission EXAFS is available from The EXAFS Materials Company, Danville, CA, USA. The transmission method is well-suited for *in situ* measurements of materials under industrially relevant conditions of extreme temperature and controlled atmosphere. Specially designed reactors for catalysis experiments and easy-
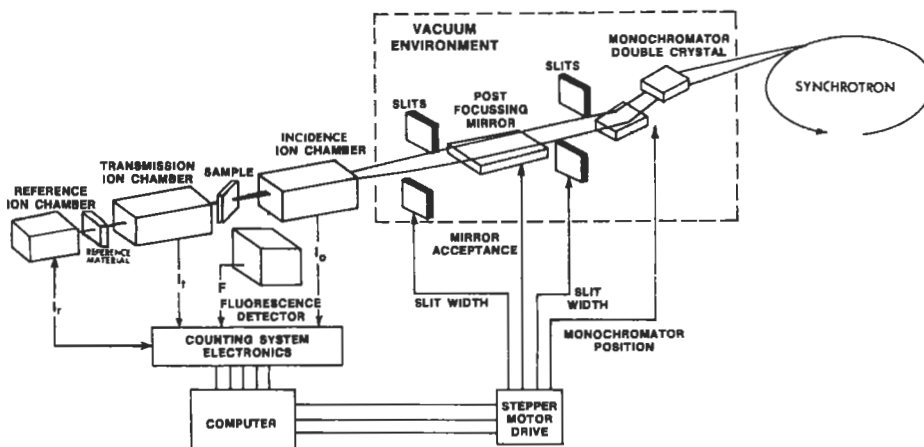
Figure 1 Schematic view of a typical EXAFS experiment at a synchrotron radiation facility. Note that it is possible to record transmission and fluorescence EXAFS simultaneously with reference EXAFS.

to-use detectors are commercially available from The EXAFS Company, Seattle, WA, USA.

In addition to transmission, EXAFS data can be recorded through the detection of

1 X-ray fluorescence

2 Electron yield

3 Ion yield

4 Optical luminescence

5 Photoconductivity

6 Photoacoustic signals.

The last three detection schemes apply only under very special circumstances.[3-6] Transmission EXAFS is strictly a probe of bulk structure, i.e., more than about a thousand monolayers. The electron- and ion-yield detection methods, which are used in reflection rather than transmission schemes, provide surface sensitivity, ~1–1,000 Å, and are inherently insensitive to bulk structure. X-ray fluorescence EXAFS has the widest range of sensitivity—from monolayer to bulk levels. The combination of electron or ion yield and transmission EXAFS measurements can provide structural information about the X-ray absorbing element at the surface and in the bulk, respectively, of a sample.

Without exception, the highest quality EXAFS data are acquired at synchrotron radiation facilities. There are 20 operational facilities throughout the world.[10] Each has unique instrumentation: The interested user is encouraged to contact the facil-
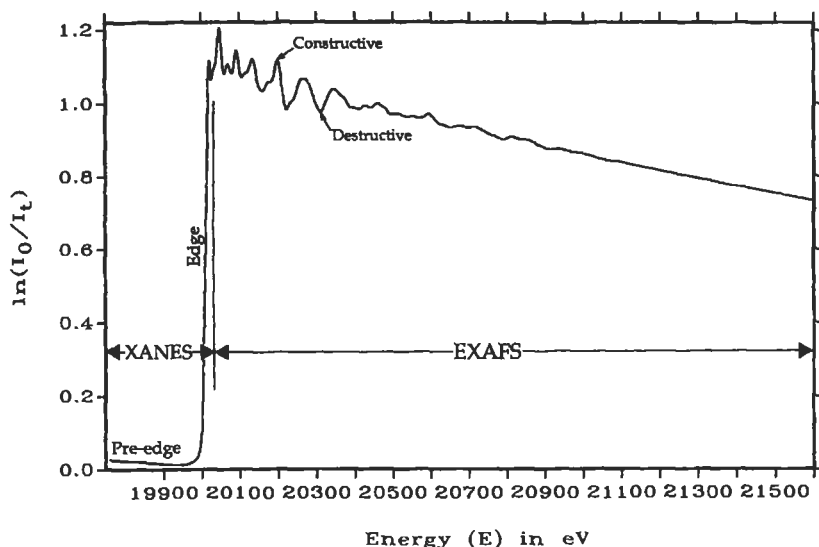
Figure 2 Molybdenum K-edge X-ray absorption spectrum, $\ln(I_0/I_t)$ versus X-ray energy (eV), for molybdenum metal foil (25-μm thick), obtained by transmission at 77 K with synchrotron radiation. The energy-dependent constructive and destructive interference of outgoing and backscattered photoelectrons at molybdenum produces the EXAFS peaks and valleys, respectively. The pre-edge and edge structures marked here are known together as X-ray absorption near edge structure, XANES and EXAFS are provided in a new compilation of literature entitled *X-ray Absorption Fine Structure* (S.S. Hasain, ed.) Ellis Horwood, New York, 1991.

ity for detailed information, such as is available in Gmur.[11] In general, "hard" X-ray beam lines (approximately ≥ 2,000 eV) employ flat-crystal monochromators to scan the X-ray energy over the region of interest, whereas "soft" X-ray beam lines (approximately ≤ 1,000 eV) employ grating-type monochromators for the same purpose. The monochromatization of X rays with energies between approximately 1,000 and 2,000 eV is a difficult problem—neither crystal nor grating monochromators work particularly well.

Basic Principles

Both inner-shell (K and L) and outer-shell (M, N, etc.) electrons can be excited by the absorption of X rays and by the inelastic scattering of electrons. In either instance, at an electron binding energy characteristic of an element in a sample,
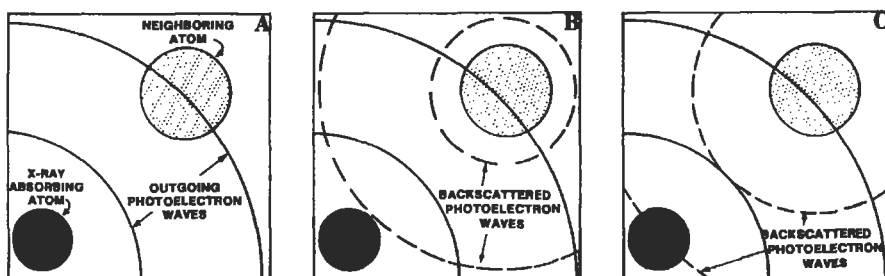
Figure 3 Schematic illustration of the EXAFS phenomenon: (A) outgoing photoelec-
tron (solid curve) from X-ray absorbing atom; (B) destructive interference at
the absorbing atom between outgoing (solid curve) and backscattered
(dashed curve) photoelectron from neighboring atom; (C) constructive inter-
ference at the absorbing atom between outgoing (solid curve) and backscat-
tered (dashed curve) photoelectron from neighboring atom. Adapted from T.
M. Hayes and J. B. Boyce. *Solid State Phys.* 37, 173, 1982.

absorption occurs and a steeply rising absorption edge is observed. For example,
molybdenum exhibits an X-ray absorption edge at 20,000 eV, which is the 1s elec-
tron binding energy (K edge) , see Figure 2. The pre-edge and edge features are col-
lectively referred to as XANES or NEXAFS, depending upon the application.
These data are valuable for probing the site symmetry and valence of the X-ray
absorbing element, but will not be discussed further here.

For X-ray energies greater than the binding energy, the absorption process leads
to the excitation of the core electron to the ionization continuum. The resulting
photoelectron wave propagates from the X-ray absorbing atom and is scattered by
the neighboring atoms, as illustrated in Figure 3. The EXAFS spectrum results
from the constructive and destructive interference between the outgoing and
incoming photoelectron waves at the absorbing atom. The interference gives rise to
the modulatory structure (i.e., peaks and valleys) of the X-ray absorption versus
incident X-ray energy, as in Figure 2. This process also makes EXAFS unique—the
absorbing atom acts as both the source and detector of the interference that is the
EXAFS phenomenon.

EXAFS is a probe of the structural distribution, e.g., interatomic distances,
numbers of neighboring atoms (the so-called coordination number), and degree of
disorder—and identity of atoms in the immediate vicinity (~5 Å) of the X-ray
absorbing atom. A simplified schematic representation of several descriptive fea-
tures of EXAFS is presented in Figure 4. The frequency of EXAFS oscillations is
related to the distance between the X-ray absorbing atom (filled circles) and the
backscattering atoms (open circles). For large interatomic distances ($R_1 > R_2$), the
EXAFS has shorter periods (higher frequencies) than for small distances; see curves
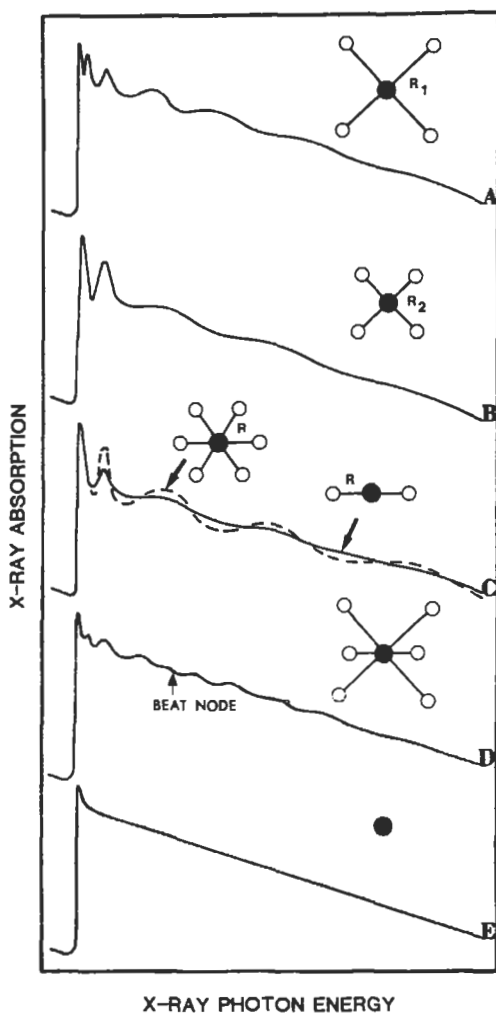
Figure 4 Descriptive aspects of EXAFS: Curves A–E are discussed in the text. Adapted from J. Stohr. In: *Emission and Scattering Techniques: Studies of Inorganic Molecules, Solids, and Surfaces.* (P. Day, ed.) Kluwer, Norwell, MA, 1981.

A and B, respectively, in Figure 4. The periodicity is also related to the identity of the absorbing and backscattering elements. Each has unique phase shifts.[12]

EXAFS has an energy-dependent amplitude that is just a few % of the total X-ray absorption. This amplitude is related to the number, type, and arrangement of backscattering atoms around the absorbing atom. As illustrated in Figure 4 (curve C), the EXAFS amplitude for backscattering by six neighboring atoms at a distance R is greater than that for backscattering by two of the same atoms at the same distance. The amplitude also provides information about the identity of the

backscattering element—each has a unique scattering function[12]—and the number of different atomic spheres about the X-ray absorbing element. As shown in Figure 4, the EXAFS for an atom with one sphere of neighbors at a single distance exhibits a smooth sinusoidal decay (see curves A–C), whereas that for an atom with two (or more) spheres of neighbors at different distances exhibits beat nodes due to superposed EXAFS signals of different frequencies (curve D).

The EXAFS amplitude is also related to the Debye-Waller factor, which is a measure of the degree of disorder of the backscattering atoms caused by dynamic (i.e., thermal–vibrational properties) and static (i.e., inequivalence of bond lengths) effects. Separation of these two effects from the total Debye-Waller factor requires temperature-dependent EXAFS measurements. In practice, EXAFS amplitudes are larger at low temperatures than at high ones due to the reduction of atomic motion with decreasing temperature. Furthermore, the amplitude for six backscattering atoms arranged symmetrically about an absorber at some average distance is larger than that for the same number of backscattering atoms arranged randomly about an absorber at the same average distance. Static disorder about the absorbing atom causes amplitude reduction. Finally, as illustrated in Figure 4 (curve E), there is no EXAFS for an absorbing element with no near neighbors, such as for a noble gas.

Data Analysis

Because EXAFS is superposed on a smooth background absorption μ_0 it is necessary to extract the modulatory structure μ from the background, which is approximated through least-squares curve fitting of the primary experimental data with polynomial functions (i.e., $\ln(I_0/I_t)$ versus E in Figure 2).[7, 12] The EXAFS spectrum χ is obtained as $\chi = [\mu-\mu_0]/\mu_0$. Here χ, μ, and μ_0 are functions of the photoelectron wave vector $\mathbf{k}$ (Å^{-1}), where $k = [0.263\ (E-E_0)]^{1/2}$; E_0 is the experimental energy threshold chosen to define the energy origin of the EXAFS spectrum in k-space. That is, $k = 0$ when the incident X-ray energy E equals E_0, and the photoelectron has no kinetic energy.

EXAFS data are multiplied by k^n ($n = 1$, 2, or 3) to compensate for amplitude attenuation as a function of k, and are normalized to the magnitude of the edge jump. Normalized, background-subtracted EXAFS data, $k^n\chi(k)$ versus k (such as illustrated in Figure 5), are typically Fourier transformed without phase shift correction. Fourier transforms are an important aspect of data analysis because they relate the EXAFS function $k^n\chi(k)$ of the photoelectron wavevector $\mathbf{k}$ (Å^{-1}) to its complementary function $\Phi_n(r')$ of distance r'(Å). Hence, the Fourier transform provides a simple physical picture, a pseudoradial distribution function, of the environment about the X-ray absorbing element. The contributions of different coordination spheres of neighbors around the absorber appear as peaks in the Fourier transform. The Fourier transform peaks are always shifted from the true distances r to shorter ones r' due to the effect of a phase shift, which amounts to ~0.2–0.5 Å, depending upon the absorbing and backscattering atom phase functions.