THE ADVANTAGE OF THE APPLICATION OF X-RAY ABSORPTION SPECTROSCOPY

RAKESH KUMAR RANJAN

Department of Physics,Veer Kunwar Singh University Ara , Bihar, India 802312

ABSTRACT

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS),is a type of absorption spectroscopy that indicates the feature in the X-ray absorption Spectra (XAS) of condensed matter due to the photo absorption cross section for electronic transitions form an atomic core level to final state in the energy region 50-100 ev above the selected atomic core level ionization energy. The K edge x-ray absorption spectrum of most elements of the periodic table can be performed through full multiple scattering calculations. Then, on the basis of a linear combination of the XANES spectra of reference compounds, the presence of the different phases present inside the materials can be quantified. Here, we show that for nanometer scale metallic clusters, it is not sufficient to consider only the electronic state of the metal of interest to perform a linear combination analysis. In the case of these peculiar materials, special attention has to be paid to different structural parameters, for example, the size and morphology of the cluster, the interatomic distance (taking into account contraction/dilatation processes), and the presence of hetero metallic bonds (in the case of bimetallic clusters). Moreover, this approach is not specific to the metallic state. As a conclusion, the quantitative measurement of the structural parameters coming from EXAFS analysis constitutes an invaluable starting point for the FEFF-PCA simulation. The advantages and limitations of the methods are discussed. Recent advances in extended EXAFS and polarized EXAFS using oriented membranes and single crystals are explained. Developments in theory in understanding the XANES spectra are described. The application of X - ray absorption spectroscopy to the study of the Mn_4Ca cluster in Photosystem II is presented.

KEYWORD : X-ray absorption, XANES, EXAFS.

INTRODUCTION

Theory of X-ray Absorption Spectra

X-ray absorption spectra of any material be it atomic or molecular in nature are characterized by sharp increases in absorption at specific X-ray photon energies, which are characteristic of the absorbing element. These sudden increases in absorption are called absorption edges, and correspond to the energy required to eject a core electron into the LUMO or to the continuum thus producing a photoelectron. The absorption discontinuity is known as the K-edge, when the photoelectron originates from a $1s$ core level, and an L-edge when the ionization is from a $2s$ or $2p$ electron. L-edge spectroscopy is, in general, more sensitive to the electronic, structural, and the spin state changes of the metal cluster compared to the K-edge spectroscopy, however, there are experimental difficulties in applying this technique to biological samples.

X-ray Absorption Spectroscopy

EXAFS and XANES X-ray absorption spectroscopy encompasses the techniques of extended x-ray absorption fine structure (EXAFS) spectroscopy and x-ray absorption near edge structure (XANES) spectroscopy (see Amorphous Materials : X-ray Absorption Spectroscopy). EXAFS spectroscopy is widely used in the study of materials, in particular disordered and amorphous materials, including heterogeneous catalysts, glasses, amorphous semiconductors, microporous materials and other solid-state materials, where no long-range order exists but where there exists a well-defined coordination around a central atom. It is also particularly suited to the study of dilute systems, such as doped materials and promoter species in heterogeneous catalysts, where the element of interest is present in very low concentrations. This arises from the combination of the element specificity of EXAFS and the high sensitivity of the technique that has come with the advent of synchrotron radiation sources, which provide ever-increasing intense photon fluxes. EXAFS provides reliable structural information concerning the local, short-range coordination environment and the chemical and electronic structure of specific sites within materials, including the number, chemical nature, and distance of neighboring atoms from the atomic site of interest. The near-edge structure arises from the excitation of core electrons into discrete unoccupied valence orbitals, that is, bound state transitions. The XANES or near-edge x-ray absorption fine structure (NEXAFS) is difficult to analyze, the main problem being to assign correctly the observed transitions and to interpret the energy

and intensities of these transitions. It does, however, relatively straightforwardly give information concerning the oxidation state of the central absorbing atom of interest since an absorption feature moves to higher energies as the oxidation state of the absorbing atom becomes more positive. In theory, analysis of the positions and relative intensities of the near-edge features does give details concerning metal site symmetry and the local coordination environment, but as noted above, the interpretation is extremely complex.

X-ray Absorption Edges

X-ray Absorption Edges An absorption edge by itself is of little value beyond elemental identification.[1,2] This is illustrated by the schematic absorption edge shown in Figure 1.
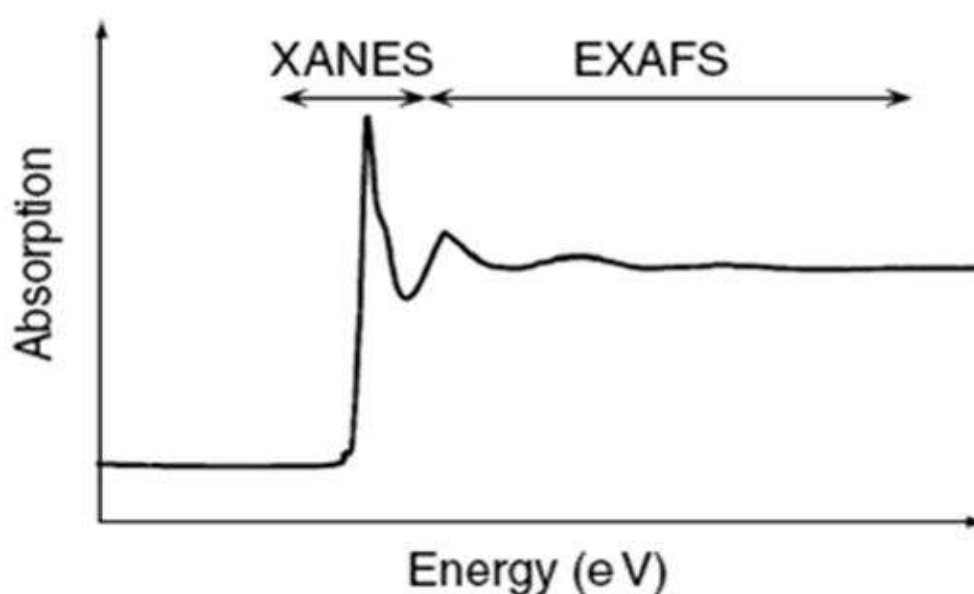

Figure 1 Schematic illustration of an X-ray absorption spectrum, showing the structured absorption that is seen both within ca. 50 eV of the edge (the XANES) and for several hundred to >1,000 eV above the edge (the EXAFS).

But in fact shows significant structure both in the immediate vicinity of the edge jump and well above the edge. The structure in the vicinity of the edge is sometimes referred to as X-ray absorption near-edge structure (XANES). The oscillations above the edge, which can extend for 1,000 eV or more, are often referred to as extended X-ray absorption fine structure (EXAFS). The distinction between XANES and EXAFS is arbitrary, since the same fundamental physical principles govern photo absorption over the entire XAS region and there is no unambiguous definition that distinguishes between ''near-edge'' and ''extended'' structure. In an attempt to emphasize the essential similarity of these regions, the term XAFS (X-ray absorption fine structure) has gained some currency as a reference to the entire structured absorption region. Nevertheless, the terms EXAFS and XANES

remain the most widely used, with some justification, since the XANES and EXAFS regions are generally analyzed differently. As described in detail below, the XANES region is sensitive to oxidation state and geometry, but is not, in most cases, analyzed quantitatively. The EXAFS region is sensitive to the radial distribution of electron density around the absorbing atom and is used for quantitative determination of bond length and coordination number. A fourth acronym, which is popular in the soft X-ray and surface science communities, is NEXAFS, standing for near-edge X-ray absorption fine structure. This acronym is redundant, since NEXAFS and XANES are used to refer to the same features, and is potentially confusing, given its similarity to EXAFS.

X-ray absorption spectroscopy (XAS) is the measurement of transitions from core electronic states of the metal to the excited electronic states and the continuum; the former is known as X-ray absorption near-edge structure (XANES), and the latter as extended X-ray absorption fine structure (EXAFS) which studies the fine structure in the absorption at energies greater than the threshold for electron release. These two methods give complementary structural information, the XANES spectra reporting electronic structure and symmetry of the metal site, and the EXAFS reporting numbers, types, and distances to ligands and neighboring atoms from the absorbing element[3].

X-ray absorption spectroscopy (XAS) theory has been developed to an extent that it can be applied to complicated molecules of known structure[4]. Although it is less straightforward to apply it to the OEC, where its molecular environment is not yet precisely defined, the basic XAS equation allows us to interpret EXAFS spectra to considerable advantage. X-ray spectral properties to be expected from specified cluster geometries can be calculated and compared with experimental measurements. Density-functional theory (DFT) can be applied to issues like the stability of a proposed cluster arrangement or the likelihood of postulated reaction paths. Moreover, the time-dependent DFT calculations provide an important insight into the electronic structure of the metal site combined with the analysis of the XANES pre-edge region.

Process of X-Ray Absorption Spectra

When the continuous X-rays having energy less than 1.02 MeV is allowed to pass through the absorbing material; absorption of X-ray takes place within the material .The intensity of the transmitted rays from the absorbing material is reduced due to (i) Photoelectric effect (ii) Auger effect and (iii) X-ray scattering effect, etc. These variations of intensity of the transmitted rays are gradual. But when the energy of the incident X-rays becomes just sufficient to promote one of the inner electrons to an orbit outside the system of the filled

orbits (i.e., outside the absorbing atom) the intensity variations become abrupt. The absorption of X-rays is given by the classical exponential law:

$$I = I_0 e^{-\mu} 1^x$$

Where,

I & Io : Intensities of the transmitted and incident X-rays beams respectively.

μ_1 : Linear absorption co-efficient (i.e. the attenuation of the beam per unit length traveled). It is a measure of the tendency of a material to absorb X-rays.

X : Thickness of the absorbing material through which the beam passes.

As the wave length of the incident ray increases (i.e. the energy of the incident X-ray decreases) the absorption coefficient increases gradually. But at particular wave lengths an abrupt change in absorption takes place where high absorption occurs. This results into an abrupt change in transmitted intensities. These abrupt discontinuities are called absorption discontin- unities or absorption edges. Thus the external structure of the atom affects the absorption spectrum. Therefore the absorption spectrum gives the ideas of the way in which an atom is influenced by the physical and chemical environment of the absorbing atom.

The edge corresponding to the most tightly bound initial state of the photo absorbing atom is known as the K-edge, followed by the L-edge having three components (L_I, L_{II} and L_{III}), in turn followed by the M-edge having five components (M_I, M_{II}, M_{III}, m_{IV} and M_V), and so on. These edges correspond to the excitation potentials of the energy levels of the concerned atom.

Measurement of X-ray Absorption Spectra :

In the simplest case, measurement of an X-ray absorption spectrum involves only measurement of the incident and the transmitted X-ray flux. This can be accomplished, for example, with an, At higher resolution, these can be resolved into $K_{\alpha1}$, $K_{\alpha2}$, with the splitting due to spin–orbit coupling. A similar pattern,with much greater complexity, is seen for L edge excitation. Redrawn from data in.[5] For a more complete list of emission lines, X-ray Absorption Spectroscopy [6]ionization chamber[7] in front of and behind the

sample, using Beer's law to convert to absorption coefficient. This approach is limited to moderately concentrated samples (greater than ca.10mM or 500 ppm) and, depending on the energy of the absorption edge, even these concentrations may not be accessible. For example, sulfur or chlorine containing solvents are nearly opaque to lower energy X-rays and thus interfere with XAS measurements. To avoid the limitations of absorption, XAS spectra are frequently measured as fluorescence excitation spectra.[8] This is particularly important for dilute samples such as catalysts, biological samples, or environmental samples.

Providing the sample is dilute or thin ,the intensity of the fluorescence X-rays is proportional to the X-ray absorption cross-section[9].
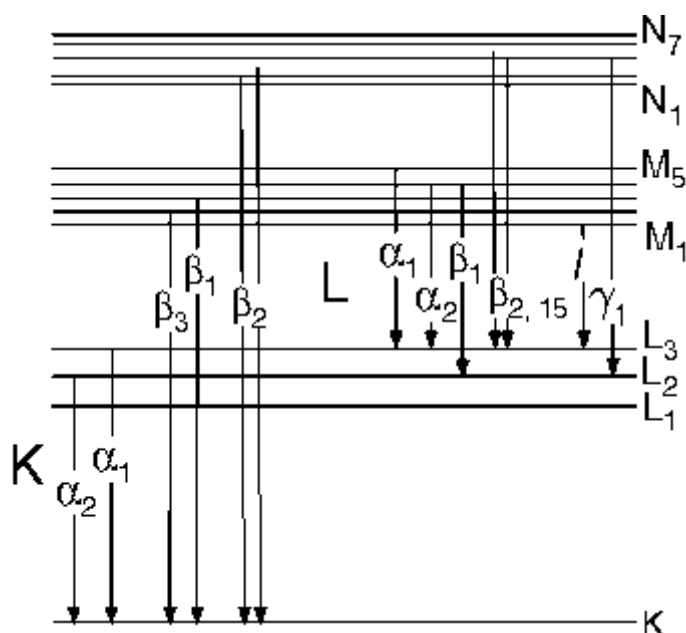

Figure 2 Nomenclature for selected X-ray emission lines. Excitation of a K shell results in K and K emission lines (originating from n = 2 and n = 3, respectively).

In most cases, the sample will emit a variety of X-rays, both the fluorescence X-rays of interest and a background of scattered X-rays. In order to have good sensitivity, the fluorescence detector needs some kind of energy resolution to distinguish between the signal and background X-rays. In some cases, energy resolution can be provided by a simple low-pass filter[10,11] although for the ultimate sensitivity it is necessary to use higher resolution in order to more effectively exclude background radiation. This is typically an energy-resolving solid-state fluorescence detector,[12-14] although recent advances with wavelengthresolving detectors may be important in special cases.[15,16] In principle, any

physical property that changes in proportion to X-ray absorption could be used to measure XAS spectra. In addition to X-ray fluorescence, properties that have been used include photoconductivity,[17] optical luminescence,[17-19] and electron yield,[20.21] although only the latter is widely used. Electron yield detection of XAS is particularly important for studies of surfaces. Since the penetration depth of an electron through matter is quite small, electron yield can be used to make XAS measurements surface sensitive.[22,23] Although XAS can be studied for virtually any X-ray absorption edge, experiments are simplest when they can be performed at atmospheric pressure. This limits the accessible X-ray energies to those greater than approximately 5 keV (for air) or 2 keV (for a He atmosphere). Lower energy measurements require that the sample be in vacuum in order to avoid excessive attenuation of the incident X-ray beam. Similarly, it is difficult, although not impossible, to make XAS measurements at energies above approximately 30 keV . However, this does not limit XAS significantly, since elements that are heavy enough to have K edge energies >30 keV have readily accessible L edge energies .This means that XAS spectra can be measured for virtually every element, although measurements for elements lighter than phosphorus generally require that the sample be made vacuum compatible. X-ray absorption spectra can be measured for solids, liquids, or gases and do not require that samples have long-range order or that samples possess particular magnetic properties .Measurements can be made at low temperature for studies of unstable samples, or at high temperature and/or pressure, for example for studies of catalysts under reaction conditions or of geochemical samples under conditions that approximate the inner mantle.

Advantage of X- Ray Absorption Spectra

1. X-ray absorption spectroscopy (XAS) is element *specific*, so one can focus on one element without interference from other elements present in the sample. In a protein, which has more than one metal like cytochrome oxidase (Cu and Fe), or nitrogenase (Fe and Mo), it is possible to study the structural environment of each metal atom selectively. The element specificity and the fact that it is always possible to obtain an X-ray spectrum of an element also means that one 'sees' all of the metal of interest, which is present in the sample. This makes it imperative that one is sure of the biochemical homogeneity of the sample and, if there is more than one site for the same metal, to resolve the structural parameters of the different sites.

2. Another important advantage of XAS is that the metal of interest is never '*silent*' with respect to X-ray absorption spectra. The system could be '*silent'* with respect to EPR, optical, or other spectroscopic methods, but one can always probe the metal site structure by XAS.

3. X-ray absorption spectroscopy (XAS) is not limited by the state of the sample, because it is sensitive only to the local metal site structure. The sample can be prepared as a powder, a solution or, as is done most often, as a frozen solution for biological samples. It is not necessary to obtain single crystals of the material to examine the local structure of the metal. However, having oriented crystals such as membranes and single crystals significantly increases the structural information obtained from the XAS method. This will be discussed in a latter section. The more important aspect is that one can either trap intermediates in the enzymatic cycle or modify the site by the addition of inhibitors or substrate or generate other chemical modifications. Such samples can be made as frozen solutions, avoiding the problems of trying to obtain single crystals. The study by this technique of trapped intermediates and treated samples has yielded insights into the mechanism of the reaction involved, in several biological systems.

4. Damage to biological samples by X-rays is cause for serious concern for X-ray crystallography and XAS experiments. However, with the right precautions one can successfully perform these experiments leaving the materials largely intact. The most serious damage is produced by the reaction with free radicals and hydrated electrons that are produced in biological samples by X-rays. The diffusion of the free radicals and hydrated electrons can be minimized by the use of low temperatures. The use of a liquid He flow cryostat or liquid He cryostream, where the samples are at atmospheric pressure in a He gas atmosphere, has greatly reduced the risk of sample damage by X-rays. XAS experiments require a lower X-ray dose than X-ray crystallography, and radiation damage can be precisely monitored and controlled, thus allowing for data collection from an intact metal cluster.[24,25]

Limitations

1. It is also important to realize the intrinsic limitations of EXAFS, beyond those of a purely experimental nature. A frequent problem is the inability to distinguish between scattering atoms with little difference in atomic number (C, N, O or S, Cl, or Mn, Fe). Care must also be exercised when deciding between atoms that are apart in Z, as frequently, it is possible to obtain equally good fits using backscattering atoms which are very different in Z (e.g., Mn or Cl), but which are at different distances from the absorbing atom. This is more acute when dealing with Fourier peaks at greater distances. In bridged multinuclear centers, it is not always possible to unequivocally assign the Fourier peaks at >3 Å.

2. Distances are usually the most reliably determined structural parameters from EXAFS. But the range of data that can be collected, often-times due to practical reasons like the presence of the K-edge of another metal, limits the resolution of distance determinations to between 0.1 and 0.2 Å. Also it is difficult to determine whether a Fourier peak should be fit to one distance with a relatively large disorder parameter or to two distances, each having a small disorder parameter. Careful statistical analysis, taking into consideration the degrees of freedom in the fits, should precede any such analysis. The resolution in the distance Δr can be estimated from the relation that $\Delta r \Delta k \sim 1$.

3. Determination of coordination numbers or number of backscatterers is fraught with difficulties. The Debye–Waller factor is strongly correlated with the coordination number and one must have recourse to other information to narrow the range that is possible from curve-fitting analysis alone. It is useful to compare the spectra from the unknown complex to some known model complexes (assuming that there is evidence that the structure resembles that of the model complex) and then use Debye–Waller parameters obtained from the model complexes in the fits. This method works reasonably well, when the structure of the system being studied is well-modeled by inorganic complexes.

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