X-Ray Absorption Fine Structure (XAFS) Spectroscopy – A Review

ABHIJEET GAUR*1, B D SHRIVASTAVA1 and H L NIGAM2
1School of Studies in Physics, Vikram University, Ujjain 456010, India
2Department of Chemistry, University of Allahabad, Allahabad 211 002 (UP), India

(Received 01 March 2013; Revised 21 August 2013; Accepted 29 August 2013)

X-ray absorption spectroscopy (XAS) refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. The absorption of X-rays on the high energy side of absorption edges does not vary monotonically in condensed matter but has a complicated behavior which extends past the edge up to about ~1 keV. This non-monotonic variation has received the name of X-ray absorption fine structure (XAFS). The X-ray absorption fine structure is typically divided into two regimes: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). This review describes the basic phenomenon of XAFS, theory of EXAFS and the method of extracting structural parameters by EXAFS which relate to the local environment surrounding the absorbing atom. Also, it has been pointed out that XANES can be used to extract information about the oxidation state, three dimensional geometry, and coordination environment of elements under investigation. There are numerous examples of the applications of the XAFS in various fields in the literature. Some selected examples are cited here and discussed so as to give the reader a glimpse of the usefulness and versatility of the XAFS. The two types of EXAFS beamlines available at the synchrotron facilities have been described. The details of BL-8 dispersive EXAFS beamline at 2 GeV Indus-2 synchrotron source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India have been given. For the last fifty years research workers in India have been doing XAFS experiments on laboratory set-ups. Now, it is hoped that research workers from Indian laboratories will do experiments on synchrotrons. Hence, details regarding experiment and analysis of the XAFS data have been given in this review so that any one who wants to do research work in the field of XAFS may get necessary information at one place. This is important because the EXAFS beamlines at the Indus-2 synchrotron have become easily available to Indian workers which were not available until now.

Key Words : X-Ray Absorption Spectroscopy; Synchrotron; EXAFS; XANES; XAFS Beamlines; Data Analysis; FEFF; Application of XAFS; Copper Metal

1. X-rays

X-rays are electromagnetic waves in the wavelength range from ~25 Å to 0.025 Å, i.e., having wavelengths much shorter than visible light, but longer than high energy gamma rays. The conventional source of X-rays is X-ray tube, which can be sealed fixed target tube, rotating anode tube or demountable tube. In an X-ray tube, the electrons emitted from the cathode are accelerated towards the metal target anode by an accelerating voltage of typically 50-100 kV. The high energy electrons interact with the atoms in the metal target. Sometimes the electron comes very close to a nucleus in the target and is deviated by the electromagnetic interaction. In this process, which is called bremsstrahlung (braking radiation), the electron loses much energy and a photon (X-ray) is emitted. The energy of the emitted photon can take any value up to a maximum corresponding to the energy of the incident electron. The process can be thought as if the electron is emitting a series of photons with varying energies. These emitted photons

*For Correspondence: E-mail: abhijeetgaur9@gmail.com
are ‘continuous X-rays’. The high energy electron can also cause an electron close to the nucleus in a metal atom to be knocked out from its place. This vacancy is filled by an electron further out from the nucleus. The well defined difference in binding energy, characteristic of the material, is emitted as a mono-energetic photon. When detected, this X-ray photon gives rise to a characteristic X-ray line in the energy spectrum. Thus, the spectrum of the radiation emitted from an X-ray tube consists of characteristic spectrum of the target superimposed over the continuous spectrum. The wavelength of X-rays is well suited to study crystal structures and details of the human body. Because of the many varied properties of X-rays, they have been used in various applications in science and industry. X-rays are used a lot in medicine to the great benefit of mankind.

2. Synchrotron as X-ray Source

The modern and most intense source of X-rays is a synchrotron. The flux of X-radiation obtained from synchrotron sources are up to 10^10 larger than that obtained from X-ray tubes. In a synchrotron, the electrons are accelerated and are directed into storage ring which has auxiliary components such as bending magnets and insertion devices (undulators or wigglers). These supply the strong magnetic fields perpendicular to the electron beam which are needed to convert the high-energy electron energy into light or some other form of electromagnetic radiation. The electrons can be maintained for many hours in the storage ring. In a synchrotron storage ring, in which the electrons have more than 1 GeV energies, radiations are obtained in the X-ray region. The most important property of synchrotron radiation is its brightness. Apart from this, the broad spectral range, pulse time structure, natural collimation, high vacuum environment, high polarization, small source-spot size and stability make synchrotron radiation a unique and rather extraordinary source for a wide variety of science and technological experiments (Winick and Doniach, 1980). An important point which should be noted is that the synchrotron radiation consists of only continuous X-rays and no characteristic X-rays. The XAFS spectra obtained using synchrotron radiation are much more cleaner (very little noise) than those obtained from X-ray tubes (large noise). With these characteristics, the synchrotron radiation has become extremely useful for X-ray absorption spectroscopic work in the past four decades. In the present article, studies which can be carried out on X-ray absorption fine structure (XAFS) spectra using X-rays from synchrotrons have been reviewed.

3. X-rays Absorption

A monochromatic beam of X-rays of the energy E, which passes through a homogeneous sample of the thickness x, is attenuated (Fig. 1). In analogy to the Lambert-Beer law (Agarwal, 1989), this attenuation can be described by:

$$I(E) = I_0(E) e^{-\mu(E)x}$$

where I_0(E) and I(E) are the incident and transmitted X-ray intensities, and μ(E) is the linear absorption coefficient, which describes how strongly X-rays are absorbed as a function of X-ray energy E. Generally, μ(E) smoothly decreases as the energy increases (approximately as 1/E^3), i.e., the X-rays become more penetrating. At certain energies, the absorption increases drastically and gives rise to an absorption edge. Each such edge occurs when the energy of the incident photons is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state, i.e. to produce a photoelectron. Thus, the energies of the absorbed radiation at these edges correspond to the binding energies of electrons in the K, L_I, L_II and L_III etc, shells (1s_1/2, 2s_1/2, 2p_1/2 and 2p_3/2 orbitals (states)) of the absorbing elements. Accordingly, the K absorption edge arises from the electronic transitions from innermost 1s states (K

![Fig. 1: Schematic of an X-ray absorption measurement in transmission mode. After the x ray has traversed a distance x into the slab, the intensity has been reduced to I = I_0 e^{-\mu x}, where μ is the definition of the absorption coefficient (Rehr and Albers, 2000).](image-url)
level) to unoccupied states above the Fermi energy ($E_F$) level. Beyond the absorption edge the absorption coefficient decreases monotonically with increasing energy, until the next absorption edge is reached.

4. X-ray Absorption Spectroscopy – XANES and EXAFS

Although most of the absorption spectrum is quite smooth, oscillatory features called fine structure is found directly above an edge. This fine structure is intrinsically quantum mechanical phenomenon that is based on the X-ray photoelectric effect, in which an X-ray photon incident on an atom within a sample is absorbed and liberates an electron from an inner atomic orbital (e.g., 1s). The “photoelectron” wave scatters from the atoms around the X-ray absorbing atom, creating interferences between the outgoing and scattered parts of the photoelectron wave function. These quantum interference effects cause an energy-dependent variation in the X-ray absorption probability, which is proportional to the X-ray absorption coefficient, a measurable quantity. This fine structure contains a wealth of local structural information. When properly decoded these modulations provide information about the structure, atomic number, structural disorder, and thermal motions of neighboring atoms.

Traditionally, this fine structure is split into two energy regions. The first termed as X-ray absorption near edge structure (XANES), occurs in the region from the edge to approximately 40 eV above the edge, while the second termed as the extended X-ray absorption fine structure (EXAFS) extends from ~40 eV to 1000 eV above the edge. The reason for this division into the XANES and EXAFS regions is that the XANES region is theoretically difficult to describe, while the EXAFS region is relatively simple to interpret. XANES is sensitive to the treatment of interactions between the photoelectron and the core hole, while the effects of the core hole on the EXAFS are relatively weak. Quantitative analysis of EXAFS has been available since the 1970s and standard techniques have been developed to extract the parameters of interest. Quantitative XANES analysis has only been available for a few years and is not a widely used technique. (Kas 2009).

X-ray absorption spectroscopy (XAS) refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. XAS is the modulation of an atom’s X-ray absorption probability due to the chemical and physical state of the atom. Following the division of fine structure into the two energy regions, i.e., XANES and EXAFS, the X-ray absorption spectroscopy is also divided into two regimes: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS). The term “XAFS” is a broad one that comprises several different techniques: EXAFS (extended X-ray absorption fine structure); XANES (X-ray absorption near edge structure); NEXAFS (near edge XAFS); and SEXAFS (surface EXAFS). (Bunker 2010).

X-ray absorption fine structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. For this reason, XAFS is a very important probe of materials, since knowledge of local atomic structure, i.e., the species of atoms present and their locations, is essential to progress in many scientific fields: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology.

5. Absorption Edge and its Position

X-ray absorption edge is an arctangent curve (Richtmyer et al. 1934). The inflection point on this curve gives the position of the absorption edge. The energy of this point corresponds to the binding energy of the inner shell from which the electron has been ejected during the absorption process.

When the absorption edge is found to split in two or more components, the inflection point of the first rise in the absorption edge corresponds to the binding energy corresponding to that edge. In case the absorption edge is found to split in two components $K_1$ and $K_2$, the energy ($E_{K_1}$) of the inflection point on the $K_1$ edge corresponds to the binding energy $E_0$ or $E_K$ of the $K$ level.
The best method to determine the exact position of the inflection point is to compute the first derivative of the $\mu(E)$ versus $E$ curve. The first maximum on the first derivative curve gives the position of the inflection point and hence the position of the absorption edge. An alternative method is to compute the second derivative of the $\mu(E)$ versus $E$ curve. The first zero crossing point on this second derivative curve also gives the position of the absorption edge correctly. The second derivative spectrum is generally used whenever there is any difficulty in measuring the position of the edge from the first derivative spectra. The above procedure holds good even in those cases where the absorption edge is found to split in two or more components. For the K absorption edge, the position of the edge is written as $E_K$ in eV.

The determination of the position of the absorption edge can be illustrated by taking an example, say, of K-absorption edge of copper metal. Fig. 2(a) shows the Cu metal K absorption spectra ($\mu(E)$ vs. $E$ spectra). This figure also shows the pre-edge, XANES and EXAFS regions. Fig. 2(b) shows the small portion (i.e., the XANES region) of Fig. 2(a). The first derivative spectra of Fig. 2(b) is shown in Fig. 2(c), while the second derivative spectra is shown in Fig. 2(d). Some of the different terms defined above have been depicted in these figures and the reasons for their existence are discussed below (Kau et al. 1987).

The K absorption edge of Cu metal (LMA in Fig. 2(b)) is found to split in two components $K_1$ and $K_2$. The initial rise LM in the Cu metal K-edge (often called the $K_1$ edge) arises from the transitions from 1s states to unoccupied states having admixed 4s-4p-3d symmetry. The energy $E_{K1}$ of the inflection point of this initial rise, as determined from the first peak in the derivative spectra, corresponds to the Fermi energy $E_F$ (8980.5 eV). The second absorption rise MA (often called the $K_2$ edge) arises from the transitions to the Laporte-allowed states of nearly pure 4p symmetry. As the inflection point on $K_1$ locates the Fermi level $E_F$, above $E_F$ the s-p-d admixed states first acquire pure s symmetry just around M and finally pure 4p symmetry around the inflection point on $K_2$. The kink at M arises because the transition probability suddenly decreases for the pure s character of states at M and this causes a decrease of the absorption. The structure $K_2$ that ends peak A is assigned 1s $\rightarrow$ 4p transitions, and the region beyond A shows maxima of absorption, corresponding to the transitions 1s $\rightarrow$ np, n = 5, 6, 7, etc. The energy $E_A$ of this peak A can be called the principal absorption maximum, as determined from the second zero crossing in the derivative spectra. Because the curve between M and A is called the $K_2$ edge, the energy of the inflection point of this second rise, as determined from the second peak in the derivative spectra, is written as $E_{K2}$.

The difference between the energies $E_A$ and $E_{K1}$, i.e., $E_A - E_{K1}$ is called the edge-width.

There is no pre-absorption features in the Cu metal K absorption spectra. Such a feature is a characteristic of K absorption spectra of Cu(II) compounds and is attributed to the dipole forbidden, quadrupole allowed, 1s $\rightarrow$ 3d transition.

The value of $E_{K1}$ for Cu metal is 8980.5 eV (Deslattes et al. 2003). However, for EXAFS data analysis this value is generally taken as its theoretical value, i.e., 8979 eV.

6. Chemical Shift (Shift in the Position of the Absorption Edge)

It is an established fact that absorption edge shifts towards higher or lower energy side relative to metal edge, depending upon whether the absorbing atom bears positive or negative charge.

The shift of the X-ray absorption edge $i$ ($i = K, L, M$ ...) of an element in a compound with respect to that of the pure element is written as:

$$\Delta E_i = E_{i \text{ (compound)}} - E_{i \text{ (element)}} \quad (2)$$

In general, the shift “$E$ is positive (towards high energy) for cation and ranges usually from $\sim 1$ eV to $\sim 15$ eV. Thus, the chemical shift of the K-absorption edge in any sample can be written as

$$\Delta E_k = E_{k \text{ (sample)}} - E_{k \text{ (pure metal)}} \quad (3)$$

On compound formation usually charge flows from metal atom (cation) to the other atom of the
ligand (anion) due to redistribution of valence electrons. This results in the increase of binding energy of K electrons on account of increase in the effective nuclear charge. Consequently, the K absorption edge of the cation is shifted towards high energy side with respect to that in the pure metal. The shifts in the edge of the metal ion in the complex are primarily influenced by the oxidation state of the metal ion and are known to undergo a systematic shift towards higher energy with an increase in the oxidation state. By comparing the observed chemical shift in the sample under consideration with the earlier data on the edge-shift measurements in different oxidation states of a metal, the metal oxidation state in a sample can be assigned.
Agarwal and Verma (1970) suggested an empirical rule for the chemical shift: in general, the chemical shift is towards the high-energy side of the metal edge; it increases progressively with increase of the valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of a metal-metal bonding. The first part of the rule, namely the valence dependence of the shift, is well known and several workers have used this dependence to determine the valences of the absorbing ions in the compounds. Sapre and Mande (1972) tested this rule and found that the covalence suppresses the shift, not only for the cations but also for the anions and unless other factors intervene, the metal-metal bond results in large shift.

A quantitative correlation of chemical shift of the absorption edges is difficult because many parameters enter the argument. Assuming that the main factors are valence and effective charge of the absorbing atom empirical correlations have been attempted. Ghatikar et al. (1977, 1978) have surveyed considerable data on chemical shifts of different elements in a large number of compounds and proposed the following relations between the chemical shift $\Delta E$ and the effective ionic charge $q$: $\Delta E = c_1 + c_2 q$.

7. Extended X-ray Absorption Fine Structure (EXAFS)

The EXAFS process can be thought of as an in situ electron diffraction, in which the X-ray absorbing atom is the photoelectron source. When the kinetic energy of the ejected photoelectron is great enough to enable it to escape the bound state, it interacts with electrons in the bound states of other atoms within the local chemical environment surrounding the absorber. Energetically, the ‘continuum’ is up to several hundred electron volts (eV) above the absorption edge. Interactions between the ejected photoelectron and other electrons produce secondary sources of scattering and interference on return of the backscattering waves to the absorber. Interferences between outgoing scattering and incoming backscattering waves result in low frequency oscillations between ~50 and ~1000 eV above the absorption edge. These oscillations constitute EXAFS and are of interest as they contain structural and chemical information specific to the scattering atomic shells. An atomic shell is a group of atoms of the same species at the same distance from the absorbing atom. Qualitatively, the EXAFS oscillations are of higher frequency for long interatomic distances between the backscattering elements and the absorber, and of lower frequency for shorter interatomic distances. Quantitatively, the amplitudes of EXAFS oscillations can identify the type and number of backscattering atoms as well as the distribution of these atoms about a mean distance from the absorbing atom. Because a XAFS spectrum is taken over a range of increasing X-ray energies, single- and multiple-scattering events dominate in different portions of the spectrum. The higher energy portions of EXAFS spectra are dominated by single-scattering events within only some tenths of nm (5-6 Å) from the absorber, and contain information specific to the local structure surrounding the absorber. On the other hand, XANES spectra, being centered close to the absorption jump, are dominated by multiple-scattering events extending a few nm from the absorber. (Newville, 2004; Gates, 2006; Kelly et al. 2008)

XAFS can be measured either in transmission or fluorescence geometries. The geometry for Auger measurements is typically the same as for fluorescence. The absorption coefficient $\mu(E)$ in transmission is

$$\mu(E) x = \log(\frac{I_0}{I_t})$$

and in X-ray fluorescence (or Auger emission) is

$$\mu(E) x \propto \frac{I_f}{I_0}$$

where, $I_t$ and $I_0$ are the intensities of the transmitted and incident radiations respectively, $x$ is the thickness of the absorber and $I_f$ is the monitored intensity of a fluorescence line (or, again, electron emission) associated with the absorption process.

For EXAFS, we are interested in the oscillations well above the absorption edge, and define the EXAFS function $\chi(E)$, as

$$\chi(E) = \frac{I_f - I_0}{I_0}$$
\[ \chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)} \]  

(6)

where, \( \mu(E) \) is the measured absorption coefficient, \( \mu_0(E) \) is a smooth background function representing the absorption of an isolated atom, and \( \Delta \mu_0(E) \) is the measured jump in the absorption \( \mu(E) \) at the threshold energy \( E_0 \). It is common to convert the X-ray energy to \( k \), the wave number of the photo-electron, which has dimensions of 1/distance and is defined as

\[ k = \sqrt{\frac{2m(E - E_0)}{h^2}} = 0.263 \sqrt{(E - E_0)} \text{(in eV)} \]

\[ k \text{ (in Å}^{-1} \text{)} \]  

(7)

where, \( E_0 \) is the absorption edge energy and \( m \) is the electron mass. The primary quantity for EXAFS is then \( \chi(k) \), the oscillations as a function of photo-electron wave number, and \( \chi(k) \) is often referred to simply as “the EXAFS”.

### 8. EXAFS Equation

The observed EXAFS, \( \gamma(k) \), oscillations can be described by an equation popularly called the EXAFS equation. Though, several derivations of the EXAFS equation are available in literature, a simple derivation based on the one given by Newville (2004) is given here.

Fig. 3 shows the photoelectric effect in which an X-ray is absorbed by a core-level electron with binding energy \( E_0 \), and a photo-electron with wave number \( k \) is created and propagates away from the atom. The photo-electron can scatter from the electrons of this neighboring atom and the scattered photo-electron can return to the absorbing atom (Fig. 4). Since the absorption coefficient depends on whether there is an available electronic state (that is whether there is an electron at the location of the atom and at the appropriate energy and momentum), the presence of the photo-electron scattered back from the neighboring atom alters the absorption coefficient: This is the origin of XAFS.

Since X-ray absorption is a transition between two quantum states (from an initial state with an X-ray, a core electron, and no photo-electron to a final state with no X-ray, a core hole, and a photo-electron), the \( \mu(E) \) can be described with Fermi’s golden rule:

\[ \mu(E) \propto \langle i | H | f \rangle \]  

(8)

where, \( \langle i \rangle \) represents the initial state (an X-ray, a core electron, and no photo-electron), \( | f \rangle \) is the final state (no X-ray, a core hole, and a photo-electron), and \( H \) is the interaction term. If we expand \( | f \rangle \) into two pieces, one that is the “bare atom” portion \( | f_0 \rangle \), and one that is the effect of the neighboring atom \( | \Delta f \rangle \) as

![Fig. 3: Cartoon of X-ray absorption through the photoelectric process. When an X-ray has the energy of a tightly bound core electron level, \( E_0 \), the probability of absorption has a sharp rise. In the absorption process, the tightly bound core-level is destroyed, and a photo-electron is created. The photoelectron travels as a wave with wave number proportional to \( (E-E_0) \). (Newville, 2004) ![Fig. 4: XAFS occurs because the photo-electron can scatter from a neighboring atom. The scattered photo-electron can return to the absorbing atom, modulating the amplitude of the photo-electron wave-function at the absorbing atom. This in turn modulates the absorption coefficient \( \mu(E) \), causing the EXAFS. (Newville, 2004)
$|f\rangle = |f_0\rangle + |\Delta f\rangle$  
\[ \mu_0 = \left|i \langle H | f_0 \rangle \right|^2 \]

\( \mu_0 \) can be assigned as the “bare atom absorption”, which depends only on the absorbing atom - as if the neighboring atom wasn’t even there and the fine-structure \( \chi \) can be written as \( \chi(E) \propto \langle i | H | \Delta f \rangle \). This can be worked out (at least roughly) as an integral equation fairly easily. The interaction term \( H \) represents the process of changing between two energy and momentum states. Hence, interaction term needed is the p-A term, where A is the quantized vector potential. Here, this reduces to a term that is proportional to $e^{ikr}$. The initial state is a tightly bound core-level, which can be approximated by delta function \( \delta(r) \) (a 1s level for atomic number \( Z \) extends to around \( a_0/Z \), where \( a_0 \) is the Bohr radius of ~ 0.529 Å). The change in final state is just the wave-function of the scattered photo-electron, \( \psi_{\text{scatt}}(r) \). Putting all these terms together, a simple expression for the EXAFS is obtained:

\[ \chi(E) \propto \int dr \delta(r) e^{ikr} \psi_{\text{scatt}}(r) = \psi_{\text{scatt}}(0) \]  

(10)

In words, this simply states the physical picture shown in Fig. 4: the EXAFS \( \chi(E) \) is proportional to the amplitude of the scattered photo-electron at the absorbing atom.

One can describe the outgoing photo-electron wave-function \( \psi(k,r) \) travelling as a spherical wave:

\[ \psi(k,r) = \frac{e^{ikr}}{kr} \]  

(11)

travelling a distance \( R \) to the neighbouring atom, then scattering from a neighbor atom, and travelling as a spherical wave a distance \( R \) back to the absorbing atom. All these factors are simply multiplied together to get:

\[ \chi(k) \propto \psi_{\text{scatt}}(k,r = 0) = \frac{2f(k)}{kR^2} \]

\[ e^{i[2kR+\delta(k)]} + e^{-i[2kR+\delta(k)]} \]  

(12)

where, \( f(k) \) is called backscattering amplitude and \( \delta(k) \) is the phase factor, both of which depend on the \( Z \) of the neighbouring atom, as shown in Fig. 5. These scattering factors make EXAFS sensitive to the atomic species of the neighbouring atom. The real part of this complex function is

\[ \chi(k) = \frac{f(k)}{kR^2} \sin[2kR +\delta(k)] \]  

(13)

(a) Number of Atomic Pairs, Thermal and Static Disorder

The treatment here was for one pair of absorbing atom and scattering atom, but for a real measurement we’ll average over millions of atom pairs. Even for neighbouring atoms of the same type, the thermal and static disorder in the bond distances will give a range of distances that will affect the EXAFS. As a first approximation, this disorder will change the EXAFS equation to

Fig. 5: Functional forms for \( f(k) \) (top) and \( \delta(k) \) (bottom) for O, Fe, and Pb showing the dependence of these terms on atomic number \( Z \). The variations in functional form allow \( Z \) to be determined (±5 or so) from analysis of the EXAFS. (Newville, 2004)
\[ \chi(k) = \frac{N}{kR^2} f(k) e^{-2k^2\sigma^2} \sin[2kR + \delta(k)] \]  
(14)

### (b) Number of Neighbouring Atoms

Real systems usually have more than one type of neighboring atom around a particular absorbing atom. This is easily accommodated in the EXAFS equation by summing the contributions from each scattering atom type (or coordination shell, as it is often called - the terms coordination sphere and scattering path are also used),

\[ \chi(k) = \sum_j \frac{N_j}{kR_j^2} f_j(k) e^{-2k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)] \]  
(15)

where, \( j \) represents the individual coordination shell of identical atoms at approximately the same distance from the central atom.

### (c) Core-hole Lifetime

One of the most important approximations made above has to be corrected. To account for both the inelastic scattering and the core-hole lifetime, a damped spherical wave

\[ \psi(k,r) = \frac{e^{ikr} e^{-2\tau/\lambda(k)}}{kr} \]  
(16)

can be used as the photo-electron wave-function where \( \lambda \) is the mean-free-path of the photo-electron (that is, how far it typically travels before scattering inelastically and before the core hole is filled). The mean-free-path is typically 5 to 30 Å and has a significant but fairly universal dependence on \( k \), shown in Fig. 6. Including the \( \lambda(k) \), the EXAFS equation becomes:

\[ \chi(k) = \sum_j \frac{N_j}{kR_j^2} f_j(k)e^{-2k^2\sigma_j^2}e^{-2R_j/\lambda(k)} \sin[2kR_j + \delta_j(k)] \]  
(17)

### (d) Amplitude Reduction Factor

A constant reduction factor \( S_0^2 \) has to be added after the derivation is done. \( S_0^2 \) is an overlap factor which includes the intrinsic losses due to inelastic effects in the equation, while, \( \lambda(k) \) includes the extrinsic losses due to inelastic effects. \( S_0^2 \) is typically ~0.9. Hence, the final EXAFS equation becomes

\[ \chi(k) = \sum_j \frac{N_j}{kR_j^2} S_0^2 f_j(k)e^{-2k^2\sigma_j^2}e^{-2R_j/\lambda(k)} \sin[2kR_j + \delta_j(k)] \]  
(18)

### (e) Two Parts of the Equation

This EXAFS equation consists of two main parts.

1. The first part is the amplitude \( A_j(k) \) given by:

\[ A_j(k) = \frac{N_j}{kR_j^2} S_0^2 f_j(k)e^{-2k^2\sigma_j^2}e^{-2R_j/\lambda(k)} \]  
(19)

and contains the coordination number (\( N \)) and disorder (\( \sigma_j \)), which is the fluctuation in \( R_j \) due to thermal motion or structural disorder.

2. The second part is the sine function which accounts for the oscillations seen in the EXAFS, i.e., \( \sin[2kR_j + \delta_j(k)] \) where \( \delta_j(k) \) is the phase shift.

Fig. 6: The photo-electron mean-free-path for XAFS \( \lambda(k) \), representing how far the photo-electron can travel and still participate in the XAFS. This term includes both the inelastic scattering of the photo-electron, and the effect of the finite lifetime of the core-hole. (Newville, 2004)
(f) Phase Shift

The argument inside the sine function can be thought of as being related to the time for the electron to travel to the neighboring atom and return. In Fig. 7, 2kR would represent this time if the kinetic electron were constant across the entire R-range. However, it is altered by an amount, \( \delta_{\text{scatterer}} \) (i.e., \( 2 \delta_s \)) resulting in part from the increase in velocity of the photoelectron as it approaches the neighbouring atom and then slows again as it returns. A similar phase shift, \( 2 \delta_{\text{absorber}} \) (i.e., \( 2 \delta_a \)) results from the absorber atom itself. The velocity increases as it approaches an atom because as shown in Fig. 7, the potential that an electron experiences decreases to more negative values as the electron is attracted more by the nucleus, and hence its kinetic energy increases. For convenience, this atomic potential is “squared off” in Fig. 7. Thus, the phase factor is

\[
\delta_{f}(k) = 2 \delta_{\text{absorber}}(k) + \delta_{\text{scatterer}}(k)
\]  

(20)

From the EXAFS equation, we can draw a few physical conclusions about EXAFS. First, because of the \( \lambda(k) \) term and the \( R^{-2} \) term, EXAFS is seen to be an inherently local probe, not able to see much further than 5 or so Angstroms from the absorbing atom. Second, the EXAFS oscillations will consist of different frequencies that correspond to the different distances for each coordination shell. This will lead us to use Fourier transforms in the analysis.

(g) Fourier Transformation of \( \chi(k) \)

Although EXAFS equation provides a complete description of the EXAFS oscillations, it is not a particularly convenient form for visualizing the information content of an EXAFS spectrum. As with NMR spectroscopy, Fourier transformation can be used to decompose a frequency-space signal into its different constituent frequencies.

The Fourier transformation of \( \chi(k) \) is defined by

\[
\text{FT}(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} k^n \chi(k)e^{i2kR} dk
\]  

(21)

In Fig. 2(a) the EXAFS spectrum of Cu metal is given as an example. The Fourier transformation of this spectrum is given in Fig. 2(e). For EXAFS, the canonical variables are \( k \) (in Å\(^{-1}\)) and \( R \) (in Å), and the Fourier transform (FT) of an EXAFS spectrum gives a pseudo-radial distribution function. It is pseudo in that the FT amplitude cannot be related directly to electron density around the absorber due to the \( f(k) \) factor and the damping factors in eqn. (18), and because the distance found from the Fourier transform is about 0.2-0.5Å shorter than the actual distance due to the energy dependence of the phase factors in the sine function (eqn. (18)). The FT is a useful way of judging qualitatively what shells may be present in a system and for comparing a fit to the data. However, it is important to remember that Fourier transforms are subject to several potential artefacts. In many cases, multiple shells of scatterers do not give rise to multiple peaks in the FT (Riggs et
Similarly, interference between two different peaks in the FT may give rise to a spurious third peak. The latter results from the fact that the FT of an EXAFS spectrum is actually a complex number, with both real and imaginary components. Typically, however, only the modulus of the FT is plotted. This is useful for visualizing the major contributions to the EXAFS spectrum, but should never be used for quantitative data analysis.

8.1 Theoretical Model

In order to extract the distances and coordination numbers from the experimental EXAFS data, we need to have accurate values for the scattering amplitude and phase-shifts \( f(k) \) and \( \delta(k) \). The need for accurate scattering amplitude and phase-shifts has been a crucial issue in the field of EXAFS. In the earliest EXAFS analyses, these factors could only be determined accurately from experimental spectra in which the near-neighbour distances and species were known (generally from measurements of crystals with well known structures). Such experimental standards can be quite accurate, but are generally restricted to first neighbour shell. Until the early 1990’s, their use was quite common. In the past decade or so, calculations of \( f(k) \) and \( \delta(k) \) have become more accurate and readily available, and use of experimental standards in EXAFS analysis is now somewhat rare. Calculated scattering factors such as those from the programs FEFF, GNXAS, and EXCURVE have been shown numerous times to be accurate enough to be used in real analysis, and in some cases are more accurate than experimentally derived scattering factors. In addition, the calculated factors are not restricted to the first shell and can account for multiple-scattering of the photo-electron.

The general approach for determining the average coordination structure around the absorber atom from EXAFS data is to generate a theoretical model for the sample and calculate the theoretical EXAFS spectrum for that model using a computer program like FEFF. Currently, the software program Artemis comes with the freely available program FEFF6L (Zabinsky et al. 1995) for computing theoretical EXAFS models. Artemis can adjust the structural parameters in the EXAFS equation until a least-squares fit is obtained between the theoretical (modelled) and experimental EXAFS spectra. The model is adjusted as needed (e.g., with different atom types) until the best possible fit is obtained between theoretical and experimental spectra. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations \( N, S_0^2, \sigma^2 \) or the phase of the oscillations \( \Delta E_0 \) and \( \Delta R \) (Kelly et al. 2008).

8.2 EXAFS Data Analysis and Determination of Structural Parameters

In practice, some of the parameters in the EXAFS equation are calculated \textit{ab initio}, while others are found by fitting the model to experiment. For example, the effective scattering phases and amplitudes are generally calculated using a multiple scattering code such as FEFF (which stands for \( f_{\text{eff}} \), the effective scattering amplitude), while a variety of other parameters are used as fitting variables. Of particular interest are the half path lengths \( R \), and the path degeneracy \( N \) since for single scattering paths these parameters are directly related to structural properties (i.e. bond length and coordination number).

The standard procedures used for preprocessing of data, and the extraction of structural parameters by fitting to the EXAFS equation can be described in brief as follows (Kelly et al. 2008). First the oscillatory fine structure \( \chi(k) \) is extracted from the data by subtracting a smooth background function \( \mu_0 \). The most prevalent method for obtaining \( \mu_0 \) is to fit the curve to a cubic or other spline function which is constrained to have low curvature (Newville et al., 1993). The oscillatory EXAFS signal \( \chi(k) \) is then Fourier transformed to real (R) space which gives an amplitude that is akin to a radial distribution function, with contributions from longer scattering paths peaking at higher R value. Phase correction gives a \( |\chi(R)| \) which is akin to the radial distribution function. The peaks in the Fourier transform, appear at approximately the different shell distances. In order to obtain more accurate values for the parameters, or to obtain additional parameters, a model consisting of a few important terms from the EXAFS equation...
is fit to the data. Fitting of the model (EXAFS equation) to the data is performed in R space using a limited range of the Fourier transformed data, in order to isolate the contribution from a relatively small number of short scattering paths. Most EXAFS analysis programs use the least squares algorithm for fitting the model to the data. In practice, $f_j(k)$, $\delta_j$, and $\lambda_j$ are calculated while a number of the other parameters (i.e. $R_j$, $N_j$, etc.) may be allowed to vary during fitting (Kas, 2009). Thus, the parameters that are determined from the fitting of the theoretical model to the experimental EXAFS data are $N$, $S_0^2$, $\sigma^2$, $\Delta E_0$ and $\Delta R$.

9. Multiple Scattering

In the physical model presented above, the X-ray excited photoelectron travels from the absorbing atom to the scattering atom and back. However, far more complex scattering pathways are also possible. For example (see Fig. 8), the photoelectron may travel from the first scattering atom (S1) to a second (S2) and even a third (S3) before returning to the absorbing atom. Each scattering interaction defines an angle, e.g., $\theta_i$ that determines the intensity, and hence the significance, of that multiple-scattering pathway. The scattering of an electron by an atom is strongly focused in the forward direction ($\theta \approx 180^\circ$) and falls off very rapidly for $\theta < 150^\circ$. Multiple scattering depends on the simultaneous positions of three or more atoms, i.e., on the distances and angles between the atoms. This means that multiple scattering can, at least in principle, provide information about the three-dimensional structure around the absorbing site. For this reason, there has been a great deal of interest in developing methods to use multiple scattering in XAS analyses, and thus to avoid the limitation that EXAFS provides only radial structure information. Two obstacles confront attempts to use multiple-scattering to determine molecular geometry. The first is computational: since hundreds, and even thousands of multiple scattering pathways can contribute to the observed XAS, the theoretical description of multiple scattering can be computationally formidable. This makes it difficult to perform effective refinements of complete multiple scattering. A more fundamental problem is the limited information content of XAS spectra (Penner-Hahn, 1999).

Fig. 8: Selected single and multiple scattering pathways for a tetraatomic system. (Top) Geometry of the absorber (A) relative to the three scattering atoms. The positions can be specified by three distances and two angles (for a planar system). (Bottom) Scattering pathways for outgoing and backscattered photoelectron (indicated by arrows). Left column is for the nearest neighbor, $S_1$; Middle for $S_2$; and Right for $S_3$. For $S_1$, only the single scattering pathway is shown. For $S_2$, both double and triple scattering pathways are also indicated. For $S_3$, only two of the possible double scattering pathways are shown. Note that, for a non-planar system, several additional distances and angles are required to completely specify the scattering pathways. In general, all possible multiple scattering pathways (of which only a small fraction are shown) will contribute to the observed EXAFS, each with oscillations of slightly different frequency. (Penner-Hahn, 1999)

10. X-ray Absorption Near Edge Structure (XANES)

The physical principles that govern EXAFS apply equally in the XANES region. However, at low kinetic energy the photoelectron mean-free-path increases dramatically. Similarly, the $\exp(-k^2)$ dependence of the Debye-Waller factor means that this damping factor is negligible in the XANES region. These effects combine to render the XANES region sensitive to a wide range of absorber-scatterer distances, as compared to the (relatively) simple short-range treatment that can be used for most EXAFS. This is, in principle, an advantage since it provides the possibility of extracting three-dimensional structure information from XANES spectra. However, this also makes theoretical simulations of XANES spectra extremely difficult.
Although much progress has recently been made in the theoretical modelling of XANES, most of the applications of this energy region remain qualitative. On the low energy side of the absorption edge one frequently observes several weak transitions. In contrast with the electron-scattering model that is used to describe the EXAFS and the other XANES features, these low energy transitions arise from bound state transitions. For the first transition series metals, bound state transitions include both 1s-3d and 1s-4p transitions.

XANES is a much larger signal than EXAFS and can be obtained at lower concentrations, and at less than perfect sample conditions. The processes responsible for near-edge absorption structure are related to ejection of core electrons into ‘continuum states’, and involve single- and multiple-scattering events off the first atomic shell surrounding the absorber, as well as multiple-scattering events from more distant atomic shells. XANES is considerably harder to fully interpret than EXAFS. The interpretation of XANES is complicated by the fact that there is not a simple analytic (or even physical) description of XANES. The main difficulty is that the EXAFS equation breaks down at low-k, due to the 1/k term and the increase in the mean-free-path at very low-k. Precise and accurate calculations of all spectral features are still difficult, time-consuming, and not always reliable. This situation is improving, but at this point, quantitative analyses of XANES using ab initio calculations are very rare. Recent advances in multiple scattering formalisms have, however, shown that XANES spectra can be treated like EXAFS spectra to gain element-specific information on bonding environment, such as coordination number and interatomic distances.

Though the lack of a simple analytic expression complicates XANES interpretation, XANES can be described qualitatively (and nearly quantitatively) in terms of coordination chemistry, molecular orbitals, band-structure and multiple-scattering.

These chemical and physical interpretations are all related, of course. There is much chemical information obtainable from the XANES region, notably formal valence (very difficult to experimentally determine in a nondestructive way) and coordination environment. Clearly, the edge position and shape is sensitive to formal valence state, ligand type, and coordination environment. Hence, edge features (position and shape) reflect oxidation states and coordination environments in the vicinity of the absorber. As already pointed out in section 5, an important and common application of XANES is to use the shift of the edge position to determine the valence state. This technique is now routinely applied to discern coordination and oxidation states of metals in compounds and complexes (Berry et al. 2006). Decomposition of the spectral components can differentiate between different site symmetries and assist in quantifying oxidation states.

The heights and positions of pre-edge peaks can also be reliably used to empirically determine oxidation states and coordination chemistry. These approaches of assigning formal valence state based on edge features and as a fingerprinting technique make XANES somewhat easier to crudely interpret than EXAFS, even if a complete physical understanding of all spectral features is not available.

11. Speciation Using XANES

The species, speciation and speciation analysis are defined as follows:

**Chemical Species**: Specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.

**Speciation**: Distribution of an element amongst defined chemical species in a system.

**Speciation Analysis**: Analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample.

By taking standards of well-defined chemical species, analysis of XANES can be used to determine metal speciation, i.e., determination of the chemical forms along with the relative quantity of the different species in a given sample.

Though, the commonly used methods for speciation are principal component analysis (PCA)
with target transformation method (TT) and linear combination fitting (LCF), several other approaches for the analysis of XANES data have also been developed, which can be listed as follows: residual phase analysis (RPA), multiple dataset (MDS) fit method, derivative spectra methods and normalized difference absorption edge analysis (NDAES). Gaur et al. (2009, 2012 a, 2013 a, b) have studied the different methods of speciation to make a comparative study of these methods of speciation and to discuss their relative merits.

12. XAS and Crystallography

Despite the tremendous advances that have taken place in spectroscopic methods for structure elucidation, X-ray crystallography remains the method of choice for definitive determination of the structure of a sample. Unfortunately, X-ray crystallography cannot always be used. Some samples simply cannot be crystallized in diffraction quality crystals, despite the best efforts of skilled experimenters. In other cases, crystals may be available but the structural questions of interest involve solution structure. For example, it may be necessary to determine whether a molecule remains structurally intact in solution. Finally, there are a variety of situations, involving for example crystallographic disorder, in which X-ray crystallography is unable to provide a complete structural description. In all of these cases, XAS can provide unique structural information.

Levina et al. (2005) have given reasons as to why it is important to use XAFS, even if the XRD structure is known for a sample. Some examples of why it is important to use XAFS, even if the XRD structure is known, are outlined below:

(i) Usually, metal-ligand bond lengths are an order of magnitude more accurate and precise (0.01-0.02 Å) than those obtained using XRD (typically ~0.1Å ), except for the few XRD structures that are determined to a resolution of ~1Å.

(ii) Crystallization procedures for XRD structures can sometimes result in active sites that are not relevant due to coordination of ligands from the crystallizing medium, e.g., small molecules/ions used as buffers or to control ionic strength.

(iii) XRD structures performed on crystals where a coordinating molecule is diffused into a preformed crystal are subject to crystal packing forces that can lead to coordination geometries different from those present in the relevant solution structures.

(iv) XRD determinations are often very susceptible to photoreduction at the metal center during structural determinations, even at liquid nitrogen temperatures, when highly focused synchrotron X-ray beams are used. This often leads to changes in the structural details of the active site.

(v) There is an advantage in having XRD data for calibrating theoretical parameters for XAFS calculations.

(vi) When the XRD structure is unknown but those of related samples are known, the XRD structure can be used to build a suitable starting model of the active site of the sample with an unknown structure.

Further, X-ray absorption spectroscopy offers an effective tool for investigating many vital problems of coordination chemistry such as valency of the metal ion, symmetry of the coordination sphere, nature of the metal-ligand bond, etc., when many other methods such as X-ray diffraction (particularly when the samples are solutions or are amorphous) and magnetic measurements (where the results are often ambiguous) fail to provide a full and satisfactory solution. (Shrivastava and Nigam, 1973; Nigam 1981)

13. XAS and XPS

X-ray photoemission describes nearly the same process as X-ray absorption, i.e. the excitation of a core electron from the ground state to some excited state. The difference between the physical processes involved in X-ray photoemission spectroscopy (XPS) and XAS are twofold. First, in XPS the initial ground state valence electrons experience the full potential of an unscreened core hole, whereas in XAS the core electron can be excited into an efficient screening orbital so that the perturbation on the remaining
ground state electrons is small. Second, in XPS the various components of the spectrum are broadened by multiplet structure rather than exhibiting specific multiplets, because virtually all of the many final-state multiplets can be reached. XAS, by virtue of the dipole selection rule, is, on the other hand, quite selective in multiplet structure. Only a limited number of states are accessible and therefore become visible as separate structures in the spectrum (Van der Laan et al. 1986).

XAS measures the variation in the absorption with respect to the excitation energy, while XPS measures the variation in the kinetic energy of the emitted electron at a constant excitation energy. This immediately gives rise to the observation that one can combine XAS and XPS and measure the XPS spectra as a function of the X-ray excitation energy, for example, while scanning through an absorption edge. XAS is complementary to XPS as in the two processes, the various interactions and hybridization enter in different ways. (De Groot, 2005).

Several examples can be found in the literature where XAS and XPS have been combined to obtain complementary information. As an example, Hutson et al. (2007) have used XAS and XPS to obtain information about the speciation and binding of mercury on two commercially available brominated activated carbons. The results are compared with similar analysis of a conventional (non-halogenated) and chlorinated activated carbon. Both the XAS and XPS results indicate that the mercury, though introduced as elemental vapor, is consistently bound on the carbon in the oxidized form. In another example, Park et al., (2008) have investigated the functional groups concerned with the biosorption of Cr(VI). Core electron XPS and XAS were used to investigate the surface and bulk characteristics of the biomaterial during the biosorption of Cr(VI) under various conditions. XPS spectra indicated that the Cr(VI) bound to the biomass was completely reduced to Cr(III) at tested various conditions. XANES and EXAFS spectra of the Cr-laden biomass were very similar to those of Cr(III)-acetate, which means that the Cr bound to the biomass during Cr(VI) reduction had an octahedral geometrical arrangement.

14. Advantages and Limitations of XAS

The principal advantage of XAS as a structural probe is that it is a local structure probe. In ideal circumstances, EXAFS data can be analyzed to determine the absorber-scatterer distance with an accuracy of ca. 0.02 Å and perhaps even better. Coordination numbers can be determined with an accuracy of ca. 25% and scatterer identity can typically be defined to the nearest row of the periodic table.

XANES analysis have the ability to provide oxidation state and spin-state information that can be difficult or impossible to extract from crystallographic measurements. In comparison with other spectroscopic methods, XAS has the decided advantage that it is always detectable, without the need for specific spin states or isotopic substitution, and that it is element specific. Every element has at least one unique absorption edge. The universal detectability of XAS is, of course, a mixed blessing since it means that XAS is a bulk technique sensitive to all of the forms of an element that are present in a sample. If the element of interest occurs in multiple environments, only the average structure can be determined.

Any discussion of the advantages of XAS would be incomplete without a summary of the limitations of the technique (Penner-Hahn, 1999). Ultimately, all of these involve different limitations in experimental resolution. Several of these are widely recognized. EXAFS provides only limited chemical resolution - scattering atoms that differ by two or three in atomic number (e.g. C, O, N, and F) typically cannot be resolved. EXAFS, at least as described thus far, provides no angular resolution. It is thus not possible to learn anything directly about geometry. There are some possibilities for introducing angular resolution but this remains a limitation in most XAS studies. Finally, the finite k range of the EXAFS spectrum limits the bond-length resolution of the method. Two scattering shells can only be resolved if they differ sufficiently in frequency to cause a detectable change in the EXAFS amplitude, due to the interference between the two different EXAFS
components. For small differences in distance, the interference simply introduces an exponential damping factor. This is indistinguishable from an increase in the Debye-Waller term in EXAFS eqn (18). For perfect data, two shells of the same scatterer should become resolvable when the difference in their distances, dR, is large enough to cause a ‘beat’ in the EXAFS amplitude. This occurs for \( \frac{\partial R}{\partial k} \geq \frac{\pi}{2k_{\text{max}}} \), where, \( k_{\text{max}} \) is the maximum value of k for which a signal can be measured.

Notwithstanding the dire warnings (above) regarding the limitations of XAS, the fact remains that XAS has the ability to provide unique information about local structure of the sample under investigation.

15. Books and Review Articles on XAFS

Several books and various review articles have been published which give comprehensive, detailed and exhaustive description of the different aspects of XAFS since 1975, when the modern practice in XAFS spectroscopy was started by Prof. E. A. Stern and his group. The important books which will be helpful to those who wish to start work on this branch of X-ray absorption spectroscopy are by Nigam (1981), Bonnelle and Mande (1982), Koningsberger and Prins (1988), Agarwal (1989), Meisel (1989), Stohr (1992), Crozier (1997), Joshi, Shrivastava and Deshpande (1998) and Bunker (2010). The important review articles are by Lee et al. (1981), Stern and Heald (1983), Riggs et al. (1995), Penner-Hahn (1999, 2005), Rehr and Albers (2000), Modrow (2004), Wende (2004), Rehr and Ankudinov (2005), Levina et al. (2005), Kelly, Hesterberg, and Ravel (2008), Manceau and Matynia (2010) and Frenkel (2012).

### Proceedings of the Fourteen International Conferences on XAFS

Apart from the important books and review articles mentioned above, excellent source of information on the work done in the field of XAFS spectroscopy are the proceedings of the fourteen International Conferences on XAFS which are all published in the form of books or in the form of special issues of research journals. These fourteen conferences are listed below along with the references.

<table>
<thead>
<tr>
<th>Conf. no.</th>
<th>Year</th>
<th>Place</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAFS 1</td>
<td>1981</td>
<td>Daresbury (UK)</td>
<td></td>
</tr>
<tr>
<td>XAFS 2</td>
<td>1982</td>
<td>Frascati (Italy)</td>
<td>Bianconi et al. (1983)</td>
</tr>
<tr>
<td>XAFS 12</td>
<td>2003</td>
<td>Malmo (Sweden)</td>
<td>Proc. XAFS-12 conf. (2005), Physica Scripta 17</td>
</tr>
</tbody>
</table>
16. Laboratory X-ray Absorption Spectroscopic Set-ups

The laboratory X-ray absorption spectroscopic set-ups which have been in use, since long, specially in many Indian laboratories, employ low power (0.5kW-3kW) X-ray tubes, Cauchois-type curved mica crystal spectrographs and photographic method of registration of spectra. After obtaining a number of spectrograms, the analog and digital spectral records are obtained with the help of a microphotometer. These analog and digital spectral records are used to be analyzed manually. Several workers (Agarwal, 1989; Koningsberger and Prins, 1988; Stern and Heald, 1983) have been using such photographic technique and reporting the results about X-ray absorption edge energies, edge structures, near edge structures and extended fine structures. The data has generally been analyzed qualitatively and empirically to yield useful information about molecular structure. The data has also been analyzed through some established relations to yield information about valency, effective nuclear charge, coordination type, average bond length etc. The data has hardly been analyzed using Fourier transform and fitting procedures which have now become standard methods of EXAFS data analysis. Recently, Joshi et al. (2009) and Johari et al. (2011) have shown that the EXAFS data obtained from photographic method of registration of spectra can be analyzed by employing Fourier transformation and fitting procedures. It has been shown that the structural information obtained for the first two shells is comparable with that obtained from synchrotron X-ray spectroscopic set-ups.

17. XAFS beamlines at Synchrotrons

XAFS spectroscopy has developed hand in hand with the growth of synchrotron radiation research. The first useful synchrotron X-ray facilities were developed around 1970, about the time of Stern, Sayers, and Lytle’s modern synthesis of EXAFS spectra (Stern, 1974; Stern et al. 1975; Lytle et al. 1975). XAFS requires an X-ray beam of finely tunable energy; although it is possible to do limited experiments with a laboratory X-ray source, most experiments benefit enormously from the availability of synchrotron radiation. As a consequence, nearly all modern XAFS experiments are performed at Synchrotron Radiation Sources (SRSs).

In the laboratory set-ups one uses X-ray spectrometers for recording the X-ray absorption spectra. In synchrotron set-ups one uses beamlines. The description of the beamline is given in brief as follows:

Synchrotron beamline refers to the instrumentation that carries beams of synchrotron radiation to an experimental end station, which uses the radiation produced by the bending magnets and insertion devices in the storage ring of a synchrotron. At a large synchrotron facility there are many beamlines, each optimized for a particular field of research. The differences will depend on the type of insertion device, the beam conditioning equipment and the experimental end station. A typical beamline is 25 to 100 m long from the storage ring to the end station.

The beamline elements are located in radiation shielding enclosures, called hutch, which are the size of a small room (cabin). A typical beamline consists of two hutch, an optical hutch for the beam conditioning elements and an experimental hutch, which houses the experiment. Between hutch, the beam travels in a transport tube. Entrance to the hutch is forbidden when the beam shutter is open and radiation can enter the hutch. This is enforced by the use of elaborate safety systems, which make sure that no one is inside the hutch when the radiation is turned on. The safety system will also shut down the radiation beam if the door to the hutch is accidentally opened when the beam is on.

Elements that are used in beamlines by experimenters for conditioning the radiation beam between the storage ring and the end station include the following:

(i) Windows – They are made of beryllium and transmit almost the entire beam, but protect the vacuum within the storage ring.

(ii) Slits – They control the physical width of the beam and its angular spread
(iii) Focusing mirrors – There are one or more mirrors, which may be flat, bent-flat, or toroidal, which help to collimate (focus) the beam.

(iv) Monochromators – They are devices based on diffraction by crystals which select particular wavelengths.

(v) Spacing tubes – They provide proper space between optical elements and shield any scattered radiation, maintaining vacuum.

(vi) Sample stages – The sample under study is mounted and manipulated on the sample stages. The temperature and pressure etc. can be varied.

(vii) Radiation detectors – They are used for measuring the radiation before and after the sample.

Devices along the beamline which absorb significant power from the beam are actively cooled by water, or liquid nitrogen. The entire length of a beamline is normally kept under ultra high vacuum conditions.

The list of synchrotron facilities having XAFS beamlines across the world are listed below in Table 1 for ready reference to any user.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Asia &amp; Oceania</th>
<th>S.No.</th>
<th>Europe</th>
<th>S.No.</th>
<th>America</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Australian Synchrotron Victoria, Australia</td>
<td>1</td>
<td>ANKA Karlsruhe, Germany</td>
<td>1</td>
<td>ALS Berkeley, CA, USA</td>
</tr>
<tr>
<td>2</td>
<td>BSRF Beijing, China</td>
<td>2</td>
<td>BESSY II Berlin, Germany</td>
<td>2</td>
<td>APS Argonne, IL, USA</td>
</tr>
<tr>
<td>3</td>
<td>INDUS-2 Indore, India</td>
<td>3</td>
<td>DELSY Dubna, Russia</td>
<td>3</td>
<td>CLS Saskatoon, Canada</td>
</tr>
<tr>
<td>4</td>
<td>NSRF Hefei, China</td>
<td>4</td>
<td>Diamond United Kingdom</td>
<td>4</td>
<td>LNLS Campinas, Brazil</td>
</tr>
<tr>
<td>5</td>
<td>NSRRC Hsinshu, Taiwan, ROC</td>
<td>5</td>
<td>ELETTRA Trieste, Italy</td>
<td>5</td>
<td>NSLS Brookhaven, NY, USA</td>
</tr>
<tr>
<td>6</td>
<td>PAL Pohang, Korea</td>
<td>6</td>
<td>ESRF Grenoble, France</td>
<td>6</td>
<td>SSRL Stanford, CA, USA</td>
</tr>
<tr>
<td>7</td>
<td>Photon Factory KEK Tsukuba, Japan</td>
<td>7</td>
<td>HASYLAB Hamburg, Germany</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>SAGA Tosu, Japan</td>
<td>8</td>
<td>IS-800 Kiev, Ukraine</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>SLRI, Siam Nakhon, Thailand</td>
<td>9</td>
<td>KIPT Kharkov, Ukraine</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>SPring-8 Hyogo pref, Japan</td>
<td>10</td>
<td>KSRS Moscow, Russia</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>SSLS Singapore</td>
<td>11</td>
<td>MAXLAB Lund, Sweden</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>SSRC Novosibirsk, Russia</td>
<td>12</td>
<td>SLS Villingen, Switzerland</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>13</td>
<td>SOLEIL Saint-Aubin, France</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>14</td>
<td>TK Moscow, Zelenograd, Russia</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>
and its radius of curvature, the crystal reflects a particular central energy ($E_0$) with a certain bandwidth ($\Delta E$) and this spatially dispersed polychromatic radiation is then focused at the sample position ($S_3$). The transmitted radiation from the sample is then detected by a position-sensitive detector (D). Thus, the energy dispersed absorption spectra of the sample over the whole band width ($\Delta E$) around the central energy ($E_0$) is recorded on the detector simultaneously. The beam-line covers the photon energy range of 5 keV to 20 keV by a bent Si (111) crystal having 2$d$ value equal to 6.2709Å. The beam-line provides band widths of the order of 0.3 keV, 1 keV and 2 keV at photon energies of 5 keV, 10 keV and 20 keV respectively. The average resolution at the detector is $\sim$1 eV per channel (Das et al. 1999).

Before doing any EXAFS measurements on this beamline, calibration of the particular setting of the polychromator has to be done. Gaur et al. (2011 a) have outlined a method which is recommended to be used for finding the dispersion and then for calibrating the experimental spectra. This method involves taking the position of the first maximum of the derivative spectra of the two standards, for determining their edge positions and energies.

At this beamline, the incident intensity obtained at 2.0 GeV beam energy and 50-60 mA beam current is such that the CCD detectors get saturated even in a few microseconds when $I_0$ is measured. Hence, the typical time to record a spectrum can be kept only a few micro-seconds. If the time is increased, the detectors get saturated. Hence, a large number of spectra should be taken keeping the time as few microseconds and then sum them up. This increases the signal to noise ratio and good spectrum is obtained. Hence, it is advised that while using this beamline, a large number of spectra should be recorded for a sample and then data should be summed up. Gaur et al. (2013 c) have compared the performance of this beamline with other standard beamlines of the world. Using this beamline Gaur et al. (2011 b, 2012 b) have studied EXAFS of copper complexes.

The main advantages of dispersive EXAFS setup are the focusing optics, short acquisition time (few ms) and great stability during the measurements due to the absence of any mechanical movement. Thus, in situ and time-resolved experiments can be easily performed on such kind of set-ups (Lamberti, 2003; Smolentsev, 2009).

(b) DCM Beamline

The line sketch of a typical DCM beamline is given in Fig. 10. A double silicon crystal Si(111) is generally used as monochromator (Fixed-exit double-crystal monochromator) which selects a particular energy from the incident synchrotron beam. The monochromatic beam is made incident on the sample and the intensity of the transmitted beam passing through the sample or that of the fluorescence beam emerging out of the sample is recorded along with the incident intensity at each energy by scanning the DCM. EXAFS can be measured in transmission, fluorescence, and electron yield modes. Detectors that can be used are ionization chambers, Peltier-cooled Si(Li) detectors, multi-element germanium diode detectors.
array fluorescence detectors, Lytle fluorescence and electron yield detectors. Three ionization chambers are used for measurements in transmission mode. These are filled with optimal He, Ne, Ar, Kr gas mixture. The ionization chambers signals are amplified by picoamperomers and digitalized by a voltage to frequency converters and finally read by the counters of the data collection PC. Harmonics are rejected by using the cutoff of the reflectivity of the platinum mirror and by detuning the second crystal of the monochromator by 30% of the maximum. This type of beamline having double crystal monochromator (DCM) is being commissioned at Indus-2, RRCAT, Indore and is named as BL-9.

18. Preparation of Samples for XAFS Measurements

(a) Sample Preparation

In transmission mode, to produce a high-quality absorption signal, the sample should be uniform and the thickness should be optimized such that the partial absorption due to the absorber atoms is approximately one absorption length (\( \Delta \mu x = 1 \)) and the total absorption from all atoms in the sample is less than 2.5 absorption lengths (\( \mu x = 2.5 \)) (Heald, 1988). The partial absorption is easily measured as it corresponds to the step height of the absorption edge in transmission mode. An incident X-ray intensity of \( 10^7 \) is needed to measure a sample with a total absorption length of 2.5 and this X-ray intensity is mostly available in second-generation synchrotrons. An example of the calculation of the amount of the sample required to be spread uniformly in 1cm\(^2\) area and to be used in transmission mode is given below.

(b) X-ray Absorption Calculation

The mass absorption coefficient (\( \mu_p \)) by a sample is the sum of absorptions by each constituent element:

\[
\mu_p = \sum_i f_i \mu_{pi},
\]

where, \( f_i \) is the mass fraction of element \( i \) having mass absorption coefficient \( \mu_{pi} \). Energy dependent mass absorption coefficients for the elements are tabulated in handbooks (Elam et al. 2002) and in XAS utility programs such as Hephaestus (comes with IFEFFIT package). The mass absorption coefficient \( \mu_p \) can be either the total mass absorption coefficient (\( \mu_{p,t} \)) or the step mass absorption coefficient \( \Delta \mu_p \), across an absorption edge.

As an example, a calculation for partial absorption and total absorption of copper complex \([\text{Cu}_{2}(2,2\text{-bipy})(\text{NA})_{2}]\text{(ClO}_4\text{)}_{2}\cdot\text{H}_2\text{O}\) which has molecular formula \( \text{C}_{16}\text{H}_{13}\text{ClCuN}_3\text{O}_{6.5} \) is given in Table 2. This calculation is for making a tablet of this complex by mixing it with cellulose acetate which can be used as absorption screen for recording X-ray absorption spectra at the K-edge of copper. The tablet can be made in a palletizer using a die of diameter 12 mm with a cross-sectional area of 1.13 cm\(^2\) and a sample capacity of approximately 100 mg of cellulose acetate. The calculations are for yielding an edge step of 1.0 across the Cu K-edge (8979 eV) for the sample and having a total absorption length less than 2.5.

The mass fraction of each element in the complex is calculated from their mole fractions and atomic weights. Because the tabulated mass absorption coefficients do not include EXAFS structure, it is reasonable to choose energies several electron volts above and below the absorption edge of the absorber element (Cu in this example). Note in Table 2 that Cu shows a sharp increase in the mass absorption coefficient across the edge energy at 8979 eV, whereas the cross sections of C, H, Cl, N and O remain essentially unchanged. The Cu concentration (\( \rho x, \text{ g cm}^{-2} \)) yielding a given edge step (S) (unitless absorption) is calculated as follows:

\[
\rho x = S / \Delta \mu_p.
\]

Multiplying \( S / \Delta \mu_p \) by the cross-sectional area of the sample holder (1.13 cm\(^2\) in this example) gives the mass of Cu in the diluted sample (converted to milligrams), which is then converted to the mass of the complex through its mass fraction of Cu. For the final Cu concentration in this example, the total sample mass includes the masses of the complex and cellulose acetate.
The particles of the sample in the absorption screen should be considerably smaller than one absorption length of material at the energy of interest. To prepare fine particles, samples should be grounded by hand in a porcelain or agate (aluminium oxide) mortar and pestle. While preparing the absorption screens care should be taken that the areal density of material presented to the beam is uniform and specially the thin regions (gaps, pin holes) are minimized. Two methods are generally used to prepare absorption screens. In one of the methods used for preparing absorption screens, the fine particles of the sample are uniformly coated on a commercial adhesive tape like Scotch Magic transparent tape. Multiple layers are used to obtain the desired absorption and also to cover gaps between particles. In the second method for preparing the absorption screens the sample is uniformly mixed with a filler/binder material like cellulose acetate or boron nitride (BN). The well mixed sample is then made into a pellet using a press (pelletizer).

(c) Preparation of Absorption Screens

The particles of the sample in the absorption screen should be considerably smaller than one absorption length of material at the energy of interest. To prepare fine particles, samples should be grounded by hand in a porcelain or agate (aluminium oxide) mortar and pestle.

While preparing the absorption screens care should be taken that the areal density of material presented to the beam is uniform and specially the thin regions (gaps, pin holes) are minimized. Two methods are generally used to prepare absorption screens. In one of the methods used for preparing absorption screens, the fine particles of the sample are uniformly coated on a commercial adhesive tape like Scotch Magic transparent tape. Multiple layers are used to obtain the desired absorption and also to cover gaps between particles. In the second method for preparing the absorption screens the sample is uniformly mixed with a filler/binder material like cellulose acetate or boron nitride (BN). The well mixed sample is then made into a pellet using a press (pelletizer).

**Table 2**: Example calculation to estimate the dilution of copper complex Cu₄(2,2'-bipy)(NA)₂(ClO₄)₂H₂O which has molecular formula C₁₆H₁₃ClCuN₃O₆.5 in cellulose acetate yielding an edge step of 1.0 across the Cu K-edge (8979 eV) for a tablet making die of diameter 12 mm with a cross-sectional area of 1.16 cm² and a sample capacity of approximately 100 mg of cellulose acetate, the dominant sample component. In this example, the dilution yielding unit edge step would give a total post-edge absorption (1.50) i.e. not exceeding the desired maximum of 2.5 for a transmission sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic weight</th>
<th>Mass fraction in sample</th>
<th>Mass absorption coefficient (µ / ρ) †</th>
<th>Pre-edge (8979 eV) cm² g⁻¹</th>
<th>Pre-edge (8979 eV) cm² g⁻¹</th>
<th>Δ (m/r) cm² g⁻¹</th>
<th>Concent. for unit edge (g cm⁻²)</th>
<th>Amount in sample holders* mg</th>
<th>Mineral amount* mg</th>
<th>Mineral conc. ¶ mg g⁻¹</th>
<th>Post-edge absorption (per element) #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>63.54</td>
<td>0.144</td>
<td>38.3</td>
<td>278.3</td>
<td>240</td>
<td>0.00416</td>
<td>4.70</td>
<td>32.64</td>
<td>326</td>
<td>0.05</td>
<td>1.160</td>
</tr>
<tr>
<td>O</td>
<td>16.00</td>
<td>0.217</td>
<td>8.2</td>
<td>8.2</td>
<td>0.05</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>C</td>
<td>12.01</td>
<td>0.435</td>
<td>3.2</td>
<td>3.2</td>
<td>0.04</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>H</td>
<td>1.00</td>
<td>0.03</td>
<td>0.38</td>
<td>0.38</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>N</td>
<td>14</td>
<td>0.09</td>
<td>5.3</td>
<td>5.3</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>35.46</td>
<td>0.08</td>
<td>77.7</td>
<td>77.7</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>442.16 (mol. wt.)</td>
<td>Total post-edge absorption</td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Mass absorption coefficient (µ / ρ) below and above the Cu K-edge at 8979 eV obtained from X-ray absorption tables in Hephaestus for each element and the change in l/ρ for Cu across the edge.

‡ Calculated for Cu as 1.0/ Δ(µ / ρ), where 1.0 = the target edge step.

*Cu amount (column 8) in sample (mg) = Cu concentration (g cm⁻²) x sample cross-sectional area (1.16 cm²) x 1000 mg g⁻¹; mineral amount (column 9) = Cu amount (column 8)/mass fraction of Cu (column 3).

¶ Concentration of mineral (mg/g sample) after diluting in cellulose acetate = mass of mineral (13.46 mg)/mass sample (1.0 = 0.01346 g mineral + 0.98654 g cellulose acetate).

19. XAFS Data Processing

A number of capable analysis packages are available from a multiple of sources. Most are free/open source; a few are sold as commercial packages; others such as recent FEFF9 programs are licensed (FEFF6 is available without restrictions) for a modest fee. The open source program IFEFFIT is a flexible data reduction/fitting engine that can be used directly in command line mode, or called by external programs. Athena, Artemis and SixPack have nice integrated graphical interfaces that use IFEFFIT for most of the numerical calculations. A variety of other programs such as GNXAS and DLEXCURV, have various unique capabilities. These software packages are open-source programs that can be downloaded from
a link on the International XAFS Society (www.i-x-s.org) or XAFS.ORG (www.xafs.org) websites for use on various computer platforms. It is safe to say that there is no one single program package that offers all the features of the others, and there is no reason not to use the best tool for a particular job. It is probably advisable for most people to use one of the standard analysis packages, however.

For the analysis of the EXAFS data presented in this review, software packages Athena and Artemis have been used. These programs include AUTOBK (Newville et al. 1993) for background removal, FEFF6L (Zabinsky et al. 1995) for generation of the theoretical EXAFS models, and FEFFIT (Newville et al. 1995) for parameter optimization of the model. An advanced version of these softwares, i.e., ‘Demeter’ has recently become available and can be downloaded freely from https://github.com/bruceravel/demeter.

The following pre-processing procedures are required for refining the EXAFS data recorded at the beamline before it can be used for analysis

(a) rebinning measured data points
(b) removal of data points that are clearly in error (degitching)
(c) trimming the absorption spectra to the usable energy region (truncation)
(d) changing the energy scale to align several scans
(e) averaging several scans to produce a high quality spectrum for analysis.

After this pre-processing, the raw data is processed by following the steps outlined below (Kelly et al. 2008)

a) The measured intensities are converted to raw μ(E) data, possibly correcting systematic measurement errors such as self-absorption effects and detector dead-time.
b) The smooth pre-edge function is subtracted from μ(E) to get rid of any instrumental background and absorption from other edges.

c) Similarly, a post-edge function is plotted to determine edge step.
d) The threshold energy E₀ is identified, typically as the energy of the maximum of the first derivative of μ(E).
e) μ(E) is normalized to go from 0 to 1.
f) The XAFS χ(k) data is isolated.
g) The XAFS χ(k) is k-weighted and Fourier transformed into R-space

The steps are shown graphically in Fig. 11 by taking the case of K absorption spectrum of copper metal foil.

(i) Raw μ(E) data

Fig. 11(i) shows the raw X-ray absorption data of copper metal foil, recorded at the EXAFS beamline at ELETTRA. The absorption coefficient above the absorption edge is defined as

\[ \mu_{total} = \mu_{atomic}[1 + \chi] \] (24)

with \( \mu_{atomic} \) representing the atomic background. \( \chi \) forms the oscillatory part of the total absorption, describing the scattering of the outgoing electron against the neighbouring atoms. It is called the EXAFS function. Since the oscillatory part is created by the interference between the outgoing and backscattered waves, \( \gamma \) contains information about the local structure around the absorber atom.

(ii) Edge Energy - \( E_0 \)

The edge energy reference parameter, \( E_0 \), used for processing EXAFS data is not defined relative to the electron configuration within the solid (i.e., the Fermi level or any other level), but rather it is a parameter that is used to align the experimental spectrum to the theoretically calculated spectrum. A systematic definition of \( E_0 \) for all EXAFS spectra from the same adsorption edge is desirable since a shift in \( E_0 \) is determined in the fit of theoretical spectra to the experimental spectra. If all data sets have the same
In this case, one variable can be used to model all data sets, rather than using a separate variable for each data set. The inflection point, i.e., the maximum in the first derivative of the absorption edge, is generally considered as a systematic choice (Kelly et al. 2008). Hence, the edge position is typically chosen at the inflection point with the help of the XANES and first derivative XANES $\mu(E)$ spectra as illustrated in Fig. 11 (ii) and (iii), respectively.

The value of $E_0$ is generally taken as 8979.0 eV though the experimental value 8980.5 eV (Deslattes et al. 2003) is also sometimes preferred.

(iii) Pre-Edge Subtraction and Determination of Edge Step

Before $\mu_{\text{atomic}}$ can be determined, the pre-edge (X-ray absorption before the actual absorption edge occurs) has to be subtracted (Fig. 11(iv)). The pre-edge is normally approximated by a modified Victoreen \[ \mu_{\text{pre-edge}}(E) = C E^3 - D E^4 \] and calculated by extrapolation of the pre-edge region in the data. Similarly, a linear or quadratic function is regressed to the post-edge region (Fig. 11(iv)). These lines are extrapolated to the absorption edge, $E_0$, and the difference in absorption between these projected lines at $E_0$ is called the edge step.

(iv) Post-edge Background Removal

The atomic background ($\mu_{\text{atomic}}$) after the absorption edge has to be determined (Fig. 11(v)), normally using a cubic spline:

\[
\sum_{j=1}^{\text{NPTS}} \frac{(\mu_j - B C K_j)^2}{e^{-wE_1}} \leq SM
\]  

The cubic spline consists of four parameters that define the spline function: SM (smoothing parameters), W (weighting factor) and the start and end energy that determine the number of points (Koningsberger et al. 2000). The more data points available, the better the spline will be defined. The background is optimized using several criteria, of which the most important is not to remove any of the oscillating information from our data.

(v) Normalizing $\mu(E)$

Before $\gamma(k)$ can be obtained, the total absorption as obtained from experiment has to be normalized per absorber atom. Generally, spectra are normalized by division of the absorption data by the edge-step at 50 eV after the absorption edge (Fig. 11(vi)). The normalized K absorption spectra of copper metal is shown in Fig. 11(vii). Normalization is done by subtracting a regressed line determined by the pre-edge region from the entire spectra and dividing the measured spectra by the absorption step height at $E_0$. The step height determines the amplitude of the EXAFS oscillations and is therefore correlated to the EXAFS parameters such as the amplitude reduction factor ($S_0^2$), and the coordination number (N). That is, the step height, $S_0^2$, and N are all components of one multiplicative amplitude term in the EXAFS equation (eqn. 18).

(vi) Extraction of $\chi(k)$

The extraction of $\chi(k)$ from the experimentally obtained $\mu_{\text{total}}$ (Fig. 11(i)) follows several consecutive steps, that are visualized in Fig. 11. As defined in eqn. (24) $\chi$ can be obtained once the atomic absorption is known, by calculating

\[
\chi = \frac{\mu_{\text{total}} - \mu_{\text{atomic}}}{\mu_{\text{atomic}}} 
\]  

The value of the edge energy is used to calculate $k(\text{Å}^{-1})$ as given by the following equation.

\[
k = \sqrt{\frac{2m(E - E_0)}{h^2}} = 0.263\sqrt{(E - E_0)(\text{eV})} \]  

(in Å$^{-1}$)  

$\chi(k)$ is calculated according to eqn. (27) and is shown in Fig. 11(viii).

Hence, the pre-edge, post-edge, and resulting step height should always be checked before the $\chi(k)$ spectrum is further processed. Normalized XANES spectra can be used in EXAFS analysis to visually check the alignment of the spectra and to look for spectral changes between successive scans from the same sample.
The details of the different steps for extraction of the oscillatory part, i.e., \( \chi(k) \) vs. \( k \) data from the raw experimental \( \mu(E) \) vs. \( E \) data of an X-ray absorption spectrum are given above and are shown in Fig. 11. All these steps have been carried out using the computer software *Athena*. The Figs. 11(i)-(ix) presented here are those which are the outputs of *Athena*. A brief description of these figures is given below to summarize the procedure.

(1) Fig. 11(i) shows the raw experimental XAFS data, i.e., \( \mu(E) \) vs. \( E \) curve, obtained from \( \ln(I_0/I_t) \), where \( I_0 \) is the incident X-ray intensity and \( I_t \) is the transmitted intensity recorded by the ion chambers.

(2) The edge position \( E_0 \) has been typically chosen at the inflection point (marker); (Fig. 11(ii)).

(3) The edge position, as defined above, is determined as the first maximum in the derivative spectra. (Fig. 11(iii)).

(4) Fig. 11(iv) shows the pre-edge and post-edge lines.

(5) Fig. 11(v) shows the post-edge background curve. This atomic background (\( \mu_{\text{atomic}} \)) after the absorption edge has to be determined normally using a cubic spline (eqn. 25).

(6) The difference between the pre-edge and post-edge projected curves at \( E_0 \) determines the edge-step \( \Delta \mu_0 \). This is shown in Fig. 11(vi).

(7) Normalized \( \mu(E) \) spectrum is produced by subtracting the pre-edge line from the entire data spectrum and then dividing the spectrum by the step height. In the normalized spectrum, the pre-edge region lies along zero absorption and the edge step is 1 (Fig. 11(vii)).

(8) The \( \chi(k) \) can be obtained from the experimentally obtained \( \mu(E) \) using eqn. 27. The EXAFS \( \chi(k) \) vs. \( k \) data data is shown in Fig. 11 (viii).

(9) Fig. 11(ix) shows EXAFS \( k^1 \chi(k) \) vs. \( k \) data, obtained by multiplying the data in Fig. 11(viii) by \( k^1 \). The primary choice of the power of the weighting should be to give a constant amplitude of the weighted data over the range of the data to be transformed.

### (viii) Background Function

The EXAFS signal is defined as the normalized oscillatory part of the absorption coefficient above an absorption edge. To process the EXAFS signal, the step-like background of the absorption edge itself is removed. The background function is constructed from splines that are connected with knots. A spline is a polynomial of \( n \)th order, where order of 1, 2, or 3 correspond to a linear \( (y = Ax) \), quadratic \( (y = Ax + Bx^2) \), or cubic \( (y = Ax + Bx^2 + Cx^3) \) splines. In *Athena*, the algorithm AUTOBK uses the information content in the low \( R \) region of the spectrum to construct the background function. Information theory is used to define the transfer of information from wavenumber \( k \) to radial distance \( R \) through a Fourier transform (eq. 21). In this approach, the background function is constructed from third order (cubic) splines.

Information theory is used to constrain the background function to Fourier components that are longer in wavelength than that in the EXAFS spectrum by setting a maximum frequency component in \( R \) (called “\( R_{\text{bkg}} \)”), below which contributing Fourier components are considered to be part of the background. In the AUTOBK algorithm, the data range and the value for \( R_{\text{bkg}} \) determine the number of splines as given by \((2R_{\text{bkg}} \Delta k)/\pi\). In general, \( R_{\text{bkg}} \) is about one-half the first nearest neighbor distance. This value for \( R_{\text{bkg}} \) will allow all frequencies up to one-half the first shell distance to be removed by the background. (Kelly et al. 2008).

Fig. 12 shows the background (bkg) function obtained by varying the value of \( R_{\text{bkg}} \) in the K absorption spectrum of copper metal recorded at beamline 11.1 at Elettra, Italy. In Figs. 12 (i), (ii), (iii) and (iv), \( R_{\text{bkg}} \) has been kept as 0.5, 1, 1.5 and 2, respectively. It has been found that optimal background removal (\( R_{\text{bkg}} = 1.0 \) Å) maximizes the intensity of the first-shell peak while minimizing the amplitudes of peaks at shorter radial distances in the Fourier transform. Also, it can be seen that with \( R_{\text{bkg}} \)
Fig. 11: (Pl. see caption on p. 946)
values of 1.5 and 2 Å, the background follows the oscillatory part of the absorption coefficient above the absorption edge. Hence, we have taken \( R_{\text{bkg}} = 1 \) for further analysis of the spectrum.

20. Fourier Transformation of EXAFS Spectrum

(a) Fourier Transformation

The Fourier transformation of \( \chi(k) \) has already been defined by eq. (21). Any signal that is a sum of sine waves can be Fourier transformed to separate each frequency component in distance \( R \), i.e., a Fourier transform separates a signal into its Fourier components. Each Fourier component is defined by an amplitude and phase. The Fourier transform is a complex function containing both real and imaginary parts. The magnitude of the Fourier transform is an envelope of the real and imaginary parts of the Fourier transform.

For example, an infinite sine wave \( (k = -\infty \text{ to } +\infty) \) with a phase of 2k, which has only a single component and infinite data range, is Fourier transformed to an infinitely high and infinitely thin...
peak (a delta function) at $R = 1.0 \, \text{Å}$. The factor of 2 is divided out in the Fourier transform of the infinite sine wave, so that the peak corresponds to $R$ of one instead of two.

The Fourier transformed spectrum becomes harder to interpret with a limited data range, as in a measured EXAFS spectrum. However, any number of unique sine-wave phases can be combined and then separated by using a Fourier transform as long as the difference in the phases is greater than the spatial resolution of the spectra.

The information content of the EXAFS spectrum can be described by a sum of sine waves. Each sine wave is characterized by an amplitude and phase that depend on the distance between the absorber atom and the coordinating atoms and the type of coordinating atoms. The magnitude of the Fourier transform of an EXAFS spectrum contains peaks in $R$ that are related to the interatomic distances. All of the coordinating atoms that are at approximately the same radial distance from the absorber atom (a coordination shell) contribute to one peak in the magnitude of the Fourier transform. In EXAFS fitting analysis, theoretical models are optimized to the data using both the real and imaginary parts of the Fourier transform. This method allows a specific range of phases, corresponding to a specific range of distances about the absorber atom, to be isolated from the other signals in the data.

The magnitude of the Fourier transform is like a radial distribution function (RDF) of the atoms about the absorber atom because there is usually a peak corresponding to the first shell of atoms and the

**Fig. 12:** K absorption spectrum of copper metal recorded at beamline 11.1 at Elettra, Italy showing background (bkg) function obtained by varying the value of $R_{\text{bkg}}$. In (i), (ii), (iii) and (iv) the $R_{\text{bkg}}$ has been kept as 0.5, 1, 1.5 and 2, respectively. $R_{\text{bkg}} = 1$ has been used in further analysis.
R value for the peak is related to the bond length of the first shell. In fact, the magnitude of the EXAFS Fourier transform is not a RDF, for the several reasons. Actually, the magnitude of the Fourier transform of the EXAFS data is a complicated signal that depends only in part on the RDF. (Kelly et al. 2008).

The Fourier transform (FT) of the EXAFS signal is written as $\text{FT}[\chi(k)k^{kw}]$ indicating that the EXAFS signal written $\chi(k)$ has been multiplied by a k weighting of $k^{kw}$. The units of the Fourier transformed spectrum are $\text{Å}^{-1-kw}$. The Fourier transform of the EXAFS signal is a function of $R$ and can also be written as $\tilde{\chi}(R)$, where the tilde indicates that a Fourier transform has been applied.

(b) Information in Fourier Transformed Spectrum

Information theory is used to correlate the amount of information in the original EXAFS spectrum to the information in Fourier transform spectrum as determined from the Nyquist theorem

$$N_{\text{idp}} = \frac{2}{\pi} \Delta k \Delta R + 1$$

(28)

where, $N_{\text{idp}}$ is the number of independent points, $\Delta k$ is the Fourier transformed data range and $\Delta R$ is the region used in EXAFS data analysis. In general, a robust fitting model uses much fewer variables than $N_{\text{idp}}$. Keeping the number of variables less than $N_{\text{idp}}$ is recommended because the information contained within the EXAFS signal is not ideally packed. A useful goal in EXAFS data analysis is to have twice as many independent points as variables in the fitting model. (Kelly et al. 2008)

(c) Different Parts of a Fourier Transform

Fig. 13(i) shows EXAFS $k^2 \chi(k)$ vs. k data for copper metal. The real and imaginary parts and the magnitude of the Fourier transform of the copper metal K-edge EXAFS data are shown in Fig. 13(ii), (iii) and (iv), respectively. Fig. 13(v) shows the mirror image of the magnitude of the Fourier transform to illustrate that the magnitude is an envelope function of the real and imaginary parts.

The back Fourier transformed $\chi$ produces a $\chi(q)$ spectrum. Both q and k are measures of wavenumber in units of $\text{Å}^{-1}$. The back Fourier transform is useful for determining components from the original $\chi(k)$ spectrum that contribute to an R range in the Fourier-transformed spectrum. The back Fourier transform is shown with the original copper metal K-edge $\chi(k)$ spectrum in Fig. 13(vi). Differences in these spectra illustrate the effect of the initial Fourier transform window shown in fig. 13(i) and Fourier filtering of the high frequency noise. (Kelly et al. 2008).

(d) Window Functions Used for Fourier Transform

Many types of window functions can be used to process EXAFS data, including the commonly used Hanning and Kaiser-Bessel functions. The windows are defined by the same basic parameters: $k_{\text{min}}$ and $k_{\text{max}}$ to specify the beginning and ending k values of the window, and $dk$, to specify the width of the transition region. The value of $k_{\text{max}}$ is a convenient way to limit the Fourier transform to the region of the spectra to be used in the analysis. The Hanning window shows the transition for a dk value of 2Å$^{-1}$; values of 1Å$^{-1}$ or 2Å$^{-1}$ are typical. The Kaiser-Bessel window gradually increases from zero to one and then back to zero over the entire data range. The slope is controlled by the value of dk with typical values of 3 or 4 Å$^{-1}$. (Kelly et al. 2008)

(e) k Weights Used for Fourier Transform

The amplitude of EXAFS oscillations diminishes with increasing energy above the absorption edge. Therefore, EXAFS spectra are usually multiplied by k raised to the power of 1, 2, or 3 before the Fourier transform is performed. The power of k is called the k weight (kw). By increasing the k weight, the data at higher k are given relatively more importance, and the Fourier transform will have larger amplitude for the Fourier components that have a larger contribution at higher k values.
Fig. 13: Relationship between the different parts of the Fourier transform of an EXAFS spectrum associated with copper metal K-edge in CuO given in Fig 2.14. (i) Original $k^2 \chi(k)$ EXAFS data and the Fourier transform Hanning window, (ii) Real part of the Fourier transform, (iii) Imaginary part of the Fourier transform, (iv) Magnitude of the Fourier transform, (v) Illustration of the relationship between the real (red line) and imaginary (green line) parts and the magnitude (blue line) of the Fourier transform. The magnitude of the Fourier transform is like an envelope function of the real and imaginary parts and (vi) Back Fourier transform real part of $\chi(q)$ (red line) of the EXAFS signal is compared to the original $k^2 \chi(k)$ signal (blue line) to illustrate the effects of the original Fourier transform window function and of high frequency filtering (smoothing by limiting the $R$ range in the back transform).
Processing Fourier transforms of EXAFS data using $k$ weights of 1, 2, and 3 is useful for distinguishing between the types of atoms in the first and second shell.

(f) Usable EXAFS Data range from Fourier Transforms

A desirable effect of extending the $k$ range is increased spatial resolution of the Fourier transform signal from neighboring shells of atoms. A Fourier transform with the limited data range from 2 to 7 Å$^{-1}$ is not sufficient to resolve the two neighboring peaks. Increasing the $k$ range of the Fourier-transformed spectra increases the resolution of the spectra but does not preferentially allow the shells of atoms at greater radial distances to be resolved. All shells of atoms about the absorbing atom contribute to the EXAFS $\chi(k)$ spectra starting at $k = 0$. In principle, the amount of information within a given $\Delta R$ range and a given $\Delta k$ range are independent; that is, there is the same amount of information in a spectrum from 1 to 3 Å as there is from 3 to 5 Å. Both of these data ranges have a $\Delta R$ range of 2 Å with a $\Delta k$ range of 10 Å$^{-1}$ (e.g., $k = 2-12$ Å$^{-1}$), such that the information content as given by the Nyquist theorem (eqn. (27)) is the same. (Kelly et al. 2008)

21. Analysis of EXAFS Data Using Artemis

(a) Generating Theoretical Models

The distance found in Fourier transform is about 0.2 Å-0.5 Å shorter than the actual distance due to energy dependence of the phase factors in sine function (Koningsberger et al. 2000) of the EXAFS equation (eq. 18). Hence, to extract the information about the various parameters that can be determined from EXAFS data, the data has to be compared with accurately known “standard”, i.e., either theoretical model or experimental reference (Rehr et al. 1991). Generally, theoretical models are preferred over experimental references specially because computer programs for calculation of theoretical models are easily available.

The theoretical models can be generated using FEFF program as provided in the software Artemis. FEFF is the program that calculates the details of the scattering processes from a cluster of atoms. The theoretical models are fitted to the experimental EXAFS data using IFEFFIT (Zabinsky et al. 1995; Newville, 2001).

The general approach for determining the average coordination structure around the absorber atom from EXAFS data is to build a structural model for the chemical species being identified, and calculate the theoretical EXAFS spectrum for that model using the FEFF program. Programs such as Artemis adjust the structural parameters in the EXAFS equation until a least-squares fit is obtained between the theoretical (modeled) and experimental EXAFS spectra. The model is adjusted as needed (e.g., with different atom types) until the best possible fit is obtained between theoretical and experimental spectra.

(b) Description of FEFF

For generating theoretical model, FEFF requires an initial guess as the starting point for the placement of atoms about the absorber atom in the sample. The initial guess can be in the form of a known crystal structure, or user-defined list of x, y, z coordinates for a cluster of atoms. The use of crystal structures provides a reliable method for producing well-spaced atomic potentials needed for theoretical EXAFS computations, so this approach is used extensively to fit EXAFS data for both crystalline and non-crystalline samples. The program Artemis has a special interface called “Atoms” that converts crystal structure information into a cluster of atoms and provides a list of atom positions in x, y, z coordinates for use in FEFF computations. The Atoms interface allows the user to define a crystal structure by specifying the space group, unit cell dimensions, and the fractional positions of the atoms within the unit cell. Additional information needed includes the core atom type, the cluster size, and the X-ray absorption edge. (Kelly et al. 2008)

The Atoms interface also inserts a user defined identifier tag (e.g., N1_1 and N2_2 to distinguish nitrogen atoms in different shells), which is intended to make the list easier to read and interpret. FEFF
creates muffin tin potentials about the position of the atoms (Zabinsky et al. 1995). The radius of these potentials is defined by the placement of the coordinating atoms. Because the potentials are restricted in size by the coordinating atom, it is important to calculate the theoretical EXAFS signal from a cluster that has a radius R that is larger than the largest coordinating atom distance used to model the experimental spectrum.

(c) EXAFS Fitting Parameters

All photoelectron scattering configurations that start at the absorber atom, go to one or more neighboring atoms, and then return to the absorber atom contribute to the EXAFS signal. These configurations are called scattering paths. Single-scattering paths are from one shell of atoms. The degeneracy of a single-scattering path is the coordination number of that shell. The degeneracy of a multiple scattering path is the number of equivalent paths.

Once a path has been selected for possible inclusion in a structural model, mathematical expressions for the EXAFS parameters (eqn. 18) are defined. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations (N, S_{0}, \sigma) or the phase of the oscillations (\Delta E, \Delta R). There are many approaches that can be used to constrain the EXAFS fitting parameters such that the number of independent points in the measured spectra is greater than the number of variables determined in the model. (Kelly et al. 2008, Ravel et al. 1998, 1999; Frenkel et al. 1994, 1997, 2001; Allen et al. 1995; Haskel et al. 2005; Calvin et al. 2002). For constraining each of the EXAFS fitting parameters the common approaches (Kelly et al. 2008) are as follows:

1. \Delta R
   
   (i) The change in path length parameters can be determined independently for each path.
   
   (ii) \Delta R values can be related to unit cell dimensions or atomic moieties.
   
   (iii) \Delta R values can be defined by an isotropic expansion-contraction term as \sigma^{\Delta R_{eff}}. R_{eff} is a special key word for the effective path length R for each path from the FEFF calculation of the model structure. A single value of \sigma could be determined and applied to all path lengths included in the model, effectively reducing the number of variables for R from the number of paths to a single variable. This approach is best used for cubic crystal structures in which physical expansions/contractions are likely to be isotropic.

   (iv) R_{i} values or \alpha_{i} R_{eff} values can be grouped depending on path length or direction. This parameterization gives more freedom to account for an anisotropic expansion-contraction but also requires more variables.

2. \Delta E
   
   (i) One energy shift can be applied to all paths. This is the most common method of defining \Delta E, and it accounts for the misalignment of the data with respect to the theoretical calculation.

   (ii) Two energy shift values are sometimes used, where the value for the first path is different from the value for all other paths. This method accounts for the energy-alignment issue and for some possible charge imbalance in the FEFF calculation of the first atomic potentials as compared with all other potentials.

   (iii) Energy shifts can be assigned to atom types.

3. \Delta k
   
   (i) \sigma^{\Delta k} values can be grouped depending on atom type and bond length of a model path. This parameterization assumes that coordination shells involving similar atoms and similar interatomic distances are similar in thermal and static disorder.

   (ii) \sigma^{\Delta k} a unique value can be given to each path, which yields the maximum number of \sigma^{\Delta k} parameters in the model.

   (iii) \sigma^{\Delta k} values can be broken into two components to represent the structural and thermal disorder
in the bond lengths.

(iv) \( \sigma^2 \) values can be defined in terms of a Debye or Einstein model (Sevillano et al. 1979) with one or more characteristic temperatures.

(4) \( S_0^2 \)

(i) One value of \( S_0^2 \) is often used for all paths included in the model.

(ii) \( S_0^2 \) values are determined by fitting the measured EXAFS spectrum of a standard of known crystal structure measured under similar conditions as the sample in which unknown species are being identified.

(iii) Theoretical calculations such as those by FEFF 8.4 (Ankudinov et al, 2003) can also be used to determine \( S_0^2 \).

(5) \( N \)

(i) The degeneracy of a path, \( N \), is often determined from the coordination number in a known crystal structure or known atomic species.

(ii) The degeneracy can be independently determined for each single scattering path used in the mode. The degeneracy of multiple scattering paths is constrained in terms of the corresponding single scattering paths.

(iii) Coordination numbers can also be constrained by the stoichiometry of a particular ligand attached to the absorber.

(d) Statistical Tools Used for Comparing Models

Once a model for the EXAFS parameters has been developed, the variable EXAFS parameters and mathematical variables are adjusted to arrive at a least-squares fit between the experimental and theoretical spectra. The fitting results include the user defined variables, their best-fit values, and the uncertainties in these variables, along with important information about the statistics of the model. Statistical parameters include the number of independent points, \( N_{idp} \), the number of variables \( N_{var} \), which must be less than the number of independent points, the \( \chi^2 \) (chi-square) and \( \chi_r^2 \) (reduced-chi-square) values, and an R factor (Bevington et al. 1992). Use of these statistical parameters for EXAFS analysis is described by Stern et al. (1995). The isolated EXAFS signal is denoted as \( \chi \) (k) and should not be confused with the goodness-of-fit parameter \( \chi^2 \). Changes in the goodness-of-fit parameter, \( \chi_r^2 \), are used to compare different EXAFS models.

The R factor is defined as follows:

\[
R = \frac{\sum_i (data_i - fit_i)^2}{\sum_i data_i^2}
\]  
(29)

The \( \chi^2 \) value is calculated as

\[
\chi^2 = \frac{N_{idp}}{N_{pts}} \sum_i \left( \frac{data_i - fit_i}{data_i} \right)^2
\]  
(30)

where, \( N_{idp} \) is the number of independent points in the model fit and \( N_{pts} \) is the number of data points. To compare models with different numbers of variables, the \( \chi_r^2 \) values are used. It is calculated by the \( \chi^2 \) divided by the degrees of freedom in the fit, \( \nu \).

(e) An Example Fit: Pure Copper at 298K

Table 3 gives the list of atoms generated by Artemis using the following crystal structure of Cu atom:

- Space group : fcc,
- Cell edge \( a = 3.61 \text{ Å} \),
- Core atom: Cu, \( x = 0.0, y = 0.0, z = 0.0 \),
- Cluster size = 7.0 Å

Using the list of atoms different paths have been generated which are given in Table 4. This Table lists the scattering paths used, their half-path-length, degeneracy, number of scattering sites, and amplitude.

The fit to the 298 K copper metal data was done to the first four shells. In this case, eleven paths (1-10 and path 14) have been used for fitting. These paths have been used to fit first four shells of Cu atom (Fig. 14(a)). Both the single scattering (SS) and
Table 3: List of atoms generated by Artemis

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>ipot</th>
<th>tag</th>
<th>distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>1.805</td>
<td>1.805</td>
<td>0</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>-1.805</td>
<td>1.805</td>
<td>0</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>1.805</td>
<td>-1.805</td>
<td>0</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>-1.805</td>
<td>-1.805</td>
<td>0</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>1.805</td>
<td>0</td>
<td>1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>-1.805</td>
<td>0</td>
<td>1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>0</td>
<td>1.805</td>
<td>1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>-1.805</td>
<td>0</td>
<td>1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>1.805</td>
<td>0</td>
<td>-1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>-1.805</td>
<td>0</td>
<td>-1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>0</td>
<td>1.805</td>
<td>-1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>0</td>
<td>-1.805</td>
<td>-1.805</td>
<td>1</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>3.61</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>-3.61</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>0</td>
<td>3.61</td>
<td>0</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>0</td>
<td>-3.61</td>
<td>0</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3.61</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-3.61</td>
<td>1</td>
<td>Cu_2</td>
<td>3.61</td>
</tr>
<tr>
<td>3.61</td>
<td>1.805</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-3.61</td>
<td>1.805</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>1.805</td>
<td>3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-1.805</td>
<td>3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>3.61</td>
<td>-1.805</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-3.61</td>
<td>-1.805</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>1.805</td>
<td>-3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-1.805</td>
<td>-3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>1.805</td>
<td>1.805</td>
<td>3.61</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-1.805</td>
<td>-3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>1.805</td>
<td>1.805</td>
<td>3.61</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-1.805</td>
<td>-3.61</td>
<td>1.805</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>1.805</td>
<td>-1.805</td>
<td>3.61</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>-1.805</td>
<td>1.805</td>
<td>3.61</td>
<td>1</td>
<td>Cu_3</td>
<td>4.42133</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Cu_1</td>
<td>2.55266</td>
</tr>
<tr>
<td>3.61</td>
<td>1.805</td>
<td>3.61</td>
<td>0</td>
<td>Cu_4</td>
<td>5.10531</td>
</tr>
<tr>
<td>-3.61</td>
<td>3.61</td>
<td>0</td>
<td>1</td>
<td>Cu_4</td>
<td>5.10531</td>
</tr>
<tr>
<td>3.61</td>
<td>-3.61</td>
<td>0</td>
<td>1</td>
<td>Cu_4</td>
<td>5.10531</td>
</tr>
<tr>
<td>3.61</td>
<td>0</td>
<td>3.61</td>
<td>1</td>
<td>Cu_4</td>
<td>5.10531</td>
</tr>
<tr>
<td>-3.61</td>
<td>0</td>
<td>3.61</td>
<td>1</td>
<td>Cu_4</td>
<td>5.10531</td>
</tr>
</tbody>
</table>

Table 4: List of important paths from FEFF for copper metal at 298K. Paths are enumerated according to increasing R and are listed with half-path length $R_{	ext{eff}}$, degeneracy $N_{\text{degen}}$, number of scattering sites $N_{\text{scat}}$ and amplitude $\text{amp}$.

<table>
<thead>
<tr>
<th>Path index</th>
<th>$R_{\text{eff}}$ (Å)</th>
<th>$N_{\text{degen}}$</th>
<th>$N_{\text{scat}}$</th>
<th>$\text{amp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.553</td>
<td>12</td>
<td>1</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>3.610</td>
<td>6</td>
<td>1</td>
<td>22.98</td>
</tr>
<tr>
<td>3</td>
<td>3.829</td>
<td>48</td>
<td>2</td>
<td>10.6</td>
</tr>
<tr>
<td>4</td>
<td>4.358</td>
<td>48</td>
<td>2</td>
<td>8.65</td>
</tr>
<tr>
<td>5</td>
<td>4.421</td>
<td>24</td>
<td>1</td>
<td>55.40</td>
</tr>
<tr>
<td>6</td>
<td>4.763</td>
<td>48</td>
<td>2</td>
<td>10.62</td>
</tr>
<tr>
<td>7</td>
<td>4.7639</td>
<td>62</td>
<td>2</td>
<td>1.84</td>
</tr>
<tr>
<td>8</td>
<td>5.105</td>
<td>12</td>
<td>1</td>
<td>18.93</td>
</tr>
<tr>
<td>9</td>
<td>5.105</td>
<td>12</td>
<td>2</td>
<td>8.46</td>
</tr>
<tr>
<td>10</td>
<td>5.105</td>
<td>24</td>
<td>2</td>
<td>43.72</td>
</tr>
<tr>
<td>11</td>
<td>5.105</td>
<td>12</td>
<td>3</td>
<td>8.20</td>
</tr>
<tr>
<td>12</td>
<td>5.105</td>
<td>12</td>
<td>3</td>
<td>3.56</td>
</tr>
<tr>
<td>13</td>
<td>5.105</td>
<td>12</td>
<td>3</td>
<td>32.79</td>
</tr>
<tr>
<td>14</td>
<td>5.105</td>
<td>48</td>
<td>3</td>
<td>3.26</td>
</tr>
<tr>
<td>15</td>
<td>5.292</td>
<td>48</td>
<td>2</td>
<td>4.14</td>
</tr>
<tr>
<td>16</td>
<td>5.292</td>
<td>48</td>
<td>2</td>
<td>4.09</td>
</tr>
<tr>
<td>17</td>
<td>5.968</td>
<td>96</td>
<td>2</td>
<td>2.73</td>
</tr>
<tr>
<td>18</td>
<td>5.968</td>
<td>96</td>
<td>2</td>
<td>4.80</td>
</tr>
<tr>
<td>19</td>
<td>5.708</td>
<td>24</td>
<td>1</td>
<td>27.86</td>
</tr>
<tr>
<td>20</td>
<td>5.935</td>
<td>48</td>
<td>2</td>
<td>8.65</td>
</tr>
<tr>
<td>21</td>
<td>5.935</td>
<td>48</td>
<td>2</td>
<td>7.12</td>
</tr>
<tr>
<td>22</td>
<td>5.935</td>
<td>48</td>
<td>2</td>
<td>7.70</td>
</tr>
<tr>
<td>23</td>
<td>6.040</td>
<td>96</td>
<td>2</td>
<td>5.08</td>
</tr>
<tr>
<td>24</td>
<td>6.040</td>
<td>96</td>
<td>2</td>
<td>5.50</td>
</tr>
<tr>
<td>25</td>
<td>6.040</td>
<td>96</td>
<td>3</td>
<td>5.28</td>
</tr>
<tr>
<td>26</td>
<td>6.040</td>
<td>96</td>
<td>3</td>
<td>5.39</td>
</tr>
<tr>
<td>27</td>
<td>6.253</td>
<td>8</td>
<td>1</td>
<td>7.17</td>
</tr>
<tr>
<td>28</td>
<td>6.341</td>
<td>96</td>
<td>2</td>
<td>4.41</td>
</tr>
<tr>
<td>29</td>
<td>6.341</td>
<td>96</td>
<td>2</td>
<td>6.00</td>
</tr>
<tr>
<td>30</td>
<td>6.341</td>
<td>96</td>
<td>2</td>
<td>4.93</td>
</tr>
<tr>
<td>31</td>
<td>6.613</td>
<td>48</td>
<td>2</td>
<td>4.00</td>
</tr>
<tr>
<td>32</td>
<td>6.613</td>
<td>48</td>
<td>2</td>
<td>3.81</td>
</tr>
<tr>
<td>33</td>
<td>6.754</td>
<td>48</td>
<td>1</td>
<td>34.36</td>
</tr>
<tr>
<td>34</td>
<td>6.864</td>
<td>96</td>
<td>2</td>
<td>16.37</td>
</tr>
<tr>
<td>35</td>
<td>6.864</td>
<td>96</td>
<td>2</td>
<td>13.52</td>
</tr>
<tr>
<td>36</td>
<td>6.864</td>
<td>96</td>
<td>2</td>
<td>12.53</td>
</tr>
<tr>
<td>37</td>
<td>6.974</td>
<td>96</td>
<td>3</td>
<td>2.71</td>
</tr>
<tr>
<td>38</td>
<td>6.974</td>
<td>96</td>
<td>3</td>
<td>3.35</td>
</tr>
<tr>
<td>39</td>
<td>6.974</td>
<td>96</td>
<td>3</td>
<td>4.29</td>
</tr>
<tr>
<td>40</td>
<td>6.974</td>
<td>96</td>
<td>3</td>
<td>4.06</td>
</tr>
</tbody>
</table>

Note: Though the total number of paths is from 1 to 56, the number of paths given in the table are only 41. The intermediate missing paths are insignificant and have not been included in further calculations.
multiple scattering (MS) paths for Cu metal have been used. For the present analysis, the input parameter that determines the maximum frequency of the background $R_{bkg}$ was set to 1.25 Å. The background subtracted, normalized $\chi (k)$ data was then imported into the Artemis and the corresponding Fourier transformed data was obtained. The Fourier transform parameters used were $kw = 2$, $k_{min} = 2.3$ Å$^{-1}$, $k_{max} = 14.3$ Å$^{-1}$ and $dk = 1$ for this data. The theoretical model for copper metal was generated in Artemis using the software Atoms, available in Artemis. Theoretically modeled data were fitted to the experimental data in the R space and the corresponding fit is shown in Fig. 14(b). The data was fitted using $kw = 2$. Fit was performed in the R ranges of 1.5-5.0 Å.

The results obtained from fitting, which gives the local structure parameters obtained from the EXAFS analysis for copper metal are shown in Table 5. As the coordination number for copper metal is well known, we have constrained $N$ to its crystallographic value for the first shell and used $S_0^2$ as fitting parameter. For the other shells we have fixed the $S_0^2$ value thus obtained. The $S_0^2$ value obtained for the present analysis is 0.72. The del $E_0$ value obtained is 2.9 eV. The value of goodness-of-fit parameter, i.e., reduced chi-square ($\chi^2$) is 369.

It can be easily seen that a small number of paths from FEFF will give a very good approximation to the EXAFS with a suitably small number of adjustable parameters. It is not possible to fit more shells as the experimental data is limited to four shells. Therefore, the experimental data should be good for getting a nice fit for more number of shells. This can be done by recording the XAFS spectra at lower temperatures.

### 22. Reporting EXAFS Analysis

After the EXAFS spectra have been processed and analyzed according to the procedure mentioned above, the report regarding the EXAFS results should contain information about the following points. (www.xafs.org)

(a) Data Collection Information

The following data collection parameters should be

<table>
<thead>
<tr>
<th>N</th>
<th>R(Å)</th>
<th>del r (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st shell</td>
<td>12</td>
<td>2.54</td>
<td>-0.011 (0.004)</td>
</tr>
<tr>
<td>2nd shell</td>
<td>6.0</td>
<td>3.69</td>
<td>0.08 (0.007)</td>
</tr>
<tr>
<td>3rd shell</td>
<td>24</td>
<td>4.44</td>
<td>0.020 (0.0100)</td>
</tr>
<tr>
<td>4th shell</td>
<td>12</td>
<td>5.13</td>
<td>0.026 (0.008)</td>
</tr>
</tbody>
</table>

Table 5: Local structure parameters for copper metal (at $T = 298$ K) obtained from fitting of the theoretical model to the experimental EXAFS data

![Fig. 14(a): The theoretically calculated contribution to $|\chi(R)|$ by the single scattering paths and multiple scattering paths for Cu metal. Eleven paths are used for fitting the experimental $|\chi(R)|$ is also shown in this figure](image)

![Fig. 14(b): Fourier transformed EXAFS data for Cu metal. Blue line is experimental data and red line is modeled fit for four shells as explained in the text](image)
reported in a manuscript where EXAFS results are included.

i. The synchrotron should be listed and the acknowledgements should include the funding mechanism for the synchrotron.

ii. The beamline should be given including a reference for the standard operating procedures.

iii. The mechanism for X-ray energy selection, such as monochromator type (double crystal Si(111) monochromator with pre-monochromator slits of 0.6 mm).

iv. The mechanism for harmonic x-ray energy rejection (detune the second monochromator crystal by X%, Rh coated harmonic rejection mirror).

v. Detectors used to monitor I_0 and I_t, including fill gasses for ionization chambers and filters.

vi. The cross section of the incident x-rays on the sample.

vii. Method used to calibrate the monochromator energy.

a. Reference sample placed after I_t.

b. Scattered x-rays used to monitor reference sample.

viii. Sample type (powder, paste, aqueous, solid).

a. Powder-particle size, tape mount, pellet method within sample holder size.

b. Paste-sample holder size, concentration, and components of paste.

c. aqueous-concentration and components.

d. solid - concentration, size.

(b) XAFS Analysis Information

i. The data range in k, and the fit range in R.

ii. A method for accounting for each EXAFS parameter for each path included in the model (S_0^2, N, R, σ^2, E_0).

iii. A description of the software and/or procedures used to perform the analysis.

(c) Information About Results

i. The data overlayed with the model fit (in k or R)

ii. A table of EXAFS results with the uncertainties

23. Depiction of Coordination Geometries as Determined from EXAFS Analysis

The EXAFS analysis gives bond distances of the near neighbours around the central metal atom. The bond angles can be calculated using the obtained bond distances. From these two data, the depiction of coordination geometry around the central metal atom is difficult. However, if the crystal structure for that sample or an analogous sample is available from crystallography, then the coordination geometry for the sample can be depicted showing the values of bond distances and bond angles obtained using EXAFS. (Gaur et al. 2011 b)

24. Application of XAFS in Different Fields

XAFS can be applied not only to crystals, but also to materials that possess little or no long-range translational order: amorphous systems, glasses, quasicrystals, disordered films, membranes, solutions, liquids, metalloproteins and even molecular gases. This versatility allows it to be used in a wide variety of disciplines. In this review, an effort has been made to illustrate the application of XAFS in the fields of catalysis, nanomaterials, magnetism, material science, chemistry, energy, environment and life science.

(a) Catalysis

XAFS spectroscopy has been a stalwart in catalyst characterization for about 40 years. Thousands of manuscripts have been published in the field of catalysis worldwide where XAFS has been used as a primary characterization technique. The reason for the widespread use of the technique is a result of several factors. It is known that the reaction environment can change the structure of the catalyst.
The power of XAFS is its ability to probe specific elements within a catalyst under relevant reaction conditions, e.g. elevated temperature and pressure (in situ characterization of the catalyst). Often there is no other way to obtain the structural information provided by this technique that allows one to develop specific structure-activity relationships in catalysis. XAS is applicable to a broad range of elemental concentrations (from tens of ppm to wt% levels), and therefore is used to characterize both high-surface-area supported catalysts and bulk catalysts. The element-specific information provided by XAFS is coupled with the catalytic activity of the catalyst and used to develop structure-activity relationships.

The use of XANES spectroscopy for the study of catalysts under in situ or in operando conditions allows to obtain useful information concerning the symmetry of the formed complexes. The use of dispersive XANES spectroscopy allows to follow, in real time, the evolution of a system in working conditions. The simultaneous determination of the catalyst activity and of the average oxidation state of metal in the catalyst allows the evolution of a system in working conditions to be followed in real time. The specific advantages of a dispersive experimental set-up, compared to the standard XANES set-up, make this method useful to investigate time resolved processes. Concerning XANES spectroscopy applied to catalysis, two main improvements have been achieved with the appearance of third-generation synchrotron radiation sources. First they have facilitated an improvement in the energy resolution of XANES spectra collected in the conventional geometry. In the second place they resulted in a significant reduction in the acquisition time of a single spectrum, allowing the time scale needed to follow a reaction under operando conditions to be explored. Evans (1989) have given an excellent review on the application of EXAFS in the field of catalysis.

As an example, Stotzel et al. (2009) have studied the structure of copper catalysts on alumina support in situ and time resolved during reduction and re-oxidation at different temperatures with the quick-scanning EXAFS. The high time resolution provided new insights into the dynamics of the catalysts e.g. revealing Cu(I) as intermediate state during re-oxidation.

Matsumura et al. (2009) have studied the local structure of Pd metal fine particles on LaFeO₃. It was recognized that, under the reductive atmosphere, Pd atoms show similar speed of movement from oxide to metal state both on the two supports. However, under the oxidative atmosphere, Pd atoms on LaFeO₃ show faster movement from metal to oxide state than those on Al₂O₃.

Lamberti et al. (2003) have illustrated the use of XANES spectroscopy, both in DCM and in dispersive geometries, for the study of copper-based catalysts under in situ or in operando conditions. As case studies, copper-exchanged MFI zeolites and CuCl₂/g-Al₂O₃ systems are considered. The simultaneous determination of the catalyst activity and of the average oxidation state of copper in the catalyst allows the evolution of a system in working conditions to be followed in real time.

(b) Nanomaterials

Nanoscale materials are of great importance because of their potential applications in electronics, optics, and catalysis. The properties of these nanoscale materials can be expected to be between those of the bulk and isolated atoms. To exploit their full application potentials, it is important to thoroughly investigate the structure of these nanomaterials. EXAFS is a bulk probe and provides information only about the first few coordination shells and therefore does not reveal nanometer-scale structure (Ramaker and Koningsberger, 2010). However, it contains crucial chemical-specific local structural information and is sensitive to dilute species. Thus, it is a natural complement to the nanoscale, but chemically unresolved data. EXAFS and XANES, have been used as powerful tools for studying the structures and dynamics of the nanoscale materials, as these techniques are well suited for determining the local structures of both non-crystalline and crystalline materials.

A number of colloidal nanocrystals have been characterized by EXAFS and XANES, including
CdS, CdSe, SnO2, manganese oxides, MoS2, Au and cobalt nanoparticle catalysts (Cheng et al. 2004). The experimental measurements of XAS spectra for three different sizes of Conanoparticles have shown that the smaller the nanoparticles are, the more reactive they are. The existence of the disorder phase (or boundary) in the nanocrystalline structure is found to cause sharp decreases in the EXAFS patterns and Fourier transformations for nanoparticles.

Antoniak et al. (2009) have studied the influence of structural and compositional changes within FePt nanoparticles on their magnetic properties by means of XANES and its associated magnetic circular dichroism as well as by analysis of the EXAFS. The magnetic moments at the Fe sites were found to be a sensitive monitor to changes of the local surrounding.

Sun et al. (2009) have developed an in situ EXAFS method aiming at the study of nucleation and growth progresses of nanocrystals by using a microfluidic reactor. They measured the Se K-edge EXAFS spectra for CdSe nanocrystals along the reactor channel and found strong time-dependence of the nucleation and growth at the beginning of the reaction. A rapid increase of the reaction yield of CdSe nanocrystals within several seconds was observed. It is found that after injection of starting materials, the nucleation occurs abruptly and the CdSe nuclei concentration reaches a maximum and then declines rapidly.

Considering several examples Frenkel (2012) has demonstrated that bimetallic nanoparticles can be analyzed with EXAFS-based methods at very high level of detail, yet reliably, i.e., by accounting for experimental and theoretical uncertainties and artefacts.

Modrow (2004) has reviewed experimental evidence for the influence of the way of stabilization and the course of the synthesis on nano-particle properties using XAS. The obtained results indicate that not only size-dependent phase transitions, but also chemical interaction between the core of the nanoparticle and its surfactant molecules are responsible for the observed spectral changes, which can be explained when constructing detailed models of core-surfactant interaction. Also, it is observed that the surfactant can influence the course of the synthesis of a given nanoparticle notably.

(c) Magnetism

XAS and X-ray magnetic circular dichroism (XMCD) are state-of-the-art methods to determine both the electronic and magnetic structure of materials including site and valence band information as well as element-specific structure and magnetization. XMCD is a difference spectrum of two XAS taken in a magnetic field, one taken with left circularly polarized light, and one with right circularly polarized light. In addition to the chemical selectivity of XAS, XMCD gives information on the magnetic spin and orbital moments of the excited atoms. XMCD originates from coupling between the photon spin and the atomic magnetic moments, which gives rise to a difference between the absorption cross sections measured with the magnetic field parallel or antiparallel to the photon wave vector.

In the case of transition metals such as iron, cobalt, and nickel, the absorption spectra for XMCD are usually measured at the L-edge. For example in case of iron, this corresponds to excitation of 2p electron to 3d state by an X-ray of about 700 eV. Because the 3d electron states are the origin of the magnetic properties of the elements, the spectra contain information on the magnetic properties. XMCD is best suited for the study of ferromagnets and ferrimagnets. XAS and XMCD have been applied with great success in the investigation of magnetic properties of thin Fe layers on different metallic substrates such as Cu, Ag, Au and Rh, Pd, and Pt (Cammelli et al. 2009; Vaz et al. 2008).

Symmetry breaking and bonding at interfaces leads to a variety of anisotropy phenomena in transition metal sandwiches and multilayers. The charge density, the spin density and the orbital moment become anisotropic. These effects can be studied by the XMCD technique.

The valence and spin states of the doped ions and their magnetic interaction have been revealed by XAS and XMCD measurements of the transition-
metal core levels. Also, both the surface sensitive total-electron-yield mode and the bulk-sensitive total-fluorescence yield mode have been employed to extract the valence and spin states of the surface and inner core regions of the nano-particles separately. The experimental results indicate that doped holes rather than doped electrons are involved in the occurrence of ferromagnetism in these systems.

Transition metal thin films and surfaces may exhibit a variety of interesting magnetic phenomena. One of the most important magnetic phenomena is magnetocrystalline anisotropy (MCA). The opportunity to directly observe the magnetocrystalline anisotropy (MCA) as an anisotropy of the orbital moment, first suggested by Bruno (1989), comes from the development of X-ray magnetic circular dichroism (XMCD) spectroscopy. The technique which was pioneered by Schütz et al. (1987) has been developed both experimentally and theoretically into a quantitative magnetometry tool. It has several capabilities not afforded by traditional magnetics techniques. Its foremost strengths are the element-specific, quantitative separation and determination of spin and orbital magnetic moments and their anisotropies.

Recently, Borek et al. (2012) have done first-principles calculations to study x-ray absorption spectra and XMCD of the multiferroic system Fe/BaTiO$_3$(001). They have studied both the influence of structural and magnetic properties of the Fe films and the dependence on the polarization direction of BaTiO$_3$. They have shown that x-ray absorption spectroscopy and XMCD measurements are essential to understand the complex magnetic behaviour at the interface and surface of this system.

The induced magnetism in 3d and 5d metals at interfaces of ultrathin films was investigated by Wende (2004) employing XAS. The temperature-dependent analysis of the magnetic EXAFS provided a deeper understanding of the effects of local spin dynamics on the dichroic fine structure in the extended energy range.

**Material Science**

XAFS spectroscopy has contributed significantly to a better understanding of the properties of materials on the macroscopic and microscopic scale over the last decades. One particularly interesting application is the study of isotopic effects. Recently, Purans et al. (2009) has measured temperature-dependent EXAFS on the two isotopes $^{70}$Ge and $^{76}$Ge. The analysis of the first coordination shell has evidenced the effect of isotopic mass difference on the low temperature difference of Debye-Waller factors, and on the difference of nearest neighbor average interatomic distances, measured with femtometer accuracy.

Ganguli et al. (2009) have detected the possible existence of different Be-Se bond lengths in Zn$_{1-x}$Be$_x$Se mixed crystals. The EXAFS data has been analyzed to determine the composition dependence of the nearest neighbor distances in Zn$_{1-x}$Be$_x$Se and probe the possibility of the direct observation of the different bond lengths for the Be-Se bond in these mixed crystals. Their analysis shows that the EXAFS data are consistent with the interpretation of the Raman data in terms of a two mode behaviour.

Binstead and Edwards (2009) have shown that EXAFS is a useful tool in the evaluation of Ni superalloy structures. They have studied seven Ni-superalloy foils using EXAFS together with X-ray diffraction and electron microprobe fluorescence mapping. Changes during heat treatment and in differences in the host phase of minor elements has been demonstrated to give reliable and accurate information on local lattice distortions in these alloys.

Structural investigations of Ba$_{1-x}$La$_x$TiO$_3$ have been done using XRD and XAS techniques by Kamon et al. (2009). The Ba L$_{III}$-edge XANES measurements show the shape, position, and intensity of the XANES spectra are almost identical at all La content, indicating that the local atomic structure around Ba$^{2+}$ in BaTiO$_3$ does not alter with La doping. The Ti K-edge measurements show that there is no change in both intensity and position of the pre-edge peak, suggesting that La doping does not displace Ti ion from its centrosymmetry point.
(e) Chemistry

Earlier reviews of the work done on the use of XAS in chemistry are by Shrivastava and Nigam (1973) and Nigam (1981). The valence dependence of the position of the absorption edge has been demonstrated in these reviews. Nigam and Shrivastava (1971a) have extended the study of valence dependence of the position of absorption edge to systems involving mixed valence. Two distinct edges have been observed in case of copper thiovanol, copper thiomalic acid and copper penicillamine complexes (Nigam et al. 1978) involving Cu(I) and Cu(II), the energy separation between the absorption maxima assigned as 1s-4p* transitions corresponding to Cu(I) ans Cu(II) respectively, being in fair agreement with calculations of Beeman et al. (1945). Measurements on a number of Cu(II) complexes known to involve metal-metal exchange interaction have shown that the abnormal boosting of edge shifts resulting from such interaction as reported by earlier workers cannot be made a criterion for the presence of metal-metal interaction (Prasad et al. 1976 a, b; 1977 a, b). They have shown that the totality of edge shift data indicate a prominent role of many other factors besides the valence state of the metal ion. A doublet structure has been observed in the main peak of copper in some Cu(II) acetyl-acetonates and have been assigned 1s → A_{2u} and 1s → E_{u} transitions (Krishna et al. 1977). In case of Cu(II) thiopropionic acid (D_{2h}) and Cu(II) thiosalicylic acid (D_{4h}) complexes, the main peak due to the former splits into two broad peaks whereas the latter shows a single broad peak (Nigam and Shrivastava, 1971 b). They have pointed out that a more reliable criterion for correct assignment of the oxidation state would be the relative energy of the main peak rather than that of the edge. They have also given an empirical correlation between edge-width and coordination stoichiometry expressed in terms of overall metal nearest neighbours electronegativity difference (Nigam and Shrivastava, 1971 c; Shrivastava and Nigam, 1971). The use of X-ray absorption spectroscopy in chemical characterization has been reviewed by Nigam (1988).

XAS has been used to probe the local structure of copper(I) complexes containing scorpionate ligands by Giorgetti et al. (2009). Copper is found to be 4-fold coordinated with two sets of Cu-N and Cu-P interactions describing a quasi planar figure. An additional coordination is revealed for the copper complex of bis(1,2,4-triazol-1-yl) acetate due to the interaction of the copper with the acetate of the scorpionate ligand. XANES spectra behaviour confirms the occurrence of copper in the +1 oxidation state.

Using XANES and EXAFS spectroscopy, along with supporting thermodynamic equilibrium calculations and structural and steric considerations, Manceau and Matynia (2010) have shown evidence at pH 4.5 and 5.5 for a five-membered Cu(malate)$_2$-like ring chelate at 100-300 ppm Cu concentration, and a six-membered Cu(malonate)$_1$-like ring chelate at higher concentration. A “structure fingerprint” is defined for the 5.0-7.0 Å$^{-1}$ EXAFS region which is indicative of the ring size and number (i.e., mono- vs. bischelate), and the distance and bonding of axial oxygens (O$_{ax}$) perpendicular to the chelate plane formed by the four equatorial oxygens (O$_{eq}$) at 1.94Å.

Aquilanti et al. (2011) have investigated using XAS, both in the solid state and in aqueous solution, the coordination environment and stability behaviour of four macrocyclic ligands (three N$_2$S$_2$ and one N$_3$S$_2$) and of the corresponding Cu(II) complexes. Copper is found to be 4-fold coordinated with a CuN$_2$S$_2$ environment with different Cu–S distances depending on the size of the macrocyclic ring. The study of the copper(II) complex with the N$_3$S$_2$ ligand confirms the 4-fold coordination with an additional long Cu–N interaction.

Using EXAFS and XANES spectroscopy, Gaur et al. (2011 b, 2012 b, c, 2013 d, e) have obtained useful information about copper complexes. They have shown that if the crystal structure is not available for a complex, then the crystal structure of a similar or an analogous complex can be used satisfactorily for generating the theoretical model for the EXAFS data analysis of that complex, even if different ligands are attached to the central metal atom.

Penner Hahn (2005) has reviewed the use of
X-ray absorption to characterize the roles of spectroscopically quiet metals in biology. He has discussed the application of XAFS for determining ligation, coordination number, geometry, metal-site nuclearity and oxidation of metalloproteins.

(f) Time Resolved Studies

Among many types of reactions that occur very fast, several alternatives to the real time approach, such as freeze-quench, stop-flow, methods of physical trapping and ligand-binding, structural encapsulation, and site-directed mutagenesis methods of chemical trapping have been commonly used. The time resolution in these experiments is achieved by either stopping the reaction rapidly at a certain moment of time or lower the free energy for a particular intermediate. However, these intermediate phases are not measured in situ and thus the authenticity and the very interpretation of trapped phases as true intermediates are questionable since the reaction pathway is modified. XAFS can be applied in situ under realistic reaction conditions e.g., the gas atmosphere and pressure or sample temperature in real time. Time resolved XAFS contains relevant information about real time phase composition and structure in the course of reaction, which cannot be uncovered by static techniques. XAFS is limited to those reaction systems where metals play important roles e.g., catalysts in reactions. XAFS can also be used to probe laser excited samples to obtain the excited state structural and electronic dynamical information not available through other techniques. Stern and Brew (2009) have shown that XAFS contributes new insights to time resolved measurements of Ge in addition to distinguishing between the classical vibration mode and incoherent phonons excitations. The important result discovered by time-resolved XAFS measurements is the laser power-independent 11ps time delay before the excited electron/hole (e/h) start decaying by interacting with incoherent phonons. The delay in the e/h interaction with incoherent phonons indicated that there is a surprising metastable binding between electrons and holes when they are initially excited.

The study of Van der Veen et al. (2009) has demonstrated that accurate structural changes in photoexcited molecules can be determined by fitting the transient EXAFS spectrum directly in energy space and that additional non-structural information, such as the excitation yield and chemical shift, can be extracted from the fit due to the largely reduced parameters space in a model-based analysis. The analysis has been applied to the transient L$_3$-edge EXAFS data of the photoexcited [Pt$_2$(P$_2$O$_5$H$_2$)$_4$]$_4$ anion.

(g) Energy, Environment and Life-Science

Bulk XAFS has been successfully applied to characterize metal-contaminated environmental samples. This technique probes a volume of several cubic millimeters, providing only one spectrum of the average species of the metal of interest. The bulk XAFS spectrum represents an average of multiple phases that may be present. Using a complete database of reference spectra, the single contributions to such an average spectrum can be deciphered. One of the most promising techniques to examine heterogeneous soil and environmental samples is micro focused XAFS, which is able to identify crystalline or noncrystalline species within a complex mixture on a micron scale. Microscopic techniques may resolve the different reactive sites in soil at the micron level, thus allowing for a more selective approach to speciation. (Kong et al. 2012).

XAS has been used for elucidating the function of hemeprotein. Arcovito et al. (2009) have demonstrated the feasibility of a structural study combining polarized XAS and XRD on the same protein crystal of the ferric cyanomet derivative of sperm whale Mb (Mb+CN). They have determined both the 1.4 Å X-ray structure of the protein and, by XANES, the local structure around the Fe ion with enhanced resolution, comparable to that of atomic resolution XRD.

XANES spectroscopy has been used by Franz et al. (2009) to investigate whether polymeric sulfur is also the preferred sulfur species in other purple sulfur bacteria belonging to the families Chromatiaceae and Ecothiorodospiraceae. The cultures were fed with 50
mM of elemental sulfur consisting of 68% polymeric sulfur and 30% cyclo-octasulfur. XANES spectroscopy revealed that only the polymeric sulfur fraction was taken up by all cultures investigated. This strongly indicates that polymeric ‘chain-like’ sulfur is the form preferably used by phototrophic sulfur bacteria.

Borghi et al. (2002) have characterized the binuclear copper sites of the met and met-azido derivatives of Octopus vulgaris and Carcinus aestuarii hemocyanins at pH 7.5 by high-resolution X-ray absorption spectroscopy in the low energy region (XANES) and in the higher region (EXAFS). They have found that the comparison between the protein’s and the complexes’ XAFS data, supported a description of the met-derivatives as a five-coordinated O-bridged binuclear copper(II) center and favored, for both species, a bis(hydroxo) structure with a 3 Å Cu-Cu distance.

Ravel et al. (2009) have presented the results of an XAS study of a mercury sensor which illustrates the nature of the Hg–DNA interaction. They have found a strong affinity to a single binding site on the Hg-selective DNA. Analysis of the Hg-edge EXAFS has shown that the Hg is bound directly to a six-member ring.

Yano et al. (2009) have reviewed the application of XAFS pertaining to photosynthesis. 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. The application of XAS to the study of the Mn$_4$Ca cluster in Photosystem II is presented.

25. Conclusions

Over the past four decades, the technique of XAFS has made great strides toward the goal of providing information about the absorbing atom. The existence of intense new synchrotron X-ray sources alone was not enough to achieve this goal, even though such facilities spurred considerable progress. In addition, the full success of the XAFS technique must be attributed in large part to advances in theory, which have led ultimately to a highly quantitative understanding of the phenomena.

The EXAFS beamline BL-8 has become operational at Indus-2 synchrotron at Raja Ramanna Center for Advanced Technology (RRCAT), Indore which is a dispersive EXAFS beamline. Another beamline BL-9 which is a DCM beamline is being commissioned and will become operational soon. Now, it is hoped that research workers from Indian laboratories will do XAFS experiments at synchrotrons. Hence, details regarding experiment and analysis of the XAFS data have been given in this review so that any body who wants to do research work in the field of XAFS may get necessary information at one place.

Acknowledgements

The authors (AG and BDS) are thankful to Madhya Pradesh Council of Science and Technology (MPCST), Bhopal (India) for a research grant. The authors are thankful to Dr. D Bhattacharya and Dr. S N Jha of Applied Spectroscopy Division, Bhabha Atomic Research Centre, Mumbai for their constant help and cooperation while performing experiments at RRCAT, Indore.

References

Zwick B D Multinuclear NMR, Raman, EXAFS, and X-ray diffraction studies of uranyl carbonate complexes in near-neutral aqueous solution. X-ray structure of [C(NH$_2$)$_3$)$_6$[(UO$_2$)$_3$(CO$_3$)$_6$].cntdot.6.5H$_2$O Inorg Chem 34 (1995) 4797-4807
Abhijeet Gaur et al.

Correlation of magnetic moments and local structure of FePt nanoparticles J Phys Conf Ser 190 (2009) 012118


Bhattacharyya D, Poswal A K, Jha S N, Sangeeta and Sabharwal S C First results from a dispersive EXAFS beamline developed at INDUS-2 synchrotron source at RRCAT, Indore, India Nucl Instrum Meth A 609 (2009a) 286-293


Bonnelle C and Mande C (eds) Advances in X-ray spectroscopy, Pergamon (1982)


Coulon-Ginet C and Brookes N B (eds) Proceeding of the IX international conference on X-ray absorption fine structure, XAFS IX, Grenoble France J de Physique IV 7 (1996)


Evans J EXAFS in the study of catalysts Catalysis 8 (1989) 1-41
Franz B, Lichtenberg H, Dahl C, Hornes J and Prange A


Ganguli T, Mazher J, Polian A, Deb S K, Pages O and Firszt F (2009) An EXAFS study of the structure of the Zn\textsubscript{1-x}Be\textsubscript{x}Se alloy system J Phys Conf Ser 190 012064


Gaur A and Shrivastava B D Speciation of mixtures of copper (I) and copper (II) mixed ligand complexes by X-ray absorption fine structure spectroscopy Spectroscopy Lett 46 (2013a) 375-383


Gaur A, Shrivastava B D, Jha S N, Bhattacharyya D and Poswal A A comparative study of the spectra recorded at RRCAT synchrotron BL-8 dispersive EXAFS beamline with other beamlines Pramana – J Phys 80 (2013c) 159-171


Gaur A, Shrivastava B D and Joshi S K Copper K-edge XANES of Cu(I) and Cu(II) oxide mixtures J Phys Conf Series 190 (2009) 012084

Gaur A, Shrivastava B D and Khalid S Study of XAFS spectroscopic methods of speciation using mixtures of Cu(I) and Cu(II) chlorides J Phys Conf Ser 430 (2013b) 012045


Ghatikar M N, Padalia B D and Nayak R M Chemical shifts and effective charges in ternary and complex systems J Phys C 10 (1977) 4173


Hasnain S S (ed) Proceeding of the VI international conference on X-ray absorption fine structure, XAFS VI, Daresbury Laboratory, Warrington UK (1991)


Journal de Physique Colloques EXAFS and near edge structure IV 47C8 (1986)


Matsumura D, Okajima Y, Nishiha Y, Mizuki J, Taniguchi M, Uenishi M and Tanaka H. Dynamic structural change of Pd particles on \(\text{LaFeO}_3\) under redox atmosphere and CO/NO catalytic reaction studied by dispersive XAFS. J Phys Conf Ser 190 (2009) 012154

Meisel A. X-ray spectra and chemical binding. Springer-Verlag (1989)


Nigam H L. Proceedings of the 68th session of the Indian Science Congress

Presidential Address, Varanasi, Section of Chemistry 1 (1981)


Nigam H L and Shrivastava U C. K-Absorption Spectroscopic
X-ray Absorption Fine Structure (XAFS) Spectroscopy – A Review

Investigations on Mixed Valency Canad J Chem 49 (1971a) 3229-3231
Nigam H L and Shrivastava U C Co-ordination stoicheiometry and edge-width in X-ray absorption spectra—a correlation Chem Comm 14 (1971c) 761-762
Park D, Yun Y-S, Park J M XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption J Colloid Interface Sci 317 (2008) 54-61
Prasad J, Krishna V and Nigam H L Ind J Chem 15 (1977a) 768
Richtmyer F K, Barnes S W and Ramberg E The widths of the L-series lines and of the energy levels of Au(79) Phys Rev 46 (1934) 843-860
Sapre V B and Mande C Chemical shifts in the K-absorption discontinuity of arsenic J Phys C 5 (1972) 793
Shrivastava U C and Nigam H L X-ray absorption edge spectrometry (xaes) as applied to coordination chemistry Coord Chem Rev 9 (1973) 275-310
Shrivastava UC and Nigam H L Ind J Chem 9 (1971) 1301


Stohr J NEXAFS spectroscopy, Springer-Verlag (1992)


