X-ray absorption Spectroscopy with Synchrotron Radiation

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Introduction

X-ray absorption spectroscopy (XAS) generally deals with measurement of absorption coefficient, as a function of X-ray photon energy, around an X-ray absorption edge of an element, in a material. X-ray absorption spectrum consists of two parts: (i) The spectrum near the absorption edge (viz., the X-ray near edge structure or the XANES part) gives information about the external perturbations in the valence states to which electrons make transitions from core levels, upon absorption of X-ray photon energy and hence can yield information regarding hybridization of orbitals in case of molecule or long range order existing in a crystalline sample, apart from the oxidation states of the absorbing atom in the material. (ii) The second part of the spectrum which extends from 50 eV to ~700 eV above the absorption edge, is generally called the Extended X-ray absorption fine structure (EXAFS) part, which is generally characterized by the presence of fine structure, oscillations and can give precise information regarding the short range order and local structure around the particular atomic species in the material. This determination is confined to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5-7 Å radius from the element. The above characteristics along with the fact that EXAFS is an element specific tool, makes EXAFS a powerful structural local probe. With the advent of modern bright Synchrotron radiation sources, this technique has emerged to be the most powerful local structure determination technique, which can be applied to any type of material viz. amorphous, polycrystalline, polymers, surfaces and solutions. Furthermore, EXAFS does not require any particular experimental conditions, such as high vacuum and hence, samples of various physical forms can be adapted for measurements in the experimental stations [1-5].

Theoretical formulation

The X-ray absorption coefficient for an atom in the photon energy range of 1-100 keV is generally dominated by Photoelectric effect as shown in Fig. 1, which is a monotonically decreasing function of energy, with several discontinuities known as absorption edges. These discontinuities occur when the energy of the incident photons equals the binding energy of different core levels of the atom and are classified with capital letters (K,L,M...) according to the principal quantum number of the core level ground state \( n = 1, 2, 3... \). The edge energy is characteristic of each atom. In the case of an isolated atom (monatomic gas), the absorption coefficient decreases monotonously between two subsequent edges. However, in a real material the spectrum always shows oscillations as shown in the inset of Fig. 1 for Ge K edge. An incident photon is able to extract a core electron, if its energy is equal to or greater than the edge energy. If the absorbing atom is isolated in space, the photoelectron propagates as an unperturbed isotropic wave, but in a real material since the absorber is surrounded by several neighbouring atoms, photoelectrons get backscattered and the final state of the photoelectron can be described, by
the superposition of the original and scattered waves. This leads to an interference phenomenon that modifies the interaction probability between core electrons and incident photons. Constructive interference increases while destructive interference decreases the absorption coefficient of the atom. This interference phenomenon, for a given energy of the photoelectron, depends on the distance between emitting and scattering atoms and their scattering strengths and coordination numbers.

Since the oscillations in the absorption spectra are important, the experimentally obtained \( \mu \) versus \( E \) data is first plotted as \( \chi(E) \) versus \( E \), where \( \chi(E) \) is defined as follows:

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)}
\]

(1)

where, \( E_0 \) is the absorption edge, \( \mu_0(E) \) is the bare atom background and \( \Delta \mu_0(E_0) \) is the step in the \( \mu(E) \) value at the absorption edge. The energy scale is also converted to the wave number scale \( k \), given by:

\[
k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}
\]

(2)

\( \chi(k) \) is weighted by \( k^2 \) to amplify the oscillations at high \( k \) and finally the \( \chi(k)k^2 \) versus \( k \) spectra is Fourier transformed to generate the \( \chi(R) \) versus \( R \) spectra in terms of real distances from the centre of the absorbing atom.

Under the dipole approximation, an analytical expression of the EXAFS signal can be derived as follows [6]:

\[
\chi(k) = \sum N_j f_j(k) e^{-2\sigma_j} e^{\frac{2kR_j}{\lambda}} \sin \left[ 2kR_j + \delta_j(k) \right]
\]

(3)

where, \( N_j \) is the number of \( j \)th neighbours of the absorbing atom sitting at a distance of \( R_j \), having a scattering amplitude of \( f_j \) and creates a phase change of \( \delta_j \) as the photoelectron get scattered by its potential. The term \( \sigma_j \) represents the fluctuation at the atomic positions (having both structural as well as thermal effect) and \( \lambda \) is the mean free path which determines the probability of the scattering photoelectron to come back at the absorber, after being backscattered by the neighbour.

Different relevant parameters from the EXAFS signal are determined by fitting the experimental EXAFS spectra with the above theoretical expression. The amplitude, distance, phase and degeneracy of the different contributions corresponding to different interactions (nearest neighbour and further interactions), are used as fitting parameters.
for fitting the experimental data. Different codes for EXAFS data analysis programme are available among which, IFEFFIT package is mostly commonly used [7].

References