Theoretical analysis of EXAFS data of copper (II) complexes of isoxezol series

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A newly approached method has been employed for analysis of the K-absorption X-ray spectra of mixed ligand complexes and verification of structural parameters obtained experimentally. Extended X-ray absorption fine structure (EXAFS) data is generated using standard EXAFS equation and EXAFS curves are plotted for some copper (II) mixed ligand complexes of isoxezol series. Fourier transform of calculated EXAFS data has been taken to calculate bond lengths theoretically. These bond lengths are compared with bond lengths obtained using other methods from experimental EXAFS data. Imaginary part of Fourier transform is compared with the amplitude of Fourier transform to verify consistency of experimentally obtained phase shift parameter with calculated data.

Keywords: EXAFS, Copper (II) mixed ligand complexes, Isoxezol series, Fourier transform

1 Introduction

The phenomenon of extended X-ray absorption fine structure (EXAFS) refers to the oscillation of the X-ray absorption coefficient as a function of X-ray energy above threshold. It has been attributed to an interference of the ejected photoelectrons at the site of the absorbing atom. For K-shell excitation, the modulating part of the absorption coefficient (EXAFS) is described by:

\[
\chi(k) = \frac{m}{4\pi^2 k} \sum_j N_j t_j (2k) \exp \left( -R_j / \lambda \right) \times \sin 2 \left( k R_j + \delta_j (k) \right) \exp \left( -2k^2 \sigma_j^2 \right) \]

\[ \text{... (1)} \]

where \( k \) is the electron wave vector, \( N_j \) is the number of atoms in the \( j \)th coordination shell, \( R_j \) is the average radial distance to the \( j \)th atom, \( t_j (2k) \) is the back-scattering matrix element encountered by the electrons, \( \lambda \) is the mean free path of the electron, the \( 2^n \) exponential containing \( \sigma_j^2 \) is a Debye-Waller-type term where \( \sigma_j \) is the rms fluctuations of the atom about \( R_j \), and \( \delta_j (k) \) is a phase shift. The form of this equation is a sine like scattering from each shell of atoms at \( R_j \) with the EXAFS signal proportional to the number of atoms surrounding the absorbing atom and inversely proportional to \( R_j \). Each coordination shell contributes a sine like term of period \( 2k R_j \). The total result is a summation overall the coordination shells within the range of the effect.

Several attempts have been made to extract structural information from EXAFS. The most general methods used are fitting procedures¹ and Fourier transform methods²-⁴. The Fourier transform method can be applied to more complicated structures. From \( \chi(k) \) a radial function \( \phi_n (R) \) can be derived given by:

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

\[ \text{... (2)} \]

where \( n \) is usually either 1 or 3, and \( k_{\text{min}} \) and \( k_{\text{max}} \) are the minimum and maximum values of \( k \), respectively. The \( n = 3 \) transform weights less the low-energy portion of \( \chi(k) \), where the undesirable uncertainties occur, while it weights most the high-energy portion of \( \chi(k) \). For this reason, \( \phi_3 (R) \) has been employed as standard transform in this paper.

The maxima of this function are generated by shells of scattering atoms surrounding the absorbing atom. The positions of the peaks in \( |\phi_3 (R)| \) are shifted compared to true distances due to contribution of scattering phases that depend on \( k \).

The present study deals with a theoretical analysis of K absorption X-ray spectra of copper (II) mixed ligand complexes of isoxezol series. The mixed ligand complexes are: copper (II) 4-(2-Cl) Phenylehydrozono-3-Methyl isoxazol-5-Ones (Cu 42Cl-PMO); copper (II) 4-(4-OH) Phenylehydrozono-3-Methyl isoxazol-5-Ones (Cu 44OH-PMO); copper (II) 4-(4-Cl) Phenylehydrozono-3-Methyl isoxazol-5-Ones (Cu 44Cl-PMO); copper(II) 4-(4-CH₃) Phenylehydrozono-3-Methyl isoxazol-5-Ones (Cu...
copper (II) 4-(2-NO$_2$) Phenylhydrozono-3-Methyl isoxazol-5-Ones (Cu 42NO$_2$-PMO); copper (II) 4-(4-NO$_2$) Phenylhydrozono-3-Methyl isoxazol-5-Ones (Cu 44NO$_2$-PMO).

The theoretical tools for the interpretation of EXAFS in various complex compounds are provided and structural parameters obtained experimentally on conventional X-ray fixed target source are verified. The EXAFS data is generated and curves are plotted for copper (II) mixed ligand complexes of isoxezol series using MathCAD programming. Fourier transform of calculated EXAFS spectra is taken to calculate bond lengths for copper (II) mixed ligand complexes and compare with corresponding bond lengths obtained by LSS method$^3$, Lytle’s method$^4$ and Levy’s method$^5$. Imaginary, real and magnitude part of Fourier transform is calculated to show consistency of experimental phase shift parameter with calculated data.

2 Results and Discussion

The feature of EXAFS that makes it particularly attractive is the ability to determine the environment around each type of atom separately. This occurs because the X-ray absorption edges of many atoms are far enough separated in energy and their EXAFS do not overlap. Since EXAFS measures the immediate environment around a given type of atom, it does not require that the sample be single crystal or even crystalline. Thus amorphous, liquid and other disordered states can be investigated in addition to crystalline forms. The greatest usefulness for EXAFS should be in measuring materials, which are composed of many different types of atoms in a disordered form such as biological systems, amorphous solids, complicated alloys and compounds.

The method employed in the paper for analysis of EXAFS and verification of various structural parameters using MathCAD programming is simpler than commonly used FEFFIT (Fitting of EXAFS by Fast Fourier Inverse Transform) programming$^6$. In contrast to conventional EXAFS fitting analysis or FEFFIT, other kind of EXAFS analysis computation originated from the Tikhonov regularization method$^7$ is the iterative solution projection method using numerical recipe and algorithm$^8$ of manipulating matrix inversion computation under the ill-posed mathematical problem.

The EXAFS spectra obtained by using Eq. (1) in MathCAD programming for copper (II) mixed ligand complexes of isoxezol series are shown in Fig. 1. Experimental spectra for these complexes are shown elsewhere$^9$. Fourier transform of the EXAFS data of copper (II) mixed ligand complexes are calculated by using Eq. (2). The imaginary, real and magnitude parts of Fourier transform of calculated EXAFS data of Cu 42Cl-PMO complex are shown in Fig. 2. Bond length is calculated from magnitude of Fourier transform and is shown in Fig. 3 for copper (II) mixed ligand complexes of isoxezol series.

Results indicate that bond lengths determined by Fourier transforming of the calculated data resembles with the bond lengths obtained by LSS method, Levy’s method and Lytle’s method (Table 1). The imaginary part of Fourier transform coincides with the amplitude of Fourier transform (Fig. 2). This verifies that experimentally obtained
Thus the fact that theory and experiment agree well means that the parameterized theoretical calculation of the EXAFS spectra describes well the physical reality.

3 Conclusions

The calculated EXAFS curves for Cu (II) complexes of isoxezol series resemble with experimental EXAFS curves for all complexes studied within experimental error. A perusal of bond length values in Table 1 as obtained by magnitude of Fourier transform of calculated EXAFS data indicates that the calculated values are in good agreement with the values obtained by LSS method, Levy’s method and Lytle’s method.

References