

EXAFS study of Fe (II) complexes using Dispersive EXAFS beamline

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Abstract: Extended X-ray absorption fine structure (EXAFS) spectra have been recorded at the K-edge of Fe (II) complexes using the energy dispersive EXAFS beam line at 2.5GeV Indus -2 synchrotron source at RRCAT, Indore, India. A theoretical EXAFS data analysis is also carried out by Fourier analysis of experimental EXAFS data of the two iron (II) complexes. This analysis includes details of the Fourier transform of the data and the extraction of metal-ligand bond length. Bond lengths determined from data analysis methods are compared with the bond lengths obtained from several other known existing techniques. These data have also been calibrated by derivative method and bond lengths have also been obtained from Fourier transformation method and the results have been compared with the each other. The EXAFS data have been analysed using the computer software *Athena*.

1. Introduction

In the present work, the X-ray absorption spectra have been recorded at the K-edge of Iron in two macro-cyclic complexes. The coordination chemistry of macro-cyclic ligand is a fascinating area of research. The extended X-ray absorption fine structure (EXAFS) spectroscopy is an effective technique for selectively investigating the local coordination environment around the metal active site

of complexes [1]. The EXAFS K-edge of Fe (II) complexes were recorded at 7112eV and also determined the bond length between metal-ligand of (a) Fe 1-Fe(II)2-methyl-3[(bis-orthonitrophenyl)]-3H 1, 5 benzodiazepine chloride, (b) Fe 2-Fe(II)2-methyl-3[(bis-meta nitrophenyl)]-3H 1, 5 benzodiazepine chloride.

A method for determining the metal-ligand bond length by an appropriate Fourier analysis of the K-edge data has been presented. This is illustrated by a detailed analysis of the data for a series of metal organic based on pyridine ligand systems, which model active centres of natural copper containing metal proteins [1]. The Fourier transform of the experimental EXAFS data is done using the IFEFFIT program [2] and metal-ligand bond length is determined. Applications of EXAFS can be found in literature on a variety of fields, namely, chemical reactions at the solid state [3], surface treatments [4] and structural studies of thin films [5]. A structural analysis of X-ray absorption fine structure (XAFS) spectroscopy has been used for a local structural refinement on an atom of interest [6]. In general, the small pre-edge peaks of the K-edge absorption spectra for transition metal compounds have been assigned to the transition from 1s to nd orbital, even though it is a dipole forbidden transition. Since the transition is very sensitive to chemical environment, the pre-edge feature in XAFS studies has been used to infer the local structure around the central atom. Some molecular orbital calculation studies have been reported that the pre-edge peak intensity is related to 3d and 4p orbital mixing by



perturbation of site symmetry and increases gradually with the departure from a centro-symmetric environment [7]. In this context, the extended X-ray absorption fine structure (EXAFS) spectra have provided many quantitative structural characterizations such as inter-atomic distance, coordination number and Debye-Waller factor. Since the EXAFS refinement does not depend on the long-range order of atomic arrangement and is very sensitive to atomic local sites, it is a powerful technique for local structural analysis of partially substituted inorganic compounds.

2. Material Synthesis

Preparation of ligand (L)

Iron Complexes have been prepared by chemical root method. The chemicals used are of pure grade. O-phenylenediamine (0.05 mol, 5.0g), substituted aniline (R) (0.05 mol, 6.9g) dissolved in ethanol (25 mL), and ethyl acetoacetate (0.05 mol, 6.7g) dissolved in ethanol (25 mL). The mixtures of both reactants were refluxed for 6 hour. The volume concentrated on the steam bath until white colored crystals began to form. The product was purified by crystallization from hot alcohol. Thus white crystalline pure macro-cyclic ligand was collected.

Preparation of [Fe (II)-L-Cl₂]

Hot ethanol solution of ligand (L) (0.01 m. mol, 0.2 g), hot ethanol solution of Iron chlorides [FeCl₃.2H₂O] with few drops of hydrochloric acid was added. The solution mixture was then refluxed for 4h. On cooling, colored precipitates were then filtered and washed with cold water and dried in vacuum [8].

3. Experimental

The complexes were finely powdered and then absorption screens were prepared by carefully spreading calculating amount of the powdered on 1 cm area of kapton tape. The Iron K-edge EXAFS spectra of these absorption screens have been recorded at BL-8 dispersive EXAFS beamline at 2 GeV Indus -2 synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India [9-12]. The energy calibration of beam line for a particular setting of the polychromator can be done by recording the absorption spectra of two standards, whose absorption edge energies are well established. For example for recording the absorption spectra of Fe sample, the two standards can be Fe metal foil and Gd oxide powder. The absorption spectra of Fe K edge and Gd 2O₃ L₃-edge have been recorded under the same setting of crystal bender and goniometer. In the present work we are taking the values of the energies of Fe K-edge in metal and Gd L₃ -edge in Gd₂O₃ as 7709 eV and 7243 eV respectively [13].

4. Results and discussion

The X-ray absorption spectra, i.e., normalized $\mu(E)$ vs. E curve of Iron complexes is shown in figure 1. The bond lengths have been determined using the following four methods, i.e., Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation methods and the results were obtained.

4.1 Levy's method

The bond lengths According to Levy's method [14], are given by Bragg relation $R_1 = [151/\Delta E]^{1/2}$ Å, where ΔE is the difference in eV of the energies of the EXAFS maximum B and minimum. R_1 is the radius of the first coordination sphere. The R_1 calculated bond length value of Fe foil, Fe1 complex and Fe2 complex are 2.25, 2.22 and 2.20 Å respectively.

4.2 Lytle's method

According to Lytle [15] method the bond length (R_s) is evaluated by the radius R_s of equivalent polyhedron through the relation $R_s = [37.60 / M]^{1/2}$, where M is slope of E vs Q plot, energy values (E) is EXAFS maxima and $Q = 2.04, 6.04, 12.0, \text{ and } 20.0$ are constant. The R_s calculated bond length value of Fe foil, Fe1 complex and Fe2 complex are 1.85, 1.82 and 1.80 Å respectively.

4.3 Lytle, Sayers and Stern's (LSS) method

In the LSS method [16], for determination of the nearest neighbour distances, gives the value of $(1/2 + n)\pi = 2k(R_1 - \alpha_1) + 2\beta_1$, where R_1 is the bond length. ($R_1 - \alpha_1$) is the phase uncorrected bond length value of Fe foil, Fe1 complex and Fe2 complex are 1.40, 1.32 and 1.30 Å respectively. Although, Fourier transform of EXAFS data is a general and powerful technique to determine many

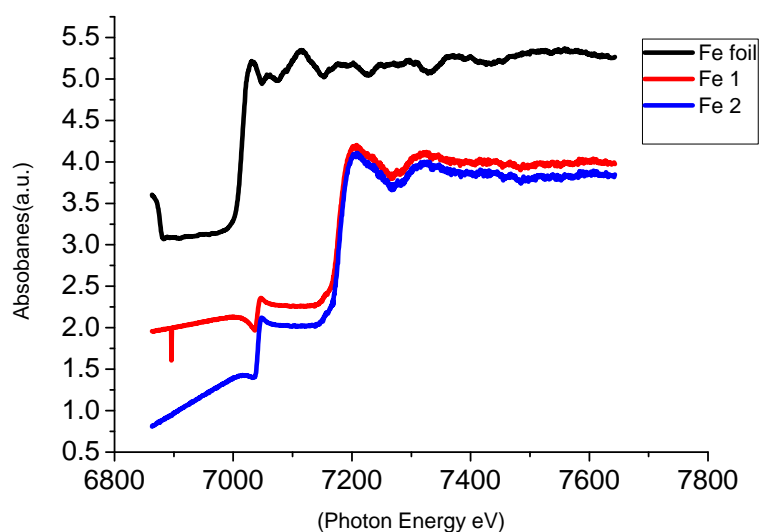


Figure 1- EXAFS spectra of Fe (II) complexes.

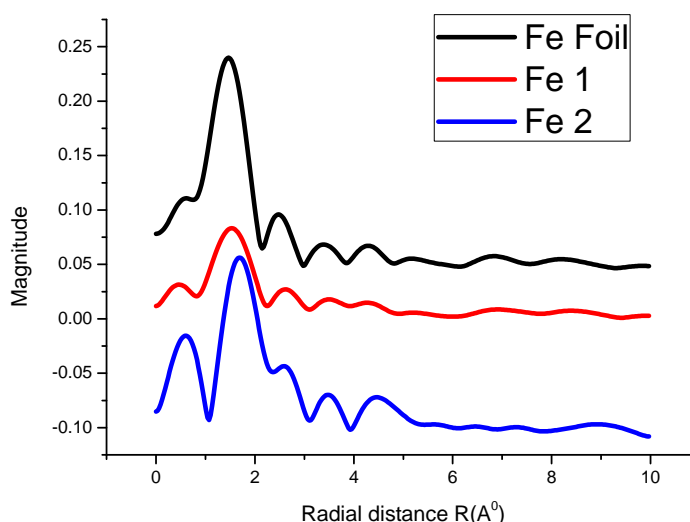


Figure 2- Magnitude of Fourier transformation in first shell maxima for Fe (II) complexes.

physical parameters; however, it is possible to determine nearest-neighbour distances and phase shifts from a simple graphical technique. This is possible because the first shell scattering usually dominates the EXAFS curves; then, if only the major EXAFS peaks are used, the period will be that of the first coordination shell. In this method, the energy positions of the maxima and minima of the main EXAFS are measured with respect to the inflection point on the main absorption edge, which signifies the Fermi level in metals and the first unoccupied level of suitable symmetry available for the absorption of the ejected electron in the case of compounds.

4.4 Fourier transformation method

The magnitude of Fourier transform spectra are shown in figure 2. The Fourier transforms peak at the radial distances of the neighbouring atoms from the absorbing atom. The bond length value of Fe foil, Fe1 complex and Fe2 complex are 1.95, 1.92 and 1.90 Å respectively. The distances found in Fourier transform are, however, shorter by 0.2-0.5 Å than the actual distances due to energy dependence of the phase factors in sine function of the theoretical expression for EXAFS, which is known as the EXAFS equation [17]. The peaks in the Fourier transform are shifted towards the origin

by an amount α_j and hence the peaks are at distances $R_j - \alpha_j$. For the first peak $j=1$ and hence the position of the first peak determines the distance $R_1 - \alpha_1$. There are some subtleties associated with doing the FT of EXAFS data but techniques for dealing with these are well developed. 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.

5. Conclusion

Calibration of particular setting of the polychromator has to be done and it has been shown by derivative method, and after this EXAFS spectra has been recorded and comparison of the values of bond length R_s is seen to have slightly lesser values than the corresponding bond lengths obtained by Levy's method. This may be described to the fact that Levy's method gives the radius of coordination sphere

directly whereas Lytle method does not. In later method, the inter atomic spacing is obtained by multiplying R_s with a factor appropriate to the geometry of the system. The value of the bond length

obtained from LSS method are closer to obtained by Levy's method and Fourier transformation method.

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References

- [1] Vlasenko V G, Uraev A I, Zubavichus Ya V, Chernyshov A A, Garnovskii A D, & Mamin R K 2008 *Bull. Russian Acad. Sci.: Phys.* **72** 468.
- [2] Newville M 2001 *J. Synch. Rad.* **8** 322.
- [3] d'Acapito F, Ghigna P, Alessandri I, Cardelli A, & Davoli I 2003 *Nucl Instrum Methods: Phys Res B.* **200** 421.
- [4] Lutzenkirchen and Frahm R 2005 *Physica B.* **357** 213.
- [5] d'Acapito F, Milita S, Satta A, and Colombo L 2007 *J Appl Phys.* **102** 043524.
- [6] Rehr J J, Leon J M, Zabinsky S I, Albers R C 1991 *J Am Chem Soc.* **113** 5135.
- [7] Westre T E, Kennepohl P, DeWitt J G, Hedman B, Hodgson K O, Solomon E I 1997 *J Am Chem Soc.* **119** 6297.
- [8] Mayura Panchbhai A et al. 2008 *E-Journal of Chemistry.* **S15**.
- [9] Bhattacharyya D, Poswal A K, Jha S N, Sangeeta, Sabharwal S C 2009 *Bull. Mater. Sci.* **32** 103.
- [10] Bhattacharyya D, Poswal A K, Jha S N, Sangeeta, Sabharwal S C 2009 *Nucl. Instrum. Meth. A*; **609** 286.
- [11] Das N C, Jha S N, Bhattacharyya D, Poswal A K, Sinha A K and Mishra V K 2004 *Sadhana* **29** 545.
- [12] Lee P L, Beno M A, Jennings G, Ramanathan M, Knapp G S, Huang K, Bai J, Montano P A 1994 *Rev. Sci. Instrum.* **65**.
- [13] Matthew A. Marcus, Andrew J. Westphal and Sirine C. Fakra 2008 *J. Synchrotron Rad.* **15**, 463.
- [14] Levy R M 1965 *J. Chem. Phys.* **43** 1846.
- [15] Lytle F W 1966 *Advances in X-ray Analysis.* **9** 398.
- [16] Lytle F W, Sayers D E and Stern E A 1975 *Phys. Rev. B.* **11** 4825.
- [17] Stern E A, Sayers D E and Lytle F W 1975 *Phys. Rev. B.* **11** 4836.