

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES
ANALYSIS OF K-ABSORPTION SPECTRA OF SOME COPPER COMPLEXES USING
ATHENA**A.Rammaiya^{*1}, N. Parsai², P. Sharma³ & A. Mishra⁴**^{*1}B L P Govt P G college, Mhow²Shri Vaishnav Institute of Management, Indore³Govt Holkar Science college, Indore⁴School of Physics, Devi Ahilya University, Indore**ABSTRACT**

A simplified method has been presented for the analysis of extended X-ray absorption fine structure (EXAFS) data and determining the first shell bond length. In the present EXAFS analysis, we have taken the available experimental EXAFS spectra of some copper compounds recorded at room temperature at the synchrotron EXAFS beamline. The theoretical EXAFS data have been generated employing computer software Athena, for the first coordination shell around the absorbing atom, using the EXAFS equation. For the input in this equation, the phase shift for the backscattered photoelectron wave has been obtained from the experimental data, the backscattering amplitude has been taken from the available tabulations and other parameters have been taken from crystallographic data. Fourier transforms of both the experimental and theoretical data have been computed and they agree well with each other in case of all the compounds. The first shell bond lengths in all the compounds have been computed from the Fourier transforms and LSS method and they have been found to agree well with the crystallographic values.

Keywords- EXAFS, Athena, Fourier transform, Bond length

I. INTRODUCTION

During the last 15 years, X-ray absorption spectroscopy (XAS) has found extensive application in determining the local atomic and electronic structure of the absorbing centers (atoms) in the materials science, physics, chemistry, biology, and geophysics. Rapid advance in the XAS method is caused by appearance of synchrotron sources all over the world, as well as by considerable achievement in the theory and its practical realization in convenient and easily available software packages¹.

When X-ray of energies close to the electron binding energies are absorbed, features known as absorption edges are observed. The typical X-ray absorption spectrum exhibits an oscillating fine structure, which extends far from the absorption edge. For convenient interpretation, two regions are often separated: (i) the X-ray absorption near-edge structure (XANES) and (ii) the extended X-ray absorption fine structure (EXAFS). The region upto 50-100 eV beyond an absorption edge is known as XANES region and it is determined by the local density of vacant states in an absorbing atom, as well as by multiple-scattering effects, i.e., scattering of an excited photoelectron on several atoms. The farther EXAFS region is dominated by the single scattering processes and extends up to 400-2000 eV from an edge. Its upper bound is determined by the signal-to-noise ratio and/or another absorption edge.

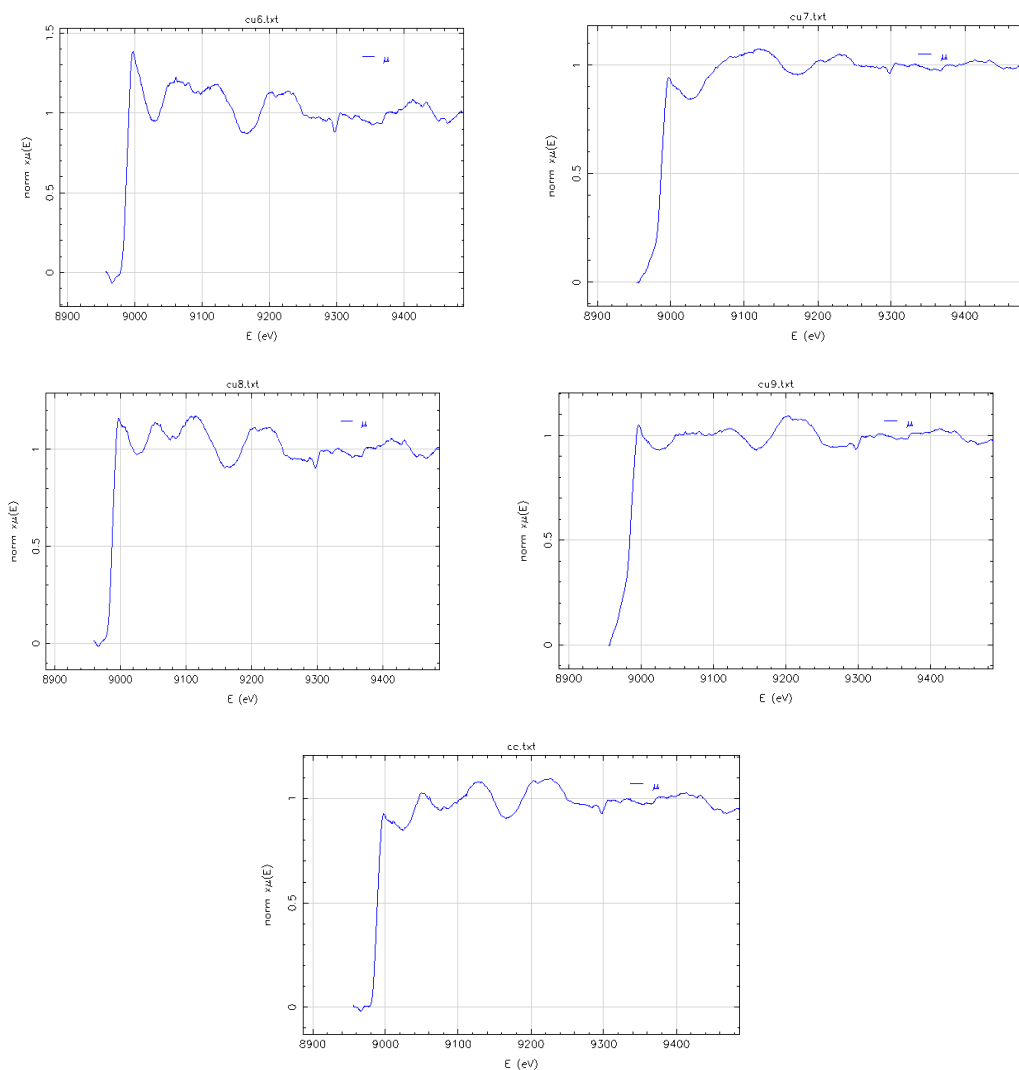


Fig. 1 (a) The normalized XAFS spectrum for Cu(II) Schiff base and pyridine ligands complexes.

The present communication is aimed to provide a simpler technique of EXAFS analysis by using computer software Athena. Earlier the same technique has been demonstrated to yield satisfactory results for copper and nickel metal foils.² In the present work the technique has been described by using the available EXAFS data of some of the copper complexes obtained at room temperature at the synchrotron EXAFS beamlines. For calculation the backscattering amplitude has been taken from the standard table of Teo and Lee³, in which backscattering amplitude has been calculated by plane wave approximation. The similar calculation has been done by using backscattering amplitude from a more accurate table of Mckale⁴, which is based on curved wave approximation. The phase shift has been calculated using LSS method⁵.

II. METHODOLOGY

Several authors have given derivations for the EXAFS theory⁶⁻⁹. The simplest theory is based on the single-scattering plane wave approximation. In this approximation the electron wave is viewed as a plane wave, rather than a spherical wave to simplify the mathematical derivation. In the single scattering event, the electron is assumed to be

scattered only once before it returns to the absorber atom. This simplification is sufficient to describe and analyze the EXAFS signals in most experimental data. The EXAFS function $\chi(k)$ can be given as a summation over all interference patterns scattered off of all neighbouring atoms:

$$\chi(k) = \sum_j \frac{(N_j S_0^2) F_j(k)}{k R_j^2} \sin(2kR_j + 2\delta_j(k)) \exp(-2\sigma_j^2 k^2) \dots (1)$$

$$\times \exp(-2R_j / \lambda(k))$$

where k is the wave vector for the photoelectron, N_j is the number of atoms of type j at distance R_j from the absorber. The exponential term $\exp(-2\sigma_j^2 k^2)$ takes account of the fluctuations of distances due to structural and/or thermal disorder, under the assumption of small displacements and Gaussian distributions of distances. The exponential term $\exp(-2R_j / \lambda(k))$ takes account of the finite mean free paths $\lambda(k)$ of the photoelectrons (between 5 and 10 Å for photoelectron energies from 30 to 1000 eV). S_0^2 is an average amplitude reduction factor; its value is the percent weight of the main excitation channel with respect to all possible excitation channels; its value is usually 0.8–0.9. $|F_j(k)|$ is a scattering amplitude function characteristic of the j^{th} atom, $\delta_j(k)$ is a phase function that takes account of the varying potential field along which the photoelectron moves.

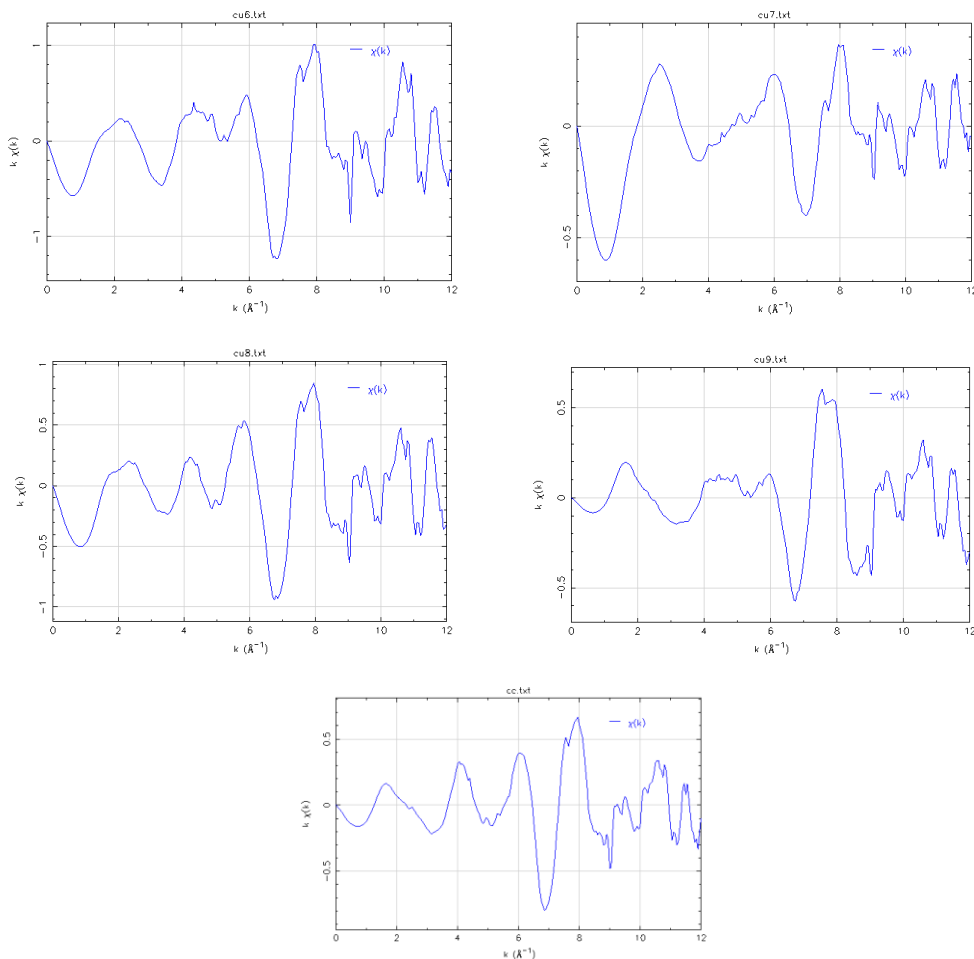


Fig. 2 $\chi(k)$ versus k curve for Cu(II) Schiff base and pyridine ligands complexes.

It can be seen from Eq. (1) that many parameters determine the final $\chi(k)$ function. In addition to the coordination number, distance and disorder, the backscattering amplitudes and phase shifts have to be known. On first sight, this seems to make data analysis rather complicated as so many parameters are unknown. However, it was found that the backscattering amplitude and phase shifts are transferable from one compound to the other, if the same absorber-backscatterer pair is involved¹⁰. Thus if a copper complex is studied, a copper foil can be used as a reference compound for Cu-Cu scattering amplitude and phase shifts.

Fourier transform of the EXAFS function $\chi(k)$ results in a radial distribution function⁸. The Fourier transformation is defined by

$$\phi_n(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} k^n \chi(k) \times \exp(2ikR) dk \quad \dots (2)$$

The radial distribution function is defined in R-space and will have peaks at $R = R_j$ corresponding to average radial distance (R) of the j^{th} atom from the absorbing atom. Thus, the positions of the peaks in the Fourier transform of the EXAFS signal are related to the distance between the absorbing atom and the neighbouring atoms, and the height is related to the number of neighbouring atoms at this distance. The distance found in the Fourier transformation is about 0.2-0.5 Å shorter than the actual distance due to the energy dependence of the phase factors in the sine function of Eq.(1).

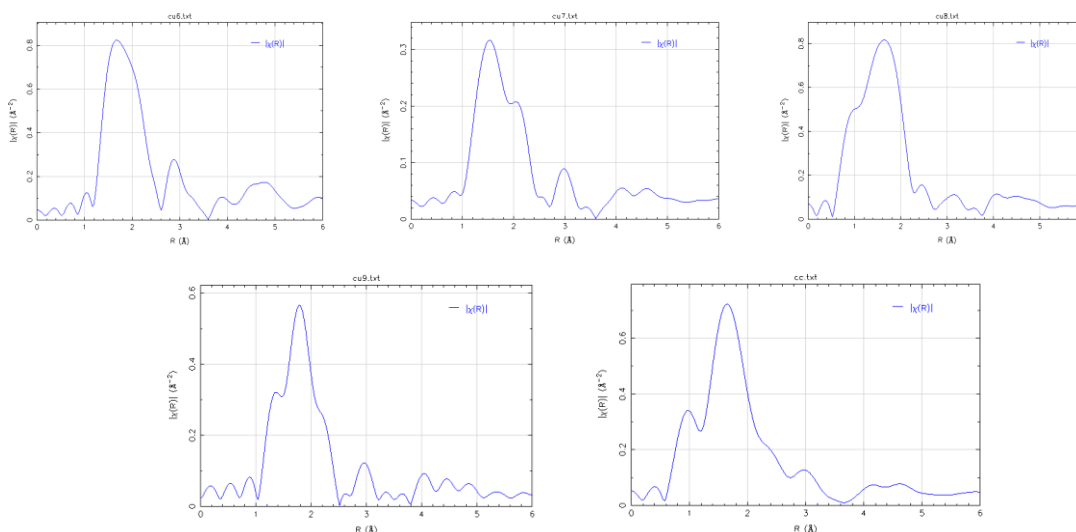


Fig. 3 Magnitude of Fourier transform of the $\chi(k)$ versus k curve for Cu(II) Schiff base and pyridine ligands complexes

In the present work, we have developed a simplified analysis procedure for extracting bond length for the first coordination shell from the experimental EXAFS data using the computer software Athena. The theoretical model is generated through the standard EXAFS equation given in Eq. (1) for the first shell. The values of N_j , σ_j^2 and λ are taken from crystallographic data^{11,12}. The backscattering amplitude $F_j(k)$ has been taken from the tables of Mckale³ as well as of Teo and Lee⁴. The phase shift has been extracted from the experimental data using LSS method⁵.

III. RESULTS AND DISCUSSION

Figs. 1(a-d) show experimental normalized XAFS curves for copper complexes in some mixed ligand copper complexes having Schiff base and pyridine ligands as shown in table1, respectively. For the computation of the data for Figs. 1(a-d), the phase factor has been extracted from the experimental data and the back scattering amplitude has been taken from the theoretical tables of Mckale³ for a distance of 2.5 [Å] from the central absorbing atom. Figs.

2 (a-d) show $\chi(k)$ versus k curves. Though the two formalisms have been reported to give similar values of backscattering amplitude for lower Z elements, yet we have used both of them in the present work to compare the theoretical curves obtained from both of them.

The $\chi(k)$ versus k spectra are then Fourier transformed. The amplitudes of the Fourier transform of the experimental XAFS curves of Figs. 2(a-d) are shown in Figs. 3(a-d) respectively. It is seen from Figs 1 to 3 that the $\chi(k)$ curves as well as their Fourier transforms are in reasonable agreement with their experimental counterparts, showing that the simplified method presented in this work is quite satisfactory to analyze copper complexes.

The values of the bond length for the first shell in these copper complexes have been reported in Table 3 for both types of computations, i.e., by using the back scattering amplitudes from the theoretical tables of Mckale³ and those of Teo and Lee⁴. The values of the bond lengths have been found to be in good agreement with the experimental values and the values obtained by LSS method⁵, which are also given in Table 1.

TABLE 1. Copper (II) complexes of Schiff base and pyridine ligand, their abbreviation.

Complexes	Abbreviation
Cu1	Cu(II) simple aniline Schiff base and 3-Hydroxypicolinamide
Cu2	Cu(II) P-toluidine Schiff base and 3-Hydroxypicolinamide
Cu3	Cu(II) 4-cl aniline Schiff base and 3-Hydroxypicolinamide
Cu4	Cu(II) 4-Nitro aniline Schiff base and 3-Hydroxypicolinamide
Cu5	Cu(II) P-anisidine aniline Schiff base and 3-Hydroxypicolinamide

TABLE 2. Wave vector k (\AA^{-1}) for EXAFS maxima and minima at the K-absorption edge of copper (II) complexes of Schiff base and pyridine ligands and their corresponding values of n .

n	Cu1 k (\AA^{-1})	Cu 2 k (\AA^{-1})	Cu 3 k (\AA^{-1})	Cu4 k (\AA^{-1})	Cu5 k (\AA^{-1})
0	2.25	2.25	2.40	1.70	1.75
1	3.40	3.40	3.55	3.25	3.15
2	4.35	4.35	4.85	4.40	4.05
3	5.15	5.15	5.65	5.40	5.10
4	5.90	5.90	6.70	6.75	6.85
5	6.75	6.75	7.55	7.65	7.65
6	7.90	7.90	8.70	8.90	8.90
7	8.80	8.80	9.80	9.80	9.80
8	9.85	9.45	10.60	10.60	10.80
9	10.70	10.70	11.90	11.90	11.90

TABLE 3. Values of first shell bond lengths (in Å) calculated from LSS and Fourier transform methods for copper (II) complexes of Schiff base and pyridine ligands.

Complex	LSS method $R_1-\alpha_1$	F.T. method R (phase uncorrected)
Cu1	1.69	1.65
Cu2	1.72	1.55
Cu3	1.52	1.66
Cu4	1.42	1.78
Cu5	1.38	1.66

IV. CONCLUSION

In this paper one of the more innovative and simple method of EXAFS data analysis has been presented and demonstrated using some copper complexes. The $\chi(k)$ data computed by this method agree well with the experimental $\chi(k)$ data. The Fourier transforms of the computed $\chi(k)$ data fit well with the Fourier transforms of the experimental $\chi(k)$ data for all these complexes. The first shell bond length determined by the present method shows good agreement with the experimental value and the value calculated using LSS method⁵ for all the copper complexes studied.

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