Comparative Study of Experimental and Theoretical Analysis of EXAFS Data of Copper (II) Complexes Using IEEFFIT Method

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Abstract - The X-ray absorption spectra at the K-edge for a series of copper mixed ligand, having Coumarine as one of the ligands, have been investigated in the laboratory with X-ray spectroscopic set-up. The X-ray absorption edge fine structure parameters bond length using modified Lytle & Levy's method were calculated. In the present study the bond lengths are calculated by Fourier Transform method theoretically using IFEFFIT software and have also been compared with experimental results. IFEFFIT is an interactive program for XAFS Data Analysis. It runs like a command-line 'shell' in which commands are entered to process and manipulate data. IFEFFIT has a fairly high-level command language so that one can do the complex manipulation needed for XAFS analysis (such as background subtraction and Fourier transforms) with simple commands.

Keywords – EXAFS, IEEFFIT Method.

I. INTRODUCTION

The transition metal Schiff base complexes of copper have been playing an important role in the development of coordination chemistry. Schiff base metal complexes have been widely studied,
because of their antifungal and biological applications. [1]. In the present studies we have taken Series of copper (II) complexes Coumarine as ligand have been taken.
The structure extending from 40 to 1000eV from the edge is called extended X-ray absorption fine structure (EXAFS) and it gives information about the local structure of the complexes. The aim of the present investigation is to measure the spectra of copper complex, and to compare first shell inter atomic distance using the programmed called IFEFFIT.

II. PROPOSED ALGORITHM

Experimental Technique –
Material Synthesis –
Preparation of Schiff Base Ligand-
Standard method was adopted for the preparation of the complexes. The series of the copper (II) complexes with Coumarine as ligand is shown below.

Table-1 Series of Copper Complexes Coumarine as Ligand.

S. No.	Name of Ligand	Abbreviation	Mol. Formula
1	3-(4-chloro) phenylazo-7-hydroxy 4-methyl coumarine	34CPA7H4MC	C16H11N2O3Cl
2	3-(2-chloro) phenylazo-7-hydroxy 4-methyl coumarine	32CPA7H4MC	C16H11N2O3Cl
3	3-(3-chloro) phenylazo-7-hydroxy 4-methyl coumarine	33CPA7H4MC	C16H11N2O3Cl

X-ray absorption fine structure studies were carried out using a conventional Siefert sealed X-ray Tube with Tungsten target operating 20 kV and 40 mA. After this process, the scanning of the X-ray films was completed on Carl-Ziess microdensitometer coupled with computer to convert the data into IFEFFIT. The FEFF series of programs for the calculation of X-ray absorption spectra has had a transformative impact on EXAFS analysis because of its accuracy, flexibility, and portability. Its primary use has been in supporting a path by path analysis of experimental data using auxiliary programs such as IFEFFIT, Artemis, Six Pack, etc. In this paper alternative strategies for XAFS analysis that combine FEFF are described[2].

III. RESULT & DISCUSSION

A. EXAFS analysis

The bond lengths of copper complexes were calculated using IFEFFIT method and compared with LSS, Levy's, lytle's methods [3, 4, 5]. According to LSS method, the bond lengths can be detrmine using the slope of n vs k plot. The phase parameter $\alpha_1$and β_1, the metal ligandbond length R_1 have been estimated with expression

$$(1/2+n)\pi=2k\ (R_1-\alpha_1)+2\ \beta_1-\pi$$

The EXAFS curves are shown in figure1.1a Using the Levy's method, the bond length has been obtained from the expression

$$r = (151/\Delta E)^{1/2}$$

where, ΔE is the energy difference between first maxima and first minim [8]. Lytle method is modification of LSS method and the bond length is given by the expression

$$R= (37.60/M)^{1/2}$$

where M is slope between E vs Q plots. In FEFFIT programming the EXAFS data were analyzed by the standard procedure. The pre edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interest background above the edge was removed from the spectrum using spline fit. The data converted to energy space and then to k space.

A Fourier transform is applied to these data to convert into the r-space . The bond lengths of copper complexes calculated by IFEFFIT programming is compared with LSS, Lytle and Levy's methods as depicted in table2.

The theoretical analysis of EXAFS of copper complexes having Coumarine as ligand has been done and compared with experimental values. The results of the average values of metal ligand bond length are reported in table 2.

Table-2 The average values of metal-ligand bond length in ($\overset{0}{A}$)$^{-1}$ for copper complexes

Comp.	Experimental Values By R^a_{Levy}	Experimental Values By R^a_{Lytle}	Experimental Values By R^a_{LSS}	Values By IFEFFIT
34CPA7H4MC	**1.9**	**1.8**	**1.7**	**1.6**
32CPA7H4MC	**3.1**	**1.8**	**1.7**	**1.1**
33CPA7H4MC	**1.9**	**1.7**	**1.6**	**1.4**

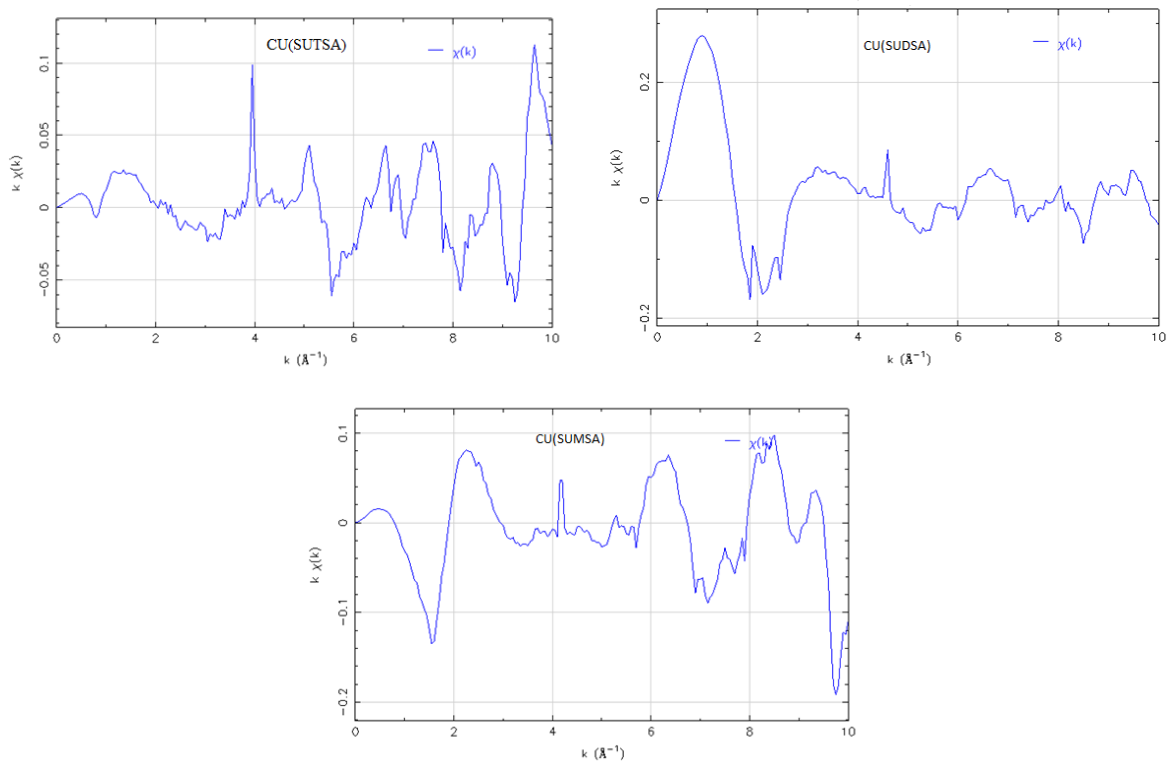

Figure-1 Shows EXAFS spectra of Cu(II) complexes.

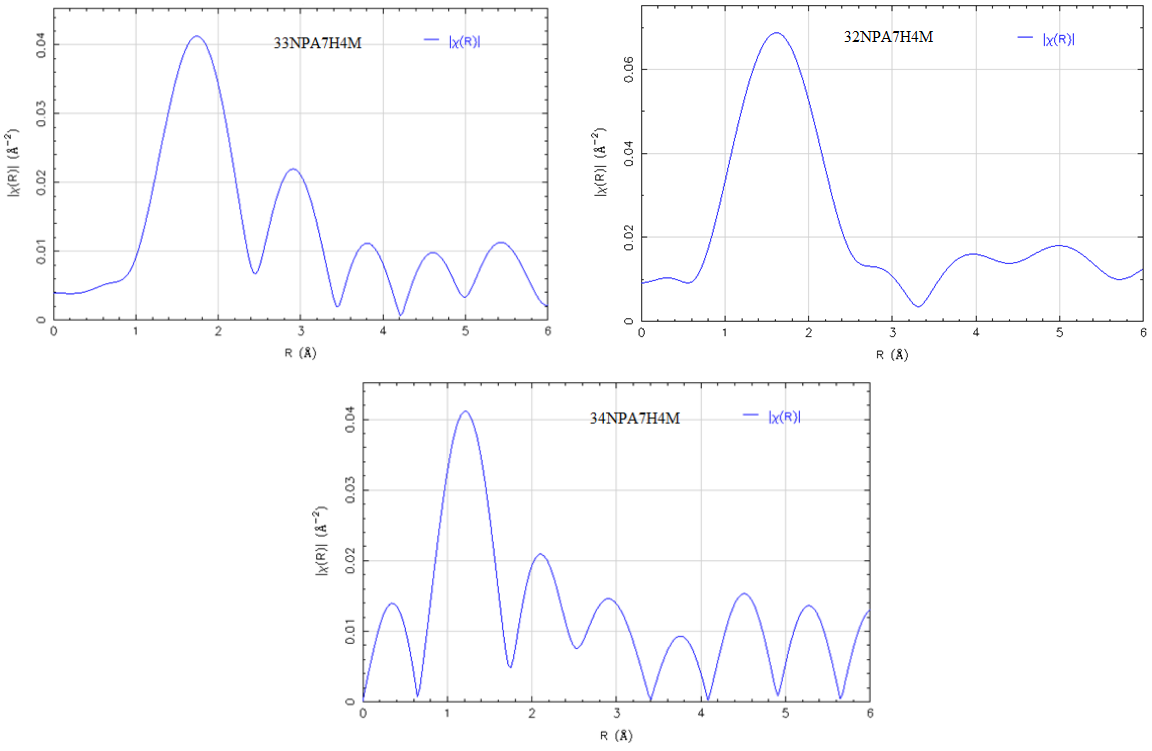

Figure-2 Magnitude of F.T of $k^2\chi(k)$ for copper (II) complexes

IV. CONCLUSION

As is evident from the analysis that the bond lengths determined by Fourier transforming the FEFFIT programming are comparable with the bond length obtained by LSS, Levy's and Lytle methods. The theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of the EXAFS spectra of copper complexes described here is in good agreement with physical reality.

REFERENCES

[1] Kekre P A, Joshi K P and Mishra A, 1996 Indian Journal of Pure and applied Physics 34306
[2] Alternative Strategies forXafs Data Analysis using Feffand Mathematica 7JCPDSInternational Centre for Diffraction Data 2011 ISSN 1097-0002
[3] Konningsberger D C, R. Prins (Eds.), "X-ray Absorption Principle, Technique of EXAFS, SEXAFS, XANES" Wiley, New York, 1998.
[4] Cullity B D, Element of X-ray Diffraction, ewville M 2001 J Synchrotron Rad.8 322
[5] Stern E A, Sayers D E and Lytle F W 1975 Physical Review B 11 4836
[6] Stern E A, 1974 Physical Review B 10 3027
[7] Stern E A, Sayers D E and Lytle F W 1975 Physical Review B 11, 4825