X-ray absorption fine structure (XAFS) spectroscopy using synchrotron radiation

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Abstract. The X-ray absorption fine structure (XAFS) spectra are best recorded when a highly intense beam of X-rays from a synchrotron is used along with a good resolution double crystal or curved crystal spectrometer and detectors like ionization chambers, scintillation counters, solid state detectors etc. Several synchrotrons around the world have X-ray beamlines dedicated specifically to XAFS spectroscopy. Fortunately, the Indian synchrotron (Indus-2) at Raja Ramanna Centre for Advanced Technology (RRCAT) at Indore has started operation. A dispersive type EXAFS beamline called BL-8 has been commissioned at this synchrotron and another beamline having double crystal monochromator (DCM) is going to be commissioned shortly. In Indian context, in order that more research workers use these beamlines, the study of XAFS spectroscopy using synchrotron radiation becomes important. In the present work some of the works done by our group on XAFS spectroscopy using synchrotron radiation have been described.

1. Introduction
X-ray absorption fine structure (XAFS) spectroscopy refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. At certain energy, the absorption increases drastically and gives rise to an absorption edge. Although most of the absorption spectrum is quite smooth, oscillatory features called X-ray absorption fine structure (XAFS) is found directly above an edge. This fine structure is intrinsically quantum mechanical phenomenon that is based on the X-ray photoelectric effect, in which an X-ray photon incident on an atom within a sample is absorbed and liberates an electron from an inner atomic orbital. The “photoelectron” wave scatters from the atoms around the X-ray absorbing atom, creating interferences between the outgoing and scattered parts of the photoelectron wave function. These quantum interference effects cause an energy-dependent variation in the X-ray absorption probability, which is proportional to the X-ray absorption coefficient, a measurable quantity. Traditionally, this fine structure is split into two energy regions. The first, termed as X-ray absorption near edge structure (XANES), occurs in the region from the edge to approximately 40 eV above the edge, while the second, termed as the extended X-ray absorption fine structure (EXAFS), extends from 40 eV to 1000 eV above the edge. The higher energy portions of EXAFS spectra are dominated by single-scattering events within only some tenths of nm (5-6 Å) from the absorber, and contain information specific to the local structure surrounding the absorber. On the other hand, XANES spectra, being centered close to the absorption jump, are dominated by multiple-scattering events extending a few nm from the
Figure 1. Normalized EXAFS spectra at the K-edge of copper in the four complexes.

absorber. XANES is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom, while the EXAFS is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom. As a result, XAS provides a practical and simple way to determine the chemical state and local atomic structure for a selected atomic species. The significant advantage of X-ray absorption spectroscopy over the X-ray crystallography is that the local structural information around the element of interest can be obtained easily and quickly even from disordered samples, such as powders and solutions. To be specific, single crystals of samples are not required in XAS spectroscopy as are necessary in the case of X-ray crystallography. This versatility allows it to be used in a wide variety of disciplines: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology [1].

2. Transition from X-ray tubes to synchrotron sources

X-ray absorption spectroscopy (XAS) has been extensively used in the past to obtain information about molecular structure viz., the valency, bond type, ionic charges, coordination stoichiometry etc. Many research centers in Indian universities and institutes have been doing extensive research work in this field since 1950 or so. At all of these centers, the laboratory X-ray spectroscopic set-ups were in use which employ photographic method of registration of spectra. These types of set-ups comprise of low power (0.5kW - 3kW) X-ray tubes and Cauchois-type curved mica crystal spectrographs employing X-ray films as detectors. After obtaining a number of spectrograms, the analog and digital spectral records were obtained with the help of microphotometers. These analog and digital spectral records were used to be analyzed manually. The results about X-ray absorption edge energies, edge structures, near edge structures and extended fine structures were being reported. The data was used to be generally analyzed qualitatively and empirically to yield useful information about molecular structure. The data was also analyzed through some established relations to yield information about valency, effective nuclear charge, coordination type, average bond length etc. To our knowledge, such photographic EXAFS data has not been analyzed by Fourier transforming and fitting with theoretical standards. Only recently, we have made such an attempt [2, 3]. Unfortunately, nearly all of these centers ceased to work in 1980s because research workers around the world had started using X-rays from synchrotron instead of X-ray tubes for recording the X-ray absorption spectra.

The experimental X-ray absorption spectroscopic data obtained from X-ray tube sources is plagued by noise and systematic errors. It wasn't until the 1970s that high brilliance synchrotron radiation began to be used to obtain absorption spectra. Experimental techniques have continued to develop over the years, and due to the exponential increase in brilliance over time, high quality XAFS data is now routinely collected at a variety of second and third generation synchrotron sources. Over the past three decades, the technique of XAFS has made great strides toward the goal of providing such information. The existence of intense new synchrotron X-ray sources alone was not enough to achieve this goal, even though such facilities spurred considerable progress. In addition, the full success of the XAFS technique must be attributed in large part to advances in theory, which have led ultimately to a highly quantitative understanding of the phenomena.

X-ray absorption spectroscopic measurements with synchrotron radiation are generally carried out on two different types of beamline set-ups. In the first type of XAFS beamline set-up, a double crystal
3. Analysis of EXAFS data using theoretical model

The data obtained from EXAFS beamline is generally analyzed using available computer software packages like Athena and Artemis (available from website www.xafs.org). These programs include AUTOBK for background removal, FEFF6L for generation of the theoretical EXAFS models, and FEFFIT for parameter optimization of the model. A brief description of the recommended analysis procedure is given below. [4]

For normalizing the µ(E) vs. E spectra, a linear function is regressed to the pre-edge region, and a linear or quadratic function is regressed to the post-edge region. Normalized µ(E) spectra are produced by subtracting the pre-edge line from the entire data spectrum and then dividing the spectrum by the step height. µ(E) data is then converted to χ(k) data. The χ(k) data is then Fourier transformed in Artemis. The distance found in Fourier transform is about 0.2 Å - 0.5 Å shorter than the actual distance due to energy dependence of the phase factors in sine function of the EXAFS equation (given below). Hence, to extract the information about the various parameters that can be determined from EXAFS data, the data has to be compared with theoretical model. This can be done through the software Artemis. The program Artemis has a special interface called “Atoms” that converts crystal structure information into a cluster of atoms and provides a list of atom positions in x, y, z coordinates for use in FEFF computations. This trial structure is given as input to the FEFF code to generate a theoretical EXAFS model.

The theoretical model is written as a sum of paths of the contribution from all scattering paths of photoelectron that travels from the absorbing atom and then is scattered from one or more neighbouring atoms and finally returns to the absorbing atom.

$$\chi(k) = \sum_i \left[ N_i S_i^2 F_{\text{eff} i}(k)/kR_i^2 \right] \sin\left[2kR_i + \phi_i(k)\right] \exp(-2\sigma_i^2k^2) \exp[-2R_i/\lambda_i(k)]$$

with $R_i = R_{i0} + \Delta R_i$ and $k^2 = [2m_i(E - E_{i0} + \Delta E_0)/\hbar]$

In the above equations, the terms $F_{\text{eff} i}(k)$, $\phi_i(k)$ and $\lambda_i(k)$ are the effective scattering amplitude of the photoelectron, the phase shift of the photoelectron and the mean free path of the photoelectron,
Figure 3. Coordination geometry about the copper (II) ions in complexes 1 and 2 as deduced from the EXAFS data analysis and following Haddad et al [7]. respectively, all of which can be calculated by a computer program such as FEFF. The term $R_i$ is the half path length of the photoelectron (i.e., the distance between the absorber and a coordinating atom for a single-scattering event). The value of $R_{0i}$ is the half path length used in the theoretical calculation which can be modified by $\Delta R_i$. Each path has several adjustable parameters optimized by the computer code FEFFIT to fit the data. These parameters include the passive electron reduction factor ($S_0^2$), the number of identical paths ($N_i$), the relative mean-square displacement of the atoms included in path ($\sigma_i^2$), an energy shift for each path ($\Delta E_0$), and a change in the path length ($\Delta R_i$).

The theoretical model is adjusted as needed (e.g., with different atom types) until the best possible fit is obtained between theoretical and experimental spectra. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations ($N$, $S_0^2$, $\sigma_i^2$) or the phase of the oscillations ($\Delta E_0$ and $\Delta R_i$).

In the following, some of the works done by our group on X-ray absorption spectroscopy using synchrotron radiation have been described.

4. Calibration of dispersive EXAFS beamline at RRCAT, Indore:
Before doing any XAFS measurement on the recently developed energy dispersive EXAFS beamline at the Indus-2 synchrotron source, RRCAT, Indore, calibration of the particular setting of the polychromator has to be done. We have outlined a method which should be used for finding the dispersion and then for calibrating the experimental spectra [5]. This method involves taking the position of the first maximum of the derivative spectra of the two standards, for determining their edge positions and energies. Also, the performance of the beamline for the particular setting should be checked by recording the EXAFS of a standard and by fitting the EXAFS data with a theoretical model. By recording the K-absorption spectra of copper metal foil and a copper complex on this beamline, it has been shown by analysis and extracting information about the various parameters that the performance of the beamline is quite satisfactory [2, 3].

5. Application of EXAFS spectroscopy using synchrotron radiation - EXAFS study of binuclear hydroxo-bridged copper (II) complexes
As an example of the application of EXAFS, a study carried out by us on copper complexes [6] is being presented here. The EXAFS spectra of binuclear monohydroxo-bridged copper(II) complex [(bpy)$_2$Cu-OH-Cu(bpy)$_2$](ClO$_4$)$_2$ (1), its analogous complex [(phen)$_2$Cu-OH-Cu(phen)$_2$](ClO$_4$)$_2$ (2) and dihydroxo-bridged copper(II) complex [Cu$_2$(μ-OH)$_2$(bpy)$_2$]SO$_4$·5H$_2$O (3), its analogous complex [Cu$_2$(μ-OH)$_2$(phen)$_2$]SO$_4$·5H$_2$O (4) (where bpy and phen are 2,2’-bipyridine and 1,10-phenanthroline, respectively) have been recorded at dispersive EXAFS beamline BL-8 on Indus-2 synchrotron, RRCAT, Indore.

The energies of the K-edge of copper are found to be 8989.69 eV, 8990.01 eV, 8988.30 eV and 8988.11 eV for complexes 1, 2, 3 and 4, respectively. Taking the energy of copper metal K-edge as 8980.5 eV, the chemical shifts are found to be 9.19 eV, 9.51 eV, 7.80 eV and 7.61 eV for complexes 1, 2,
Table 1(a). The EXAFS fitting results for complexes 1 and 2. The XRD results for complex 1 (from Haddad et al. [7]) are also given.

| Atomic pair | EXAFS results | XRD results | EXAFS results |
|-------------|---------------|-------------|---------------|
|             | N  | R(Å) | delr(Å) | σ(Å²) | R  | N  | R(Å) | delr(Å) | σ(Å²) |
| Cu1-O1      | 1  | 1.86 | -0.06   | 0.0101 ± 0.0026 | 1.92 | 1  | 1.83 | 0.0134 ± 0.0017 |
| Cu1-NA      | 1  | 2.18 | -0.17   | 0.0123 ± 0.0099 | 2.00 | 1  | 2.09 | 0.0091 ± 0.0033 |
| Cu1-NB      | 1  | 2.18 | -0.17   | 0.0123 ± 0.0099 | 2.01 | 1  | 2.10 | 0.0091 ± 0.0033 |
| Cu1-NA      | 1  | 2.36 | 0.12    | 0.0123 ± 0.0099 | 2.34 | 1  | 2.10 | 0.0091 ± 0.0033 |
| Cu1-Cu2     | 1  | 3.60 | -0.04   | 0.0014 ± 0.0049 | 3.64 | 1  | 3.42 | 0.0087 ± 0.0100 |

Table 1(b). The EXAFS fitting results for complexes 3 and 4. The XRD results for complex 3 (from Casey et al. [8]) are also given.

| Atomic pair | EXAFS results | XRD results | EXAFS results |
|-------------|---------------|-------------|---------------|
|             | N  | R(Å) | delr(Å) | σ(Å²) | R  | N  | R(Å) | delr(Å) | σ(Å²) |
| Cu1-O1      | 1  | 1.91 | -0.01   | 0.0082 ± 0.0065 | 1.92 | 1  | 1.86 | 0.0082 ± 0.0065 |
| Cu1-O2      | 1  | 1.91 | -0.01   | 0.0082 ± 0.0065 | 1.92 | 1  | 1.86 | 0.0082 ± 0.0065 |
| Cu1-N1      | 1  | 1.98 | -0.01   | 0.0082 ± 0.0065 | 1.99 | 1  | 1.94 | 0.0082 ± 0.0065 |
| Cu1-N2      | 1  | 1.99 | -0.01   | 0.0082 ± 0.0065 | 2.00 | 1  | 1.94 | 0.0082 ± 0.0065 |
| Cu1-O4      | 1  | 2.29 | -0.09   | 0.0066 ± 0.0059 | 2.37 | 1  | 2.38 | 0.0157 ± 0.0063 |
| Cu1-Cu2     | 1  | 2.76 | -0.08   | 0.0075 ± 0.0028 | 2.84 | 1  | 2.78 | 0.0046 ± 0.0022 |

3 and 4, respectively. These values of the chemical shifts suggest that copper is in +2 oxidation state in all of these four complexes. The EXAFS data have been analyzed and theoretical models have been generated for the complexes 1 and 3, and then fitted to their experimental EXAFS data to obtain the bond-lengths, coordination numbers and thermal disorders. As the crystallographic data for the complexes 2 and 4 are not available in literature, we have determined the structural parameters for these complexes by fitting their experimental EXAFS data with the same theoretical models which were generated for their corresponding analogous complexes, i.e., 1 and 3 respectively.

5.1. Complex 1
For the analysis of the EXAFS data of 1, the input parameter R₃₉₅, that determines the maximum frequency of the background, was set to 1.0 Å. Fourier transform was performed over k-range: kₘₐₓ=2.30 Å⁻¹, kₘᵓₙ=8.38 Å⁻¹. Theoretically modeled data was fitted in the R-space to the experimental data using kw = 2. Fitting was performed for the coordination shells in the R range of 1.0 - 5.0 Å. In the fitting procedure, we have used the first 16 paths obtained from FEFF calculations. The value of goodness-of-fit parameter, i.e., reduced chi-square (χ²) is 76.31. The results obtained from fitting are given in table 1(a), which gives the local structure parameters for complex 1 obtained from the analysis. The S₀² value obtained is 1.57 ± 0.31. ΔE₀ value is also reasonable, i.e., 5.43 eV ± 1.75. Also, the σ² values are quiet high as the measurements have been performed at room temperature.

Our results for the bond distances in 1, with ΔR ranging from -0.04 to 0.17, are given in the table 2(a) and these distances are in agreement with the crystallographic bond distances reported by Haddad et al. [7]. The Cu-O-Cu bridging angle calculated from the obtained distances is 150.8° which is in the range of 135.4° - 165.6° reported for binuclear monohydroxo-bridged complexes. The value of this angle as reported by Haddad et al. is 141.6°. Hence, the theoretical model generated by us for 1 appears to be quite reasonable. Using the present results the inner coordination spheres around the two copper (II) centers have been depicted in figure 3(a). This figure is based on the figure given by Haddad et al. but shows the distances and the bridging angle obtained by us in the present study.
5.2 Complex 2

As the theoretical model generated by us for 1 fits well to its experimental EXAFS data and as 1 and 2 are analogous to each other, we have used the same theoretical model generated for 1 to fit the experimental EXAFS data of 2. The data analysis procedure used for 1, as explained above, has also been applied to 2 and the input fitting parameters were kept the same during fitting. The $S_0^2$ value obtained is 1.17 ± 0.24. $\Delta E_0$ value is also reasonable, i.e., -1.25 eV ± 2.78. The structural parameters so obtained for 2 are reported in table 2(a). The Cu-O-Cu bridging angle calculated from the obtained distances is 138.2˚ which is in the range of 135.4˚ - 165.6˚ reported for binuclear monohydroxo-bridged complexes. Using the obtained results, the inner coordination spheres around the two copper (II) centers in 2 have been depicted in figure 3(b).

5.3 Complex 3 and 4

The crystallographic data is available for 3 [8], using which the theoretical model for the complex has been generated. This theoretical model is then fitted to its experimental EXAFS data to obtain the structural parameters for 3 and the results obtained from fitting are given in table 1(b). The results have been found to be comparable with the crystallographic results. The Cu-O-Cu bridging angle calculated from the obtained distances comes out to be 91.8˚, while the range reported for binuclear dihydroxo-bridged complexes is 95.6˚ - 104.1˚. The value of this angle as reported by Casey et al. [8] is 97.0˚.

As the crystallographic data for 4 is not available in the literature, we have applied the same method as in the case of 1 and 2, i.e, we have used the theoretical model generated for 3 to fit the experimental EXAFS data of its analogous complex 4. The structural parameters so obtained for 4 are also reported in table 1(b). The Cu-O-Cu bridging angle calculated from the obtained distances is 96.71˚ which is in the range of 95.6˚ - 104.1˚ reported for binuclear dihydroxo-bridged complexes.

Using the present results the inner coordination spheres around the two copper (II) centres have been depicted in figures 4(a) and 4(b) for complexes 3 and 4, respectively. Figure 4(a) is based on the figure given by Casey et al. but shows the distances and the bridging angle obtained by us in the present study.

The metal-metal coordination number in the four complexes has been found to be unity (table 1 (a) and (b)) which points to the presence of a stable binuclear complex. Thus, on the basis the analysis of the EXAFS data, the four complexes have been shown to be binuclear, i.e., they contain two metal atoms per cluster.

Thus, it has been demonstrated that if crystal structure is available for a complex from X-ray crystallographic studies (which require single crystals), structural parameters like bond-length, coordination number and Debye-Waller factor can be determined for any of its analogous complex from EXAFS studies (which do not require single crystals).
6. Application of XANES spectroscopy using synchrotron radiation - A comparative study of the methods of speciation using X-ray absorption fine structure

As an example of the application of XANES, study carried out by us on speciation of copper compounds in their mixture is being presented here. XANES spectrum reflects the local structure around the absorbing atom and provides information about oxidation state of an excited atom and the coordination symmetry. By taking standards of well-defined chemical species, analysis of XANES can be used to determine metal speciation, i.e., determination of the chemical forms along with the relative quantity of the different species in a given sample. For speciation using XANES, the commonly used methods are: principal component analysis (PCA), target transformation (TT) and linear combination fitting (LCF). Other methods which can be used are: methods based on derivative spectra, method based on the relative position of the absorption edge, residual phase analysis (RPA) and normalized difference absorption edge spectra analysis (NDAES).

We have made comparative studies of the above mentioned different methods of speciation and discussed their relative merits by taking example of mixture of cuprous oxide and cupric oxide in a specific ratio [9, 10]. The X-ray absorption fine structure (XAFS) spectra for these standards and the mixture were recorded using the EXAFS set-up at the synchrotron wiggler beamline 4–1 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, California, USA.

The normalized (energies normalized to the elemental Cu edge, baseline, and background corrected) XANES spectra of copper metal, cuprous oxide, cupric oxide and their mixture are shown in figure 5. The edge position, defined as the maximum point of the first derivative function in the rapidly rising edge step of the absorbance vs. energy plot, have been found to be 8979.0, 8980.6 and 8983.6 eV for Cu foil, Cu$_2$O and CuO, respectively. The different characteristic features obtained in the present investigation in the XANES region for two copper oxides, which are used as standards, are also shown in figure 5. These features are important as they are ultimately used for speciation purpose.

In the present study, for PCA and target transformation, SIXPack data analysis software has been used. (Details can be found at www.ssrl.slac.stanford.edu/swebb/sixpack.htm). LCF has been performed using Athena. The position of the edge corresponding to the point having $\mu x = 0.5$ in the normalized spectrum has been determined using Athena. The difference spectra and the derivative spectra for the analysis were also constructed using Athena. EXAFS data analysis program Artemis has been used for optimizing the theoretical model to the measured spectrum.

![Figure 5. XANES spectra of copper metal, cuprous oxide, cupric oxide and their mixture.](image-url)
By applying PCA and target transformation, the number and identity of components in the mixture have been confirmed. Then, five methods have been used by us for determining the proportions of the CuO and Cu$_2$O in the mixture. The methods of speciation and the results obtained are discussed below.

6.1 Principal component analysis (PCA): PCA determines the minimum number of significant components required to satisfactorily regenerate the data matrix, using a reduced space. PCA assumes that the absorbance in a set of spectra can be mathematically modeled as a linear sum of individual factors, called as eigenvalues and eigenvectors. PCA has been performed in both XANES and EXAFS regions. However, the results of PCA have been presented in figure 6 only for the EXAFS region in the range 2 to 12 Å$^{-1}$. The figure shows the different components weighted by their eigenvalues. It can be seen from the figure that the first two components clearly dominate the spectra and the third component appears to be noise.

Figure 6. First three components from PCA calculation performed in the EXAFS region and weighted by eigenvalues.

Figure 7. Predicted targets obtained through target transformation of the Cu Kedge EXAFS spectra for (a) Cu$_2$O and (b) CuO

| S.No. | Method of speciation | Percentages of components in the mixture | Max. % error |
|-------|----------------------|-----------------------------------------|--------------|
|       |                      | Cu$_2$O | CuO               |              |
| 1.    | LCF                  | 73      | 27                | ± 2 %        |
| 2.    | NDAES                | 71      | 29                | ± 5 %        |
| 3.    | RPA                  | 70      | 30                | ± 5 %        |
| 4.    | Der. Cu(I)$^+$      | 74      | 26                | ± 2 %        |
| 5.    | Edge$^{**}$          | 79      | 21                | ± 5 %        |
|       | As prepared          | 75      | 25                | -            |
6.2 Target transformation (TT): In target transformation, which is also known as transformation factor analysis (TFA), the spectra from reference compounds are individually compared with the collection of mathematical principal components (PCs). The experimental reference spectra are transformed to fit the number of PCs selected from PCA. The degree to which the reference must be changed to fit the PCs is measured by SPOIL value. A high SPOIL value indicates a poor fit, suggesting that this standard is not well represented in the collection of sample spectra (represented by the PCs) [4]. Target transformation has been performed in both XANES and EXAFS regions. However, the results of TT have been presented in figure 7 only for the EXAFS region in the range 2 to 12 Å⁻¹. One of the standards, i.e., copper metal has been rejected as a potential target because its SPOIL value has come out to be > 6. Cu₂O has proved to be a very good target, with a SPOIL value < 3 and CuO has come out as marginal candidate in the SPOIL test, with SPOIL value between 3 and 6.

6.3 Method based on derivative spectra: The derivative spectra of the mixture and the standards Cu₂O and CuO are shown in figure 8. The derivative spectrum of a mixture has a distinct feature: ‘γ’ at 8981 eV corresponding to the Cu(I) component. It is the most intense feature of the derivative XANES spectra of Cu(I) species and can be used to determine the percentage of a species in the mixture. Also, it lies in a region (from 8980 to 8984 eV) where the Cu(II) species have a null derivative. The intensity of this peak varies as the amount of Cu(I) species is varied. If Iₘ and I Cu₂O are the intensities of the first maximum in the derivative spectra at 8981 eV in the mixture and Cu₂O respectively, then the ratio of Iₘ to I Cu₂O gives the fraction of Cu(I) in the mixture. The percentages of Cu₂O and CuO in the mixtures as obtained from this method are 74% and 26% respectively with an error of ± 2%.

6.4 Method based on position of the edge: It is well known that position of the absorption edge varies with the oxidation state of central metal atom. Also, significant difference between the positions of the Cu K-edges of Cu(I) and Cu(II) has been observed. In a mixture the position of the Cu K-edge is between the positions of the edges of Cu(I) and Cu(II). This shift in the value of edge energy of the mixture w.r.t. Cu(I), can be used to measure percentage of Cu(II) present in the mixture.
Figure 10. Normalized difference absorption edge spectra for copper K-edge XANES. The ratio of the height of positive peak β to that of peak α gives the proportion of Cu(I) in the mixture.

For this method, the position of the edge is taken as the point corresponding to $\mu x = 0.5$ in the normalized spectrum. Writing $E_{Cu_2O}$, $E_{CuO}$ and $E_{m}$ as the energies of the position of the edge in $Cu_2O$, CuO and the mixture respectively, the fraction $x_m$ of Cu(II) in the mixture can be determined from relation: $x_m = \Delta E_m/\Delta E_{CuO}$, where $\Delta E_m = (E_m - E_{Cu_2O})$ and $\Delta E_{CuO} = (E_{CuO} - E_{Cu_2O})$ are the edge energy shifts w.r.t. $Cu_2O$. The percentages of $Cu_2O$ and CuO in the mixtures as determined from this method are 79% and 21% with an error of ±5%.

6.5 Linear combination fitting (LCF): In least-squares LCF, one determines the proportions of the spectra for selected standards that, when summed, yield the least fit to the spectrum for an unknown sample. Also, least-squares LCF can be done across a wide energy range of the spectrum, i.e., even in the EXAFS region and thus enhances the discrimination of different species having identical spectral features at a given energy but distinct features at other energies.

The results of LCF are shown in figure 7. The fractions of the $Cu_2O$ and CuO making up the fitted spectra are also shown in this figure. The percentages of $Cu_2O$ and CuO in the mixture, as determined from LCF method are 73% and 27% respectively with an error of ±2%. In the case of LCF method, R-factor and chi-square values are 0.00016 and 0.02309 respectively. The little difference between the experimental data and LC fitted data can be seen from the difference curve which is also shown in figure 9.

6.6 Normalized difference absorption edge analysis (NDAES): In this method, to quantitate copper content, the normalized difference edge absorption spectra have been calculated by subtracting normalized edge of Cu(II) from that of normalized edge of the Cu(I) which produces characteristic derivative shaped spectra. The difference spectrum has a positive peak at 8983-8984 eV and a broad negative feature at 8990-9000 eV. The amount of cuprous ion present can be determined from the height of the positive peak. In other elements, similar characteristic features are present which can be used for the purpose of speciation.

The results of NDAES are shown in figure 10. In this figure, $\alpha$ is the positive peak obtained when CuO spectrum is subtracted from $Cu_2O$ spectrum and $\beta$ is obtained when the spectrum of mixture is subtracted from the $Cu_2O$ spectrum. The heights of the peaks $\beta$ and $\alpha$ have been measured very precisely. The ratio of the height of positive peak $\beta$ to that of peak $\alpha$ gives the proportion of Cu(I) in the mixture. The percentages of $Cu_2O$ and CuO in the mixture, as determined from this method are 71% and 29% respectively with an error of ±5%.
6.7 Residual phase analysis (RPA): RPA utilizes one of the known components as a “starting phase.” The “starting phase” is then fractionated and iteratively subtracted from the total EXAFS signal to produce corresponding residual spectra. The individual residual spectra are analyzed to obtain the best fit as follows.

Taking pure Cu$_2$O EXAFS data as the known phase and the EXAFS data of mixture as total EXAFS signal, the residual phase data has been constructed, for all y (adjustable mixing fraction) between 0 and 1, with an increment of 0.1. The statistical chi-square values obtained in each fit were then plotted as the function of y, and the minimum has been obtained as shown figure 11. The corresponding mixing fraction is found from the position of the minimum. The percentages of Cu$_2$O and CuO in the mixture have thus been found to be 70% and 30% respectively with an error of ± 5%.

The two studies presented here were done at two different beamlines at two synchrotron facilities. As already pointed out earlier, in India, the work on EXAFS has been done on recently developed Indus-2 synchrotron facility which was not earlier available to Indian workers. For the last forty years research workers in Indian laboratories were doing experiments on laboratory XAFS set-ups. Now, it is hoped that future research workers from Indian laboratories will utilize to the maximum the XAFS facilities at Indus-2.

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