

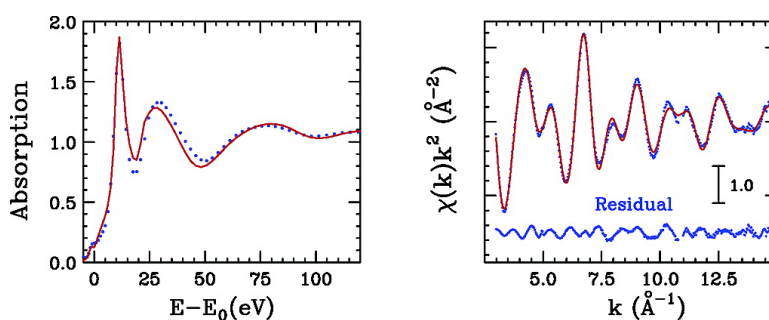
Article

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Full Quantitative Multiple-Scattering Analysis of X-ray Absorption Spectra: Application to Potassium Hexacyanoferrat(II) and -(III) Complexes

Kuniko Hayakawa,^{†,‡} Keisuke Hatada,[†] Paola D'Angelo,^{*,§} Stefano Della Longa,^{||,†} Calogero R. Natoli,[†] and Maurizio Benfatto^{*,†}

Contribution from the Laboratori Nazionali di Frascati, INFN, CP13, 00044 Frascati, Italy, Dipartimento di Biologia, Università di Padova, Padova, Italy, Dipartimento di Chimica, Università di Roma "La Sapienza", P. le A. Moro 5, 00185 Roma, Italy, and Dipartimento di Medicina Sperimentale, Università "L'Aquila", Via Vetoio 67100 L'Aquila, Italy

Received July 23, 2004; E-mail: p.dangelo@caspur.it

Abstract: A recently developed method to the full quantitative analysis of the XAS spectra extending from the absorption edge to the high-energy region is presented. This method is based on the use of two independent approaches to the analysis of the EXAFS and XANES data, the well-known GNXAS and the newly developed MXAN procedures. Herein, we report the application of this technique to two iron complexes of known structure where multiple-scattering effects are prominent, the potassium hexacyanoferrat(II) and -(III) crystals and aqueous solutions. The structural parameters obtained from refinements using the two methods are equal and compare quite well with crystallographic values. Small discrepancies between the experimental and calculated XANES spectra have been observed, and their origin has been investigated in the framework of non-muffin-tin correction. The ligand dependence of the theoretical spectra has been also examined. Analysis of the whole energy range of the XAS spectra has been found to be useful in elucidating both the type of ligands and the geometry of iron sites. These results are of particular use in studying the geometrical environment of metallic sites in proteins and complexes of chemical interest.

1. Introduction

X-ray absorption spectroscopy (XAS) is a valuable tool for investigating the local coordination environment of specific atoms in a large variety of systems. This technique is sensitive to short-range order and can be applied to any physical state, including crystals, liquid solutions, and amorphous solids. Recently, a new method (MXAN) of extracting both the metric and the angular structural information available in the XAS spectra has been developed and applied to several biological and inorganic systems.^{1–5} MXAN employs the full multiple-scattering (MS) approach to a description of the low-energy part of the X-ray absorption cross section extending up to around 100–150 eV above the threshold, the so-called XANES (X-ray absorption near-edge structure) region. Due to recent advances in the theory, it is now possible to apply the fitting procedures generally employed to interpret the extended X-ray

absorption fine structure (EXAFS) data⁶ also to the XANES region, so that the whole energy range of the absorption spectrum can be used for a quantitative determination of the structural parameters. The importance of this approach stems from the higher sensitivity of the XANES region, as compared to EXAFS, to the fine details of the geometrical arrangement of the scattering atoms around the absorber and to their chemical nature. In particular, when dealing with biological systems, the EXAFS technique is not very sensitive to the number of ligands and to their chemical nature, and the combined analysis of the EXAFS and XANES regions can provide additional insights that are key to obtaining an accurate molecular description of the system under investigation. Recently, a combined XANES and EXAFS study of Ni²⁺, Co²⁺, Zn²⁺, and Cu²⁺ ions in aqueous solutions proved the reliability of this approach.^{3,4}

Here, we intend to investigate the characteristics, advantages, and limitations of this approach by applying the method to Fe K-edge XAS data of iron coordination complexes where MS effects are quite prominent. MS effects are particularly evident for systems containing certain rigid ligands as imidazoles and porphyrines and can be of such magnitude that they dominate over single scattering signals. In particular, a thorough investigation of both XANES and EXAFS spectra of K₃Fe(CN)₆ and K₄Fe(CN)₆ crystals and aqueous solutions has been performed. These systems are characterized by the presence of six linear

[†] INFN.

[‡] Università di Padova.

[§] Università di Roma "La Sapienza".

^{||} Università "L'Aquila".

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Fe–C–N configurations giving rise to strong MS contributions, and for this reason they have been often employed to test the validity of the theoretical framework used in the XAS analysis.⁷ In this paper, we will carry out the analysis of both the ferrous and the ferric compounds, and we will compare the results obtained in the crystalline state and in aqueous solutions. The sensitivity of both EXAFS and XANES toward the number and chemical nature of the coordination groups bound to the Fe atom will be tested, this result being particularly important for biological systems. Moreover, we will discuss some effects of the muffin-tin approximation on the XANES calculations by comparing the results of the MXAN method with those obtained from a non-muffin-tin procedure. This work has been motivated, after the first successful quantitative XANES analyses made on metalloproteins,^{2,5} by the need to thoroughly test and validate the applications of the MXAN procedure to systems of biological interest.

2. Methods

2.1. Experimental Spectra. The Fe K-edge X-ray absorption spectra of 0.5 M $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ aqueous solution, and crystals were recorded at the ESRF (Grenoble, France), beam-line BM29.⁸ The solutions were prepared by dissolving weighed amounts of the salts in deionized water. The data were recorded in transmission mode using a Si(311) double-crystal monochromator, detuned to 50% of the rocking curve full width at half-maximum, for harmonic rejection. Data points were collected for 1 s each, and several spectra were recorded and averaged. The solutions were kept in cells with Kapton film windows and Teflon spacers of 1 mm. An iron foil internal energy calibration was measured simultaneously with each spectrum. The energy was defined by assigning the first inflection point of the Fe foil spectrum to 7111.2 eV.

2.2. XAS Data Analysis. The EXAFS and XANES regions of the absorption spectra have been quantitatively analyzed using two independent methods both based on multiple-scattering formalism,⁹ within the muffin-tin approximation for the shape of the potential.

The EXAFS data analysis has been performed using the GNXAS method which is based on the theoretical calculation of the EXAFS signal and a subsequent refinement of the structural parameters.^{6,10} In this approach, the interpretation of the experimental data is based on the decomposition of the $\chi(k)$ signal into a summation over n -body distribution functions calculated by means of the MS theory. The iron environment has been described by a two-body configuration associated with the six Fe–C first-shell distances and six three-body distributions accounting for the Fe–C–N configurations. We have verified that all of the signals associated with higher distance shells have negligible amplitudes. The structural parameters were the bond distance (R) and bond variance (σ^2) for the two-body signal, the two bond distances, the intervening angle (θ), and the six covariance matrix elements for the three-body signal.¹¹ Additional nonstructural parameters were minimized, namely E_0 (core ionization threshold) and S_0^2 (many-body amplitude reduction factor).

The quantitative XANES data analysis has been performed by means of the MXAN procedure which is described in detail in refs 1, 2, and 12. To include the XANES energy region starting from the edge, the scattering path operator is calculated exactly without any series

expansion. The Debye–Waller factor corrections are not included in this approach due the limited k -range used in the minimizations. Fitting procedures have been carried out assuming an octahedral arrangement of the carbon atoms around iron and minimizing only three structural parameters, the Fe–C and C–N distances, and the Fe–C–N angle. The procedure also includes three nonstructural parameters accounting for inelastic losses.¹ MXAN and the experimental data are available from the authors upon request to make it possible for users to test the program.

Least-squares fits of the XANES and EXAFS experimental data have been performed by minimizing the R_{sq} function defined as:

$$R_{sq}(\{\lambda\}) = \sum_{i=1}^N [\alpha_{exp}(E_i) - \alpha_{mod}(E_i; \lambda_1, \lambda_2, \dots, \lambda_p)]^2 \times W(E_i)$$

where N is the number of experimental points E_i , $\{\lambda\} = (\lambda_1, \lambda_2, \dots, \lambda_p)$ are the p parameters to be refined, and $W(E_i)$ is a weight function. The exact expressions of $W(E_i)$ can be found in refs 6 and 1 for the EXAFS and XANES analyses, respectively.

Phase shifts were calculated using muffin-tin potentials and advanced models for the exchange–correlation self-energy (Hedin–Lundqvist).¹⁴ The muffin-tin radii were chosen according to the Norman criterion with 1% overlapping.

A recent XAS investigation of the iron hydration complexes has shown the presence of multielectron excitations at the Fe K-edge. In particular, anomalous features at about 3.9 and 5.3 \AA^{-1} have been detected and assigned to the simultaneous excitations of the 1s3p and 1s3s electrons, and the intensities of these channels have been found to be only a few percent of the main transition edge.¹³ In the present investigation, double electron excitations have been accounted for in the EXAFS analysis by modeling the atomic background as the sum of a smooth polynomial spline, plus step-shaped functions, as described in ref 6. The parameters defining the 1s3p and 1s3s double electron channels, obtained from the EXAFS minimizations, have been found equal to those reported in ref 13. As far as the XANES region is concerned, multielectron transition edges have not been accounted for in the MXAN analysis, as their amplitude is of the order of magnitude of the present theoretical accuracy.

The full potential calculations are based on the finite difference method (FDM), which does not require any approximation for the shape of the potential. This method essentially writes the Schrödinger equation on a three-dimensional grid, obtaining a large system of linear equations connecting the values of the wave function on all of the grid points. We have used the program FDMNES developed by Y. Joly, and all details can be found in ref 15. The potential has been calculated on the basis of the $Z + 1$ approximation for the final state. To compare the theoretical results obtained by the FDM method with those obtained using muffin-tin potentials, we have modified the MXAN code for reading an external theoretical spectrum (the output of the FDMNES program calculated with real Hedin–Lundqvist potential) and performing a minimization in the nonstructural parameter space, only. The damping associated with the inelastic processes is included in the FDM calculation in the same way as in the calculations performed using the muffin-tin potential, and the resulting spectrum is compared to the experimental data.

3. Results

Figure 1 shows the comparisons between the crystal and aqueous solution XAS spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (upper and lower panels, respectively). The crystal and solution spectra are almost identical in the energy range above the main transition threshold, while small differences are detectable in

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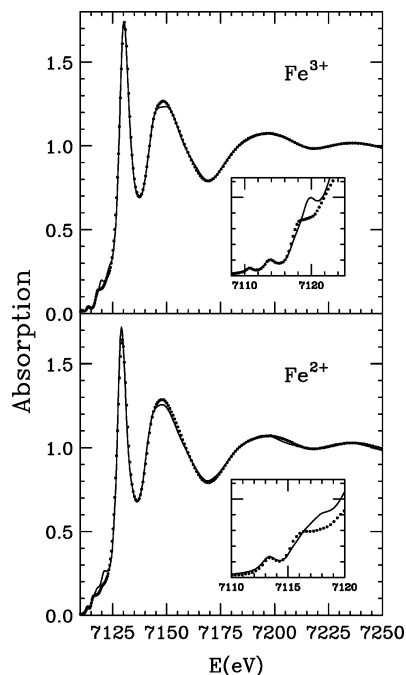


Figure 1. Upper panel: Fe K-edge XAS spectra of $K_3Fe(CN)_6$ crystal (full line) and water solution (dotted line). Lower panel: Fe K-edge XAS spectra of $K_4Fe(CN)_6$ crystal (full line) and water solution (dotted line). The insets display an expanded view of the $1s \rightarrow 3d$ pre-edge regions.

the pre-edge regions. This finding suggests that the structural environment around the ferrous and ferric ions is identical both in the crystal and in solution, within the short distance range probed by XAS. The low-spin ferrous and ferric complexes have an octahedral iron site, and, therefore, the only intensity mechanism for the $1s \rightarrow 3d$ pre-edge feature is the allowed electric quadrupole transition.¹⁶ The $K_4Fe(CN)_6$ complexes have a single feature at about 7113 eV, showing the same energy position and intensity both in the solid state and in solution. On the other hand, the feature on the rising edge of the spectra at about 7116 eV, that has been assigned as an edge transition,¹⁶ becomes less intense and appears at lower energy in going from the crystal to the solution (see the inset in the lower panel of Figure 1). The $K_3Fe(CN)_6$ complexes show a weak $1s \rightarrow 3d$ pre-edge feature at about 7114 eV with a shoulder at lower energy. These features are identical both in the crystal and in aqueous solution, while the edge transition around 7118 eV is shifted to lower energy and becomes weaker in the case of the hydrated complex (see the inset in the upper panel of Figure 1).

The modification of the structures observed in the pre-edge regions could reflect long-range order effects involving the break-down of the local octahedral symmetry due to the presence of ordered atomic shells beyond the cyanide ligands in the crystals. This can give rise to dipole transitions to empty bound states that are normally forbidden in the case of the hydrated octahedral complexes. The tentative explanation of the pre-edge features is beyond the aim of the present work. In the previous edge region, the excited photoelectron becomes rather sensitive to both the spatial and the electronic details of the potential, and it is likely that a full potential approach is necessary for a deeper understanding of these features. However, at present,

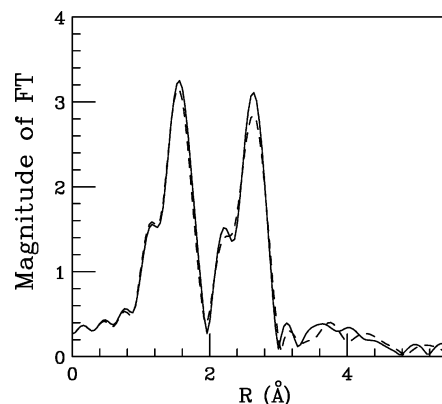


Figure 2. Nonphase-shift-corrected Fourier transforms of the EXAFS experimental data of the $K_3Fe(CN)_6$ crystal (full line) and water solution (dashed line) performed over the range $k = 3.0\text{--}15.0 \text{ \AA}^{-1}$.

the analysis performed with packages employing full potential calculation, like FDMNES, is still not possible as these procedures contain much heavier time-consuming algorithms.

Further proof of the similarity of the local iron coordination environment in crystals and in solution has been obtained by comparing the Fourier transforms (FT) of the experimental spectra. The FT moduli of the $K_3Fe(CN)_6$ crystal and of the hydration complex EXAFS spectra, extracted with a three-segmented cubic spline, are shown in Figure 2. The FT's have been calculated in the interval $k = 3.0\text{--}15.0 \text{ \AA}^{-1}$, with no phase-shift correction applied. Simple inspection of the FT spectra offers interesting insight into the structural information that can be obtained from the EXAFS technique. The first peak at about 1.5 \AA is associated with the Fe–C first-shell contribution, while the second peak at about 2.6 \AA is essentially due to the strong Fe–C–N MS signal and to the two-body Fe–N second-shell contribution.⁷ The higher-distance peaks are mainly due to cutoff effects, and no structural information is obtainable for distances longer than about 3.2 \AA from the iron atom. Therefore, due to the short-range sensitivity of this technique, only the first-shell cyanide groups contribute to the XAS spectra, and no differences are detectable between the crystalline and liquid phases. Similar results have been obtained for the $K_4Fe(CN)_6$ complex and have not been reported for the sake of brevity. The similarity of the coordination geometry around the iron ions in aqueous solution and in the crystal has been verified by performing quantitative EXAFS and XANES analyses of the spectra, and the results are reported in the following.

3.1. EXAFS Analysis. We used the GNXAS program to analyze the EXAFS data of the ferric and ferrous compounds. All of the minimizations were performed starting from the $K_3Fe(CN)_6$ crystallographic structure,^{17,18} assuming an octahedral first-shell coordination. From the crystallographic data, the Fe–C bond distance ranges from 1.93 to 1.94 \AA , while the Fe–C–N angle ranges from 177° to 179° with an average C–N distance of 1.15 \AA .^{17,18} The two-atom configurations included the Fe–C distance, while the three-atom configurations included the Fe–C–N, C–Fe–C (90°), and C–Fe–C (180°) three-body distributions. The coordination numbers were fixed to the known values, whereas the Fe–C and C–N distances and the Fe–C–N angles were allowed to vary along with the respective

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Table 1. Structural Parameters for $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ Crystals and Aqueous Solutions Obtained from the EXAFS Data Analysis^a

	R_{FeC} (Å)	σ_{FeC}^2 (Å ²)	R_{CN} (Å)	σ_{CN}^2 (Å ²)	θ (deg)	σ_θ^2 (deg ²)
Fe^{3+} aqueous solution	1.93(1)	0.0009(1)	1.18(1)	0.0007(2)	176(3)	4.4(5)
Fe^{3+} crystal	1.93(1)	0.0009(1)	1.17(1)	0.0006(2)	175(3)	4.4(4)
Fe^{2+} aqueous solution	1.92(1)	0.0014(2)	1.18(1)	0.0008(2)	177(2)	4.0(5)
Fe^{2+} crystal	1.92(1)	0.0013(2)	1.17(1)	0.0010(3)	175(3)	3.0(4)

^a The parameters are as follows: the average distance R , the distance mean-square deviation σ^2 , the three-body configuration angle θ , the angle mean-square deviation σ_θ^2 . Standard deviations obtained from the EXAFS analysis are given within parentheses.

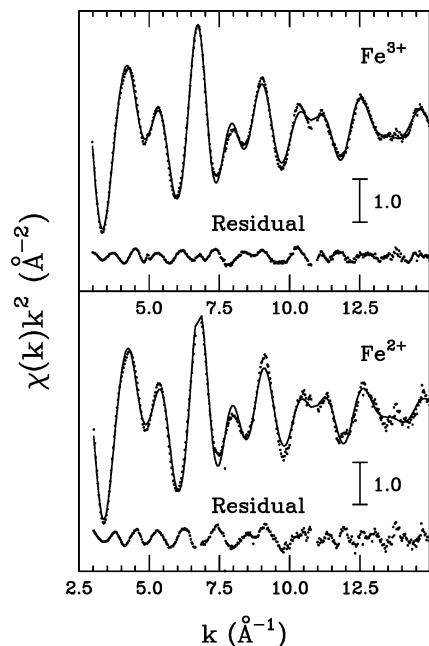


Figure 3. Upper panel: Comparison of the theoretical signal (full line) with experimental data (dotted line) of Fe K-edge k^2 -weighted EXAFS data of $K_3Fe(CN)_6$ aqueous solution, and residual function. Lower panel: Comparison of the theoretical signal (full line) with experimental data (dotted line) of Fe K-edge k^2 -weighted EXAFS data of $K_4Fe(CN)_6$ aqueous solution, and residual function.

variances. Figure 3 shows the comparison between the total theoretical signals and the experimental spectra for the Fe^{3+} (upper panel) and Fe^{2+} (lower panel) solutions, as an example. The two-body and the three-body signals are identical to those reported by Westre et al. (see Figure 9 of ref 7). Due to the presence of six linear Fe–C–N distributions and to the shortness and stiffness of the cyanide triple bond, the intensity of the MS contribution is comparable to the Fe–C single scattering first-shell signal and is about 60% bigger than the Fe–N two-body second-shell contribution. Similar results have been obtained for the crystalline samples. In all cases, the agreement between the best-fit calculations and the experimental data is very good, pointing to the reliability of the method. The trend of the residual curves reveals the presence of a systematic error probably due to the actual accuracy of the phase shift calculation. This should be also responsible for the discrepancy between the theoretical and experimental XANES spectra, as it will be shown in the following. The full set of structural parameters obtained from the minimizations is reported in Table 1. Statistical errors were estimated by looking at the confidence intervals in the parameters' space. Standard deviations and correlation effects were obtained from correlation maps calculated for the parameters of each shell. The amplitude reduction factor, S_0^2 , was found equal to 0.85 ± 0.08 in all cases. As expected for both ions, the geometry of the solution is equal to that of the crystal.^{17,18}

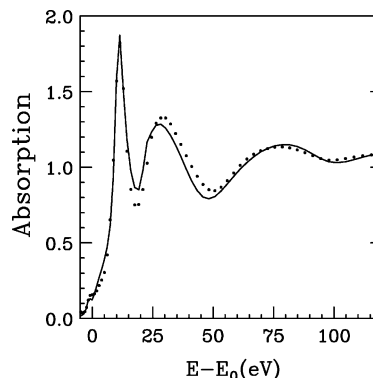


Figure 4. Comparison between the experimental Fe K-edge data of $K_3Fe(CN)_6$ in water (dotted line) and the MXAN best-fit calculation (full line).

Table 2. Structural Parameters for Fe^{3+} Complexes Obtained from the MXAN Data Analysis

	CN	CO	NO
R_{Fe-L_1} (Å)	1.93(1)	1.94(1)	1.92(1)
$R_{L_1-L_2}$ (Å)	1.15(1)	1.11(1)	1.16(1)
$\theta_{Fe-L_1-L_2}$ (deg)	180(1.3)	180 ^a	180 ^a
R_{sq}	20.8	28.8	50.0

^a Fixed parameters.

First neighbor distances deviated less than 0.01 Å from the crystallographic values, and bond distances and angles of second neighbors were accurately determined due to the proper modeling of MS contributions. Moreover, despite the different charge of the iron ions, the Fe–C first-shell distance is equal in both the $K_3Fe(CN)_6$ and the $K_4Fe(CN)_6$ complexes.

To test the sensitivity of the EXAFS technique to ligand discrimination, we have performed additional analyses using CO and NO as ligands. In these cases, the agreement between the experimental and theoretical spectra is comparable to the CN case with an increase of less than 3% of the fit index parameter R_{sq} . In particular, least-squares fits performed with the CO and NO ligands lead to the same structural parameters, enforcing the known low sensitivity of the EXAFS technique in distinguishing among backscatterers with close atomic numbers.

3.2. XANES Analysis. The MXAN program was applied to the XAS spectrum of $K_3Fe(CN)_6$ in aqueous solution considering only the contribution associated with the six CN groups. In Figure 4, we report the comparison between the experimental data and the calculation at the best-fit conditions. It corresponds to an octahedral geometry with Fe–C and C–N distances of 1.93(1) and 1.15(1) Å, respectively, and an Fe–C–N angle of 180(1.3)°. All of the refined structural parameters are reported in Table 2, together with the corresponding fit index parameters. Attempts to refine the experimental data using distorted geometries of the complex were carried out, but an octahedral symmetry was always recovered. The agreement between the

experimental data and the best-fit calculation is very good up to about 15 eV, small discrepancies are observed in the range between 15 and 40 eV, while the experimental structural oscillations are well reproduced at higher energy. Here, the agreement between the best-fit calculations and the experimental data is not of the same quality as previously found for other biological and inorganic systems.^{2–4} This result can be due to the extremely short bond length of the cyanide group and to the strong focusing effect associated with the collinear geometry of the six Fe–C–N configurations that makes the MS signals very sensitive to the potential details. Even if the agreement is not perfect in the whole energy range, the structural determination obtained with MXAN is in very good agreement with both EXAFS and crystallographic determinations, confirming that the XAS spectroscopy is dominated by the geometrical arrangement of the atoms around the photoabsorber. Note that this is the first time that all of the main features of the XANES experimental data are correctly reproduced for systems with linear geometries, and involving short bond lengths.

It is important to outline that statistical errors on all of the refined parameters obtained from the MXAN procedure are very small (see Table 2), and, in the case of the Fe–C–N angle, the error is even lower than that obtained from the EXAFS analysis. This finding indicates that the sensitivity of the XANES region to the geometrical arrangement of the atoms around the absorber is extremely high in the presence of three-body linear configurations. This allows a reliable recovery of the structural information, despite the small discrepancies between the experimental and calculated spectra described above.

To assess the sensitivity of the XANES spectra to the chemical nature of the surrounding atoms, we performed additional minimizations using CO and NO groups as ligands, as previously done for EXAFS, and the comparisons between the experimental and best-fit theoretical data are shown in Figure 5. The full set of structural parameters is listed in Table 2, together with the R_{sq} values. In the case of the CO ligand, the agreement is not remarkably worse than that obtained for CN, even if the R_{sq} value increases about 30%. This is not surprising as the only change is the substitution of the nitrogen second-shell atoms with oxygens. On the other hand, when both the first- and the second-shell atoms are varied, as in the case of the NO ligand, the agreement between the experiment and the best-fit calculation becomes significantly worse, with an R_{sq} value which is more than twice the value of the CN case. This finding quantitatively demonstrates, for the first time, the high ability of XANES in ligand discrimination for both first- and second-shell coordinating atoms. Moreover, the structure extracted from the MXAN fitting procedure is always very similar (see Table 2), enforcing the consideration that XANES features are dominated by the geometry. If a correct analysis of the XANES spectra is carried out, the possibility to identify both the exact geometry and the nature of ligands can have important implications for biological studies.

A last remark we would like to make concerns the origin of the discrepancies between the best-fit calculation and the experimental spectrum in the XANES energy range. To investigate the origin of this behavior, we performed a full-potential calculation using the best-fit geometry obtained from the MXAN analysis and optimizing the nonstructural parameters, only. Up to now, the minimization of the structural parameters

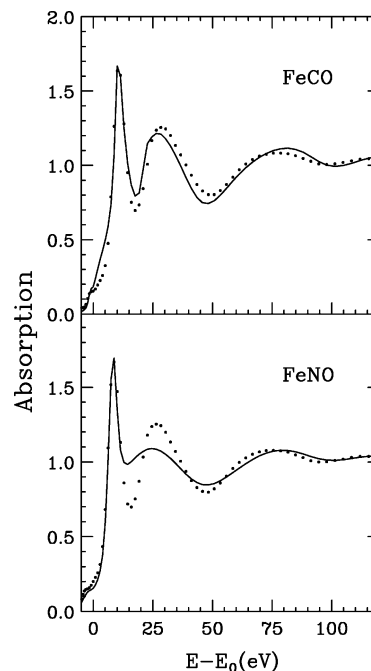


Figure 5. Upper panel: Comparison between the experimental Fe K-edge data of $\text{K}_3\text{Fe}(\text{CN})_6$ in water (dotted line) and the MXAN best-fit calculation performed using the CO group as ligand (full line). Lower panel: Comparison between the experimental Fe K-edge data of $\text{K}_3\text{Fe}(\text{CN})_6$ in water (dotted line) and the MXAN best-fit calculation performed using the NO group as ligand (full line).

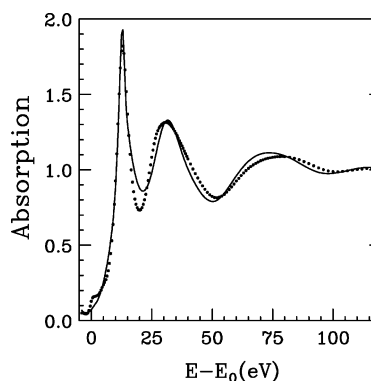


Figure 6. Comparison between the experimental Fe K-edge data of $\text{K}_3\text{Fe}(\text{CN})_6$ in water (dotted line) and the best-fit calculation performed using non-muffin-tin potentials (FMD program) (full line).

using a full-potential procedure is not possible due to the extremely long computational time required for a single FDM calculation. Figure 6 shows the results of this analysis. The agreement between experimental and theoretical data is slightly better than before (see Figure 4), and this is also confirmed by the smaller residue value obtained ($R_{\text{sq}} = 16.3$). The outstanding result of this analysis is that the improvement obtained in going from a muffin-tin to a non-muffin-tin type of potential is not as dramatic as expected for this system, where the non-muffin-tin corrections have been long recognized as fundamental. It is important to note that the use of MXAN allows a quantitative analysis of the XANES energy region and this is key to studying in detail all of the effects due to the approximations related to the potential shape. This is the first example where this type of investigations is presented in detail.

3.3. Discussion. In this paper, we performed a combined EXAFS and XANES analysis, at the Fe K-edge, of $\text{K}_3\text{Fe}(\text{CN})_6$

and $\text{K}_4\text{Fe}(\text{CN})_6$ both in the crystalline state and in aqueous solutions. The XAS spectra of both ferrous and ferric compounds in the crystalline state and in water are equal, with the exception of the pre-edge regions, where small differences have been detected and attributed to the break-down of the local octahedral symmetry in the crystals. On the other hand, the similarity of the energy regions above the rising edges indicates that the XAS oscillations are only due to the strong MS and SS contributions associated with the six CN groups surrounding the iron atom. Note that, according to the crystallographic structure of $\text{K}_3\text{Fe}(\text{CN})_6$, the Fe^{3+} ion is coordinated by six cyanide groups up to a distance of 3.09 Å, and six potassium atoms are coordinated at distances of 4.2, 4.4, and 4.6 Å, giving rise to a quite irregular second coordination shell. Additional atoms are located at distances longer than 4.8 Å.^{17,18} Therefore, it is not surprising that only the carbon and nitrogen atoms of the cyanide group contribute to the XAS spectra. As far as the solution data are concerned, the contribution associated with the water molecules is not detectable due both to the long water coordination distance and to the disorder of the hydration shell.

For the first time, a combined quantitative EXAFS and XANES analysis has been carried out for a system that is dominated by MS effects. The structural results obtained from the MXAN and GNXAS analyses are identical within the statistical errors, pointing to the reliability of both procedures in the analysis of systems where the MS signal persist up to high k -values. The full set of structural parameters, including distances and Debye Waller factors, has been determined for the ferrous and ferric ions both in the crystals and in water. The structural determinations obtained from XAS for the $\text{K}_3\text{-Fe}(\text{CN})_6$ crystal are in perfect agreement with crystallographic results.^{17,18}

One important limitation of the EXAFS technique that has to be mentioned is its difficulty in discriminating among backscatters having close atomic numbers. On the other hand, we have shown that this information is contained in the XANES

energy region of the absorption spectrum, and the quantitative analysis performed by MXAN allows the discrimination of the coordinating ligands despite the approximations in the theory. It is important to stress that, despite the not perfect agreement between the XANES theoretical and experimental data, a correct extraction of the metrical and angular structural information has been obtained from the low-energy region of the spectra. As shown in Figure 5, the discrepancies arising from the inclusion of wrong ligands are much stronger than the systematic error of the theory (see Figure 4). This result suggests that reliable structural information can be obtained from XANES also in the case of samples with unknown structure.

Moreover, we have studied the effects of the non-muffin-tin corrections in the theoretical calculation of XAS spectra of a system having strong MS effects. We have shown that these effects are weak and they do not hamper the extraction of correct structural parameters from the XANES energy region using a fitting procedure, notwithstanding the presence of small discrepancies between the experiment and theoretical data. Therefore, the quantitative analysis of the whole XAS spectrum ranging from the edge to the far EXAFS region can be performed and allows a complete extraction of both the short-range geometrical arrangement and the chemical nature of the atoms around the absorber. This is particularly important for biological systems, and in particular metallo proteins, where detailed structural information around the metal centers is often difficult to obtain by other experimental techniques, and where the ligands are always formed by atoms with close atomic numbers.

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