Double-channel excitation in the XAS spectra of divalent and trivalent iron complexes in water solution

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We present a detailed analysis of XAS spectra of divalent and trivalent iron complexes in water solutions. The interpretation of the spectra has been provided by multi-channel multiple scattering approach. On this basis, good agreement between experimental data and theoretical calculations has been obtained in both cases including two excitation channels in the final state.

Keywords: XANES, multiple scattering theory

1. Introduction

The wealth of electronic and structural information that the X-ray Absorption Near Edge Structure (XANES) spectrum contains has attracted much attention for more then twenty years from both experimental and theoretical standpoints. Many efforts have been made to extend our understanding of this spectral regime so as to exploit its usefulness as fully as possible. Regarding the theoretical description of XANES spectra, the most important approach is the multiple-scattering (MS) theory within the one-electron approximation. Although this method gives an excellent theoretical background to analyze experimental data, several important points have not been properly addressed up to now. One of these open problems concerns the failure of standard MS computation to reproduce the relative intensities of XANES structures within the first 10 eV of the spectrum in several systems. This effect is essentially linked to the difficulties to generate realistic atomic charges in an “ab-initio” XANES calculation like the one used in the MS approach.

Transition metal water complexes have commonly been used as model compounds due to the well-defined geometry and formal oxidation state of the transition metal. The shape of the XANES spectra depends essentially on the coordination geometry around the metal ion. In particular the spectra of octahedral coordinated complexes are characterized by a large resonance at the edge a very weak peak at the pre-edge region due to quadrupole transitions, dipolar ones being forbidden because of the presence of an inversion-symmetry center (Garcia et al. 1986). The interpretation of these spectra has been provided on the basis of MS approach taking into account only the six oxygen atoms around the metal ion. Although good agreement is achieved for the relative energy positions of the spectral features, the relative intensities are not well reproduced. Very recently we have shown that the inclusion of the hydrogen atoms improves these results, leading to better agreement with the experimental data as far as the intensity of the spectral features is concerned (Benfatto et al. 1997). However, whereas satisfactory reproduction of the XANES spectra was obtained for divalent transition metal complexes, computational results are poorer in the case of trivalent complexes with additional features appearing in the experimental spectrum that are not reproduced by the standard MS calculation.

In this paper we present an extensive experimental and theoretical investigation of the divalent and trivalent iron complexes in water solution on the basis of multi-channel multiple scattering theory.

2. Results and discussion

The experimental XANES spectra of trivalent and divalent iron complexes are shown in Fig. 1.

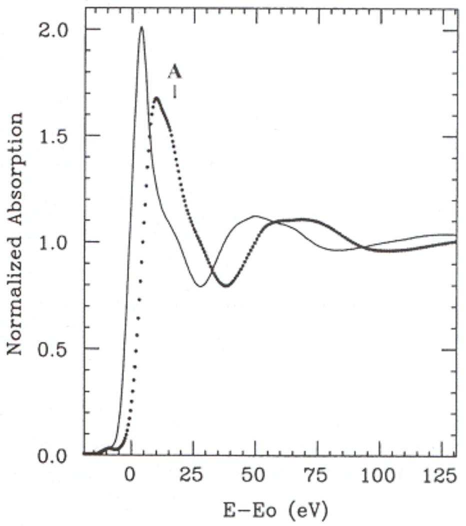

Figure 1
Normalized XANES spectra of Fe^{2+} (solid line) and Fe^{3+} (dots) in water solution at pH=1.

The shape of the spectra of both complexes does not exhibit any variation as a function of pH value (experimental data are not reported here for brevity). This is a clear experimental indication that the acidity of the solution does not influence the local geometry around the absorber, so that the six-fold coordination is maintained. The spectrum of the aqueous Fe^{2+} complex is very similar to that of other divalent transition metal complexes and it has been well accounted for by considering an octahedral arrangement of the water molecules (Benfatto et al. 1997). Although divalent and trivalent systems possess the same local geometry, their XANES spectra exhibit marked differences with the apparition of a shoulder at the higher energy part of the rising edge, called A in the text, and the increase of the width of the main resonance in the Fe^{3+} case. The energy difference between peak A and the main resonance is 6 ± 1 eV. An experimental chemical shift of about 4.5 eV between Fe^{3+} and Fe^{2+} has been also observed.

The understanding of the reason of the observed differences in the spectra is the main objective of the present study. To this end we have calculated the absorption cross section for the $[FeO_6]^{9-}$ and $[FeO_6]^{10-}$ clusters using a Spin Polarized Self Consistent Field (SCF) potential in the final state. The high spin electronic configurations, i.e. $(t_{2g}\uparrow)^3(t_{2g}\downarrow)^1(e_g\uparrow)^2$ for Fe^{2+} and $(t_{2g}\uparrow)^3(e_g\uparrow)^2$ for Fe^{3+}, has been stabilized and used to generate the charge density. Details on the calculation will be described in a forthcoming paper. The $[Fe(H_2O)_6]^{2+}$ spectrum is accurately reproduced by theoretical calculation, as it has been found in other divalent transition metal complexes. However, the computation fails to account for the experimental spectrum of $[Fe(H_2O)_6]^{3+}$; in particular, feature A is absent in the calculation. Indeed the theoretical $[FeO_6]^{9-}$ cluster spectrum is very similar, except for the chemical shift, to that of the $[FeO_6]^{10-}$ case. No appreciable improvement on the previous result has been achieved by changing the exchange-correlation potential or by including hydrogen atoms as done in the previous study of divalent complexes. In addition, small distortions of the octahedral symmetry do not produce peak A. We notice that the energy difference between peak A and the main resonance is such to imagine a lowering of the distance of about 0.25 A according the rule $(E-E_0)R^2$ = const. In other word we should find some oxygen atoms at about 1.80 A that is rather unphysical in such systems. These considerations, together with the EXAFS results which do not show any evidence of such small distance and the experimental fact that the XANES spectra are not sensitive to the pH value, indicate the need to find different reasons for the presence of peak A.

The failure to account for the XANES spectrum of the Fe^{3+} complex addresses the inadequacy of the one-electron approximation indicating the presence of possible different electronic configurations in the final state of such system. Using a spin-polarized SCF procedure we can stabilize different electronic configurations starting from the fully relaxed one E_{fr}. In particular, the excited configuration E_{exc} can be made by moving an electron from the low spin down $(t_{2g}\downarrow)$ bonding level, which is full and is located at about –5.3 eV in an X-α SCF scheme, to the last empty spin down t_{2g} orbital, located at about –0.8 eV. The energy difference between E_{fr} and E_{exc} is about 4.7 eV. In the final state the presence of the core hole moves in a different way the electronic configurations due to the different Coulomb interaction between core-hole and d electrons of the two different energy levels. In this case the energy differences becomes about 6.5 eV, number very close to the energy difference between peak A and main resonance. This result indicates that the first resonance is due to the contribution of the E_{fr} electronic configuration while peak A comes from the contribution of the E_{exc} electronic configuration. A similar behavior has been recently found in several copper compounds (Wu et al. 1996) looking at the Cu K-edge. A similar analysis can be done for the Fe^{2+} complex starting from the fully relaxed high spin configuration. In this case the energy difference between E_{fr} and E_{exc} is about 1.4 eV in the final state, i.e. within the core-hole plus the experimental resolution. In other word our experiment cannot reveal the presence of some extra feature in the data.

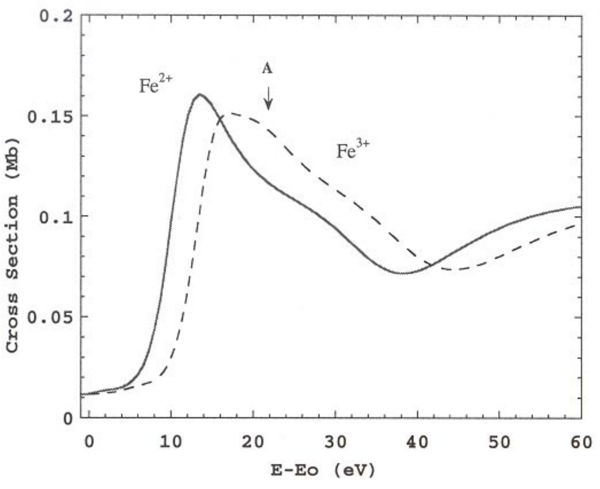

Figure 2
Comparison between two theoretical calculations related to trivalent (dashed line) and divalent (solid line) complexes.

In Fig. 2 we report the comparison between the calculated spectra of Fe^{2+} and Fe^{3+} complexes, taking into account the presence of the two electronic configurations in both cases. The calculations have been done on the basis of MS multi-channels theory in the sudden limit (Natoli et al. 1990) with weights of 0.8 and 0.2 for the excited and fundamental electronic configurations respectively. The agreement with the experimental data is now rather good for both systems. In summary we have carefully analyzed the XANES spectra of divalent and trivalent iron complexes in water solution. The peculiar behavior of the Fe^{3+} system has been explained on the basis of multi-channels excitation.

References

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Received 31 July 2000 • Accepted 30 November 2000