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Theoretical analysis of x-ray absorption near-edge structure of transition-metal aqueous complexes in solution at the metal *K* edge

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We present a detailed analysis of x-ray absorption near-edge structure spectra (XANES) of transition-metal aqueous complex in solution. The metal K edges of Ni^{2+} and Co^{2+} are analyzed by multiple-scattering theory using clusters of different size and different final-state potentials. On this basis, the effect of hydrogen atoms of the water molecules on the theoretical XANES spectra has been investigated. The calculations show that the intensity ratio and width of the main features of the spectrum are sensitive to the presence and the geometrical position of hydrogen atoms. A very good agreement between experimental data and theoretical calculations has been obtained using final-state potentials built on the basis of the self-consistent field procedure and clusters with a well-defined geometrical position of hydrogen atoms. [S0163-1829(97)05329-0]

I. INTRODUCTION

In the last few years the x-ray absorption near-edge structure (XANES) spectra at the metal K edge of transition metal (TM) aqueous complexes in solution have been the object of extensive studies. This interest has been motivated by the possibility to use these materials as both test compounds of theoretical calculations of XANES spectra and reference compounds in the analysis of other materials.[1–3] These complexes present a well-known very simple geometry and well-defined formal valency of the ionic species. The XANES spectrum has a well-defined shape which depends essentially on the coordination geometry around the metal ion:[4] (i) spectra of complexes with tetrahedral coordination show an intense pre-edge peak, which corresponds to the dipole transition from the $1s$ to an antibonding state of T_2 symmetry, followed by the absorption jump due to the transition to continuum state of p-like symmetry;[5] (ii) spectra of octahedral coordinated compounds present a very big resonance at the edge and a very weak pre-edge peak due to a quadrupole transition. In this case, dipolar transitions are forbidden because the first unoccupied bound states have T_{2g} and E_g symmetries.[6]

In both cases, the succesfully interpretation of the continuum part of these spectra has been provided on the basis of the multiple-scattering (MS) theory,[7,8] indicating the presence of relevant MS signals of different order up to several hundred of electron volts (eV) above the edge with a different degree of interference depending on the geometry.[9] For example, the strong resonance at the edge of octahedral complexes results to be formed by a coherent sum of all MS contributions which, due to the particular geometrical coordination, happen to be all in phase at the resonance energy.[9,10] All the calculations about these complexes were made till now by taking into account only the first oxygen shell around the transition metal and neglecting any contribution coming from the hydrogen atoms of the water molecule. On this basis, a rather good agreement between experimental data and theoretical calculation has been obtained for what concerns the shape of the spectra and the relative energy separation of the various features. However, the relative intensities of the peaks of the theoretical spectra disagree for the first tenth of eV with the experimental data. In the case of octahedral complexes, the calculated resonance at the edge has a higher intensity and a smaller width than the experimental counterpart.[1,11,12] This is a general behavior of the MS calculations of XANES spectra of aqueous TM complexes and different choices of final state potential do not give any substantial improvement.

The influence of hydrogen in the XANES spectra was to be considered very weak because of the low scattering power of this specie, so that it is usually neglected in theoretical calculations and data analysis. The effect of hydrogen in the XANES spectra has been considered, in some cases, in an indirect way through the modification of electronic states of the host atoms. As, for example, in cerium compounds after hydrogen absorption[13,14] and in the case of metal hydrides,[14,15] where the presence of hydrogen modifies the electronic band structure of the system inducing new states above the Fermi level that give rise to extra features in the XANES spectrum compared with that of the pure metal. Only a few examples are reported in the literature where the presence of hydrogen atoms must be taken into account in the data analysis procedure. Considering the extended x-ray absorption fine-structure (EXAFS) part of the absorbing spectrum, hydrogen was detected in an indirect way in Ni and Cr hydrides, since it is located in between the absorber and the backscatterer affecting the photoelectron wave in magnitude and phase. It acts as a lens producing either focusing effect of the outgoing photoelectron wave function and a change, through multiple-scattering events, in phase shifts and backscattering amplitudes.[16] This effect allowed the determination of the hydrogen site in the lattice. Recently, EXAFS spectra of bromine in metanol solution[17] and

Sr^{2+} in aqueous solution[18] have been analyzed including the hydrogen EXAFS signal.

In this paper, we report a careful theoretical analysis of the K-edge XANES spectra of Ni^{2+} and Co^{2+} octahedral aqueous complexes based on MS theory. The aim is to assess the influence on the theoretical calculation of the different procedures to generate the final-state potential and to include hydrogen atoms of water molecules. We show that the use of the self-consistent field procedure to generate the potential instead of the normal $Z+1$ approximation, the real Hedin-Lundqvist potential for the exchange part, and a well-defined geometrical position of hydrogen atoms in the cluster, allows us to obtain a very good agreement with the experimental data. Moreover, the sensitivity of the calculation to the hydrogen can be used to give an insight on the water molecule position around the metal ion in this class of compounds.

II. EXPERIMENTAL AND THEORETICAL DETAILS

X-ray absorption spectra of Ni^{2+} and Co^{2+} water solutions, $5mM$, were recorded in the transmission mode, at the Ni and Co K edge, at beam station 7.1 of the Daresbury Laboratory. A double-crystal Si(111) monochromator was used and harmonic rejection of about 50% was achieved by slightly detuning the second crystal from the parallel alignment. The storage ring was operated at 2 GeV with an average current of 150 mA. The new spectra coincide in shape and intensity with those previously reported.[1,3,4,12]

In the following we outline some details of the theoretical methods used for the calculations. The computation of the XANES spectra was carried out using the multiple-scattering code CONTINUUM (Ref. 19) based on the one-electron full-multiple-scattering theory.[5,7,8] In this scheme the total potential is represented by a cluster of nonoverlapping spherical potential centered on the atomic sites and the molecule (in our case the transition-metal complex) is enveloped by an ''outer sphere.'' Three regions can be identified in the partitioning: atomic regions (spheres centered upon nuclei), extranuclear region (space beyond the outer sphere radius), and an interstitial region of complicated geometry in which the molecular potential is approximated by a constant ''muffin-tin'' potential. The atomic region is defined by the muffin-tin radii that are chosen according to the Norman's criterion with a 10% overlapping factor.[20] The Coulomb and exchange part of the input potential were calculated on the basis of the total charge density by superimposing the atomic charge densities. For the exchange potential, several approximations were used. The independent Slater X_α approximation, the energy-dependent Hedin-Lundqvist (HL), and the Dirac-Hara potentials. A complete discussion of the above methods exceeds the nature of this paper and can be found in Refs. 10, 21, 22, and references therein. Regarding the final-state potential two choices have been used: (i) the screened $Z+1$ approximation and (ii) the self-consistent field (SCF) potential. For this last case a NiO_6^{10-} cluster has been stabilized simulating hydrogen atoms by an outer sphere with a 10^+ charge to neutralize the whole cluster. The relaxed final state was calculated by removing an electron from the $1s$ state and taking constant the number of electrons of this state during the SCF procedure. The potential of the NiO_6H_{12} cluster was built by adding the contribution of the hydrogen atoms, according to some specific geometrical configuration of the water molecule, to the previous SCF potential. This procedure, whose validity has been demonstrated on extended systems,[22,23] gives us the possibility to save computer time accounting for hydrogen contribution and performing the SCF procedure.

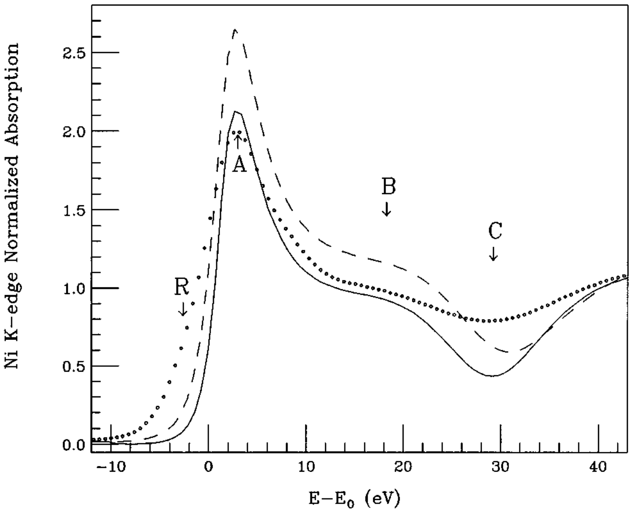

FIG. 1. Normalized K-edge XANES spectrum of Ni^{2+} complex (o) compared with different calculations obtained by using a NiO_6 clusters, self-consistent potential and different choices for the exchange and correlation potential: (a) Hedin-Lundqvist real potential (solid) and (b) Dirac-Hara potentials (dashed).

III. RESULTS AND DISCUSSION

As a first step, we have calculated the absorption cross section for the octahedral cluster of oxygen atoms surrounding the transition-metal atom using the $Z+1$ approximation. As well known, the valence state of the TM is not taken into account in this approximation. Figure 1 shows the comparison between experimental data at the Ni K edge and two calculations of the spectrum of NiO_6 cluster using different exchange potentials. The theoretical spectra are very similar to each other and qualitatively reproduce the shape of the experimental spectrum, nevertheless the relative intensity of the main resonance and the big deep, C, are not reproduced. The relative energy position of the features is quite good for the X_α potential, and it is even better, coinciding with experiment, when the HL exchange potential is used. The Dirac-Hara potential seems instead inadequate to describe this system and the energy position of the resonances disagrees with the experimental data. However, in all the cases the theoretical calculation is unable to reproduce the width of the absorption spectrum at the raising edge (R). The influence of SCF potentials and of hydrogen atoms is shown in Fig. 2. Three calculations performed for a NiO_6 cluster with both $Z+1$ and SCF potentials, and for a NiO_6H_{12} cluster with an SCF potential, according to the procedure previously described, are reported. The geometrical configurations of hydrogen atoms used in this work are depicted in Fig. 3. In the first calculation, hydrogen atoms of the water molecules were added maintaining the geometry of the water molecule and arranged in such a way that the symmetry plane of the water molecule contains the TM-O bond direction [Fig.

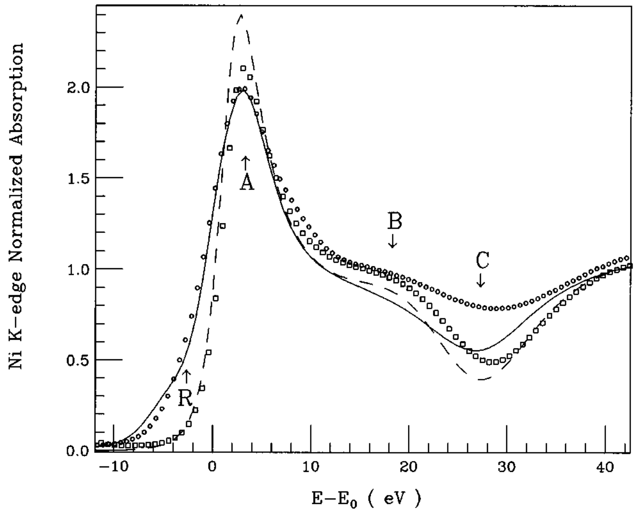

FIG. 2. Comparison between three different calculations referred to $Ni(H_2O)^{2+}$ complex and the experimental spectrum (dots). The dashed line indicates the calculation for a NiO_6 cluster using the $Z+1$ approximation for the final-state potential. The same calculation performed using a self-consistent potential for the final state is also shown (□). The solid line refers to the calculation obtained by including the hydrogen atoms of water molecules according to the geometrical configuration shown in Fig. 3.

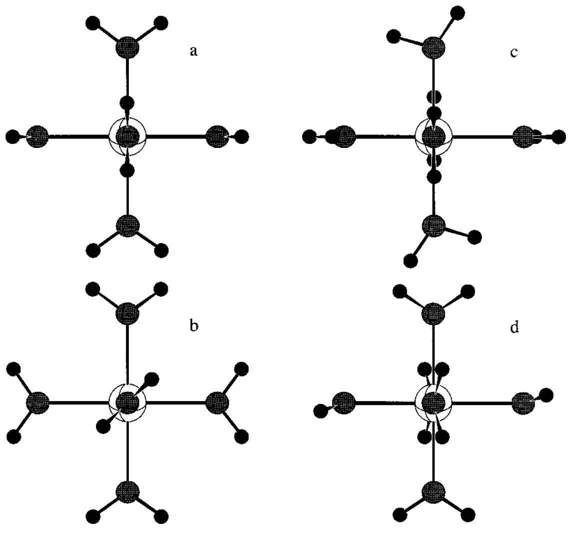

FIG. 3. Geometrical configuration of the $Ni(H_2O)_6$ cluster used in the calculations. The white circle represents the transition-metal atom (TM), while the black and dashed circles stand for the hydrogen and oxygen atoms, respectively. The octahedral cluster is seen from the O-TM-O axis which is perpendicular to the page plane. Four O atoms lie together with TM in the figure plane, the sixth O atom being hidden at the rear part of the projection. Four different possible positions of the H atoms are depicted. (a) symmetrical position of the H_2O molecule; (b) rotation of the H_2O molecule plane around the direction defined by the axis of the octahedron; (c) the H atoms are tilted 20° in the plane containing the H_2O molecule; (d) the H atoms are tilted 20° in the plane perpendicular to the H_2O molecule.

3(a)]. The use of the SCF potential improves the agreement between theory and experiment but is far from reproducing the relative intensities of the peaks. On the contrary, the inclusion of the hydrogen atoms induces minor but significant changes in the spectrum. On one hand, it creates new states at the left-hand side of the main peak, making the width of the resonance R equal to the experimental one. On the other part, the valley C is less pronounced than in the previous calculations giving a better agreement between calculation and experiment. This result corresponds to a calculation with a specific geometrical configuration of the water molecules. In order to check the dependence of the spectrum on the imposed geometry for the water molecules, we have performed further calculations using different configurations. The calculation for different symmetries of the water molecules but always maintaining the orientation of the water molecule related to the TM-O bond [see Figs. 3(a),(b)] is shown in Fig. 4, left panel. All the theoretical calculations coincide, indicating that the effect of hydrogen atoms is independent of the rotation of the water molecule around the TM-O axis. This result indicates that the hydrogen contribution comes only from the single scattering contribution, i.e., the H-TM distance remains unaltered after rotation of the water molecule around the octahedral axis. In addition, the contribution of the multiple-scattering processes including the hydrogen atoms as scatterers is negligible, as expected due to its low scattering power. Although it is not previsible from an experimental point of view, we have also performed calculations tilting the plane of the water molecule from the TM-O axis. Two different arrangements of the molecule were considered, i.e., perpendicular and parallel to the water plane [see Figs. 3(c),(d)]. The comparison of the original configuration with two calculations in which we have tilted by 20° the axis of the molecule is shown in Fig. 4, right panel. It can be observed that the tilting of the molecule plane modifies only very slightly the shape of the ‘‘distorted’’ spectra. On the other hand, the motion on the water plane induces a new shoulder at the rising edge and the intensity of the main resonance decreases dramatically. These two simulations indicate that the water molecule tends to lie perpendicular to the nickel oxygen bond and also shows the sensitivity of the XANES spectra to the hydrogen atoms.

Notwithstanding the improvement in the agreement between theory and experiment is rather satisfactory when including the water molecules, we want to briefly comment on the possible limitation to this agreement due to the use of the muffin-tin approximation. The muffin-tin corrections depend only on a series of integrals whose domains are calculated in the interstitial area.[24] Since the use of a closed atomic arrangement implies a strong reduction of the interstitial region, the non-MT corrections should be expected to be very weak. Consequently we do not expect any significant change in the calculation of NiO_6 or CoO_6 clusters with and without non-MT corrections. Moreover, it should be noted that in a closed system (like MnO_4^-), the calculated energy differences between electronic-bound levels obtained within the MT framework are in a very good agreement with the experimental data,[25] while these corrections seem to be important to obtain the right energy levels in open systems, as it is the case of the H_2^+ system.[26] Up to now, only few non-MT calculations of the x-ray absorption cross section have been made, and all of them deal with open systems. The common results to these calculations are controversial: it seems that non-MT corrections lead to better energy positions for the

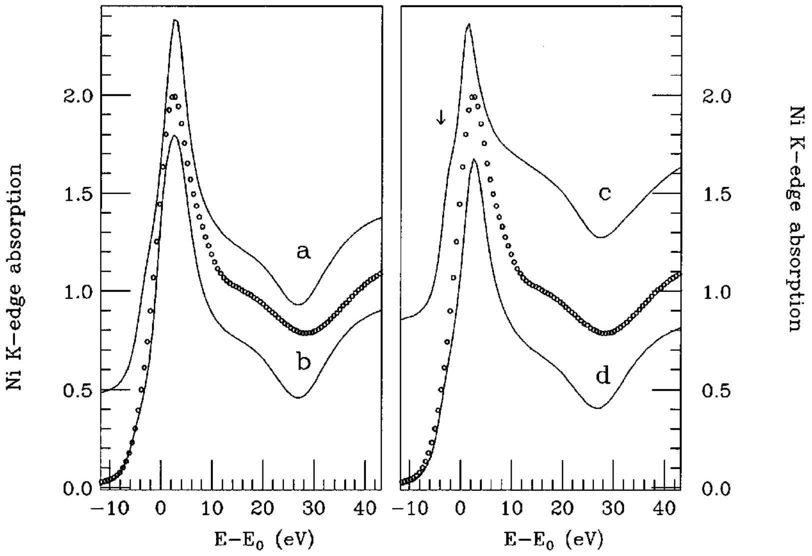

FIG. 4. Comparison between the experimental spectrum (dots) and different calculations of NiO$_6$H$_{12}$ cluster obtained using different orientations of water molecules, as shown in Fig. 3. Curves (a) and (b) refer to the cases where the symmetry plane of the water molecule contains the Ni-O axis. In (c) and (d) the water molecule has been tilted by 20°.

spectral features below the raising edge, i.e., transitions to bound-state levels; while their effect on the continuum part of the absorption spectrum is very small or even unfavorable.[27]

In order to clarify what is the origin of the effect induced by hydrogen in the spectrum we calculated the single-scattering signal of the different contributions. The total EXAFS components and their Fourier transform for the NiO$_6$, NiO$_6$H$_{12}$, and the EXAFS contribution due to hydrogen scattering are plotted in Fig. 5. As it is observed, the oscillatory contribution coming from the hydrogen scattering is mainly relevant in the first 30 eV being very small at higher energies, and it interferes destructively with the oxygen contribution causing the decrease in the intensity of the main resonance. At the same time, it induces new states at the rising edge. The Fourier transform of the EXAFS signal shows a small peak at 2.8 Å coming from the scattering of the hydrogen. We can observe that this signal is very small and comparable to the multiple-scattering contributions.[3] This result, added to the effect of the large thermal disorder related to the hydrogen motion, makes the detection of the hydrogen EXAFS contribution very difficult. It has been experimentally observed indeed, only in few cases.[17,18]

For sake of consistency we have also performed the same calculations to reproduce this study for the Co(H$_2$O)$_6$ system. The comparison between the experimental spectra of Ni^{2+} and Co^{2+} water complexes and the theoretical simulations including SCF potentials and the hydrogen atoms of the water molecules are shown in Fig. 6. In the case of the Co^{2+} complex similar effects were obtained, showing the need of including the hydrogen atoms in the calculations to obtain a quantitative agreement with the experiment. In this case, however, we note the appearance of a small prepeak which does not exist in the experimental data. This discrepancy may be due to the non-MT corrections that can be important in the calculations of clusters with hydrogen atoms. Although we cannot make a quantitative assessment of the effect, it is possible to make some qualitative considerations. From a theoretical point of view, the non-MT absorption cross section can be written as a sum of two pieces: the first is the MT part, i.e., it is the cross section calculated on the basis of MT approximation, the second is a correction which depends on the volume of the interstial region and the magnitude of the deviation from the constant value of the inter-

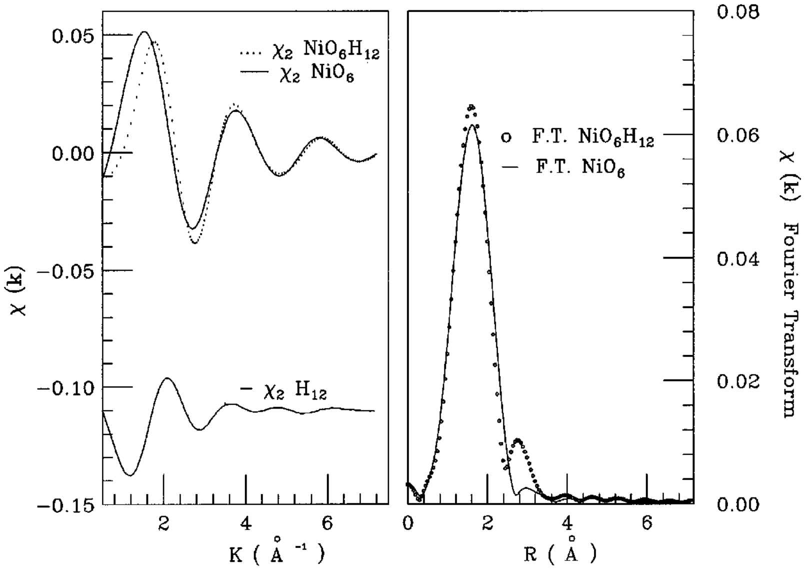

FIG. 5. Theoretical EXAFS signals of NiO$_6$ and NiO$_6$H$_{12}$ clusters showing the EXAFS contribution coming from hydrogen atoms. The Fourier transform of the NiO$_6$ and NiO$_6$H$_{12}$ EXAFS contributions is also shown.

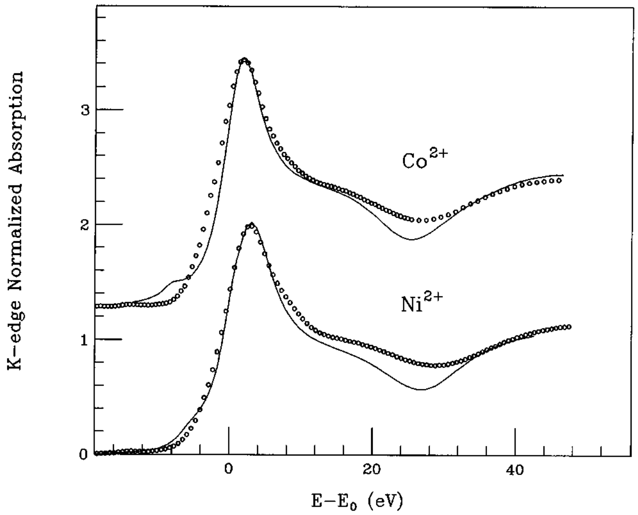

FIG. 6. Comparison between experimental data (dots) and theoretical calculations of K-edge XANES spectra of Ni^{2+} and Co^{2+} water complex. Theoretical calculations are made by using the self-consistent potential and including hydrogen atoms.

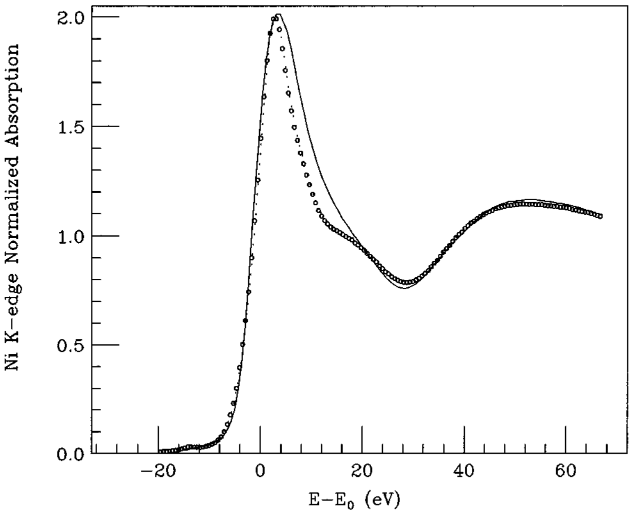

FIG. 7. Comparison between the experimental spectrum of Ni^{2+} water complex (dots) with the theoretical data related to a NiO$_6$H$_{12}$ cluster and using the self-consistent potential and complex Hedin-Lundqvist exchange and correlation potential.

stitial potential.[24,29] In other words, the non-MT absorption cross section is the MT one plus corrections that depend on the system. From this point of view, we expect that the non-MT calculation is essentially the one presented in this paper with small modifications coming from the non-MT part of the cross section.

It is also important to note that in all the cases it is impossible to reproduce the correct intensity of valley C. In order to investigate the origin of this discrepancy, which probably comes from inelastic losses, we have performed the same calculations using the Hedin-Lundqvist complex potential. In a small molecular cluster the inelastic losses can be mainly due only to the excitation of electronic configurations other than the relaxed one that subtracts intensity to the main elastic channel. This type of inelastic losses can be approximated by plasmonlike excitations only when the photoelectron energy is bigger than the energy difference between the various electronic configurations.[28]

The results of this calculation for the nickel cluster is shown in Fig. 7. The quantitative agreement of the relative intensity of the various features of the spectrum is quite remarkable now, although the shoulder B tends to disappear. This behavior is not surprising because it should be noticed that the inelastic losses in a HL-type of potential are due to the plasmonlike excitations.

IV. SUMMARY AND CONCLUSIONS

Hydrogen atoms are, in most cases, not detectable by x-ray absorption spectroscopy. This is generally true for the extended part of the spectrum, where the low scattering power of hydrogen, added to the expected high thermal disorder, makes the hydrogen contribution very small and sometimes mixes it with other more relevant contributions. In the case of the near-edge structures, the thermal disorder has no significance and the intensity of the hydrogen contribution is not negligible giving a more relevant contribution which can be detected. The effect of the hydrogen atoms in the XANES spectra of the transition-metal complex is confined in the low-energy part of the spectrum, i.e., very close to the rising edge. Including the hydrogen contribution in the theoretical calculations is essential to get a quantitative agreement between theory and experiment in what concerns intensity and width of the resonances.

We have shown in this work the improvements obtained by using self-consistent-field (SCF) methods to describe the final-state potential and the different treatments of the exchange-correlation part. It has been shown that the use of SCF potential improves the intensity ratio among the different structures of the calculated absorption spectrum as compared to the experimental A/C ratio. The introduction in the model of water molecules changes the theoretical result not only by improving the $A/B/C$ ratio, but also by matching the width of the raising edge region (R) that cannot be obtained without the hydrogen atoms. These theoretical calculations also indicate that (i) the effect of hydrogen atoms is independent of the rotation of the water molecule around the TM-O axis, and (ii) the tilting of the water molecule plane from the TM-O axis far from improves the experiment vs calculation agreement, inducing new features at the rising edge, and leading to a worse $A/B/C$ ratio. From these results we can conclude that the water molecule lies, as can be easily expected from the symmetry of the system, perpendicularly to the Ni-O bond disregarding other arrangements. Furthermore, we have shown how the discrepancy in the intensity of feature C is overcome by including inelastic losses in the calculation, that are not relevant in the raising edge region.

In conclusion, in this work we stress two main points in the simulation of the XANES spectra. On one hand, the use of realistic models using self-consistent potentials and the inclusion of the details of the real system, as for example, in our case the inclusion of hydrogen atoms of the water molecule, clearly improve the theoretical simulation making it near quantitative. On the other hand, taking into account the inelastic losses in a general form is still an open problem, being strongly dependent of the considered system. We think that the results here presented provide a new insight into the study of these transition-metal complexes by means of the full multiple-scattering approach, leading to a quantitative analysis of the problem through the inclusion of a more ''realistic'' system which includes the water molecules.

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[29] This result can be deduced with little manipulation from Ref. 24. More details will be published in a subsequent paper.