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A computational study on the X-ray absorption spectrum of proton-ordered crystalline ice IX

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Abstract

The cluster model commonly used in the simulation of X-ray absorption spectra is examined for water in a crystalline environment. The proton-ordered crystalline ice IX was chosen as an example. Effects of the size of the quantum cluster, long-range electrostatic interactions and the quality of the atomic basis sets are examined in detail. It is found that both the size of the quantum cluster and the Madelung potential due to long-range electrostatic interactions in the ordered crystal strongly influence the calculated spectrum while the quality of the basis set only has a very minor effect. For ice IX, it is shown that the features observed in the pre- and near edge region are described reasonably well but the main and post-edge absorption profile is more difficult to reproduce.

Keywords: X-ray absorption spectra; Density functional theory; Crystalline ice

Article Outline

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1. Introduction

Since the energy of a core electron level depends not only on the element but also on their chemical environment and the spatial confinement of the core hole, X-ray absorption spectroscopy (XAS) provides a sensitive element specific probe on the local electronic structure of a given atom. Moreover, the X-ray absorption process being faster than a femto-second (much faster than the vibrational and translational motions), XAS captures the electronic structure in a frozen geometry around the probed atom and the spectrum becomes a sum of snapshots of the instantaneous environment [1].

For convenient, a core level excitation spectrum usually divided into three different regions depending on the types of excitations involved [1]. In the first region, the excited electrons do not have enough energy to leave the absorbing atom and are promoted to bound unoccupied valence states. These transitions give rise to the pre-edge peaks which are located below the ionization threshold. In the second and third regions, the excited electrons have sufficient energies to escape into the continuum (ionized). In the second region, the kinetic energy is relatively low and the electrons can be trapped in quasi-bound continuum states, and it is often referred as the near- or sometimes main-

edge region. In the third region the energy of the exciting photons is significantly higher than the ionization energy, and the photoelectrons are weakly backscattered by neighboring atoms. In this post-edge region, interferences between the outgoing electron wave from the probed atom and the backscattered electron waves from its nearest neighbors creates sinusoidal variations of the absorption coefficient.

The absorption cross-section, σ , is defined as the number of electrons excited per unit of time divided by the number of incident photons per unit of time per unit of area and can be calculated from Fermi's Golden Rule:

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_f |\langle \Psi_f | \hat{\Theta} | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (1)$$

where α is the fine structure constant, $\hbar\omega$ is the energy of the incoming photon, $\hat{\Theta}$ is a transition operator coupling the initial state Ψ_i of energy E_i with the final states Ψ_f of energies E_f . The calculation of Ψ_i , a core orbital, is relatively straightforward. The difficulty lies in the calculation of the final states Ψ_f . Under normal experimental conditions when the momentum transfer is small and higher order excitations (e.g., quadrupolar, etc.) can be neglected, core shell photo-absorption can be described approximately by an independent electron model obeying the dipole approximation. Since the initial core 1s orbital is spatially localized, the dipole selection rule governs that the difference in the angular momentum of the initial and final orbital must differ by one quantum unit ($\Delta l = \pm 1$). Thus, K-shell excitations can be treated approximately by transitions from 1s to unoccupied orbitals with a local p-orbital contribution although the overall symmetry is not atomic-like.

Neglecting vibrational effects, the intensity of the transition I_{if} where $\hat{\mu}$ is the dipole moment operator can be expressed as:

$$I_{if} = \frac{2}{3} \omega_{if}^2 |\langle \Psi_f | \hat{\mu} | \Psi_i \rangle|^2$$

Eq. (2), in particular, in conjunction with density functional theory and a cluster approximation, has been used with success in the simulation of XAS in a variety of systems [2], [3], [4] and [5]. A difficulty of this one-electron model is the proper treatment of the excitations near and above the ionization threshold where the wavefunctions cannot be adequately represented using localized basis sets. In this region, a wavefunction is energy normalized and energy dependent self-energy is needed to describe the electron correctly [6]. Although a proper theoretical treatment of in the continuum region, at least for molecular systems, is well known [7], the computation is complex and it is common to resort to an *ad hoc* energy dependent line broadening scheme to mimic the absorption profile in this region.

Recently the high resolution XAS of liquid water has been reported [8]. It was pointed out that a distinct feature of the liquid is the presence of a pre-edge absorption peak. Through comparison with water adsorbed on surfaces and theoretical simulation of the XAS, a surprising conclusion was proposed that hydrogen-bonding (H-bond) network of water molecules in the liquid phase is not completed. This conjecture challenges the accepted model derived from experimental diffraction studies and theoretical Monte Carlo and molecular dynamics simulations that each water molecule should participate in full H-bonding, forming 2 donors and 2 acceptor bonds [9], [10] and [11]. This new finding [8] has a significant impact on the understanding of many anomalous properties of water. In this work, the methodology and approximations employed in the theoretical calculations of the XAS are examined. We have chosen to study crystalline ices since their structures and H-bond networks have been well characterized by neutron diffraction analysis and the conventional 4-coordinated H-bond water model is not in dispute. In this paper, various approximations, such as the cluster size, effects of long-range electrostatic interactions and the quality of the basis sets, that may affect the accuracy of the computed XAS are examined. We will focus on ice IX since it is proton-ordered and the experimental XAS spectrum has been reported [12]. As will be discussed below, the results show that in crystalline ices, long-range electrostatic effect cannot be neglected.

2. Computational details

The computational techniques employed in this study are analogous to previously described for liquid water [5]. Calculations were performed within the DFT framework as

implemented in the program deMon-StoBe [13] employing the gradient-corrected exchange and correlation functional developed by Becke, Perdew and Enzerhof (PBE) [14]. The following (standard) basis sets were used since it has already been demonstrated from previous studies that they perform well on water and related systems. For the central (ionized) oxygen atom, an all electron Huzinaga 11s 7p basis set contracted according to the 5111111/211111 scheme and augmented with two sets of d polarization functions, (i.e. the IGLO III basis set (O (11s, 7p, 2d) $\rightarrow$ [7s, 6p, 2d]) [15]), was used for the calculation the ground state orbital wavefunctions prior to excitation. For the calculation of dipole transition probabilities, a more extended and diffuse (19s, 19p, 19d) basis set augmented with 19 diffuse even tempered basis shells was used for the central oxygen in order to mimic the continuum wavefunctions in extended region above the ionization potential [16]. The 1s electrons of the remaining oxygen atoms (chemically inert core electrons) were replaced with effective 1s core potentials and a more moderate 311/211 split valence [5] basis set. All the hydrogen atoms are represented by a polarized split valence 311/1 basis set.

To examine truncation effects and long-range electrostatic interactions, different cluster models each consisting of an isolated quantum region with or without surrounding point charges to mimic the electrostatic field were studied. Atomic positions of these clusters were constructed from the respective proton-ordered crystal structures [17]. For each crystallographically distinct oxygen center, all water molecules within a chosen cut-off radius were explicitly included in the electronic (quantum) calculation. The cut-off radius was selected such that the total TIP3P dipole moment ($-0.834e$ on the oxygen atom and $+0.417e$ on each hydrogen atom) [18] of the cluster is minimized. In ice IX, there are two distinct oxygen sites. For site 1, the quantum clusters have radii of 3.3, 4.8, 5.4, 6.7, and 7.3 Å while for site 2, the radii chosen are 3.6, 4.1, 5.8, 6.9, and 7.2 Å. The oxygen atom positioned at the center of the cluster is the excited atom.

In the quantum mechanical (QM) region (quantum cluster), relaxation effects due to charge transfer (screening) accompanying the core ionization is accounted for through the (re)optimization of the electronic wavefunctions. Beyond the quantum cluster, a Madelung potential is used to model the electrostatic field by embedding the quantum cluster in a region of with screened point charges $1/(1+e^{(R-R_0)/D}) q$ [19] placed at the hydrogen and oxygen lattice positions, where R is the distance from the central (ionized) oxygen atom and q is the TIP3P oxygen and hydrogen charges for water. The oxygen and hydrogen charges are scaled by the same factor for the same molecule to retain the overall charge neutrality of the cluster. For ice IX, depending on the size of the quantum cluster, the constants R_0 and D (see ref. [19] for the definition of these terms) were chosen to be 15–40 Å and 2–4 Å, respectively.

To simulate the XAS, core–valence and core–virtual transition energies and corresponding dipole transition probabilities were calculated within the dipole approximation where both initial and final state orbitals were generated from the transition-state potential obtained from a SCF calculation with half an electron removed from the core 1s orbital of the ionized O atom [20], [21] and [22]. In principle, the transition-state approximation accounts for the relaxation effect to the second order [20]. This procedure often produces excitation energies in good agreement with experiments. Experimental lifetime and vibrational broadening were simulated by convoluting the calculated oscillator strengths with Gaussian functions. These Gaussian functions have a constant width below the ionization threshold. For transitions below 540.1 eV, linewidths (full width at half maximum, fwhm) of 0.3, 0.5, 0.7 and 0.9 eV were used to illustrate the influence of the experimental resolution on the observed lineshape. Above the ionization threshold (between 540.1 and 550.1 eV), the linewidth was interpolated linearly between the two limiting values. At higher energy (above 550.1 eV) the fwhm is again set to a constant value of 4.5 eV.

To complement the cluster calculations, we have also used a periodic model to compute the XAS of ice IX. The calculations follow the procedure described in Ref. [23]. For these calculations, the pseudopotential plane wave CPMD code was used [24]. The core electrons for oxygen atoms were replaced with the Troullier–Martins norm-conserving pseudopotentials [25]. The valence orbitals were represented by a plane wave basis set with an energy cut-off of 90 Ryd. The model system consisted of 96 water molecules supercell with the atomic positions taken from the experimental crystal structure [17]. As in the cluster model, the Perdew, Burke, and Enzerhof exchange–correlation functional was employed. Similarly, electronic excitations were calculated with the transition-state

approximation [20], [21] and [22] employing a pseudopotential with half an electron removed from the O 1s core orbital of the photoionized oxygen atom to mimic the partially screened core hole. Brillouin zone sampling was performed at the zone center (Γ point) only. XAS spectra were calculated from the local p-projected density of states of the empty orbitals and convoluted with Gaussian functions using the same procedure described earlier [23].

3. Results and discussions

There are two crystallographically distinct oxygen sites in proton-ordered ice IX. There are twice as many oxygen atoms in site 2 than in site 1. X-ray excitation intensities were calculated for each crystallographically non-equivalent oxygen and the XAS ice IX was calculated by adding the spectra at each atom site and weighing them by their respective multiplicity. The calculated ionization potential (the energy required to promote the O 1s electron from the core to the continuum) from the transition potential for site 1 is 538.23 eV and 538.06 eV for site 2.

The first point to consider in this study is the influence of the cluster size and the Madelung potential on the calculated XAS spectrum. An exhaustive study was performed on ice IX to determine the sizes of the quantum cluster and of the Madelung potential required to reach convergence in the calculated spectral features. Since the number of water molecules in the cluster increases with the third power of the cut-off radius, it is computationally impractical to exceed more than 70 water molecules (~ 210 atoms) in ice IX, the upper limit for the cluster radius is thus chosen to be around 7–8 Å. In the construction of the cluster model, we have avoided model structures which have a large net dipole moment. The calculated XAS for bare quantum cluster models with cut-off radius of ~ 3 –7 Å are obtained through an averaging of the individual XAS for the two crystallographically distinct oxygen sites of ice IX. As mentioned above, this averaging is necessary since the XAS for the two different sites are not identical. This is clearly shown in the calculated XAS of individual oxygen site in [Fig. 1], [Fig. 2], [Fig. 3] and [Fig. 4] where the absorption band from 541 to 543 eV is slightly broader at site 1 than in site 2. A cursory examination of the calculated XAS for different cluster models shows that the calculated XAS may not have converged even with the largest bare cluster. Perhaps, fortuitously, the application of line broadening functions washout the finer details and removes some of the discrepancies between different cluster calculations. However, intensities of the absorption bands are obviously quite different between the XAS computed with different cluster sizes. For example, the absorption peak at 541 eV calculated for the 7.3 Å cluster is noticeably much broader than predicted for the 3.3 Å cluster. Moreover, an absorption band starts to emerge at 537 eV when the cluster size is increased from 3.3 Å to clusters larger than 5.4 Å. Moreover, this feature is becoming more prominent with the cluster size. It is significant to note that quite prominent pre-edge excitations were predicted at 535 eV in all the cluster models.

[Full-size image \(132K\)](#)

Fig. 1.

Comparison of calculated XAS of ice IX with 3.3 Å (site 1, left panel) and 3.6 Å (site 2, right panel) of bare quantum cluster (top) and embedded in Madelung potential of different sizes.

[Full-size image \(141K\)](#)

Fig. 2.

Comparison of calculated XAS of ice IX with 4.8 Å (site 1, left panel) and 4.1 (site 2, right panel) of bare quantum cluster (top) and embedded in Madelung potential of different sizes.

[Full-size image \(144K\)](#)

Fig. 3.

Comparison of calculated XAS of ice IX with 5.4 Å (site 1, left panel) and 5.8 (site 2, right panel) of bare quantum cluster (top) and embedded in Madelung potential of different sizes.

[Full-size image \(139K\)](#)

Fig. 4.

Comparison of calculated XAS of ice IX with 7.3 Å (site 1, left panel, right panel) and 7.2 (site 2, right panel) of bare quantum cluster (top) and embedded in Madelung potential of different sizes.

Embedding the quantum cluster in the electrostatic field of the surrounding oxygen and hydrogen point charges has a dramatic effect on the calculated XAS. [Fig. 1], [Fig. 2], [Fig. 3] and [Fig. 4] compares the calculated XAS with different quantum clusters and size of the electrostatic (Madelung) potential. A major feature is a significant increase in the intensity of the absorption band at 537 eV. It should be noted that the absorption band at 537 eV already appears in the smallest quantum cluster of 3.3 Å but with much weaker intensity. Moreover, for a quantum cluster with constant size the calculated XAS converges quickly with increasing cut-off radius of the Madelung potential. The results presented here clearly show that the absorption features in the XAS are not solely dominated by the local environment. Intermediate range electrostatic interactions cannot

be neglected and must be taken into account in the calculation of the ice cluster XAS. Apart from changes in the shape of the overall absorption spectra, the Madelung potential has a drastic effect on the orbital energy levels as well. The calculated energy level diagrams from the transition-state potential for oxygen site 1 from different model clusters of ice IX with and without electrostatic field are compared in Fig. 5. It is well known that the local-density approximation often underestimates the energy (band) gap between occupied and unoccupied orbital. For example in liquid water the calculated band gap from a gradient-corrected function (GGA) is 4.5 eV [26] which is much lower than the experimental HOMO–LUMO gap determined by Grand et al. [27] and Coe et al. [28] to be 7 and 6.9 eV, respectively. It is not too surprising that DFT calculations on the bare quantum clusters seriously underestimate the gap energy. Interestingly, the calculated band gap decreases with as the size of the quantum cluster increases. The calculated HOMO–LUMO energy difference decreases from 4.17 to 3.26 to 2.80 eV when the cut-off radius of the cluster increases from 3.3 to 6.4 to 7.3 Å. Embedding the cluster in an electrostatic field (Madelung potential) resulted in a significant improvement on the band gap over the quantum cluster. For example, in the 3.3 Å cluster, the energy gap increases from 4.16 to 6.24 eV. For larger quantum clusters, the HOMO–LUMO gap decreases gradually. The largest quantum cluster considered here is 7.2 Å. When this cluster is embedded in a Madelung potential with a cut-off of 70 Å, the calculated HOMO–LUMO gap of 5.08 eV is now in better agreement with the band gap energy of 5.4 eV obtained from band structure calculations [29]. A smaller band gap predicted from DFT is not unexpected and it is due to a well-known deficiency of the local-density approximation [30].

Fig. 5.

LUMO-HOMO energy level diagrams for bare and embedded quantum clusters of different sizes for oxygen atom in site 1 of ice IX. In each panel, the energy level diagram on the left represents the bare quantum cluster and that on the right represents the embedded cluster.

The large change in the HOMO–LUMO gap due to the Madelung potential manifests in the dramatic changes in the character of the unoccupied orbitals. This point is illustrated in Fig. 6 on the iso-surface contour plot of the LUMO wavefunction (this orbital is not related to the strong pre-edge peak) of site 1 oxygen of ice IX at different cluster sizes with and without the presence of the point charges in Fig. 6. As vividly depicted in the figures, the nature of the LUMO orbital is strongly dependent on the model. The nature of the orbital wavefunction is evidently strongly modified by the size of the cluster and the electrostatic field. It is important to note that the contour plots are not intended to follow the evolution of a particular orbital with the different cluster size and the presence of the electrostatic field. The results only serve to demonstrate that the LUMO character can change significantly due to energy reordering as the result of different cluster size and the electrostatic field. It is observed that the larger the quantum cluster the more spatially disperse the LUMO. The delocalized nature of the LUMO has also been revealed in a recent study on the electronic structure of liquid water [26]. Changes in the orbital character are expected to affect the calculated XAS. It was often expected that the first coordination shell surrounding the excited oxygen atom was the primary origin of the spectral profile with low excitation energies, such as pre-edge features. The results presented here demonstrate that the

nature of the unoccupied states in the condensed phase is much more complicated.

Fig. 6.
Effect of Madelung potential on the LUMO orbital. Iso-surface plots of the LUMO orbital from site 1 of the ice IX structure for a 3.3 Å radius cluster without (a) and with (b) 70 Å radius point charges (iso-value 0.05), 7.2 Å radius cluster without (c) and with (d) 70 Å radius point charges (iso-value 0.07).

Since the nearest neighbors have a major influence on the XAS spectra, it may be expected that the convergence of calculated spectra is dependent on the quality of the basis sets used in the calculations. To investigate this effect, more diffuse basis sets were added on the nearest neighbor atoms of the excited oxygen to examine possible modifications in the pre-edge features. To this end, IGLO II (O (9s, 5p, 1d) → [5s, 4p, 1d]) or IGLO III (O (11s, 7p, 2d) → [7s, 6p, 2d]) [31] and [32] were used to replace the “standard” basis set on the nearest oxygen atoms. The computed XAS were compared in Fig. 7 to results which employ the “standard” basis set. The comparison shows that additional diffuse functions on the nearest neighbors has little effect and does not alter the gross features of the calculated spectra. The pre-edge, near-edge and the post-edge absorption profiles are not modified to any substantial extent. These results indicated that the “standard” basis sets used here and in many previous studies are adequate to describe the empty orbitals in the core hole state.

Fig. 7.
Comparison of the effect of basis set on the calculated XAS of ice IX (see text). (a) standard basis set; (b) IGLO-II and (c) OGLO-III.

A recent study by Prendergast et al. which employed a screened-full core hole approximation, with an electron included in the lowest occupied orbital, also found that the unoccupied states are sensitive to finite-size effects [26] and [33]. The same work demonstrates that the electronic structure of water is relatively insensitive to the long-range disorder and that the saturation of all hydrogen bonds in crystalline ice leads to a more delocalized state compared to water. This observation is consistent with the present results for crystalline ice IX. The near-edge and post-edge features will be more prominent in a crystalline structure where the delocalization plays a major role. Disruptions in

periodicity in disordered systems (e.g. amorphous ices and water) are expected to increase localization and the enhancement of the pre-edge feature in the XAS spectra. It was shown recently from experiment that the near-edge intensity at 539–540 eV reduces from crystalline to amorphous ices [34]. The present study demonstrates the importance of the Madelung potential on the calculation of XAS, particularly on the pre- and near-edge features.

Finally, the theoretical XAS computed using a quantum cluster of 7.3 Å embedded in a Madelung potential of 70 Å with the “standard” basis set and convoluted with Gaussian functions of fwhm of 0.9 eV is compared with the experimental spectrum measured at 0.25 GPa and 100 K in Fig. 8 with an instrumental resolution of 175 meV [12]. To facilitate the comparison, the calculated XAS were shifted to match the main feature in the observed spectrum. Three features can be identified from the experimental spectrum (indicated by arrows)—a weak pre-edge absorption at 535.07 eV and two additional absorption bands one near the ionization threshold of 538.0 and another at 541.5 eV which is above the *K*-absorption edge. The calculated spectrum reproduces the observed absorption features qualitatively. The theory seems to underestimate the near-edge feature at 538.0 eV. The intensity of the second band increases with the size of the cluster size (see [Fig. 1], [Fig. 2], [Fig. 3] and [Fig. 4]). This discrepancy, as discussed above, can be traced back to the insufficient size of the quantum cluster even at the largest cluster of *ca.* 7.0 Å studied here. The XAS spectrum computed assuming a periodic model using the pseudopotential plane wave method is also shown in Fig. 8 where the peak positions in the calculated spectra were shifted in order to match the edge jump around 539 eV. The absorption profile is in reasonable agreement with the cluster calculations. Namely, the periodic model reveals quite similar pre-edge features followed by a band around 537 eV and then a broad and more intense post-edge band. However, the intensities and peak positions are not identical between the cluster and periodic models. It is noteworthy that the intensity of the near-edge band at 537 eV is much enhanced in the periodic calculations, thus bringing the calculated spectrum in closer agreement with experiment.

[Full-size image \(41K\)](#)

Fig. 8.

A comparison of experimental and calculated XAS for ice IX using the embedded quantum cluster and periodic models (see text).

4. Conclusions

The effects of cluster size, long-range electrostatic interactions and quality of the basis sets on the calculated XAS for ice IX have been studied in detail. It is found that the crystalline environment has the most important effect on the calculated XAS. This is likely due to the crystalline and ordered proton positions. In disordered structure, such as proton disordered ice *Ih* and/or water, the randomized electrostatic field may already be largely screened at a short distance and therefore does not influence the calculated XAS. This has been demonstrated by the reasonable agreement in the calculated XAS of crystalline but proton disordered ice *Ih* [23]. For disordered system, the electrostatic field may be neglected in the cluster calculations. Equally important is the size of the quantum cluster. However, in this study we show that a small cluster can be used as long as it is embedded in a sufficiently large electrostatic field to simulate the crystalline environment. This success is partially due to the broadening procedure employed that, perhaps fortuitously, removes discrepancies in the fine details of the calculated excitations. This study also

shows that the standard basis sets used in previous studies are able to reproduce the unoccupied orbitals in the core hole state adequately. The computational approach employed here seems to reproduce well the pre-edge absorption features involving more localized excitations in proton-ordered crystalline ice IX. It is much less reliable in reproducing the absorption profile in the near-edge and post-edge regions when more diffuse wavefunctions are included. This is probably due to an incomplete treatment of (multiple) continuum states using a localized basis set approach near or beyond the ionization threshold [6]. There are, of course, other factors that might affect the calculated XAS. The use of the transition potential approximation may not be always appropriate [35]. Depending on the system, it has been shown that the use of full core hole potential, with [32] and without screening [34] by adding an electron into the conduction band, can reproduce experimental XAS better than the transition-state approximation. This study reveals that the quantitative simulation of the XAS for proton-ordered structures remains a theoretical challenge.

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