

X-Ray Absorption Spectra of Water from First Principles Calculations

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We present a series of *ab initio* calculations of the x-ray absorption cross section (XAS) of ice and liquid water at ambient conditions. Our results show that all available experimental data and theoretical results are consistent with the standard model of the liquid as comprising molecules with approximately four hydrogen bonds. Our simulations of ice XAS including the lowest lying excitonic state are in excellent agreement with experiment and those of a quasitetrahedral model of water are in reasonable agreement with recent measurements. Hence we propose that the standard, quasitetrahedral model of water, although approximate, represents a reasonably accurate description of the local structure of the liquid.

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Understanding the hydrogen bonding in liquid water is fundamental to a thorough comprehension of the driving forces behind many physical, chemical and biological processes. For the past 40 years, water has been modeled as having a local structure not dissimilar to that of the solid phase. In crystalline ice, each molecule is hydrogen bonded to exactly four others, in an approximately tetrahedral arrangement [1]. In the standard model of the liquid the local, molecular coordination is also approximately tetrahedral, with about 3.6 hydrogen bonds per molecule [2]. Classical potentials, fitted to x-ray and neutron scattering data and to measured thermodynamic properties, yield a quasitetrahedral local structure of the liquid when used in molecular dynamics (MD) simulations, and simultaneously reproduce many other physical properties [3]. Recently, first principles calculations based on density functional theory (DFT) [4] have confirmed the quasitetrahedral coordination of water molecules in the liquid. However, when neglecting proton quantum effects, converged DFT-MD simulations using gradient corrected exchange-correlation functionals and performed at the experimental equilibrium density produce a more icelike structure for the liquid [5] than that inferred from experimental estimates of the radial distribution functions [2].

Recently, x-ray absorption spectroscopy (XAS) techniques have been used to elucidate the local structure of liquid water. In particular, by comparing measured XAS spectra of bulk ice, the ice surface and water with those calculated using DFT and specific structural models, it was suggested [6] that the liquid contains significantly more broken hydrogen bonds than previously thought. The authors of Ref. [6] suggested that chains instead of tetrahedral units are the basic constituents of the fluid. The measured spectra reported in Ref. [6] are consistent with those obtained in independent experiments [7], however, their interpretation remains controversial.

In this work, we report on first principles DFT simulations of the XAS of ice and liquid water at ambient pressures, which explicitly include the lowest lying excitonic state. Our approach can reliably predict the near *K* edge structure of oxygen in crystalline ice and, in using a quasitetrahedral model of the liquid [3], yields good, qualitative agreement with all existing XAS experiments. Hence we propose that the standard model of water provides a reliable, though approximate, description of the liquid structure, and that the proposition of the fluid as being mostly composed of chainlike structures is not justified, based on the theoretical and experimental information available at present.

We calculated the x-ray absorption cross section of ice and water to first order, using Fermi's golden rule:

$$\sigma(\omega) = 4\pi^2\alpha_0\hbar\omega \sum_f |M_{i \rightarrow f}|^2 \delta(E_f - E_i - \hbar\omega).$$

Here $\hbar\omega$ is the energy of the absorbed photon, which should match the energy difference $E_f - E_i$ between initial and final electronic states; α_0 is the fine structure constant; and $M_{i \rightarrow f}$ are the matrix elements of the transition between initial and final states $|\Psi_i\rangle$ and $|\Psi_f\rangle$, evaluated within the electric-dipole approximation as

$$M_{i \rightarrow f} = \langle \Psi_f | \hat{\epsilon} \cdot \mathbf{R} | \Psi_i \rangle \approx S \langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} | \psi_i \rangle,$$

where $\hat{\epsilon}$ is the polarization direction of the electromagnetic vector potential, \mathbf{R} and \mathbf{r} are the many-electron and single-electron position operators, respectively, and $|\psi_{i,f}\rangle$ refer to the pair of single-particle states involved in the transition. Here the initial state is fixed as the $1s$ eigenstate of the oxygen atom. Single-particle approximations of the many-electron matrix elements are accurate up to a factor S , approximately constant for all transitions [8].

In our approach the final state of the electronic system is calculated in the presence of the core hole which results from the x-ray excitation. To reduce the computational cost, we occupy only the first available empty band with the excited electron and relax the DFT electronic structure within this constraint [9]. We then use the corresponding self-consistent potential to generate unoccupied levels higher in energy than the first excitation. We use the pseudopotential approximation, and model the x-ray excited atom with a pseudopotential derived from an oxygen atom with one electron removed from the $1s$ level. We employ norm-conserving Hamann pseudopotentials [10] for oxygen and a Gaussian pseudopotential for hydrogen by Giannozzi. The breaking of spin degeneracy accompanying a single-electron excitation is not included. The matrix elements $M_{i \rightarrow f}$ between the atomic core level and the excited conduction band are computed using a frozen-core approximation [11–13]. We employ DFT within the generalized-gradient approximation using the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE-GGA) [14] and the PWSCF code [15]. The single-particle wave functions are expanded in a plane-wave basis with an energy cutoff of 85 Ryd.

We first compare calculated and experimental XAS spectra for ice. Recent near-edge x-ray absorption fine structure (NEXAFS) experiments [6,16] reported x-ray absorption of crystalline ice samples prepared by molecular deposition on the Pt[111] surface. Helium scattering indicates [17] the presence of molecular crystals with surfaces consistent with either the (0001) surface of hexagonal ice (*Ih*) or the (111) surface of cubic ice (*Ic*). (Recent work [18] indicates that coverage of crystalline ice on Pt[111] may not be uniform).

In our simulations, we used lattice constants of ice *Ih* yielding a density of 1.00 g cm^{-3} with a c/a ratio of 0.945. The density of ice *Ic* was fixed at the experimental value of 0.931 g cm^{-3} using $c/a = 1.0$ [19]. The primitive cell atomic structures were relaxed, with these constraints on the unit cell volumes, until the forces computed using PBE-GGA were less than 10^{-3} Hartree/bohr. The primitive cell of ice *Ih* (*Ic*) contains 12 (8) water molecules and we constructed a $2 \times 2 \times 2$ supercell of 96 (64) molecules for our calculations [20]. The excited state electronic structure, including the excited electron in the lowest available conduction band, was converged using a uniform grid of 27 (64) k points in the Brillouin zone containing 10 (36) symmetry-inequivalent points. All absorption cross sections were averaged over the three Cartesian directions.

The agreement between calculated and measured XAS (see Fig. 1) is very good, with all qualitative features reproduced accurately. The computed spectrum is aligned with an onset energy of 535 eV associated with the lowest computed transition (at the zone center), broadened using a Gaussian line shape with 0.4 eV standard deviation, and renormalized to reproduce the peak height of experiment.

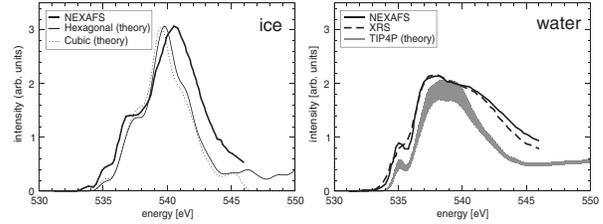


FIG. 1. Left: NEXAFS spectrum of crystalline ice I from Ref. [6] (thick, solid) and calculated XAS of hexagonal ice *Ih* (solid line) and cubic ice *Ic* (dotted line). Right: NEXAFS (thick solid line) and XRS (thick dashed line) spectra of water from Ref. [6], and calculated XAS of water (gray line) from the TIP4P MD simulation at 300 K. Vertical thickness of the calculated curve is the associated standard error from a sample of 32 water molecules.

We note that the agreement with experiment is good but not perfect. The width of the computed peaks is too narrow in comparison with experiment. This is consistent with the general underestimation of band width within current local approximations to DFT and originates from an approximate description of exchange and correlation interactions. Improvements are possible using self-interaction-corrected DFT calculations [21] or by using *GW* quasiparticle corrections [22]. Note that ice *Ih* and *Ic* differ structurally only beyond first nearest neighbor molecules and consequently have very similar spectra.

We now apply the same theoretical framework used for ice to calculations of liquid water spectra. We choose to model water using one of the popular classical potentials fitted to experiment, which can reproduce many characteristics of the phase diagram. The particular, detailed choice of the potential is not key to this study. The important, qualitative point is that the potential chosen here gives a quasitrahedral structure of the fluid in accord with the standard model. In particular we have modeled liquid water using the classical, TIP4P point charge model [3], which qualitatively reproduces the phase diagram of water [23], and which we have previously used to analyze the electronic structure of the liquid [24]. In this model water molecules are treated as rigid. We have taken 10 snapshots of 32 water molecules from a 200 ps MD simulation [25] spaced 20 ps apart. To approximate the XAS experiment, we average computed spectra from each molecule in a given snapshot and further average over all snapshots. In total we have combined the results of 320 spectral calculations to approximate the XAS of the liquid. We found very little variation between the XAS of individual, uncorrelated snapshots computed using only the zone-center k point. Therefore, we picked one representative snapshot of 32 molecules, and carried out calculations using 27 k points in the Brillouin Zone, for each excited molecule. Each spectrum of discrete transitions is broadened with a Gaussian line shape with a standard deviation of 0.3 eV. The averaged XAS is compared in Fig. 1 with the experi-

mental NEXAFS and x-ray Raman spectroscopy (XRS) spectra of water at 300 K [6]. Our calculation is in good qualitative agreement with experiment, indicating that the tetrahedral local model of the liquid accounts reasonably well for measured XAS [26].

We now turn to examining the contribution to the computed XAS spectra of broken hydrogen bonds and of disorder in the oxygen lattice. The contribution from molecules with broken or distorted hydrogen bonds (HB) is compared to that of the entire liquid in Fig. 2. Our model contains approximately 20% of molecules with broken HB, which are defined according to two definitions: (I) exceeding a maximum separation of oxygen atoms of 3.5 Å and a maximum angle of the donated hydrogen from the line joining both oxygens of 40°; (II) exceeding a maximum oxygen-oxygen separation which depends on the angle as outlined in Ref. [6]. There is a clear, qualitative difference between the signal arising from species with broken HB and the averaged spectrum. Such qualitative differences were also observed in Ref. [6]; however, contrary to our investigations, the authors of Ref. [6] concluded that the liquid should contain about 80% of broken HB species in order to reproduce the measured XAS, when using DFT-based approaches. Here we reproduce all of the experimentally detected qualitative features by having only 20% hydrogen bonds in our sample.

The effect of disorder of the oxygen sublattice on computed spectra can be estimated by comparing XAS calculations for ice, amorphous ice, and the liquid. In Fig. 2 we compare the XAS of ice *Ih* and of a rather primitive model of amorphous or disordered ice, generated using the TIP4P potential by quenching a 300 K liquid sample of 32 molecules down to 100 K. We considered one snapshot at this temperature as our structural model to generate the XAS in Fig. 2. The signal arising from broken HB species are qualitatively similar in the disordered sample and in the liquid. However, only one (two) of the molecules in our amorphous ice snapshot had less than two donor HB according to definition I (II), and yet the XAS is qualitatively different from that of the crystalline sample. We therefore conclude that disorder plays a key role in reduc-

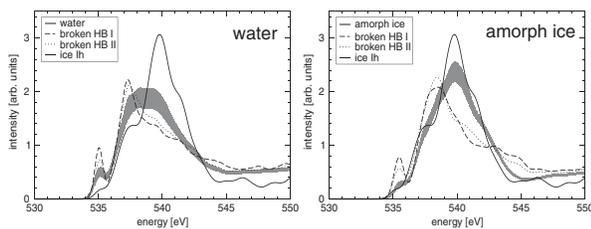


FIG. 2. Left: Comparison of the calculated XAS of water and crystalline ice *Ih* indicating qualitative spectral differences between liquid and solid phases. Right: A similar comparison between ice *Ih* and a model of amorphous ice. Also indicated in both panels are the characteristic spectra from water molecules with at least one broken donor hydrogen bond (see text).

ing the peak height at 539–540 eV, when going from ice to the amorphous structure. We also observe an increase in intensity around 538 eV in the amorphous sample, and at much higher energies above 545 eV. Both of these trends are also seen in going from ice to the liquid, and can thus be associated with disorder in the oxygen sublattice. On the other hand, the significant increases in intensity at the onset (535 eV) and the main edge (537–538 eV) found in the liquid can be associated with broken HB, of which there are approximately 4–6 times as many in the liquid sample, compared to the amorphous. Therefore we have identified two important effects accounting for the difference between XAS of ice and XAS of the liquid: broken HB and disorder of the oxygen sublattice.

Finally, we would like to comment on approaches different from ours used in the literature to compute XAS of water in various phases: the full core hole (FCH) and half-core hole (HCH) approaches. The FCH technique [11] is analogous to the one adopted here, except that it neglects a self-consistent inclusion of the excited electron. Such an approach should accurately reproduce the higher energy excitations to progressively more delocalized states, and at high energy yield the same results as our approach, which we call excited-state-core hole (XCH). However, accounting for the impact of a localized excited electron at low energies leads to differences between FCH and XCH results; these are shown in Fig. 3. FCH tends to overestimate the absorption cross section at and near the onset, consequently underestimating the main peak height, by virtue of the oscillator strength sum rule.

In the HCH approach, adopted in Ref. [6], only half an electron is removed from the core state, thereby simulating a transition state in the x-ray excitation process. We have found that in the presence of the HCH pseudopotential, inclusion of half an excited electron at the conduction band

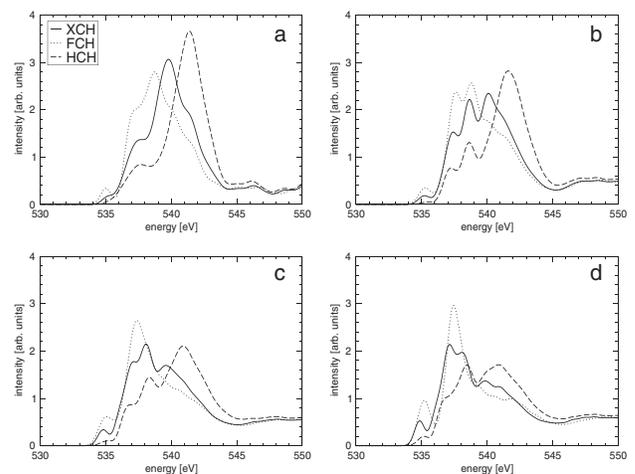


FIG. 3. Comparison of DFT XAS within various approximations for the x-ray absorption process, viz XCH, FCH, and HCH. (a) hexagonal ice; (b) amorphous ice; (c) liquid water; (d) liquid water sampling only broken-hydrogen-bonded species.

minimum has almost no impact on the calculated XAS. The HCH spectra tend to overemphasize the main peak and underestimate the excitonic near-edge intensity. This is consistent with the reduced binding energy of the half-core hole in the excited oxygen atom.

We note that the same spectral trends exist in all approaches (FCH, XCH, and HCH) with respect to increasing disorder and number of broken HB: a decrease in the main peak height and an increase in intensity at the near edge are observed. However, in the limit of converged k -point sampling and when employing homogeneous numerical broadenings, we find that only the XCH approach provides a consistent agreement with experiment. Note that the calculated HCH spectrum of a standard, quasitetrahedral liquid water model appears icelike in comparison with experiment; however, it is still clearly distinguishable within the same approximation from the XAS of the solid.

In summary, using DFT electronic structure calculations, we find very good agreement between the calculated and experimentally measured XAS of ice. Using a classical potential to simulate a standard, quasitetrahedral model of liquid water we find reasonable agreement between our DFT calculations and experiment, indicating that the standard model yields a reasonable description of liquid water. Therefore we conclude that the percentage of broken HB in the standard model is consistent with experimental observations. We have identified two major effects responsible for the difference between computed ice and water spectra: disorder of the oxygen sublattice and broken hydrogen bonds. The signature of these two effects is qualitatively the same, irrespective of the details of the models used to describe the core hole interactions in DFT calculations.

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 [26] Our theoretical XAS calculations permit absolute comparisons between XAS of different phases of water, and so we choose only one normalization and absorption onset for all our spectra, determined by fitting our calculated XAS for ice I to that measured in Ref. [6], since this structure is known. However, experiments performed on different phases may necessitate different experimental techniques, and a quantitative comparison may not be possible, if the measured spectra of the different phases have no common features. We adopt the same relative normalization in Fig. 1 between the measured XAS of liquid and ice as that provided in Fig. 1 of Ref. [6].