

X-ray absorption spectrum of liquid water from molecular dynamics simulations: Asymmetric model

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We address the question of the local structure in liquid water by computing the x-ray absorption (XA) spectrum explicitly averaging over configurations from classical and Car-Parrinello molecular dynamics (MD) simulations. We confirm the prediction by Wernet *et al.* [Science **304**, 995 (2004)] that the resulting spectra are not representative for liquid water due to a too large fraction of molecules with two donating hydrogen bonds. The H-bond criterion given by Wernet *et al.* is, however, not sufficient to predict the XA spectrum for general structures from MD simulations. Only by selecting specific single-donor MD configurations is it possible to represent the liquid water spectrum; this results in an improved and more restrictive geometrical connection between local structure and spectral features in the simulation. The configurations, with one strong and one weak donating hydrogen bond, need to be even more asymmetric than previously assumed. This bonding situation is strongly underrepresented in the simulations.

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I. INTRODUCTION

The local coordination and structure of liquid water is presently under strong debate.¹⁻¹¹ The established picture, derived from molecular dynamics (MD) simulations, that water is mainly four-coordinated in the liquid, was recently challenged by Wernet *et al.*¹ The x-ray absorption (XA) spectrum of liquid water has a characteristic pre-edge peak (at 535 eV) and a pronounced main-edge (at 537-538 eV); the spectrum resembles the XA spectrum of the surface of ice with unsaturated hydrogen bonds (H bonds) rather than that of fully coordinated bulk ice¹ which instead shows a strong post-edge (540 eV) with weak pre-edge contributions from proton disorder, possible surface contributions, and remaining defects.^{1,12} Based on XA and x-ray Raman scattering (XRS) spectra and spectrum simulations it was concluded that most of the molecules in the liquid only have two strong H bonds; the remaining bonds are weakened through a combination of elongation and angular distortion. This asymmetric H bonding (e.g., one strong and one weak donating H bond) was shown to be compatible with neutron data, but at strong variance with present theoretical MD simulations which predict bulk icelike x-ray spectra as a consequence of the high coordination.¹

This interpretation was challenged in an independent temperature-dependent XA study using total electron yield detection (TEY) (Ref. 2) to determine the energetics required to give the characteristic pre- and main-edge features. The low value, 1.5 kcal/mol, led Smith *et al.*² to conclude that only very small distortions from tetrahedral symmetry would be required to produce the typical features of the liquid water XA spectrum. However, we have argued that the quality of their experimental data in terms of spectra reproducibility is rather poor due to saturation effects; this, together with the simplified theoretical analysis, invalidates their conclusions.³ An evaluation of different techniques to obtain the XA spectrum of water has recently been published together with a

critical analysis of saturation effects;⁶ the techniques based on photon detection [fluorescence yield (FY), XRS, transmission mode (T mode)] were shown to give consistent spectra while the electron detection modes, TEY and Auger electron yield (AEY) show major discrepancies in their application to liquid water. In the case of TEY this is mainly due to the occurrence of saturation effects which must be corrected before an analysis can be made. The AEY technique is not bulk sensitive enough and has large spectral contributions from the surface region. Saturation effects are absent in T mode and XRS spectra and negligible in ice measurements of thin films using either fluorescence or electron detection, but must be considered and corrected when using the other techniques to obtain bulk liquid water XA spectra.^{6,13-15}

Due to the importance of MD simulations for our understanding of, e.g., water, aqueous solutions and proteins interacting with water, it becomes imperative to reconcile the simulations with the XA data. The analysis of MD structures as well as a recent study of the energetics in MD simulations¹¹ supports the interpretation of an essentially tetrahedral local hydrogen bond coordination in contradiction to the interpretation of the experimental XAS/XRS data. Although MD simulations have successfully reproduced several dynamical and structural properties of liquid water it is clear that a successful reproduction of an experiment does not prove that the model used is the correct one; for this conclusion to be valid it is also necessary to show that alternative models can be excluded.⁷ In this context it is interesting to note the recent reevaluation of available neutron- and x-ray diffraction data by Soper¹⁰ which shows that the experimental data can be fitted equally well by a symmetrical and a range of asymmetrical models; i.e., based on the diffraction data it is not possible to discriminate between a symmetric tetrahedral H-bond coordination and more asymmetric local structures. However, MD simulations have the potential to provide atomistic level information on both the

local and extended structure of liquid water as well as on the energetics and dynamics in the H-bonded network. Information from MD simulations is thus an essential and well established complement to the experimental data and it is necessary to investigate how the conflicting experimental XAS/XRS data can be fitted into the picture.

The fundamental conclusion in Ref. 1 of an asymmetric local coordination is based on the experimental comparison with the XA spectra of bulk and surface of ice. However, density functional theory (DFT) calculations of spectra for models of the liquid were used to interpolate between the two limiting experimental models and to determine geometrical H-bond criteria upon which the studied MD simulations were evaluated. Although these criteria are similar to standard definitions and the calculations were shown to describe well the limiting bulk ice and ice surface, the connection between structure and spectrum for the intermediate cases could still be questioned. One such attempt was made by Hetényi *et al.* who reported agreement with the XAS/XRS experiment within the pseudopotential-based Car-Parrinello MD (CPMD) approach after modifying the core-hole potential to include the full effect of the core hole.⁴ The pseudopotential method eliminates the inner shells and as a result the computed XA spectra have to be shifted for comparison with experiment, whereas in an all-electron description an accurate energy scale is available. As is evident from a direct comparison of all-electron calculations with experiment, the full core-hole potential is not appropriate for water neither in its gas, nor liquid, or solid phases.⁵ Thus the disagreement between experiment and MD simulations remains and in the present work we will further delineate what geometrical parameters characterize the structures that are underrepresented in the MD simulations and that can give spectra in accordance with experiment.

For the understanding of the interactions of liquid water and the interpretation of its XA spectrum, it would be desirable to analyze the XA spectral response in terms of energetics, but the XA spectrum is mainly sensitive to the exchange repulsion in the intermolecular interactions. Therefore a geometric (H bond) criterion for the response in the XA spectrum is more appropriate than an energetic criterion; this is furthermore easily applicable to analyze MD structures. A geometric cone region (around each hydrogen) within which the XA spectroscopy is sensitive to H bonding has been given.¹ This was derived from XA spectrum calculations on 11 molecules clusters and provides an operational “H-bond” criterion [$\delta_{OHO} (< 45^\circ)$ is the OH-O angle in degrees and distances are in Å], Eq. (1); an acceptor molecule within this cone is considered to be H bonded.

$$r_{OO} < r_{OO}^{max} - 0.00044 * \delta_{OHO} * \delta_{OHO}; (r_{OO}^{max} = 3.3 \text{ \AA}). \quad (1)$$

According to this criterion only water molecules with one donating H bond will give a “liquid-water-like” signature in the pre-edge and main-edge features in the computed XA

spectrum.¹ Water molecules in non (ND), single (SD), and double (DD) H-bond donating configurations according to Eq. (1), have different characteristic XA spectra.

In the present work we have used this cone definition to select configurations from MD simulations, representative of specific H-bond arrangements, such as the single-donor and single acceptor configurations (D1A1) which should dominate according to Ref. 1.

A fundamental prerequisite is that the spectrum calculations are sufficiently accurate. This has been investigated for specific cases with known structures such as the bulk and surface of ice (including H-bonded NH_3),¹ for gas phase and condensed water,⁵ and for gas-phase molecules such as, e.g., pyridine¹⁶ as well as methanol.¹⁷ The effects on the spectra from H-bond formation have been studied and compared with experiment for the ordered (3x2) overlayer of glycine on Cu(110) (Ref. 18), and the monolayer of water on Pt(111),¹⁹ as well as for bulk methanol.²⁰ For liquid water, calibration calculations comparing with experiment are more difficult since the structure itself is under debate. However, it has been shown that for general structures taken from CPMD simulations a fully periodic plane-wave calculation of the XA spectra is in complete agreement with the localized basis set cluster model calculation of the same structure once the unit cell and cluster sizes are large enough.²¹

Although in Ref. 21 we show that the spectra computed from the small 11 molecules clusters are not very sensitive to systematic enlargements of the cluster size we still find (see below) that SD species from extended models taken from MD simulations may give ice-like spectra with strong post-edge (at 540 eV) rather than the enhanced pre- (at 535 eV) and main-edge (at 537–538 eV). The cone criterion is thus not a sufficient requirement to predict liquid-water-like spectrum contributions from general structures. In the present work we will thus strengthen this criterion to give reliable predictions also in the case of extended and more disordered structures from MD dumps.

II. METHODS

In the analysis of the XA spectrum, we have used two complementary approaches to the spectrum simulations both aiming at interpreting the XA spectrum of water in terms of geometric parameters. On the one hand, spectra of configurations from MD simulations can be used to evaluate the liquid structure as obtained by the MD simulations and to investigate effects of long-range interactions. Spectrum simulations on well-defined molecular cluster models derived from the ordered ice Ih structure, on the other hand, make it possible to systematically study how the XA spectrum responds to specific geometrical changes. By combining the two approaches, models for the spectral response can be proposed and evaluated on configurations from the MD simulations. The MD configurations were taken from trajectories of the classical (SPC) (Ref. 22) and *ab initio* (CPMD) (Refs. 23 and 24) MD simulations that were presented in our recent work on water¹ and described in the on-line additional material of that reference. Both simulations were performed at room temperature and at experimental liquid water density

with fully flexible molecules at periodic boundary conditions. The configurations for sampling the XA spectrum were taken from snapshots of the classical MD simulation of 256 molecules, which was equilibrated for 100 ps with a time step of 0.1 fs, and the *ab initio* simulation of 64 molecules [after 9 ps of CPMD simulations starting from a classical (SPC/E) model²⁵]. In the CPMD simulation, the parameters for the pseudopotential description of the core electrons were taken from Ref. 26 with the modification that the cut-off radius for the Troullier-Martin-type pseudopotential²⁷ for oxygen was 1.05 a.u. A 70 Ry kinetic energy cutoff was applied for the plane-wave expansion and the BLYP gradient-corrected exchange (Becke)-correlation (Lee-Yang-Parr) functional was used in all calculations.^{28,29} Nosé-Hoover thermostats^{30,31} were used to regulate the ionic temperature. A time step of 0.144 fs, together with a fictitious electronic mass of 700 a.u., was used in the CPMD algorithm.²³

The configurations were selected either to sample over molecules in a single time-frame representative of the average H-bond statistics over the trajectory, or to sample a specific H-bond arrangement. The spectrum contribution from the selected molecule was computed using 32 molecule clusters taken out from the MD simulations, in which the neighboring molecules were selected based on an O-O distance criterion considering the periodic boundary conditions. On the other hand, for the systematic study of the response of the XA spectrum to geometric changes, model cluster configurations with 17 molecules in idealized geometries based on the ice Ih structure were used; this size corresponds to the complete first and second hydration shells. The H bonds were linear (with O-O=2.75 Å) and the internal O-H distances and H-O-H angles were 0.95 Å and 109.41°, respectively. All XA spectrum calculations were performed with the StoBe-deMon code³² using the transition potential method³³⁻³⁵ within the same computational framework as in previous studies.^{1,5} A Δ Kohn-Sham (Δ KS) correction^{5,16} is applied to the lowest state resulting in a uniform energy shift of each individual spectrum to which also a relativistic correction of +0.33 eV was added.³⁶ The discrete spectra of the 17 molecule clusters were convoluted with a Gaussian broadening linearly increasing from 0.5 to 8.0 eV over the interval 535.5 to 550 eV. Due to the introduction of the Δ KS correction this interval is somewhat different from what we have previously employed. The spectrum averages from CPMD trajectories involve between 40 (each of the constrained D1A1 classes) and 32 (each of the SPC, CPMD, and D1A1) configurations. For the sampling over MD configurations, the broadening due to the temperature is explicitly taken into account through the averaging over several configurations and a smaller additional broadening of the spectra can be applied. Therefore, we used a convolution with a Gaussian broadening linearly increasing from 0.5 to 2.0 eV over the interval 535.5 to 540 eV; to study the effect of the broadening we compare to spectra convoluted using Gaussians with constant full width at half maximum of 0.5 eV for all transitions. The spectra are normalized in the displayed energy region and the error bars denote the standard deviation in the spectra.

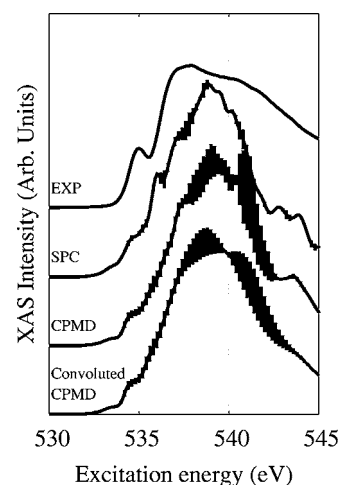


FIG. 1. Comparison of experimental (EXP) and simulated XA spectra for liquid water (Ref. 1). Averages for a classical (SPC) MD simulation and an *ab initio* (CPMD) MD simulation using constant broadening of 0.5 eV. The convolution scheme applied to the CPMD data (Convoluted CPMD). The spectra are normalized in the displayed energy region and the error bars denote the standard deviation in the spectra.

III. RESULTS

In Fig. 1 we show the simulated XA spectra obtained through explicit configurational averaging for the SPC and CPMD simulation models. The resulting XA spectra are clearly not in agreement with the experimental liquid water XA spectrum, but are consistent with our predictions based on their H-bond statistics which are 70:27 (DD:SD) and 79:20, respectively, for the SPC and CPMD simulations to be compared with 15:80 from the XA experiment.¹ The simulation models have too many fully H-bond-coordinated OH groups to correctly reproduce the experimentally observed intensity in the pre- and main-edge regions. The effect of the convolution is shown for the summed spectra based on the CPMD structures. The convoluted CPMD XA spectrum shows only a modest down-shift of the main intensity compared to the summed spectrum using the constant 0.5 eV convolution for the individual spectra. From plots of the orbitals involved in the respective excitations (not shown) we observe that the states corresponding to the pre-edge and post-edge features in the XA spectrum are very similar to the corresponding molecular orbitals in the water dimer presented in Fig. 2 in Ref. 17. Thus, the pre-edge spectral feature is related to states localized around the uncoordinated OH group, whereas the post-edge spectral feature originates from H-bonded OH groups and is due to excitations into antibonding combinations of internally antibonding OH orbitals on different molecules. As seen in Fig. 2, the energy position of this peak is thus strongly dependent on the H-bond length (O-O distance) with a roughly linear factor of almost 8 eV/Å for the donating H bonds. We have confirmed that the influence of the bond length for the accepting H bonds is modest, as is the effect of the next neighbor H-bond lengths. The vibrations in the internal O-H bond are

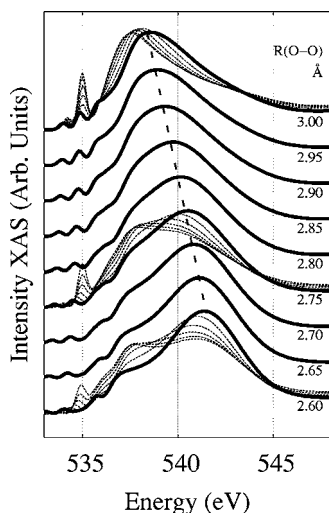


FIG. 2. The XA spectrum for the 17 molecules cluster (ice structure) as function of the donating H-bond (oxygen-oxygen) distance. In thin lines, an asymmetry is introduced by increasing one of the donating H bond distances by 1.0 Å in steps of 0.2 Å, keeping the intact H bond distance constant.

of less importance (as seen from the on-line additional material to Ref. 1). The effect of introducing an asymmetry through elongation of one of the donating H bonds is also presented in Fig. 2 for different initial O-O distances. The position of the induced pre-edge peak is independent of the length of the intact H bond and the larger the asymmetry in the H bonding the more well-defined is the pre-edge feature. States from uncoordinated H bonds at the surface of the cluster give rise to the small features below the pre-edge in Fig. 2 and may also result in an artificial splitting of the pre-edge. In the present case we only consider asymmetry imposed through elongations, but similar results are obtained also for angular distortions which are essential for realistic models of liquid water.¹ It is clear that the pre-edge is due to asymmetric distortions in the local coordination. From the disagreement between the computed simulation models and the experimental XA spectrum in Fig. 1 and in accordance with the conclusions from Ref. 1, we conclude that the number of strong donating H bonds would have to be reduced in the existing simulation models. This is necessarily accompanied by a reduction of the average number of accepting H bonds. We can simulate the influence from reducing the number of H bonds on the XA spectrum by biasing the configurational averaging. Such a biased selection is obtained by employing the H-bond criterion Eq. (1) to, e.g., select only CPMD configurations with one donating and one accepting H bond (D1A1) from the trajectory. The resulting average D1A1 spectrum in Fig. 3 clearly shows an improvement over the full CPMD spectrum in Fig. 1. The intensity in the pre-edge and main-edge regions increases at the expense of the post-edge intensity, but the pre-edge feature does not come out as well defined as in the 11 molecules cluster calculations¹ since the criterion fails to capture more extended molecular orbital interactions; the error bar at the pre-edge is very large. The spectrum calculations in Fig. 3, based on the sub-

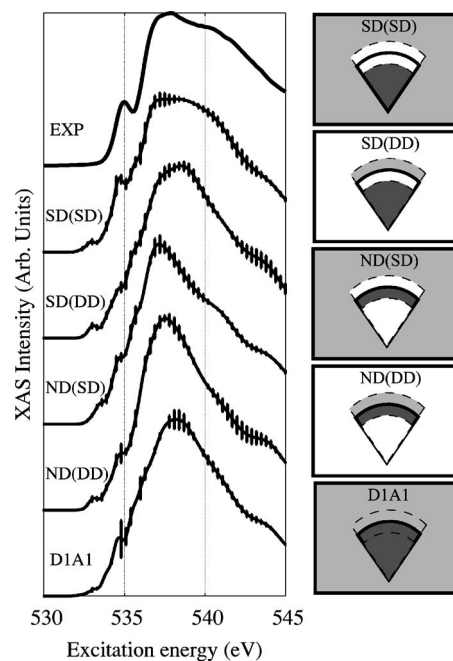


FIG. 3. Simulated XA spectra compared to the experimental data (EXP) for liquid water (Ref. 1). A schematic representation of the constraints on the H-bond definition used in the selection of configurations from the CPMD simulation: The geometrical region for the intact H-bond is depicted in dark gray and for the “broken” in light gray. (D1A1) Average over single donor and single acceptor configurations according to the original cone definition of Ref. 1. Averages over restricted classes ND(DD), ND(SD), SD(DD), and SD(SD) of distorted configurations (see the text for definitions). All spectra are normalized in the displayed energy region and the error bars denote the standard deviation in the spectra.

set of D1A1 configurations, thus show that the XA spectroscopy data put additional constraints on the possible molecular structures present in liquid water and the demarcation H-bond criterion needs to be made more restrictive; i.e., the criterion in Eq. (1) for the presence of the pre-edge peak is not sufficient when applied to larger and more disordered models.

How should the structure and the operational H-bond criterion be further refined to conform to the experimental XA spectrum and are small distortions, as suggested by Smith *et al.*,² sufficient to generate the features observed experimentally? To answer these questions, we select subsets consisting of 40 structures each from the class of D1A1 configurations from the CPMD simulation. To define the subsets we introduce a 0.4 Å margin around the H-bond criterion given by Eq. (1) which allows us to selectively study weakly and strongly distorted configurations within the class of D1A1 structures. This classification, schematically represented in Fig. 3, makes it possible to define the configurations more strictly. The least asymmetric case is given in Fig. 3 for the ND(DD) configurations which have both the intact and weakened H bonds within 0.4 Å from the defining cone border with $r_{OO}^{max} = 3.3$ Å of Eq. (1). The structures contributing to the ND(DD) spectrum in Fig. 3 are thus all single-donor configurations according to the normal H-bond

cone criterion, but nondonors with respect to an inner ($r_{OO}^{max}=3.3-0.4$ Å) cone and double donors in the sense of an outer cone ($r_{OO}^{max}=3.3+0.4$ Å); i.e., the intact H bond fulfills Eq. (1) for $r_{OO}^{max}=3.3$ Å but not for $r_{OO}^{max}=2.9$ Å, whereas the broken or weakened H bond lies outside the cone with $r_{OO}^{max}=3.3$ Å but inside an outer cone with $r_{OO}^{max}=3.7$ Å. We denote by ND(SD) in Fig. 3 configurations which are nondonors in the sense of the inner and single-donor configurations in the sense of the outer cone. These are thus more asymmetric than the ND(DD) configurations; the 40 configurations contributing to ND(SD) have the intact H bond near the border of the cone in Eq. (1), i.e., between 2.9 and 3.3 Å while the weakened H-bond is strongly weakened with $r_{OO}^{max}>3.7$ Å. The configurations giving the SD(DD) spectrum in Fig. 3 can be considered the reverse of the ND(SD) structures having instead a well-defined intact H bond, within $r_{OO}^{max}=2.9$ Å, while the weakened H bond is only somewhat weakened and within the outer cone with $r_{OO}^{max}=3.7$ Å; they are thus SD configurations in the sense of the inner cone and DD configurations in the sense of the outer cone. The actual bond lengths of the intact H bonds follow rather closely the first peak in the O-H radial distribution function of liquid water. Finally, the structures contributing to the SD(SD) spectrum in Fig. 3 are the most strongly asymmetric. They are single-donor configurations not only according to the normal H-bond cone criterion Eq. (1), but also in the sense of both the outer ($r_{OO}^{max}=3.7$ Å) and the inner ($r_{OO}^{max}=2.9$ Å) cones; i.e., the intact H bond is short and within the inner cone whereas the broken or weakened H bond is very weak with a bond distance outside the outer cone with $r_{OO}^{max}=3.7$ Å.

The ND(DD) configurations with only a weak asymmetry result in an intense main edge but the pre-edge is weak in comparison with the main edge. Enhancing the asymmetry, by having a weak intact bond and the other clearly weakened ND(SD) does not significantly alter the spectrum. Neither of the cases ND(DD) and ND(SD) shows any significant post-edge contribution as a result of the rather long intact H bond with an r_{OO}^{max} between 2.9 and 3.3 Å, while in the case of the SD(DD) species the shorter intact H-bond results in a more correct position of the post-edge peak; this is in accordance with the dependence of the post-edge position on the H-bond distance as demonstrated in Fig. 2.

Turning finally to SD(SD) with the largest asymmetry between the intact and weakened H bonds we find a very good agreement with the experimental spectrum. The ratio between the pre- and main-edge intensities is very well reproduced as is the sharpness of the pre-edge feature. It is clear that a large fraction of SD(SD)-type species, i.e., with large asymmetry in the H bonding with a well-defined intact H bond combined with a strongly distorted bond at the second hydrogen, must be present in the liquid in order to generate the observed experimental features. The structures within the D1A1 class of configurations from the CPMD simulation predominantly represent elongations in the case of the weakened donating H bond. In order to reproduce not only the XA spectrum but also the radial distribution function as determined from neutron diffraction the distortions should also include bending of the OH-O bond angle.¹ However, these

are rare in the simulation as a result of the density functional theory favoring straight H bonds over bent ones.³⁷ Since distortions through elongation and bending yield similar XA spectra¹ the studied structures are still representative for the amount of distortion in terms of a cone definition that is required to generate the observed features in the liquid; small distortions around tetrahedral symmetry are thus not sufficient. It is also important to note that in the present study we have only considered the SD species contribution to the liquid water spectrum; there are also some contributions from DD species which will somewhat enhance the post-edge region of the XA spectrum.¹

We finally note that the energy position of the computed spectra in Fig. 3 is obtained directly from the calculations plus a constant +0.33 eV shift to account for relativistic effects; no other shifts have been applied. The good agreement with the experiment in Fig. 3 in absolute energy validates the Δ KS procedure^{5,16} which furthermore is found to be essential for the reproduction of the sharp pre-edge; among the configurations in each class the Δ KS correction varies (1.3–2.7 eV) and brings the spectra into line. In analogy with Fig. 2, the small feature at ~ 533 eV in the computed spectra in Fig. 3 is due to cluster-size effects.²¹

IV. CONCLUSIONS

In conclusion we find that if the selection criterion is constrained to only very asymmetric H-bonding configurations the well-defined “water-like” pre-edge and main-edge features develop in the computed XA spectrum. This result agrees well with the results in Fig. 2 from systematic distortions of the 17 molecules cluster. The comparison in Fig. 3 shows that with a more restricted selection of asymmetrical configurations from MD simulations of liquid water we can reproduce the XA experiment and, if the distortions include bending as well, also the neutron diffraction radial distribution functions will be reproduced.¹ These bent, asymmetric configurations are strongly underrepresented in the present simulation models and it will be a challenge to develop potentials or functionals that also capture this aspect of the liquid water structure. Although the XA spectroscopy only probes the local structure, these results indicate that the liquid indeed is dominated by such asymmetrically coordinated molecules although a smaller fraction of other coordinations must also exist in the liquid.

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