Quantum Differences between Heavy and Light Water

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The structures of heavy and light water at ambient conditions are investigated with the combined techniques of x-ray diffraction, neutron diffraction, and computer simulation. It is found that heavy water is a more structured liquid than light water. We find the OH bond length in H_2O is ~3% longer than the OD bond length in D_2O. This is a much larger change than current predictions. Corresponding to this, the hydrogen bond in light water is ~4% shorter than in heavy water, while the intermolecular HH distance is ~2% longer.

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Ever since the earliest quantum simulations of water [1,2], there has been ongoing interest in the effect of quantum mechanics on the structure of water [3–11]. The main effect of including the quantum motion of the water molecule is to weaken the hydrogen bonding slightly, to give a more mobile, slightly less structured fluid than the corresponding classical liquid obtained for a given water interaction potential [9]. In particular, the main peak in the OO radial distribution function (RDF) becomes slightly broader and lower when quantum motion is included, and there are corresponding broadenings of the first peaks in the OH and HH RDFs. It is generally concluded that for the most accurate studies of water by computer simulation, quantum mechanics should be included, and that the structures of heavy and light water are similar but not identical.

The study of quantum effects in water by experiment was initiated by Egelstaff and coworkers comparing the structure of heavy water and light water using x-ray diffraction [12,13]. This is possible within the assumption that the electron form factors for heavy and light water are indistinguishable, an approximation that appears to be borne out in practice [14]. Interestingly, although the *shape* of the x-ray diffraction pattern difference, light water minus heavy water, is generally reproduced by the simulations, the *magnitude* of the predicted difference varies widely, and the observed temperature dependence of this difference is also not well reproduced by the simulations [15,16]. Most recently, the difference in structure between light and heavy water has been studied by x-ray absorption near-edge spectroscopy, XANES [17]. This last work concluded, in agreement with the previous diffraction data, that the quantum differences between light and heavy water could be represented as a temperature difference. However, the XANES data also implied increased asymmetry in the local hydrogen-bond network of light water compared to heavy water, an effect that would not be readily visible in an x-ray diffraction experiment due to the weakness of the scattering of x-rays by hydrogen.

Neutrons are of course scattered strongly by hydrogen and so in principle would be the ideal probe to look for this asymmetry in the hydrogen bond. In practice, there is a large change in neutron scattering length between H ($b_H = -3.74$ fm) and D ($b_D = 6.67$ fm) which means that the interference differential scattering cross section for water, $F_{\text{int}}^{(n)}(Q)$, changes radically with isotope even if the two structures are identical. Here,

$$F_{\text{int}}^{(n)}(Q) = c_O^2 b_O^2 S_{OO}(Q) + 2c_O c_H b_O b_H S_{OH}(Q) + c_H^2 b_H^2 S_{HH}(Q) \tag{1}$$

where c_α and b_α are the atomic fraction and neutron scattering length, respectively, of element α and $S_{\alpha\beta} = 4\pi\rho \int r^2[g_{\alpha\beta}(r) - 1]\frac{\sin Qr}{Qr}dr$, with $g_{\alpha\beta}(r)$ the radial distribution function for atom pairs (α, β), ρ the atomic number density, and Q the wave vector change in the diffraction experiment. The success of the neutron diffraction isotope experiment (NDIS) on water [18–20] relies on the assumption that heavy and light water have the same structure. There are additional complications arising from the different nuclear recoil properties of H and D. The combined circumstances of a large change in scattering length and change in recoil effect with hydrogen isotope precludes the direct observation of isotope quantum effects with neutron diffraction alone.

Recently x-ray and neutron diffraction data on water were used jointly to develop a structural model of water using empirical potential structure refinement (EPSR) [21]. This method builds on prior information, such as the water molecule geometry and the hydrogen-bond interaction, via a reference interaction potential, which is then perturbed by an empirical potential (EP) derived from the difference between simulated and measured differential scattering cross sections. The EP is refined until the residual between data and fit is minimized to the extent possible. The fact that the reference potential can build in prior information means that it may not be necessary to have a fully determinate matrix of scattering weights [e.g., Eq. (1)] in order to solve the structure. The x-ray data provide mainly information on the OO RDF, while the neutron data are dominated by the OH and HH RDFs. The extra information required to solve the structure is provided by constraints from the reference and empirical potentials.

The x-ray data (at 23 °C) were obtained from the previous work [15], with the x-ray data renormalized to the single atom form factor [21]. The neutron data were obtained (at 25 °C) on the SANDALS diffractometer at ISIS. This instrument is designed for diffraction studies of liquids containing hydrogen: the scattering angles are kept below 40° which minimizes inelasticity effects due to nuclear recoil [22]. For each of H_2O and D_2O, a cubic box of 2000 water molecules was constructed at a number density of 0.1002 atoms/Å^3, which compares with the exact number densities at this temperature of 0.10007 and 0.10000 atoms/Å^3 for H_2O and D_2O, respectively. The simulation procedure followed that described in [21].

Figure 1 shows the fits obtained to the x-ray and neutron data for the two liquids. Although some misfit between data and fit is observed, this is ascribed to systematic effects in both the x-ray and neutron experiments which have only a marginal effect on the outcome of the EPSR analysis. One feature to emerge early in the analysis was that the OH bond length, d_{OH}, in H_2O is longer than the OD bond length, d_{OD} in D_2O. This can be seen in Fig. 2 which shows the high Q fits to the respective datasets with $d_{OH} = 1.01$ Å and $d_{OD} = 0.98$ Å. Also shown is the fit to the H_2O data using $d_{OH} = 0.98$ Å. It is concluded that the OH bond length in light water must be longer than in heavy water.

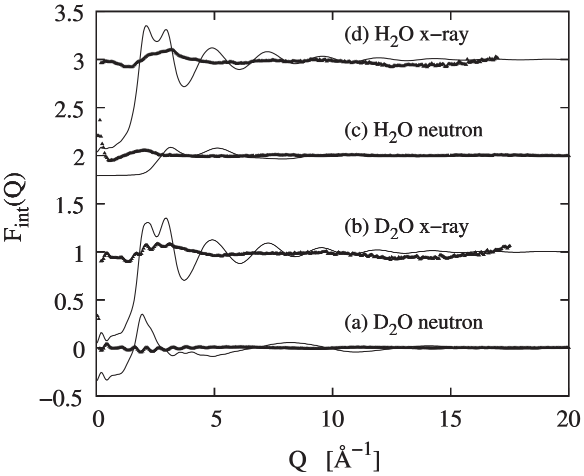

FIG. 1. EPSR fits to the neutron [(a) and (c)] and x-ray [(b) and (d)] diffraction data for heavy [(a) and (b)] and light [(c) and (d)] water. The fits are shown as the solid lines while the difference between data and fit is shown by the dots. Some systematic misfit is found for both neutron and x-ray data. In addition, truncation oscillations are found for the heavy water fits caused by finite size effects from the simulations.

To understand the role of inelastic scattering, we have performed a detailed study of the harmonic oscillator model of the dynamic scattering law [23] (A. K. Soper manuscript in preparation). One conclusion of the study is that for the single atom scattering, the effect of merging diffraction data from a range of scattering angles as is done in the SANDALS experiment is to leave only a monotonically varying background which is then removed by a simple smoothing procedure. For the interference scattering of interest here, the effect of inelasticity is to make the OH bond appear longer, by ~0.006 Å, while for OD, it appears ~0.004 Å longer. Hence, inelasticity by itself does not explain the marked difference between the two bond lengths that is observed here.

Also shown in Fig. 2 is the EPSR analysis of neutron diffraction data for deuteriated benzene, protiated benzene, and a 50:50 mixture of protiated and deuteriated benzene, measured under the same conditions as water. In this latter case, the same EPSR model of benzene was fit to all three diffraction datasets. Although there are small mismatches between model and data, there is no evidence here of a shift of C-H bond distance going from heavy benzene to light benzene [24]. Although benzene will generally have much different excitation frequencies compared to the water

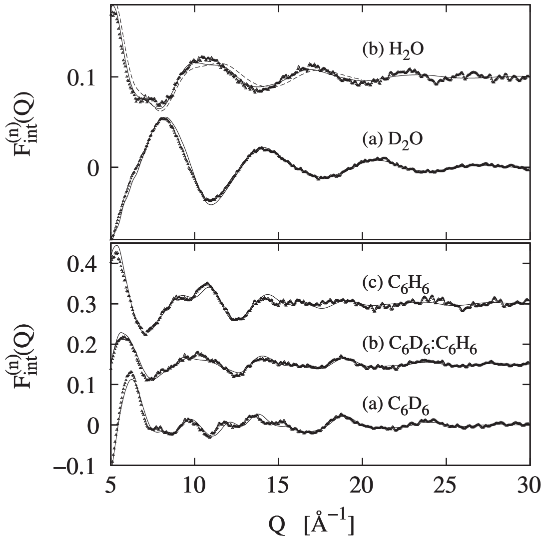

FIG. 2. Top: EPSR fits (solid lines) to the high Q region of the neutron diffraction data (dots) for heavy (a) and light (b) water. Also shown is the fit to the H_2O data assuming the same OH bond length, $d_{OH} = 0.98$ Å as for D_2O (dashed line). Bottom: EPSR fits (solid lines) to the high Q region of the neutron diffraction data (dots) for C_6D_6 (a), C_6D_6:C_6H_6 (b), and C_6H_6 (c). The benzene data have been analyzed with an assumed C-H distance of 1.06 Å. Unlike water, there is no indication of a longer C-H bond distance in C_6H_6 compared to C_6D_6.

molecule, the influential C-H stretch frequencies for benzene (~ 3100 cm^{-1}) are closely similar to those for the OH stretch frequencies in water (~3700 cm^{-1}). Hence, the increased OH bond length does not appear to be an artifact of the experiment. The OH bond length for the isolated water molecule is known accurately from microwave and infrared spectroscopies [25], with the OH bond length in the free H_2O molecule, 0.9724 Å ~0.6% longer than the OD bond in free D_2O, 0.9687 Å. An earlier measurement of the OD bond in D_2O yielded exactly the same result as the present data [26], while *ab initio* calculations for light water yielded $d_{\mathrm{OH}} = 0.99$ Å [27]. Later, Dore *et al.* [20], analyzing a series of reactor neutron data on heavy water dominated mixtures of heavy and light water, also concluded that the OH bond length might be larger than OD. Extrapolating their data to pure H_2O, one would conclude that the OH bond length was 0.02 Å longer than OD, which is quite comparable with the present results within the likely uncertainties of both datsets.

In conjunction with the longer intramolecular OH bond in H_2O, the hydrogen bond in light water is shorter and more asymmetric than in heavy water. Figure 3 compares the OO, OH, and HH RDFs for the two liquids. It can be seen that the first intermolecular OH peak for H_2O is at a significantly shorter distance (~1.74 Å) compared to the same peak in D_2O (~1.81 Å). Note however that the shortening of the hydrogen bond in H_2O by 0.07 Å is larger than the lengthening of the OH bond (0.03 Å), so there must be local geometrical changes between H_2O and D_2O. In addition, the OH peak is more asymmetric in H_2O than in D_2O, and the first HH distance in H_2O (2.42 Å) is larger than in D_2O (2.37 Å). For $g_{\mathrm{OO}}(r)$, both the first and second peaks are lower and broader in light water compared to heavy water. However, the coordination numbers for OH and OO, as measured out to the first minimum in each function (2.40 Å for OH and 3.36 Å for OO), are 1.88 ± 0.05 and 4.67 ± 0.05, respectively, for heavy water and 1.81 ± 0.05 and 4.67 ± 0.05, respectively, for light water, which means the number of hydrogen bonds per water molecule drops from 3.76 ± 0.1 in heavy water to 3.62 ± 0.1 in light water.

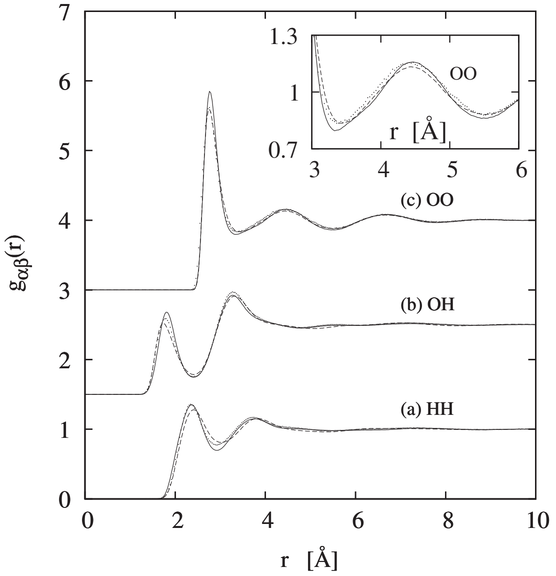

FIG. 3. Radial distribution functions for heavy (solid line) and light (dashed line) water. Also shown are the RDFs found in a previous study [21] in which both heavy and light water data were refined against the same box of molecules. The results are shown in the order HH (a), OH (b), and OO (c) and are shifted for clarity. The inset shows the second OO peak in more detail.

In order to characterize the change in local geometry between heavy and light water, we have calculated the distribution of water molecule triplets, $p(\theta_{\mathrm{OOO}})$. Here, three water molecules are regarded as a triplet if two of them lie within 3.18 Å of the third: this is the distance at which the OO coordination number reaches ~4.0. The angle calculated is the included angle made by these two molecules with the third to which they are "bonded." As can be seen in Fig. 4, this distribution is characterized by a broad peak near 100°: for light water, the peak is at 101.4°, while in heavy water, it moves outwards slightly to 103.0° and becomes slightly sharper. The same effect was seen in the quantum simulations of Guillot and Guissani [4].

The local order can also be characterized by the "q" number [28,29], which quantifies the tetrahedrality of the liquid:

$$\langle q\rangle = 1 - \left\langle\left(\cos(\theta_{\mathrm{OOO}}) + \frac{1}{3}\right)^2\right\rangle \tag{2}$$

where the average is taken over all appropriate triplets in the liquid. For the two liquids here, we find $\langle q\rangle = 0.593$ for

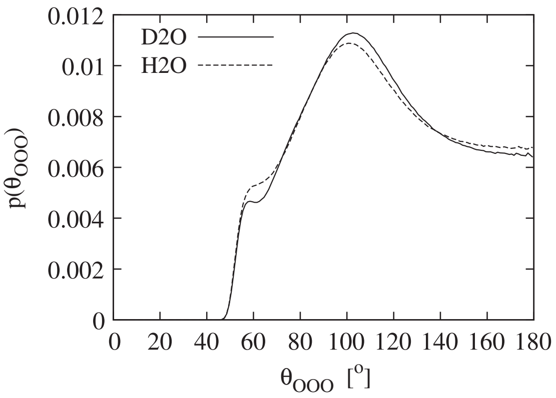

FIG. 4. Distribution of triplet angles, θ_{OOO} for triplets of water molecules, two of which are not more than 3.18 Å from a third. Heavy water is the solid line while light water is the dashed line. The results have been normalized to the $\sin(\theta_{\mathrm{OOO}})$ dependence that would occur if the triple angles were randomly distributed in space. The broad peak near 100° indicates water is broadly tetrahedral in its local neighborhood, but there are wide variations from molecule to molecule.

heavy water and $\langle q \rangle = 0.576$ for light water, confirming that heavy water is more tetrahedral than light water. (Perfectly tetrahedral local order would give $\langle q \rangle = 1$.)

In the past, it has been shown that the magnitude of the observed differences in structure are not well reproduced by the different simulations [15,16]. The general broadening of structural features in going from heavy to light water has been predicted by the quantum simulations, but the lengthening of the OH bond in H_2O compared to D_2O by as much as $\sim 3\%$ is not predicted. In turn the hydrogen bond in H_2O is shorter by $\sim 4\%$, the first intermolecular OH peak is more asymmetric, and the first HH intermolecular distance is $\sim 2\%$ longer, in H_2O compared to D_2O. These trends are opposite to earlier predictions [3,6]. The shift to shorter distances in the OH intermolecular peak *is* predicted by *ab initio* studies [5], although the magnitude and shape may be different.

Our results can be rationalized in terms of the likely anharmonicity observed for the proton potential well in water and ice [30]. Given the increased quantization of the proton compared to the deuteron, the proton would move further away from its parent oxygen atom on average, and towards the neighboring hydrogen-bonded molecule. The finding of a more asymmetric H-bond in light water compared to heavy water is also in agreement with a recent XAS experiment on water [17]. Interpretation of XAS data in terms of structure is still controversial, while in the present instance of combining neutron and x-ray diffraction data with a computer simulation method, where a simple Fourier transform connects the observable differential scattering cross sections and the desired radial distribution functions, the room for ambiguity is smaller.

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