Oxygen as a Site Specific Probe of the Structure of Water and Oxide Materials

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The method of oxygen isotope substitution in neutron diffraction is introduced as a site specific structural probe. It is employed to measure the structure of light versus heavy water, thus circumventing the assumption of isomorphism between H and D as used in more traditional neutron diffraction methods. The intramolecular and intermolecular O-H and O-D pair correlations are in excellent agreement with path integral molecular dynamics simulations, both techniques showing a difference of $\simeq 0.5\%$ between the O-H and O-D intramolecular bond distances. The results support the validity of a competing quantum effects model for water in which its structural and dynamical properties are governed by an offset between intramolecular and intermolecular quantum contributions.

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Oxygen is a ubiquitous element [1], playing an essential role in most scientific and technological disciplines, and is often incorporated within a structurally disordered material where examples include molten silicates in planetary science [2], glasses used for lasers and optical communications [3], the insulating oxide layers in silicon-based electronic devices [4], and water in biological processes [5,6]. Establishing the structure of a liquid or glassy oxide and thereby its relation to the functional properties of a material is not, however, a trivial task owing to the complexity associated with atomic disorder [7,8]. The method of isotope substitution in neutron diffraction has provided a pivotal role in unraveling the mysteries of disordered materials [8,9]. It has not, however, found application in the case of oxygen owing to the small contrast reported in the literature between the bound coherent neutron scattering lengths b of its isotopes [10,11].

In view of the importance of oxide materials and in the absence of a suitable theory to calculate the cross section for interaction of thermal neutrons with a specific nucleus, we have applied the sensitive technique of neutron interferometry [12] to measure the b values of the isotopes ^{17}O and ^{18}O relative to oxygen of natural isotopic abundance $^{\mathrm{nat}}$O. The interferometer S18 [13] was used to find the optical path difference between a sample of $H_2{}^{17}O$ or $H_2{}^{18}O$ and a sample of $H_2{}^{\mathrm{nat}}O$ for which $b_{^{\mathrm{nat}}\mathrm{O}} = 5.805(4)$ fm is accurately known [10]. The experimental procedure is described in Ref. [14] and the full details will be reported elsewhere [15]. The measured values of $b_{^{17}\mathrm{O}} = 5.867(4)$ and $b_{^{18}\mathrm{O}} = 6.009(5)$ fm were reproduced, within the experimental uncertainties, during two interferometry experiments performed a year apart. The results reveal a factor of $\simeq 6$ increase in the scattering length contrast between ^{18}O and $^{\mathrm{nat}}$O by comparison with standard tabulations [10,11]. They suggest that it is feasible to apply the method of oxygen isotope substitution in neutron diffraction to study the coordination environment of this element in disordered materials.

Water provides an important test bed to exploit this approach since there are several elements of its structure and dynamics that remain hotly debated [6]. One aspect of the controversy is the role played by nuclear quantum effects, such as zero point energy and tunneling, on water's hydrogen bonded network. This is manifested by differences between the structure and dynamics of heavy (D_2O) versus light (H_2O) water which lead to changes in properties such as their melting and boiling points, their temperature of maximum density, and their interaction with biological systems [6,16–19]. In addition, techniques such as 2D infrared (IR) spectroscopy commonly require H to be partially substituted by D, and hence it is important to understand the difference this engenders in the structure and dynamics of water [20,21].

Theoretical predictions of the changes in the structure of water upon including quantum effects vary considerably. On the one hand, rigid or flexible harmonic models predict a large destructuring as shown by (i) a decrease in the height of the first peak in the O-O pair distribution function, which is an indicator of intermolecular ordering, and (ii) an increase in the number of hydrogen bonds broken [22–25] (Table I). The replication of this peak height reduction by using classical models requires an increase of the liquid temperature by $\Delta T \simeq 35$–40 K. The destructuring can have dramatic implications for the dynamics

TABLE I. The change in structure predicted for some common models of water when quantum mechanical effects are included by using path integral molecular dynamics [26]. The models are either rigid (R), flexible harmonic (FH), or flexible anharmonic (FA). The difference between the intramolecular bond length on substituting H for D, $\Delta r = r_{\mathrm{OH}} - r_{\mathrm{OD}}$, is compared to (i) the difference in height of the first peak in $g_{\mathrm{OO}}(r)$, $\Delta h = g_{\mathrm{OO}}(r)|^{\mathrm{cl}}_{\mathrm{max}} - g_{\mathrm{OO}}(r)|^{\mathrm{qm}}_{\mathrm{max}}$, and (ii) the fractional difference in the number of hydrogen bonds, $\Delta\bar{n}_{\mathrm{OH}} = (\bar{n}^{\mathrm{cl}}_{\mathrm{OH}} - \bar{n}^{\mathrm{qm}}_{\mathrm{OH}})/\bar{n}^{\mathrm{cl}}_{\mathrm{OH}}$, as calculated from classical (cl) versus quantum (qm) simulations for H_2O. $\bar{n}_{\mathrm{OH}}$ is the O-H intermolecular coordination number such that $\Delta\bar{n}_{\mathrm{OH}} > 0$ implies a breaking of bonds on including quantum effects. Also listed are ΔT (see the text) and the ratio of the quantum to classical diffusion coefficients $D_{\mathrm{qm}}/D_{\mathrm{cl}}$ for a given model of H_2O [27].

Model	Type	Reference	Δr (Å)	Δh	$\Delta\bar{n}_{\mathrm{OH}}$ (%)	ΔT (K)	$D_{\mathrm{qm}}/D_{\mathrm{cl}}$
TIP4P	R	[28]	0	0.30	2.62	35	1.53
SPC/E	R	[29]	0	0.31	1.79	35	1.42
SPC/F	FH	[25]	0.0011	0.35	2.24	40	1.43
q-TIP4P/F	FA	[27]	0.0038	0.20	0.14	18	1.15
TTM3-F	FA	[30]	0.0054	0.03	−1.13	5	0.95

with the diffusion coefficient changing by as much as 50% [24,25,27]. On the other hand, flexible anharmonic models and a recent first principles molecular dynamics study predict much smaller changes in the structure [17,27], corresponding to $\Delta T \simeq 5$–18 K. Our diffraction approach provides a direct probe of the changes in water's structure on substituting H for D and thus provides a test for the validity of the various models.

Neutron diffraction experiments were made using the instrument D4c [31] with an incident wavelength of $\simeq 0.5$ Å at $T = 300.6 \pm 0.5$ K. The stability of this instrument was assessed by finding the fractional change of intensity for the successive diffraction patterns measured for a given sample. This change was found to be independent of the magnitude of the scattering vector Q, and the mean value calculated for the various samples was $\pm 0.012(8)\%$, consistent with the quoted stability for D4c of $\pm 0.01\%$ over 3 days [31]. The heavy water samples were $D_2{}^{\mathrm{nat}}O$ and $D_2{}^{18}O$ (1.82% ^{16}O, 0.50% ^{17}O, 97.68% ^{18}O) with a D:H ratio of 0.9947:0.0053. The light water samples were $H_2{}^{\mathrm{nat}}O$ and $H_2{}^{18}O$ (1.4% ^{16}O, 0.5% ^{17}O, 98.1% ^{18}O). The samples were handled in a dry (<4 ppm water) argon filled glovebox. The same cylindrical thin walled (0.1 mm) vanadium container (internal radius 0.24 mm) was used to hold the samples for the diffraction experiments and was always mounted in the same orientation. The atomic number density $n_0 = 0.100$ Å^{-3}.

The measured data sets were corrected [32] to give the differential scattering cross section for each sample. These functions, for either heavy or light water, were then subtracted to eliminate either the D-D or H-H correlations along with the main contributions arising from inelastic scattering (H and D are lighter than O and twice as numerous [9,33,34]) and any systematic error arising from the background, container, or multiple scattering corrections [32]. A residual inelasticity correction of the form $\Delta P(Q) = a + bQ^2 + cQ^4$, where a, b, and c are fitted coefficients, was then applied to give the first difference functions $\Delta F_{\mathrm{D}}(Q) = c_{\mathrm{O}}^2(b^2_{^{18}\mathrm{O}} - b^2_{^{\mathrm{nat}}\mathrm{O}})[S_{\mathrm{OO}}(Q) - 1] + 2c_{\mathrm{O}}c_{\mathrm{D}}b_{\mathrm{D}}(b_{^{18}\mathrm{O}} - b_{^{\mathrm{nat}}\mathrm{O}})[S_{\mathrm{OD}}(Q) - 1]$, and $\Delta F_{\mathrm{H}}(Q) = c_{\mathrm{O}}^2(b^2_{^{18}\mathrm{O}} - b^2_{^{\mathrm{nat}}\mathrm{O}})[S_{\mathrm{OO}}(Q) - 1] + 2c_{\mathrm{O}}c_{\mathrm{H}}b_{\mathrm{H}}(b_{^{18}\mathrm{O}} - b_{^{\mathrm{nat}}\mathrm{O}}) \times [S_{\mathrm{OH}}(Q) - 1]$, where c_α is the atomic fraction of chemical species α and $S_{\alpha\beta}(Q)$ is a partial structure factor [Fig. 1(a)]. The robustness of the results for heavy water was assessed by measuring the diffraction patterns for several $D_2{}^{\mathrm{nat}}O$ samples with different D:H ratios in the range 0.9988:0.0012 to 0.9921:0.0079. It was found, for example, that a $\pm 0.1\%$ change in the D content alters $\Delta P_{\mathrm{D}}(Q)$ but does not have a material effect on the results for $\Delta F_{\mathrm{D}}(Q)$. The robustness of the results for light water was assessed by making two independent diffraction experiments a year apart. The measured $\Delta F_{\mathrm{H}}(Q)$ functions were found to be in agreement within the experimental error, and the data sets for both experiments were therefore combined to give a weighted average which is shown in Fig. 1(a).

The measured real space functions $\Delta G_{\mathrm{D}}(r)$ and $\Delta G_{\mathrm{H}}(r)$, which correspond to $\Delta F_{\mathrm{D}}(Q)$ and $\Delta F_{\mathrm{H}}(Q)$, give O-D and O-H intramolecular bond distances of 0.985(5) and 0.990(5) Å, respectively [Fig. 2(a)]. The difference in these bond lengths of $\simeq 0.5\%$ compares to $\simeq 0.4\%$ for the gas phase [35] and is much smaller than the difference of $\sim 3\%$ found in the most recent modeling of neutron and x-ray data [36]. The latter difference is much larger than found in any theoretical prediction.

To provide a comparison for our diffraction data we made path integral molecular dynamics simulations [26] of light and heavy water for a system of 1000 molecules with $n_0 = 0.100$ Å^{-3} at $T = 300$ K using 32 imaginary time replicas. The computational procedures followed Refs. [37,38]. These calculations, in which a system of quantum mechanical particles is mapped onto a simulation of classical ring polymers, provide an exact treatment of

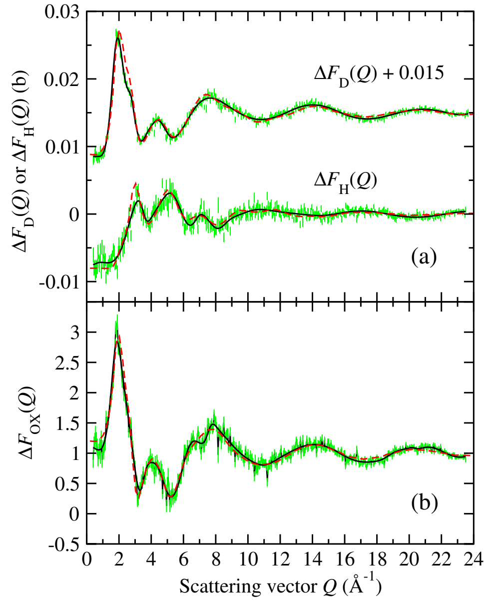

FIG. 1 (color online). (a) The first difference functions $\Delta F_D(Q)/b = 0.0059(2)[S_{OD}(Q) - 1] + 0.00262(8)[S_{OO}(Q) - 1]$ and $\Delta F_H(Q)/b = -0.0033(1)[S_{OH}(Q) - 1] + 0.00263(8) \times [S_{OO}(Q) - 1]$ and (b) the second difference function $\Delta F_{OX}(Q)$ which is constructed by subtracting $\Delta F_H(Q)$ from $\Delta F_D(Q)$ and is equal to $S_{OD}(Q)$ [or $S_{OH}(Q)$] if the O-O correlations cancel (see the text). In (a) and (b) the vertical bars give the statistical errors on the measured data points and the solid (black) curves give spline fits that were used to generate the corresponding real space functions shown in Fig. 2. The broken (red) curves show the path integral molecular dynamics results.

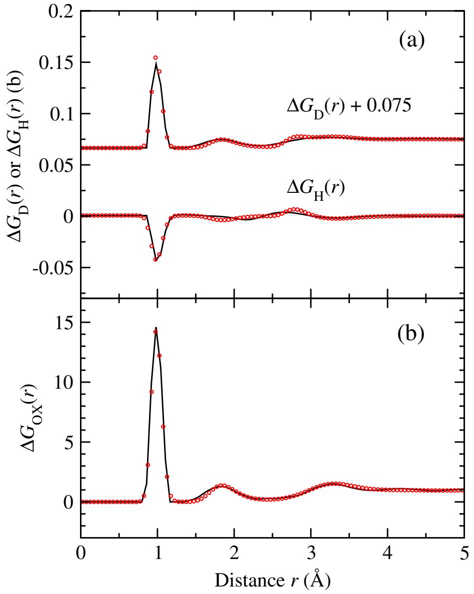

FIG. 2 (color online). (a) The first difference functions $\Delta G_D(r)/b = 0.0059(2)[g_{OD}(r) - 1] + 0.00262(8)[g_{OO}(r) - 1]$ and $\Delta G_H(r)/b = -0.0033(1)[g_{OH}(r) - 1] + 0.00263(8) [g_{OO}(r) - 1]$, where $g_{\alpha\beta}(r)$ denotes a partial pair distribution function. The O-H correlations in $\Delta G_H(r)$ have a negative weighting factor because $b_H < 0$. The first peak or trough arises from intramolecular O-D or O-H correlations and gives a measured coordination number of 1.9(1) or 2.0(2), respectively. (b) The second difference function $\Delta G_{OX}(r)$ which is equal to $g_{OD}(r)$ [or $g_{OH}(r)$] if the net quantum effects are sufficiently small that the O-O correlations cancel (see the text). The measured function gives a first peak at 0.987(5) Å with a coordination number of 2.0(1). In (a) and (b) the solid curves were obtained by Fourier transforming the spline fitted data sets presented in Fig. 1 before and after the application of a Lorch modification function. The data obtained from the first procedure were joined with the data obtained from the second procedure after the first peak or trough. The path integral molecular dynamics results are shown by circles.

nuclear quantum fluctuations in the structure of a given potential energy model for water [26]. We used several different water models [25,27–29], including the polarizable flexible TTM3-F model which was originally parametrized using *ab initio* calculations of gas phase clusters as opposed to experimental results and is therefore largely unbiased in its prediction of the liquid structure [30]. The TTM3-F model accurately reproduces the O-H stretching region of the IR absorption spectrum of liquid water as well as its diffusion coefficient [27,30,39].

Our simulations using the TTM3-F model find a difference between the intramolecular O-H and O-D bond lengths of 0.0054 Å or ≃ 0.5% [40], a significantly larger change than in most empirical models (Table I), but in excellent agreement with our diffraction data. Indeed, the comparison in Fig. 2(a) shows that theory and experiment are essentially superposed in the region where the intramolecular correlations dominate. In the case of $\Delta G_D(r)$, for which the intermolecular peak is most pronounced, the measured intermolecular O-D peak position is at 1.83(2) Å, the weighted peak position $\langle r_{OD} \rangle = \int dr r g_{OD}(r) / \int dr g_{OD}(r)$ is at 1.93(2) Å, and the corresponding O-D coordination number is 2.2(2). By comparison, the simulation results for the intermolecular O-D peak and weighted peak positions are 1.84 and 1.91 Å, respectively. The simulated intermolecular O-H peak is at 1.84 Å with a weighted peak position of 1.91 Å; i.e., the average length of a hydrogen bond barely changes between light and heavy water. It is worth pointing out that the experimental and simulation strands of our work were made independently, and were only brought together after both had been completed separately.

The quantitative agreement between the measured and calculated first difference functions, which are particularly sensitive to changes in the structure of water when H is substituted by D relative to total diffraction patterns, supports the proposal of “competing quantum effects” [17,27]. In this hypothesis intermolecular zero point energy and tunneling weaken the hydrogen bond network, as previously predicted [22–25], but quantum fluctuations in the anharmonic intramolecular O-H bond increase its length and hence the dipole moment of each water molecule. This higher dipole acts, in turn, to increase the binding between molecules, and hence the net effect of quantum fluctuations is smaller than originally suggested from rigid water simulations. As shown in Table I for a selection of water models, the extent of cancellation is strongly related to Δr, the change observed in the intramolecular bond length on substituting H for D in the path integral simulations. The largest values of Δr correspond to flexible anharmonic models which show a much smaller change upon including quantum effects in (i) the O-O peak height, (ii) the number of hydrogen bonds broken, and (iii) the diffusion coefficient. In the case of the TTM3-F model, the cancellation between opposing quantum effects is large, leading to a fall in the O-O peak height of only 0.03 and a ratio of quantum to classical diffusion coefficients of 0.95. These changes are much smaller than for rigid models which cannot exhibit any competition between intramolecular and intermolecular quantum effects. A large cancellation of competing quantum effects is fortuitous for experimental methods that exploit H/D isotope substitution such as 2D IR and NMR [20,21]. This is because when these methods are used to study either light or heavy water at 300 K the structural environments probed, as well as the quantum contribution to the dynamics, are likely to be similar.

In this spirit, and in view of the similarity between the measured intramolecular correlations for heavy and light water, the first difference functions were combined to give a second difference function $\Delta F_{\mathrm{OX}}(Q) = 1 + [\Delta F_{\mathrm{D}}(Q) - \Delta F_{\mathrm{H}}(Q)]/2c_{\mathrm{O}}c_{\mathrm{H}}(b_{\mathrm{D}} - b_{\mathrm{H}})(b_{^{18}\mathrm{O}} - b_{^{\mathrm{nat}}\mathrm{O}})$, where X represents a weighted average of H and D. The associated inelasticity correction $\Delta P_{\mathrm{OX}}(Q) = \Delta P_{\mathrm{D}}(Q) - \Delta P_{\mathrm{H}}(Q)$ is particularly small because the inelasticity corrections used to obtain the first difference functions have the same sign and are comparable in magnitude. $\Delta F_{\mathrm{OX}}(Q)$ corresponds to $S_{\mathrm{OD}}(Q)$ [or $S_{\mathrm{OH}}(Q)$] if the net quantum effects are sufficiently small that there is good cancellation of the $S_{\mathrm{OO}}(Q)$ functions for light and heavy water. The result is given in Fig. 1(b) and the corresponding real space function $\Delta G_{\mathrm{OX}}(r)$ is shown in Fig. 2(b). There is excellent overall agreement with the path integral molecular dynamics results.

In summary, it is worth emphasizing that the experimental results for water obtained in the present work originate directly from measured data sets and not from a refinement of models using diffraction data, wherein different starting points can lead to quite different conclusions [36,41]. Our approach therefore allows for a direct comparison between experiment and theory and thus provides a benchmark for improving models of water, this most essential of substances. Moreover, the experimental results show that there is great potential for applying the method of neutron diffraction with oxygen isotope substitution beyond water. Current instrumentation with a count rate stability of ±0.01% will allow for this approach to be applied to materials where the oxygen content $c_{\mathrm{O}} \gtrsim 1/3$ and the cations are formed from, e.g., monoisotopic elements such as Be, Na, Al, P, and As. With the advent of the higher count rate instrumentation that is coming online at the next generation of neutron sources, materials with even lower oxygen contents should be accessible.

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