Hydrogen Bonding in Water

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Computer simulations using density functional theory based *ab initio* path integral molecular dynamics have been carried out to investigate hydrogen bonding in water under ambient conditions. Structural predictions for both H_2O and D_2O, which include the effects of zero-point energy, thermal motion, and many body polarization effects, are contrasted with classical simulations that ignore nuclear quantum effects. The calculated effect of H/D isotope substitution on the water structure is much smaller than the difference between the classical and quantum path integral results, and is in excellent agreement with the measured H/D difference data from both neutron and x-ray scattering.

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The quest to understand and rationalize the diverse chemical and physical nature of water from first principles has been a long-standing goal of science [1–3]. For such a seemingly simple molecule, the complexity of behavior is astonishing, arising as it does from the delicate interplay between different kinds of interactions, such as hydrogen bonding, many body polarization, etc. [3,4]. The emergence of novel experimental [5–7] and theoretical techniques [8,9], plus the recent availability of multiteraflop computing platforms [10], provides a unique opportunity to utilize isotope effects to elucidate the role of zero-point energy on the hydrogen bonding in water [3]. Such an investigation is particularly timely given that data from synchrotron x-ray and neutron scattering have recently reached consensus on the structure of water as well as the effect of H/D isotope substitution [5–7].

The aforementioned data provide important benchmarks for computer simulations based on empirical force fields, as well as simulations based on *ab initio* methodologies [11,12]. Indeed, they have already stimulated a new generation of force fields that offer a quantitative modeling of the water structure and other properties. However, among the simulation methodologies available to explore the role of quantum (zero-point energy) effects on the structure of water, only first principles molecular dynamics, such as Car-Parrinello molecular dynamics (CPMD) [8,9], offers the possibility of a consistent, essentially parameter-free way of including electronic polarization and nuclear quantum effects [3]. Until very recently, these fully quantum-mechanical (electronic and nuclear) simulations were too computationally intensive to be employed in systematic comparative studies. The advent of terascale computing platforms [10] has enabled us to carry out the first *ab initio* simulation of H/D substitution on the structure of water and thereby unambiguously delineate the structural consequences of zero-point energy effects on the hydrogen bonding in water. It was found that the inclusion of zero-point energy leads to an enhancement in the water dipole moment, and thus a shorter hydrogen bond in water compared to results based on purely classical nuclear dynamics. In addition, these *ab initio* simulations have reproduced the measured H/D difference data from both neutron and x-ray scattering. The calculated very small differences between the H_2O and D_2O structure factors provide support for the common practice of using H/D mixtures as a phase contrast in a wide range of neutron scattering experiments.

Specifically, we report herein structural information on both H_2O and D_2O obtained from extensive path integral CPMD simulations. The simulation details, including the system size, the number of replicas, the simulation length, as well as the methods employed, were provided in Ref. [13]. Comparison of radial distribution functions (g_{OH}/g_{OD}) generated from the "quantum" path integral calculations with the "classical" counterpart (see Fig. 1) reveals that the hydrogen bond distance $O—H\cdots O$ in quantum water is noticeably shorter than in classical water. At first sight, this finding seems to be at odds with the notion that quantum (zero-point energy) effects should reduce the strength and directionality of hydrogen bonding and thereby lead to a softening of the water structure [2,12]. Analysis of the molecular charge distribution in the liquid, based on maximally localized Wannier functions [14], indicates that the average dipole moment of an individual water molecule in the classical liquid is 3.04 D compared to

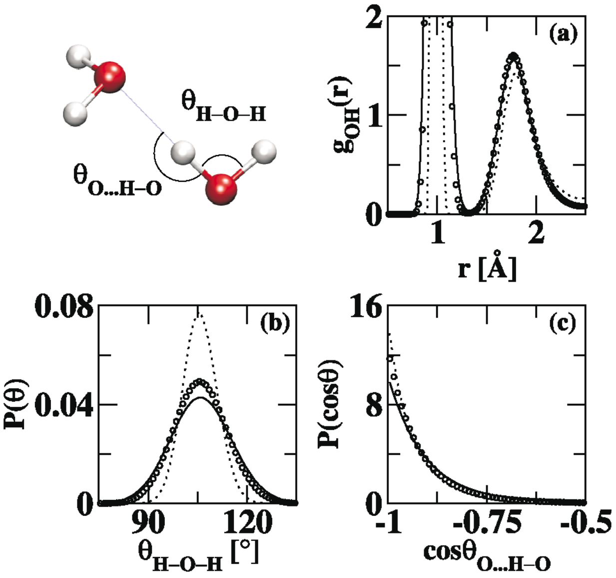

FIG. 1 (color online). Radial distribution functions for O—H atom pairs [panel (a)], distributions of the intramolecular H—O—H angle [panel (b)], and of the cosine of the hydrogen bond angle $\theta_{O\cdots H\text{-}O}$ [panel (c)] in liquid H_2O (solid line) and D_2O (circles) at 300 K generated from the quantum path integral calculations compared to the classical counterpart (dotted line). Note that the intermolecular g_{OH} hydrogen bond peak (at ~1.8 Å) shifts to shorter distances in quantum water, as a result of a higher dipole moment (see text). On the other hand, the intramolecular peak (at ~1 Å) and the H—O—H angle distribution are broadened and the hydrogen bond angle $\theta_{O\cdots H\text{-}O}$ is less linear ($\cos\theta = -1$ corresponds to linear hydrogen bonds) for the quantum water, in accord with expectations [2,12].

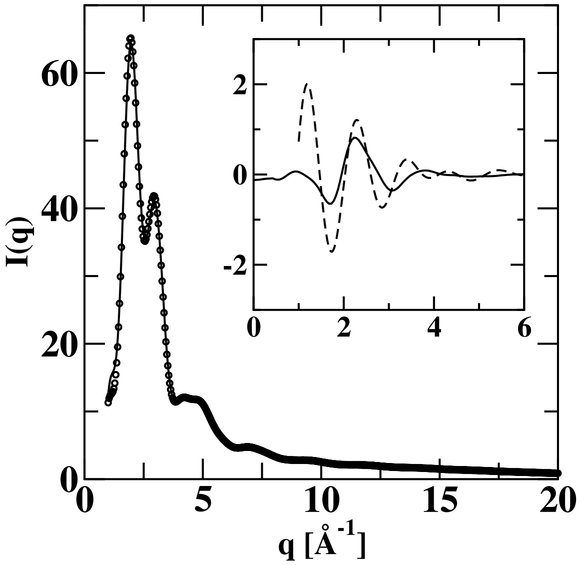

FIG. 2. Shown is a comparison between calculated and measured effects of isotopic H/D substitution on the structure of water as measured by x-ray scattering experiments. The calculated intensities for liquid H_2O (solid line) and D_2O (circles) are based on the radial distribution functions obtained from the present *ab initio* path integral CPMD simulations. The differences between these two liquids arising solely from O—O correlations are shown in the inset (dashed), as well as those measured by synchrotron x-ray diffraction experiments [7] (solid). In the calculation of the x-ray intensities, we used the modified atomic form factors developed by Head-Gordon and co-workers, which include polarization and valence-electron delocalization effects in liquid water [6].

3.18 ± 0.01 D for quantum H_2O or D_2O. The increased diffuseness of the intramolecular degrees of freedom that arises from the addition of nuclear quantum effects stretches the intramolecular O—H bond and thereby increases the polarity of the molecule [15]. The calculated ~4% increase in the molecular dipole moment and the concomitant increase in electrostatic and polarization effects rationalize the observed shortening of the hydrogen bond. Thus, even though the first (intramolecular) peaks of g_{OH} and g_{HH} are significantly broadened for quantum water, in accord with expectations [2,12], the intermolecular features appear more structured.

Isotopic substitution is a standard experimental probe for evidence of quantum effects. Shown in Fig. 2 is a comparison between the isotopic effects in water in terms of the difference in x-ray scattering intensities between H_2O and D_2O as a function of the reciprocal space coordinate q, calculated from the path integral simulations, versus those obtained from a recent synchrotron experiment [7]. The simulations reproduce semiquantitatively the experimental results, particularly the major peak at around 2.3 $Å^{-1}$. The slightly larger oscillation calculated at low q values is likely an artifact caused by the truncation of the calculated distribution functions due to the relatively modest size of the simulation cell. The observed isotope effects in x-ray scattering are mainly dominated by the oxygen-oxygen correlation functions. A close examination of the g_{OO} functions indicates that the second peak (see Fig. 3) appears to shift to larger separations from H_2O to D_2O. This again agrees with the experimental interpretations [7] as well as findings from pioneering path integral simulations, which employed an empirical rigid-molecule force field [2].

Unlike x-ray scattering intensities, the structure factors measured by neutron diffraction are heavily weighted by the contribution from the hydrogen species. Because the scattering length is isotope sensitive, H/D substitution has been routinely utilized in combination with the neutron diffraction technique (NDIS) to determine the partial structure factors for water and many other systems. The underlying assumption used by such NDIS experiments is that the water structure is isotope independent. The above comparison of path integral simulations of the g_{OO} functions for H_2O and D_2O gives the first *ab initio* demonstration that the explicit isotopic substitution effect on the structure of water is very small at constant number density. To examine the ramifications of this finding in

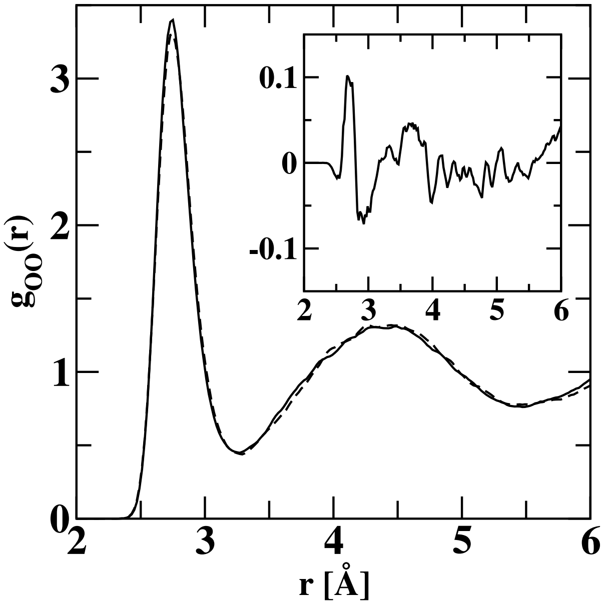

FIG. 3. Radial distribution functions (RDFs) for O—O atom pairs in liquid H_2O (solid) and D_2O (dashed) at 300 K calculated from the *ab initio* path integral CPMD simulations. The differences between these two curves are shown in the inset. Note that the two RDFs are very similar except that the first peak is slightly *lower* and the second peak shifts to slightly larger distance for D_2O compared to H_2O.

more detail, we have computed the neutron scattering function for quantum H_2O using deuterium's scattering length for the hydrogen atoms and compared it to the directly calculated function for quantum D_2O in Fig. 4. The difference between these two curves, which is solely due to quantum effects, is very small, and likely within the typical uncertainties of NDIS experiments. (Note that the experimentally measured large difference caused by the actual scattering lengths of H and D is quantitatively reproduced in the Fig. 4 inset.) Thus, the assumption used by NDIS experiments is reasonable at least around room temperature. This finding does not imply that quantum effects on the structure of water are small. In fact, the neutron scattering function calculated for water using classical nuclear dynamics simulations is quite different from the two quantum path integral results, showing much more pronounced oscillations at high q values (not shown). Overall, inclusion of nuclear quantum effects brings the calculated isotope effects on H_2O and D_2O in better agreement with experiment.

In summary, the present path integral CPMD simulations reproduce the H/D isotope effects on the structure of liquid water as observed by both neutron and x-ray experiments. The calculated radial distribution functions for O and H/D atom pairs are in reasonable agreement with synchrotron x-ray and neutron scattering data, giving added confidence in the predicted H/D isotope effects. The most significant finding is that intramolecular zero-point energy effects cause an enhancement in the water molecule dipole moment, which in turn increases the hydrogen bond strength relative to classical water via a coupling of intra- and intermolecular effects. The calculated close agreement in the structure of H_2O and D_2O provides an *a posteriori* justification for the use of H/D substitution in molecular structure determination via neutron scattering.

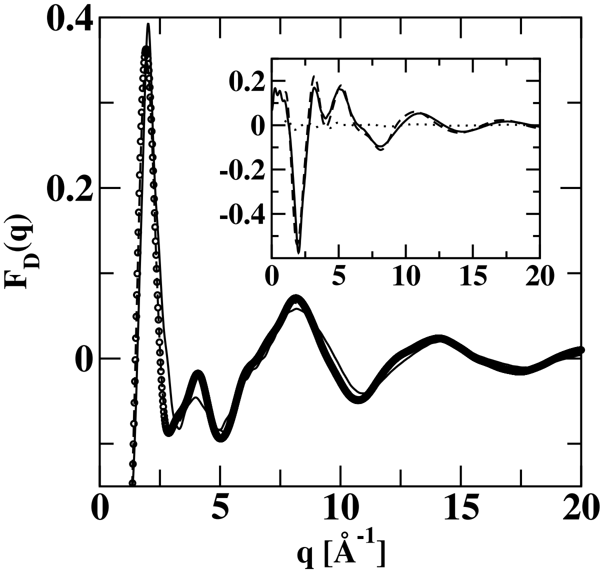

FIG. 4. The measured total structure factor for neutron scattering from liquid D_2O [13] (solid line) compared to calculated values from the ab initio path integral CPMD simulations of liquid H_2O (dashed line) and D_2O (circles) at 300 K at constant density. In order to assess the explicit influence of the nuclear quantum effects, the same (deuterium) scattering lengths are used for H and D. The differences between path integral H_2O and D_2O, which are due solely to nuclear quantum effects, are shown in the inset as a near horizontal dotted line. Also shown are the calculated (dashed) and experimental [5] (solid) differences between these two liquids, which take into account the actual scattering lengths of H/D.

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[13] The simulations were performed with the program CPMD 3.4 (J. Hutter *et al.*, MPI für Festkörperforschung and IBM Research Laboratory 1995–2000 [7]) and utilized 64 water molecules in a periodic cubic box with a dimension of 12.419 Å. The gradient corrected Becke-Lee-Yang-Parr exchange correlation functional was adopted for the present study since it has been shown previously to give a good description of aqueous systems. For all atoms, nonlocal norm-conserving Troullier-Martins pseudopotentials were used to describe the valence-core interactions. All pseudopotentials have been transformed to a fully nonlocal form using the scheme of Kleinman and Bylander. The valence electronic wave functions were expanded in a plane wave basis set up to an energy cutoff of 80 Ry. A fictitious electronic mass of 500 a.u. was employed. The path integral was discretized using $P = 16$ Trotter replicas. An equilibrated water configuration generated previously from a classical CPMD trajectory [4] was used as the starting configuration for these path integral simulations. After an equilibration of 1–2 ps, a total of 132 000 and 135 000 configurations, with time step of 5.0 a.u., were generated for H_2O and D_2O, respectively.

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