Bonding in the Superionic Phase of Water

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The predicted superionic phase of water is investigated via *ab initio* molecular dynamics at densities of 2.0–3.0 g/cc (34–115 GPa) along the 2000 K isotherm. We find that extremely rapid (superionic) diffusion of protons occurs in a fluid phase at pressures between 34 and 58 GPa. A transition to a stable body-centered cubic O lattice with superionic proton conductivity is observed between 70 and 75 GPa, a much higher pressure than suggested in prior work. We find that all molecular species at pressures greater than 75 GPa are too short lived to be classified as bound states. Up to 95 GPa, we find a solid superionic phase characterized by covalent O-H bonding. Above 95 GPa, a transient network phase is found characterized by symmetric O-H hydrogen bonding with nearly 50% covalent character. In addition, we describe a metastable superionic phase with quenched O disorder.

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The density profiles of large planets, such as Uranus and Neptune, suggest that there exists within a thick layer of "hot ice," which is thought to be 56% H_2O , 36% CH_4 , and 8% NH₃ [1]. This has led to theoretical investigations of the water phase diagram [2], in which Car-Parrinello Molecular Dynamics (CPMD) simulations [3] were conducted at temperatures and pressures ranging from 300 to 7000 K and 30-300 GPa [4]. At temperatures above 2000 K and pressures above 30 GPa, there was observed a superionic phase in which the oxygen atoms had formed a body-centered cubic (bcc) lattice, and the hydrogen atoms diffused extremely rapidly (ca. 10^{-4} cm²/s) via a hopping mechanism between oxygen lattice sites. Experimental results for the ionic conductivity of water at similar state conditions [5,6] agree well with the results from Ref. [4], confirming the idea of a superionic phase and indicating a complete atomic ionization of water molecules under extreme conditions (P > 70 GPa, T > 4000 K) [6].

More recent *ab initio* MD simulations were performed at temperatures up to 2000 K and pressures up to 30 GPa [7,8]. Under these conditions the authors found that the molecular ions H_3O^+ and OH^- are the major charge carriers in a fluid phase, in contrast to the bcc crystal predicted for the superionic phase. The fluid high pressure phase has been recently confirmed by x-ray diffraction results of water melting at ca. 1000 K and up to 40 GPa pressure [9–11]. In addition, extrapolations of the proton diffusion constant of ice into the superionic region were found to be far lower than a superionic criteria of 10^{-4} cm²/s [12]. Thus, it is clear there is a great need for further work to resolve the apparently conflicting data.

Here, we investigate the superionic phase with more extensive first principles Car-Parrinello molecular dynamics simulations. Calculated power spectra (i.e., the vibrational density of states) have recently been compared to measured experimental Raman spectra [13] at pressures up to 55 GPa and temperatures of 1500 K. The agreement between theory and experiment was very good. In particular, weakening and broadening of the OH stretch PACS numbers: 61.20.Ja, 31.15.Ar, 62.50.+p, 71.15.Pd

mode at 55 GPa were found both theoretically and experimentally.

It is the goal of this work to reevaluate the phase diagram of water by characterizing the superionic phase in terms of its structure, dynamics, and molecular composition. In the present study, we focus our efforts on an area of the phase diagram that is likely to show a transition to the superionic phase. We report results of simulations along the 2000 K isotherm, at pressures of 34-115 GPa (2.0–3.0 g/cc).

For our simulations, we used the CPMD code v.3.91, with the Becke-Lee-Yang-Parr exchange-correlation functional [14,15], and Troullier-Martins pseudopotentials [16] for both oxygen and hydrogen. A plane-wave cutoff of 120 Ry was employed to ensure convergence of the pressure, although all other properties were seen to converge with a much lower cutoff (85 Ry). The system size was 54 H₂O molecules. The temperature was controlled by using Nosé-Hoover thermostats [17] for all nuclear degrees of freedom. The importance of an appropriate choice of electron mass in Car-Parrinello molecular dynamics of water has been pointed out in recent studies [18,19]. We chose a conservative value of 200 a.u. and a time step of 0.048 fs. Initial conditions were generated in two ways: (1) a liquid configuration at 2000 K was compressed from 1.0 g/cc to the desired density in sequential steps of 0.2 g/cc from an equilibrated sample. (2) An ice VII configuration was relaxed at the density of interest, then heated to 2000 K in steps of 300° each for a duration of 0.5–1 ps. While heating, the temperature was controlled via velocity scaling. We refer to the first set of simulations as the "L" set, and the second as the "S" set. Unless stated otherwise, the results (including the pressures) from the S initial configurations are those reported. Once the desired density and/or temperature were achieved, all simulations were equilibrated for a minimum of 2 ps. Data collection simulations were run from 5-10 ps.

The calculated diffusion constants of hydrogen and oxygen atoms are shown in Fig. 1, and the inset plot shows the equation of state for this isotherm for both L and S simu-



FIG. 1. Diffusion constants for O and H atoms at 2000 K as a function of density. The lines with circles correspond to hydrogen, and the lines with squares to oxygen. The solid lines correspond to a liquid ("L") initial configuration, and the dashed lines to an ice VII ("S") initial configuration. The inset plot shows the pressure as a function of density at 2000 K, where the triangles correspond to L and the X's to S.

lations. The two results are virtually identical up until 2.6 g/cc. At 34 GPa (2.0 g/cc), the hydrogen atom diffusion constant has achieved values associated with superionic conductivity (greater than 10^{-4} cm²/s). The diffusion constant remains relatively constant with increasing density, similar to the experimental results of Chau *et al.* [6] for the ionic conductivity, although their estimated temperatures are much higher than 2000 K.

On the other hand, the O diffusion constant drops to zero at 75 GPa (2.6 g/cc) for both L and S initial configurations. The surprisingly small hysteresis (i.e., difference between the glass transition and melting transition temperatures) in the fluid to superionic transition allows us to place the transition point between 70 GPa (2.5 g/cc) and 75 GPa (2.6 g/cc). The small hysteresis is most likely due to the weak O-H bonds at the conditions studied, which have free energy barriers to dissociation comparable to k_BT (see below). Simulations that start from the L initial configurations are found to quench to an amorphous solid upon compression to 2.6 g/cc. The S simulations between 75-115 GPa have an average internal energy ca. 6 kcal/mol of O lower than that of the L simulations at the same density. This is larger than the likely entropic difference (we estimate $T\Delta S \approx 4$ kcal/mol for the entropy of amorphization) between the phases. Thus, the observed amorphous solid is metastable with respect to the bcc lattice S states [4].

Our results show that superionic conduction can exist even in a metastable glass phase. We note that amorphous states often occur under high pressure conditions [20]. Our transition pressure of 75 GPa is much higher than the value of 30 GPa predicted earlier [4]. This is likely due to their use of a much smaller basis set (70 Ry). Our results are in disagreement with simple extrapolations of the proton diffusion constant to high temperatures [12].



FIG. 2. Radial distribution functions as a function of density. At 34 GPa we find a fluid state. At 75 GPa we show a "covalent" solid phase. At 115 GPa, we find a "network" phase with symmetric hydrogen bonding.

Radial distribution functions (RDFs) for the *S* simulations are shown in Fig. 2. Analysis of the oxygen-oxygen RDF for all pressures yields a coordination number of the first peak of just over 14, consistent with a high density bcc lattice in which the first two peaks are broadened due to thermal fluctuations. The RDF was further analyzed by calculating an "average position" RDF in which the position of each oxygen was averaged over the course of the trajectory. The results for 75–115 GPa indicate the presence of bcc lattice undergoing large amplitude vibrations, even though the RDFs in Fig. 2 have widths similar to that of a liquid or a glass. The RDFs for the amorphous phase (not shown) are similar to those of the solid phase obtained in the *S* simulations.

The O-O and H-H RDFs indicate that no O-O or H-H covalent bonds are formed during the simulations at all densities. The $g(R_{OH})$ shows a latticelike structure at 115 GPa, which is consistent with proton diffusion via a hopping mechanism between lattice sites [4]. At 34 GPa, the coordination number for the first peak in $g(R_{OH})$ is 2, indicating molecular H₂O. At 95–115 GPa, however, the

coordination number for the first peak in $g(R_{OH})$ becomes 4, indicating that water has formed symmetric hydrogen bonds where each oxygen has four nearest neighbor hydrogens.

Concomitant with this is a shift of the first minimum of the O-H RDF from 1.30 Å at 34 GPa to 1.70 Å at 115 GPa. We observe a similar structural change in the H-H RDF in which the first peak lengthens from 1.63 Å (close to the result for ambient conditions) to 1.85 Å. These observations bear a strong resemblance to the ice VII to ice X transition in which the covalent O-H bond distance of ice becomes equivalent to the hydrogen bond distance as pressure is increased [21]. However, the superionic phase differs from ice X in that the position of the first peak in $g(R_{OH})$ is not half the distance of the first O-O peak [21]. We analyze the effect of the change in $g(R_{OH})$ below in terms of the molecular speciation in the simulations.

We have determined the free energy barrier for dissociation by defining a free energy surface for the oxygenhydrogen distances, viz. $W(r) = -k_B T \ln[g(R_{OH})]$, where W(r) is the free energy surface (potential of the mean force). The results are shown in Fig. 3. The free energy barrier can then be defined as the difference in height between the first minimum and second maximum in the free energy surface. The remainder of the results discussed below are for the *S* simulations.

We find that at 34 GPa, the free energy barrier is 11.4 kcal/mol. For comparison, the experimental value for the difference in the Gibbs free energy is significantly higher (21.6 kcal/mol) at ambient conditions. We attribute the lower barrier to the well-known destabilization of covalent bonds by high pressure conditions [22]. By 75 GPa, the free energy barrier has dropped significantly to 7.5 kcal/mol, which is already comparable to the value of *RT* at 2000 K (3.98 kcal/mol). At 115 GPa, the free energy barrier has increased to 8.8 kcal/mol. We speculate that this strengthening is related to the existence of a sharply defined O lattice at 115 GPa, whereas at 75 GPa the O lattice is strongly broadened [see $g(R_{OO})$ in Fig. 2]. The change in free energy surface at 115 GPa is consistent



FIG. 3. R_{OH} free energy surface. The lines are spaced by a factor of 4 kcal/mol for clarity.

with the formation of symmetric hydrogen bonds, as discussed above. Also, the lengthening of the O-H bond is consistent with greater ionic character.

We now analyze the chemical species prevalent in water at these conditions. We define instantaneous species based on the O-H bond distance. If the bond distance is less than a value r_c , we count the atom pair as bonded. Determining all the bonds in the system gives the chemical species at each point in time. Species with lifetimes less than an O-H bond vibrational period (10 fs) are "transient," and do not represent bound molecules. The optimal cutoff r_c between bonded and nonbonded species is given by the location of the maximum in the free energy surface [23].

The use of the free energy maximum to define a bond cutoff provides a clear picture of qualitative trends. As expected from the $g(R_{OH})$, at 34 GPa, the free energy peak is found at 1.30 Å, which is approximately the same value obtained from simulations of ambient water. At 75 GPa, the free energy peak maintains almost the same position, but broadens considerably. At 115 GPa, the peak has sharpened once again, and the maximum is now at 1.70 Å.

Given the above definition of a bond distance, we have analyzed species lifetimes. Above 2.6 g/cc, the lifetime of all species is less than 12 fs, which is roughly the period of an O-H bond vibration (ca. 10 fs). Hence, water above 75 GPa and at 2000 K does not contain any molecular states, but instead forms a collection of short-lived transient states. The *L* simulations at 2.6 g/cc (77 GPa) and 2000 K yield lifetimes nearly identical to that found in the *S* simulations described above (within 0.5 fs). This indicates that the amorphous states formed from the *L* simulations are closely related to the superionic bcc crystal states found in the *S* simulations.

Species concentrations are shown in Fig. 4. At 34 GPa (2.0 g/cc), H_2O is the predominant species, with H_3O^+ and OH^- having mole fractions of ca. 5%. In addition, some aggregation has occurred in which neutral and ionic clusters containing up to six oxygens have formed. The concentrations of OH^- and H_3O^+ are low for all densities



FIG. 4. Mole fraction of species found at 34-115 GPa. The filled circles correspond to H_3O^+ , while the open circles correspond to OH^- .



FIG. 5 (color). Snapshots of the simulations at 75 and 115 GPa. At 75 GPa, the water molecules are starting to cluster, and at 115 GPa, a well defined network has been formed. The protons dissociate very rapidly and form new clusters (at 75 GPa) or networks of bonds (at 115 GPa).

investigated, and are nonexistent at 95 and 115 GPa (2.8 and 3.0 g/cc). The calculated lifetimes for these species are well below 10 fs for the same thermodynamic conditions (less than 8 fs at 34 GPa). At pressures of 95 and 115 GPa, the increase in the O-H bond distance leads to the formation of extensive bond networks (Fig. 5). These networks consist entirely of O-H bonds, while O-O and H-H bonds were not found to be present at any point.

Maximally localized Wannier centers [24] of several trajectories were calculated, and a distribution function was determined. The outer peak at 0.46–0.50 Å corresponds to electrons participating in a covalent bond. Based on the above distribution, one can define the minimum at roughly 0.42 Å as a dividing surface wherein a maximally localized Wannier center located at distances shorter than this, relative to its parent oxygen atom, represents a lone pair, and those found at greater distances represent covalent bonds [7]. We used this definition to compute the percentage of O-H bonds with a Wannier center along the bond axis. Surprisingly, the results for pressures of 34-75 GPa consistently showed that 85%-95% of the O-H bonds are covalent. For 95 and 115 GPa, we find about 50%-55% of the bonds are covalent. This is consistent with symmetric hydrogen bonding, for which the split between ionic and covalent bonds would be 50/50.

In conclusion, we have performed first principles simulations of water at pressures up to 115 GPa (3.0 g/cc) and 2000 K. Along this isotherm we can define three different phases. First, from 34 to 58 GPa (2.0–2.4 g/cc), we observe a molecular fluid phase with fast diffusion of the hydrogens. Second, at 75 GPa (2.6 g/cc), we find a stable bcc oxygen lattice with superionic proton conduction. O-H bonds within this "solid" phase are found to be mostly covalent, despite their exceedingly short lifetimes of ca. 10 fs. Third, at 95–115 GPa (2.8–3.0 g/cc) we find a transformation to a phase dominated by transient networks of symmetric O-H hydrogen bonds. Given the smooth nature of the calculated P - V isotherm, the transition to the network phase does not appear to be first order. The

network can be attributed to the symmetrization of the hydrogen bond, similar to the ice VII to ice X transition.

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