

Dissociation of Water under Pressure

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The dissociation of water under pressure is investigated with a series of *ab initio* molecular dynamics simulations at thermodynamic conditions close to those obtained in shock wave experiments. We find that molecular dissociation occurs via a bimolecular process similar to ambient conditions, leading to the formation of short-lived hydronium ions. Up to twofold compression and 2000 K, the oxygen diffusion coefficient is characteristic of a fluid. Our findings do not support models used to estimate the liquid electrical conductivity and interpret Raman spectra that assume the presence of free protons.

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The phase diagram of water has been investigated for decades, yet the properties of the liquid away from ambient conditions are not well understood [1]. Few experimental data exist at extreme thermodynamic conditions on the structural and electronic properties of the liquid state, as well as on the mechanism by which molecular dissociation occurs under high pressure. In particular, whether the dissociation of water under pressure differs substantially from that at ambient conditions and how molecular dissociation affects and ultimately determines the atomic and the electronic structure of the fluid are open questions.

Under ambient conditions, the dissociation of a water molecule in the liquid phase is a rare event: A water molecule undergoes dissociation only once every 11 h [2]. This dissociation process is characterized as a bimolecular reaction, $2\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_3\text{O}^+$, where the products formed are a hydroxide (OH^-) and a hydronium (H_3O^+) ion [3]. Although rare under ambient conditions, an increase in pressure or temperature can cause the reaction to occur much more frequently [4,5], and this may be responsible for the sharp rise in the conductivity of water at pressures near 12 GPa in both static and shock wave experiments. At this pressure, about ≈ 0.5 mol% are estimated to correspond to molecular ions [5]. However, in a pioneering study of the Raman spectra of water shocked up to 26 GPa and 1700 K, the band associated with H_3O^+ was not found [6]. Such a band is visible under ambient conditions in the Raman spectra of water when the concentration of H_3O^+ is high [7,8]. For example, in the Raman spectra of an aqueous solution of 11.4M HCl, there is a broad peak centered at 2900 to 3000 cm^{-1} due to the presence of H_3O^+ [7]. The absence of a similar band in shocked water has led to the suggestion that the high pressure dissociation mechanism is different from the one at ambient conditions, and is better described by the unimolecular process $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$. However, the lack of a clear signature of H_3O^+ in the Raman spectra could also correspond to a H_3O^+ lifetime under pressure which is much shorter than at ambient conditions. Following the conclusions of Holmes *et al.* [6], recent data on the conductivity of water shocked to pressures of 70 to 180 GPa have been interpreted and modeled assuming the presence of free protons in the liquid [9].

Theoretically, the investigation of water dissociation under pressure is a challenging problem; only one study of the properties of water in a regime where dissociation plays a prominent role has appeared in the literature [10]. In particular, the simulations reported in Ref. [10] indicate that at approximately 30 GPa and 2000 K water becomes a superionic conductor, with the oxygen atoms vibrating around their crystalline ice VII positions and protons hopping between different molecular sites. However, a detailed analysis of the dissociation process was not reported.

In order to shed light on the controversial dissociation mechanism of water under pressure and to determine the structure of the liquid under conditions where molecular dissociation are dominant, we have performed a series of *ab initio* molecular dynamics (MD) simulations [11–13]. Our results show the formation of short-lived H_3O^+ , with protons hopping between diffusive molecular sites with a mechanism similar to that found at ambient conditions. Between 12–30 GPa and 600–2000 K, oxygen diffusion is found to be characteristic of a normal liquid state.

To illustrate the accuracy of our theoretical model, we first compare our results for liquid water at ambient conditions with the most recent x-ray and neutron diffraction data, and with free-energy measurements for the dissociation reaction. In Fig. 1, the oxygen-oxygen radial distribution function (RDF), $g_{\text{OO}}(r)$, obtained from a 7.5 ps simulation of 54 water molecules at ambient conditions [14], is shown together with the $g_{\text{OO}}(r)$ determined by the most recent neutron [15] and x-ray [16] diffraction measurements. The agreement between the simulation and experiment is very good; there is essentially an exact agreement between the positions of the peaks obtained by our simulation and by the experimental measurements [15,16]. In addition to the structural properties of water, we have investigated the energy profile of the molecular dissociation reaction at ambient conditions by using constrained MD techniques [17]. By integrating the force associated with constraining an O-H bond length at nine points along a dissociation reaction, we find a free energy difference for the dissociation reaction of 20.8 kcal/mol. This is in remarkable agreement with the experimentally determined difference in Gibbs free energy of 21.6 kcal/mol

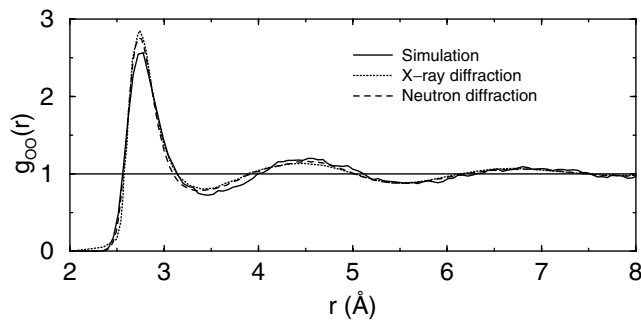


FIG. 1. Comparison between the liquid water oxygen-oxygen radial distribution function obtained by simulation (solid line), neutron diffraction (dashed line) [15], and x-ray diffraction (dotted line) [16] at ambient conditions.

[2]. Additional details of this simulation will be given elsewhere.

As mentioned above, our simulations at high pressure are focused on thermodynamic conditions close to those obtained in shock compression experiments of liquid water [5,18]. In particular, we performed 7.4 ps constant volume and energy MD simulations of liquid water at densities (ρ) of 1.72 and 1.95 g/cm³ with average temperatures of 750 and 1390 K, respectively. We then investigated the effect of raising the temperature at both densities. The simulations at $\rho = 1.72$ and 1.95 g/cm³ were carried out with 54 and 100 water molecules, respectively. The computed pressures from these simulations are 14.5 GPa at $\rho = 1.72$ g/cm³, and 26.8 GPa at $\rho = 1.95$ g/cm³, which are in good agreement with the experimental estimates at similar temperatures and densities (13 GPa [5] and 23 GPa [19], respectively).

In Fig. 2, the RDFs obtained from the simulations at $\rho = 1.72$ and 1.95 g/cm³ are shown along with the RDFs that have been previously obtained at $\rho = 1.57$ g/cm³ and

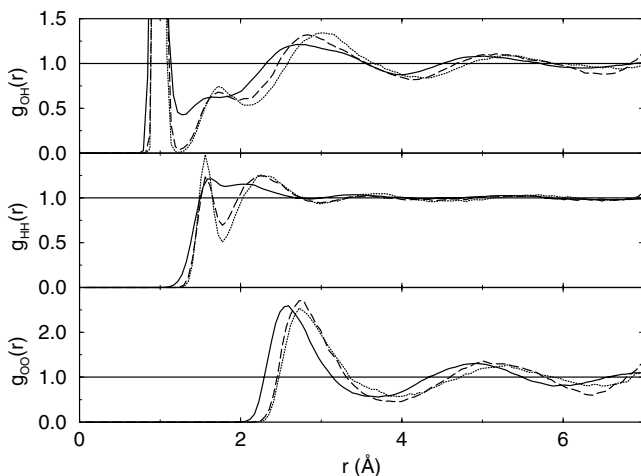


FIG. 2. The radial distribution functions of liquid water under pressure as determined by simulation. The solid line corresponds to a density of 1.95 g/cm³, the dashed line to a density of 1.72 g/cm³, and the dotted line to a density of 1.57 g/cm³.

600 K [20] ($P = 10$ GPa). The differences between the RDFs at $\rho = 1.57$ and 1.72 g/cm³ are small. As was observed in Ref. [20], the peak located at $r = 1.8$ Å in $g_{OH}(r)$ is much smaller than the corresponding hydrogen bond peak at ambient conditions, indicating a substantial reduction in intermolecular hydrogen bonding. A careful examination of $g_{OH}(r)$ in Fig. 2 reveals that the first minimum located at $r = 1.3$ Å is nonzero in the $\rho = 1.72$ g/cm³ simulation, which is an indicator of a small fraction of intramolecular dissociation at these conditions. Despite the fact that the nearest neighbor oxygen-oxygen coordination number has increased from 4.5 at ambient conditions to nearly 13 at $\rho = 1.57$ and 1.72 g/cm³, the position of the first peak in $g_{OO}(r)$ is not significantly changed from the position found at ambient conditions. In Ref. [20], this effect was attributed to a collapse of the second solvation shell into the first solvation shell, consistent with the findings of recent neutron diffraction measurements of water under ~ 0.5 GPa pressure [21].

In going from a density of 1.72 to 1.95 g/cm³ at moderate temperatures, substantial changes in the liquid structure are observed. The most dramatic change is a ~ 0.2 Å inward shift in the position of the first peak in $g_{OO}(r)$. This shift in the nearest neighbor oxygen-oxygen separation is accompanied by a loss of the intermolecular hydrogen bonding peak in $g_{OH}(r)$, a large increase in the first minimum intensity in $g_{OH}(r)$, and an almost complete loss of structure in $g_{HH}(r)$. These changes in the RDFs at nearly twofold compression and 1390 K indicate that there is a collapse of the nearest neighbor oxygen network, which coincides with a significant fraction of intramolecular dissociation. Under these conditions, the diffusion coefficient of oxygen is 4.4×10^{-5} cm²/s, with no indication of superionic behavior in the liquid.

In order to quantify the amount of dissociation in our simulations, we have compared several different approaches for the definition of O-H bond breaking. We have considered both a geometric definition of bond breaking, based on the atomic trajectories, and an electronic definition, based on a local orbital analysis of the electronic states.

We first discuss our local orbital analysis in terms of maximally localized Wannier functions (WFs) [22,23]. The eight valence electrons of an isolated water molecule result in four doubly occupied WF centers in a tetrahedral arrangement around the oxygen atoms. The centers of charge for a water molecule's four WF centers are shown in the inset of Fig. 3. Two of the WF centers are located at covalent O-H bonds and the other two correspond to lone-pair orbitals on the oxygen atom. The RDF function between oxygen atoms and neighboring WF centers (g_{OW}) is shown in Fig. 3 by the solid line, and is compared with the corresponding correlation function computed at ambient conditions (dotted line) [24]. The two peaks at 0.33 and 0.49 Å, corresponding to lone pairs and covalent bond orbitals, respectively, are much broader at twofold compression and are shifted towards shorter distances.

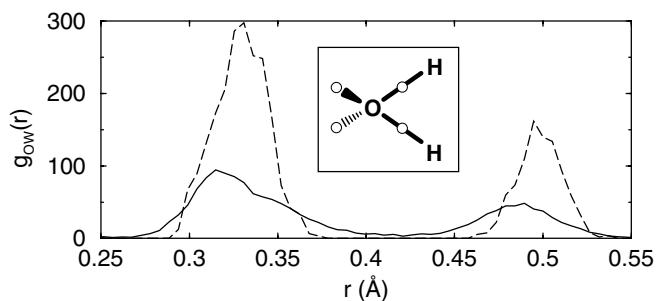


FIG. 3. The radial distribution function between oxygen and its nearest maximally localized Wannier function centers at ambient conditions (dashed line) and at a density of 1.95 g/cm^3 (solid line). The small circles in the inset show the orientation of Wannier function centers around a water molecule.

The minimum between the two peaks is slightly different from zero in the compressed fluid, to indicate the occurrence of proton transfers between orbitals; however, it is still very clearly defined. We have used the location of the first minimum of g_{OW} (0.42 \AA) as the cutoff distance to determine the number of O-H covalent bonds that each oxygen atom participates in [25]. Based on this criterion, H_3O^+ is present in the twofold compressed liquid at a concentration of 6.9 mol % at 1390 K. In addition, equal concentrations of H_3O^+ and OH^- are found, which precludes the existence of a significant concentration of free protons in the liquid.

In Fig. 4, snapshots from a typical dissociation reaction in the $\rho = 1.95 \text{ g/cm}^3$ simulation at 1390 K are shown along with the relevant WFs that participate in the reaction. In Fig. 4a, the left-hand side water molecule acts as a hydrogen bond donor (one of its O-H covalent bond orbitals is displayed) and the right-hand side molecule as a hydrogen bond acceptor (one of its lone-pair orbitals is shown). In Fig. 4b, the original hydrogen bond donor water molecule gives up a proton, which is then equally shared between the two molecules. At this point, the centers of the displayed WF orbitals are both 0.43 \AA from their respective oxygen atoms. In Fig. 4c, the proton is completely transferred to what was originally the hydrogen bond acceptor water molecule, and OH^- and H_3O^+ are formed. As this process occurs, the center of the original covalent bond WF decreases to a distance of 0.36 \AA from the oxygen, and the

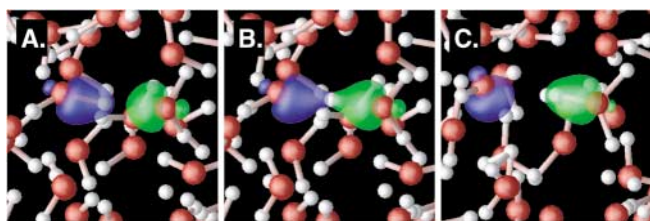


FIG. 4 (color). Snapshots of a water molecule dissociation in the simulation at a density of 1.95 g/cm^3 . Isosurfaces of the maximally localized Wannier functions that are involved are displayed in blue for the proton donor water molecule and in green for the proton acceptor water molecule.

center of the original lone-pair WF increases to a distance of 0.47 \AA . These series of snapshots are representative of the dissociation reactions observed in the simulation and illustrate that dissociation occurs between hydrogen bonded molecules via a bimolecular process leading to the formation of OH^- and H_3O^+ , similar to ambient conditions.

In addition to the maximally localized WF analysis, we have also used purely geometric criteria to identify the O-H bonding breaking and formation pattern. At a density of 1.95 g/cm^3 , there is not a clear minimum between the first and second peak in $g_{OH}(r)$ (see Fig. 2); therefore, a dissociation criterion based solely on a hard cutoff on O-H bond lengths would be inaccurate. However, O-H coordination numbers can be computed by matching each hydrogen atom to the nearest oxygen atom, rather than using a hard cutoff on the O-H bond lengths. The resulting probability distribution of oxygen-hydrogen coordination numbers yields the same H_3O^+ concentration for the $\rho = 1.95 \text{ g/cm}^3$ simulation as that obtained with a local orbital, WF criterion. We have used this geometrical definition to compute the coordination number of each oxygen atom in the simulations at $\rho = 1.57$ and 1.72 g/cm^3 . In Fig. 5, the instantaneous value of the oxygen atom O-H coordination number over a small 0.5 ps window for each of the simulations is shown. As was observed in Ref. [20], very little dissociation occurs over the simulation time scale at $\rho = 1.57 \text{ g/cm}^3$ (Fig. 5a). Although the limited time scale prevents an accurate estimate of the amount of dissociation at $\rho = 1.57 \text{ g/cm}^3$, we note that our qualitative estimate of a low H_3O^+ concentration is in accord with values inferred from experimental data under similar thermodynamic conditions (0.1 mol %) [4]. At a density of 1.72 g/cm^3 (Fig. 5b), the dissociation reaction occurs more frequently. Under these conditions, we find a concentration of 0.3 mol % as compared to 0.5 mol % measured

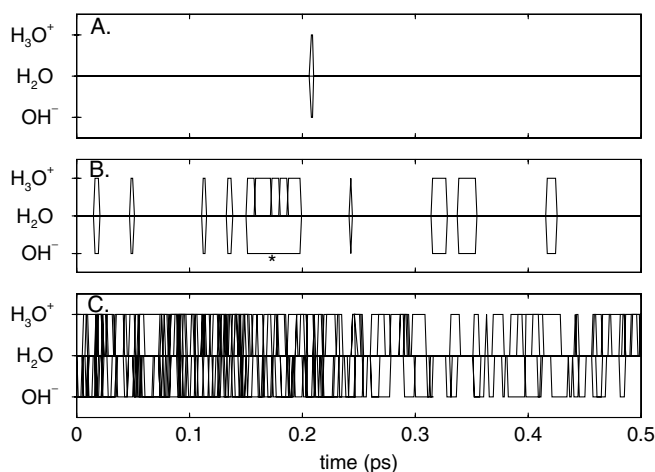


FIG. 5. The number of hydrogen atoms associated with each oxygen atom during the simulations at (A) $\rho = 1.57 \text{ g/cm}^3$, (B) $\rho = 1.72 \text{ g/cm}^3$, and (C) $\rho = 1.95 \text{ g/cm}^3$. A small subset (0.5 ps) of the total simulations are shown for clarity. In (C), the output is restricted to 54 oxygen atoms.

experimentally at a density of 1.73 g/cm^3 and a temperature of 800 K [5,18,26]. It is interesting to note (see Fig. 5b) that the majority of observed dissociation events are characterized by the formation of $\text{OH}^-/\text{H}_3\text{O}^+$ ion pairs that quickly recombine and neutralize on a time scale of 10 fs. However, occasionally a Grotthus-like proton transfer mechanism involving several molecules occurs, similar to water at ambient conditions. For example, the star in Fig. 5b indicates such an event, where the initial transfer of a proton initiates a chain of hydrogen bonded waters to undergo proton transfers (in this specific case a chain of six water molecules is involved).

Finally, we have investigated the effect of temperature on the concentration of H_3O^+ at $\rho = 1.95 \text{ g/cm}^3$ by performing a short 1 ps simulation at 1938 K. The increase in temperature causes the average pressure to increase to 30.5 GPa and the concentration of H_3O^+ to increase to 9.3 mol %. In addition, the oxygen diffusion coefficient increases by approximately a factor of 2. Under ambient conditions, where the average lifetime of H_3O^+ in water is about 3 ps [27], an H_3O^+ concentration of 6.9 to 9.3 mol % would enable the 2900 to 3000 cm^{-1} peak in the Raman spectra to have sufficient intensity to be observed [7]. However, the lifetime of H_3O^+ in the simulation at high pressure is on average only 9.8 fs, which may cause excessive broadening of the H_3O^+ band [6].

In summary, we have investigated the dissociation mechanism of water under pressure by performing a series of *ab initio* MD simulations. Our results show that molecular dissociation results in the formation of short-lived H_3O^+ and OH^- pairs, and that the diffusion of protons occurs via a transfer mechanism similar to that at ambient conditions. These findings are consistent with Raman data on shocked water, and our computed pressures up to twofold compression and 2000 K are in good agreement with experiment. However, our results do not support models used to estimate electrical conductivities and interpret Raman spectra based on the assumption that molecular dissociation occurs via a unimolecular process leading to the presence of free protons in the liquid. In addition, we find that, up to 30 GPa and 2000 K, oxygen diffusion is characteristic of a normal liquid, indicating that, if water becomes superionic under pressure, this may happen at higher pressure and/or lower temperature than that proposed in Ref. [10]. Finally, new structural data of the compressed fluid are provided for comparison with future scattering experiments.

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