

Comment on “Dissociation of Water under Pressure”

In a recent Letter, Schwegler *et al.* [1] report on an *ab initio* molecular dynamics study of autoionization in liquid water at extremely high pressures. In the course of computed ~ 10 ps equilibrium trajectories, pairs of hydroxide (OH^-) and hydronium (H_3O^+) ions form spontaneously and then rapidly recombine. This transient separation of charge occurs by proton transfer from a particular water molecule to one of its hydrogen bonded neighbors and subsequent proton hopping between surrounding water molecules. From these dynamics, Schwegler *et al.* infer that hydronium and hydroxide ions are the primary carriers of charge at high pressures. But the short lifetimes of the ionic species observed in these simulations (~ 10 fs) could preclude their ability to transport net charge in the bulk liquid. Identifying ions that truly contribute to a macroscopic conductivity may thus require order parameters beyond those used by Schwegler *et al.*, which involve only molecular geometry and local electron density.

Inadequacy of local order parameters for autodissociation has, in fact, been demonstrated for liquid water at room temperature and atmospheric pressure [2]. The autoionization mechanism at these ambient conditions, revealed by transition path sampling [3] of Car-Parrinello molecular dynamics trajectories [4], involves the formation of ion pairs by a sequence of proton transfer events. Driven by rare fluctuations in solvent electric field, this initial charge separation is essentially identical to that described by Schwegler *et al.* But the separation of ions by several neighbors is only the first step to the production of free ions that are capable of transporting charge in the liquid. A simple kinetic model introduced by Eigen [5] suggests that only about 1 out of 1000 ion pairs thus produced separates completely. Indeed, the simulations show that without a second, coincident fluctuation, rapid recombination occurs instead, typically within tens of femtoseconds. The requisite coincident fluctuation is the breaking of the hydrogen bond chain (essentially a wire) connecting the two ions. For this reason, order parameters that describe only the separation of charge are poor reaction coordinates for autoionization at ambient conditions. In order to characterize the relevant states, one must consider the solvating water molecules explicitly.

The criteria used by Schwegler *et al.* to identify ions describe charge separation, but not the arrangement of the surrounding hydrogen bond network. It is unknown whether these order parameters, insufficient to distinguish between free and transient ions at ambient conditions, are appropriate at high pressures. For the first two thermodynamic states considered in Ref. [1] ($p = 10$ GPa and $p = 14.5$ GPa), each observed ion pair independently recombines after being formed, and therefore cannot contribute to net charge transport. Evidently, these pressures do not sufficiently accelerate the breaking

of hydrogen bond wires to make free ion formation a common event on the picosecond time scale of molecular dynamics trajectories. It seems therefore likely that at these states the simulated trajectories exhibit only the first step towards full charge separation rather than complete dissociation events.

At the highest pressure considered in Ref. [1] ($p = 26.8$ GPa), however, the distinction between free and transient ion pairs may not be clear-cut. At this state, many ion pairs are typically present at once even in a sample of only 100 water molecules. Although these collections of ion pairs are short-lived, it is possible that they recombine in a permuted way that carries net charge across the system. In this case, interruption of the hydrogen bond wires that connect each ion pair may not be necessary. This interesting possibility, which is extraordinarily unlikely at ambient conditions due to the low concentration of ions, is implicit in the conclusions of Schwegler *et al.* But such an alternative mechanism for charge conduction without free ions has not been demonstrated. For this purpose, it will be necessary to consider the fates of specific ions, rather than simply the transient existence of charge separation.

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