On the recombination of hydronium and hydroxide ions in water

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Edited by Michael L. Klein, Temple University, Philadelphia, PA, and approved October 17, 2011 (received for review July 30, 2011)

The recombination of hydronium and hydroxide ions following water ionization is one of the most fundamental processes determining the pH of water. The neutralization step once the solvated ions are in close proximity is phenomenologically understood to be fast, but the molecular mechanism has not been directly probed by experiments. We elucidate the mechanism of recombination in liquid water with ab initio molecular dynamics simulations, and it emerges as quite different from the conventional view of the Grotthuss mechanism. The neutralization event involves a collective compression of the water-wire bridging the ions, which occurs in approximately 0.5 ps, triggering a concerted triple jump of the protons. This process leaves the neutralized hydroxide in a hypercoordinated state, with the implications that enhanced collective compressions of several water molecules around similarly hypercoordinated states are likely to serve as nucleation events for the autoionization of liquid water.

acid-base chemistry | concerted proton transfer | hydronium and hydroxide recombination

The mechanisms of proton transfer and transport through different media has been a subject of great interest in the fields of chemistry and biology (1–6). Several processes involving proton transfer, such as proton conduction through proton wires in proteins, and acid-base neutralization have been receiving elevated attention (7–9). Water is a common solvent for many of these processes. As an ionizable medium with hydrogen bonds that continuously break and reform, water presents a rich environment for sustaining several complex reactions. Perhaps one of the most fundamental studies in this regard is the dissociation of water and the consequent recombination of the ions. This process forms the cornerstone of textbook acid-base chemistry (10). The acid dissociation constant of water (K_w) at room temperature is 1×10^{-14} , which means that H_2O rarely autodissociates and the subsequent ionic products quickly recombine. Elucidating the molecular mechanisms of the autodissociation of water and recombination of the ions has far-reaching consequences in enriching our understanding of the anomalous conductivity of protons in different environments.

Most of the acid-base neutralization studies are interpreted within the framework of the model proposed by Eigen and de Maeyer (11). This model attributes the rate-limiting step of recombination to the approach of the solvated ionic species by a Grotthuss-like structural diffusion, until a contact distance of about 6 Å (12). At contact distance, the hydronium and hydroxide ions are separated by two water molecules, which form a water wire between the ions as shown in Fig. 1 (11, 12). The Grotthuss mechanism (13) was proposed to explain how the excess proton occurring as H_3O^+ diffuses much faster than expected from its hydrodynamic radius (13). The general consensus on the modern view of the 200-yr-old Grotthuss mechanism (13) is that the excess proton diffuses with a proton transfer from H_3O^+ to the neighboring water when the solvation conditions of the surrounding environment are suitable (3). The hydronium ion moves one molecular length at a time, continuously interconverting between covalent and hydrogen bonds, with the Eigen cation and Zundel

species as intermediates. In the context of recombination, the understanding of the diffusion of the ions up to contact distance lends itself to the ideas of the Grotthuss mechanism. Eigen and de Maeyer phenomenologically proposed that reorganization of the hydrogen bond network would drive the neutralization process from this contact distance.

The model proposed by Eigen and de Maeyer serves effectively when the ions are far away from each other; however, it does not shed light on the molecular mechanism of the recombination process once the ions reach contact distance. A representative situation at contact distance, with the H_3O^+ and hydroxide (OH^-) separated by approximately 6 Å and two intermediate waters is shown in Fig. 1. Whether the dynamics of the proton from here occurs in a stepwise fashion, transferring over one intermediate water at a time analogous to the Grotthuss mechanism, or in a concerted way (7) has been a critical missing piece in the formulation of a complete recombination mechanism of hydronium and hydroxide ions in bulk water. In this work we advance the model put forward by Eigen and de Maeyer (11) by unravelling the recombination mechanism as the ions transition from the diffusive regime to contact distance.

The time-reversed process, namely, the autoionization of liquid water, has previously been studied by using trajectories from advanced sampling methods (2, 14). These studies showed that rare electric field fluctuations resulted in ionization and a rapid structural diffusion of the proton away from the OH^- within 100 fs forming a solvent-separated hydrogen-bonded wire (Fig. 1). Our results confirm these basic features but unveils a critical slower step occurring on the subpicosecond time scale during the recombination which involves a collective motion of the wire that was not previously reported (2). We establish that, besides the fast proton transfer and formation of a hydrogen-bonded wire between the ions that was observed in earlier studies (2), the collective compression of the wire is a necessary condition for the final neutralization step. The collective compression of several water molecules is likely to be one of the critical rate-limiting steps in the autoionization of liquid water. These dynamical processes of the wire now provide a physical basis for the fast proton transfer observed in the recombination and autoionization steps which is strikingly different from the slower picosecond time scale of proton motion expected in bulk water (1, 3, 4). The specific solvent motions that we elucidate form the molecular basis for the electric field fluctuations involved in the recombination of the ions and the time-reversed process (2). This work reveals the molecular mechanism of the neutralization and demonstrates that the annihilation of the H_3O^+ and OH^- ions involves a concerted triple jump of protons through a water wire, which is

Author contributions: A.H., M.K.P., H.E., and M.P. designed research, performed research, analyzed data, and wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1112486108/-DCSupplemental.

Fig. 1. A schematic water wire linking the H_3O^+ and OH^- is shown. Within the paradigm of the modern view of the Grotthuss mechanism, the propagation of the proton is expected in three consecutive steps (1–3) resulting from sequential compressions. In contrast, we observe that it is a cooperative motion of the water wire (4) that results in a concerted motion of the protons (Fig. 2).

intriguingly different from the classical and modern views of the Grotthuss mechanism (1, 13).

Results and Discussion

Collective Compression and Proton Triple Jump. In order to understand the mechanism of recombination and to treat the proton-transfer events explicitly, we performed state-of-the-art ab initio molecular dynamics simulations. The system consists of a box of 64 waters periodically replicated in space which allows for a realistic treatment of ions separated at contact distance. The ionization of water yielding H_3O^+ and OH^- ions is an activated process and will not spontaneously occur on the time scales affordable to ab initio simulations (2). To study the recombination mechanism, we artificially constrain two different waters to exhibit the structural properties of H_3O^+ and OH^- , respectively. The initial sampling of distances between the ions ranged between approximately 5 and 9 Å. The analysis of the recombination mechanisms involves an extensive sampling of approximately 500 trajectories that were performed with energy-conserving dynamics. The simulations were performed with CP2K (15) using the Perdew-Burke-Ernzerhof (PBE) functional (16). The results we report are not sensitive to the choice of basis set and density functional. Details can be found in *SI Appendix*.

The majority of the ions that begin at contact distance recombine within 1 ps. Fig. 2 elucidates the molecular mechanisms involved in the neutralization step. Upon reaching contact distance, the hydration shells of the H_3O^+ and OH^- ions overlap and form a water wire with two waters being shared by the ions. At this point, the ions are separated by a wire linked by three hydrogen bonds, which confirms the existence of similar charge-separated solvent states observed during the autoionization of liquid water (2). The ions remain here for a short period of time before a simultaneous compression of three pairwise oxygen distances along the wire occurs (Fig. 2A and C). This process results in a concerted motion of the protons leading to the neutralization of the ions (Fig. 2B and D). In our trajectories, there are several instances where only one of the O–O pair distances undergoes a contraction. However, individual compressions of this sort were insufficient to cause recombination of the ions through either a stepwise or concerted proton transfer. Because the ultimate recombination step involves a concerted transfer of the three protons along the wire, we do not observe the formation of wires linking the ions with less than three hydrogen bonds. Once the ions reach contact distance, the overall structure of the hydrogen bond wire remains intact. Fast librational motions of the species along the wire on the femtosecond time scale will transiently agitate the water wire linking the ions. However, our results suggest that the rate-limiting step for the neutralization step is driven by the collective compression of the heavy atoms along the water

Fig. 2. (A) The collective compression of the water wire in a typical trajectory is illustrated with the sum of the three O–O distances. (B) The change in the bond lengths associated with the transferring protons is shown. The striking feature of a global compression of the water wire and the concerted flux of protons is highlighted with dashed circles and in the inset. This feature is in sharp contrast to the mechanisms expected within the framework of Grotthuss diffusion. These features are seen for an ensemble of recombination trajectories (density plots C and D), which exemplify these processes as a function of the number of ionic species in the system. The density plots for the individual pairwise oxygen distances along the wire exhibit similar trends to those shown in A. See *SI Appendix* for details along with the definition of the number of ionic species in the system and a collection of other individual trajectories.

wire. The transport mechanisms of H_3O^+ and OH^- in bulk water have been studied extensively (1, 3, 4, 17) and indicate that proton motion between two water molecules involves stepwise compressions of the oxygen atoms along the transfer coordinate, occurring on a time scale of approximately 1–2 ps. The foregoing mechanisms for the recombination of the H_3O^+ and OH^- are strikingly different from the stepwise and nonconcerted process that is anticipated within the paradigm of the Grotthuss mechanism of proton transport. The collective compression of the water wire and concerted motion of the three protons is one the central results of this work. These results are also consistent with recent experiments showing concerted proton transfer along water wires in acid-base pairs (7).

It is well established that compressing a hydrogen bond between two waters perturbs the instantaneous proton potential and increases the probability of proton delocalization and hence transfer (18–21). A collective compression of all the pairwise distances of the heavy atoms along the water wire provides a mechanism for perturbing the proton potentials along each of the hydrogen bonds along the wire. The collective compression of the oxygen atoms also plays a critical role in tuning the angular modes and the electronic structure of the species along the water wire which affect the potential of the protons. It has recently been shown that the formation of strong hydrogen bonds restricts librational modes of water (22). Hence, the collective compression of the wire damps the angular freedom of the modes associated with the transferring protons by the formation of stronger hydrogen bonds along the wire, thereby facilitating their concerted motion (see *SI Appendix*).

The effects on the electronic structure during the recombination process were analyzed by examining the changes in the positions of the Wannier centers (23) which characterize bonding properties. A water molecule, for example, is characterized by two lone-pair Wannier centers involved in hydrogen bonding in

teractions and two bonding-pair centers that are involved in covalent bonds. The evolution of the Wannier centers during the recombination elucidates the dynamical coupling of the nuclear and electronic motions. There exists a strong coupling between the wire compression and its perturbation to the electronic degrees of freedom of the species along the wire. For the two water molecules bridging the ions, most of the reorganization in the electronic structure is associated with a single lone- and bonding-pair Wannier center. The collective compression initiates a push-pull effect whereby the lone pair Wannier centers of each of the two bridging waters undergo a simultaneous *push*, evolving into bonding centers. Concurrently, a bonding center of each of these water molecules is *pulled* as it converts into a lone-pair center. The changes in the electronic structure of the ions in the wire reflect their transformation into neutral water. See *SI Appendix*. Thus the collective compression of the wire as described in Fig. 2 triggers a perturbation to the electronic structure allowing for the bridging waters to simultaneously serve as proton acceptors and donors, which facilitates the concerted proton transfer.

Hydroxide and Hydronium Solvation. Our studies reveal that the recombination of the ions at contact distance is a fast process, and hence the immediate solvent environment of the OH^- reorients on a slower time scale and retains significant orientational polarization during neutralization (24). The density map (Fig. 3) from multiple recombination trajectories exemplifies these features. Assuming that our initial conditions for the recombination studies represent an equilibrium ensemble of solvent-separated ionic states, Fig. 3 shows that a path involving reorganization of the solvent prior to the concerted proton transfer occurs with a much smaller probability. The collective compression and concerted proton transfer occurs on a subpicosecond time scale, which is much faster than the time required to reorganize the solvent environment of the hydroxide ion prior to proton transfer. The data suggest that the collective compression of the water wire provides a lower free energy path for the neutralization process that does not require significant reorganization of the solvation environment of the OH^- . This suggestion is in sharp contrast to the mechanisms of the structural diffusion of OH^- in bulk water (1). The ramifications are that the neutralization of the hydroxide forms an overcoordinated water molecule. Our analysis shows that the hypercoordinated water molecule is a short-lived species that is seen to quickly relax to the equilibrium value expected for neutral water (Figs. S11 and S12 in *SI Appendix*). This result is not surprising given that a water molecule has two lone pairs that can participate in hydrogen bond interactions.

On the other hand, we find that the relaxation dynamics of the solvent around the hydronium ion is quite different. Besides the hydrogen bonds being donated to three surrounding water molecules, the central oxygen atom of the H_3O^+ accepts a weak hydrogen bond, the strength of which increases when the hydronium converts to a transient Zundel-like species. Our simulations reveal that proton motion and the relaxation of solvent around the H_3O^+ occurs simultaneously during neutralization (25) (Fig. 3). The reorganization of the waters donating hydrogen bonds to the OH^- involves an activated process because strong hydrogen bonds need to be broken. However, for the H_3O^+ the formation of a stronger hydrogen bond being donated to the oxygen of the forming water molecule adiabatically follows the concerted proton motion.

Our equilibrium simulations of the constrained ions at different distances yield configurations where the OH^- ion is surrounded by either three or four hydrogen bond donors to it (1, 26). The solvation structure of the OH^- sitting at contact distance from the H_3O^+ is dominated by four water molecules donating hydrogen bonds (approximately 90% of the configurations). Beyond contact distance, the solvation structure of the OH^- is characterized by roughly an equal number of configurations with three or four

Fig. 3. A shows a density plot of our nonequilibrium trajectories as a function of the hydrogen bond environment surrounding the OH^- (DHB_{OH^-}) as it undergoes neutralization. DHB_{OH^-} is quantified by a difference of two switching functions. See *SI Appendix* for details. (B) A hypercoordinated water molecule immediately following neutralization is shown. The concerted proton motion during neutralization quickly changes the number of ionized species from 2 to 0 but leaves the nascent neutralized hydroxide in a hypercoordinated solvation state with a value of $\text{DHB}_{\text{OH}^-} \sim 4$. (C) A regular water molecule with two hydrogen bond donors to it is shown. After neutralization, DHB_{OH^-} quickly relaxes to the equilibrium value (approximately 2.8) of neutral water illustrated by the solid red disk. The value of approximately 2.8 was determined by calculating the average value of DHB_{OH^-} for regular bulk water molecules that are not involved in the neutralization process. D shows a similar density plot for $\text{DHB}_{\text{H}_3\text{O}^+}$ during neutralization. $\text{DHB}_{\text{H}_3\text{O}^+}$ is also quantified by a difference of two switching functions. See *SI Appendix* for details. Path (1) shows that the weak hydrogen bond donated to the H_3O^+ becomes stronger as the neutralization process occurs, approaching the equilibrium value (approximately 1.7) of neutral water. These results reveal that the initial weak hydrogen bond donated to the hydronium oxygen prior to recombination can reorganize to form a stronger hydrogen bond as the concerted transfer of protons occurs. The value of approximately 1.7 was determined by calculating the average value of $\text{DHB}_{\text{H}_3\text{O}^+}$ for regular bulk water molecules that are not involved in the neutralization process. Path (2) illustrates the path taken by a Zundel-like species with a presolvated environment hence requiring little reorganization of the solvent. The recombination of the counterions starting from these initial states are already partially presolvated and hence do not involve significant reorganization of the solvent.

hydrogen bond donors. It is worth noting again that, at contact distance, the hydration shells of the ions overlap so that the ions are sharing waters between them. This fact will certainly affect the solvent environment in the immediate vicinity of the ions. Significantly longer and larger simulations would be required to quantitatively determine the relative populations of these configurations beyond contact distance. However, our results suggest that, as the ions transit from the diffusive zone to the regime of contact distance, the overlapping hydration shells bias the immediate solvation sphere of the OH^- ion to be overcoordinated.

Revisiting the Eigen and de Maeyer model. The model proposed by Eigen and de Maeyer serves as an effective model for the recombination of the H_3O^+ and OH^- when the ions are far apart from each other. However, this model does not provide a molecular picture of the processes that occur during the neutralization step. Characterizing the nature of the transition from the diffusive re-

gime to contact distance was not the focus of previous studies on the autoionization of liquid water (2). Having procured numerous recombination events of the ions, we are now in a position to examine the kinetics of the process in greater detail. The distribution of recombination times is illustrated in Fig. 4. We find that, at contact distance, the distribution is characterized by a stepwise kinetic model with two time scales: approximately 65 fs and approximately 0.5 ps. The slower component of 0.5 ps is characterized by the mode required to collectively compress the wire. The ultrafast component is associated with the neutralization event for the compressed wire. This time scale is consistent with the 100-fs time scale observed for motion of protons during part of the autoionization step of liquid water (2). The ultrafast time scales observed deviate significantly from the picosecond time scale of proton motion observed in bulk water (1, 3, 4). The large driving force and elevated electronic coupling that is expected for a strongly hydrogen-bonded system suggest that the recombination occurs in the strongly adiabatic regime close to the barrierless region (27). The reactant ions and the transition state ensemble are best considered as being part of the same continuum of short-lived transient states.

Quantitatively probing the diffusive encounter of the ions is computationally prohibitive with *ab initio* simulations. However, we can shed qualitative light on the nature of the transition from the zone of diffusive motion to the regime of contact distance. About 40% of the trajectories that begin beyond contact distance recombine within 2 ps. The H_3O^+ and OH^- ions that begin at about 8 Å, which is close to the largest distance we can fit with our periodic boundary conditions, exhibit a lag of approximately 0.3 ps in the recombination times (see *SI Appendix* for the distribution). At this distance, the ions consist of hydrogen bond wires that are separated by 4–5 water molecules. If the motion of H_3O^+ and OH^- ions immediately beyond contact distance was described by purely diffusive bulk-like motion, we would expect a much larger lag on the order of several picoseconds, in the recombination times. These results suggest that, as the H_3O^+ and OH^- approach contact distance, there exists an intermediate zone where the mobility of the ions is enhanced relative to diffusion in the bulk. In our simulations, the approach of the ions can be facilitated by a dynamically labile, lower coordinated OH^- (1). The sensitivity of the enhanced diffusion and the mechanism of H_3O^+ and OH^- motion in the intermediate regime to finite box size effects will require modeling much larger scale systems. However, a long-range collective compression and concerted proton transport mechanism beyond contact distance involving water wires

longer than the one illustrated in Fig. 1 is not observed in our simulations.

Implications for water ionization. We have shown (Fig. 3) that the neutralization event is a fast process rendering the neutralized OH^- in a hypercoordinated state. The notion of presolvation mechanisms occurs in the context of proton and hydroxide transfer in bulk water (1, 25), and it should not be surprising that these phenomena translate to the ionization of water. Assuming microscopic reversibility, our results provide some exciting perspectives on the mechanisms involved in the ionization of water. The dissociation of water is likely to involve a presolvation mechanism involving the formation of a hypercoordinated water molecule and a collective compression of the nearby hydrogen bonds. Previous studies have highlighted the role of electric field fluctuations in initiating autoionization (2). The notion of the presolvation of water prior to ionization that emerges from our recombination studies now provides a molecular basis for these electric field fluctuations. Thus, rare states of water molecules exhibiting solvation patterns similar to those seen for OH^- are likely to serve as nucleation sites for water ionization. Indeed, it has recently been demonstrated that the local electric field on an O–H bond of a water molecule with more hydrogen bond donors to it is relatively enhanced. These studies confirm that overcoordinated water molecules are likely to serve as a pathway for the autoionization of liquid water (28). Evidently because of the difference in time scales of the ionization and recombination events, presolvation processes play a more critical role in the former than in the latter.

As illustrated earlier, the recombination of the H_3O^+ and OH^- involves a collective compression of the water wire bridging the ions, resulting in a concerted motion of the protons. We have ascertained that a contact ion pair without any intermediate water molecules results in an instantaneous recombination step. Earlier work on the autoionization of liquid water emphasized the essential role of the formation of a hydrogen-bonded chain to facilitate the stabilization of charge-separated solvent states within a time scale of 100 fs (2). However, our results highlight that, in addition to this process, a mechanism involving a collective compression of the water molecules in close vicinity to an ionizing water will be required to stabilize the H_3O^+ and OH^- along a hydrogen-bonded chain at contact distance. See *SI Appendix*. This effect is also likely to be present in the autoionization trajectories of ref. 2 if they were to be analyzed.

As seen in Fig. 24, once the concerted proton transfer is completed during the recombination, the water wire instantaneously decompresses, which implies that the contracted state of the wire during the time-reversed process has a very short lifetime. This decompression facilitates the rapid shuttling of the proton during the autoionization of liquid water, as described previously, with the ions situated at contact distance (2). However, the separation of the ions beyond this point was not previously addressed. Our studies indicate that, as the H_3O^+ and OH^- approach contact distance during the recombination step, there exists an intermediate zone where the mobility of the ions is enhanced relative to diffusion in the bulk. This zone implies that, during autoionization, bulk-like Grotthuss diffusion will begin only once the ions separate beyond this intermediate zone.

Nuclear quantum (QM) effects. In our simulations, the nuclei are treated classically. Nuclear quantum effects, through both tunneling and zero point energy (ZPE), can be important when considering the motion of protons. The recombination studies we perform in this work are dynamical processes and hence cannot be repeated by using a canonical path integral formalism. However, we can examine the effect of nuclear quantum effects on structural equilibrium properties of the water wire shown in Fig. 1. A promising way of incorporating nuclear quantum effects in

Fig. 4. A histogram of the distribution of recombination times is shown along with the fit (solid red line).

classical simulations is through thermostating the effective temperature of the high-frequency modes associated with the protons (29). We have ascertained by using a quantum thermostat (29) that ZPE does not significantly change the equilibrium structure of the water wire (see Table 1). The data shown in Table 1 confirm that nuclear quantum effects through zero point energy do not alter the structural properties of the water wire in a manner that would qualitatively change the phenomena reported in this work. We find, however, that the O-H bond lengths along the water wire exhibit more enhanced fluctuations with the quantum thermostat, as expected (30). The molecular mechanism of the recombination is governed by the structural properties of the wire, and hence the overall features of the neutralization should be correctly described by classical trajectories (1, 31).

Experimental validation of mechanism. It is tantalizing to explore the possibility of experimentally validating the mechanism of the recombination of the ions reported in this work. Earlier experiments on the recombination of H_3O^+ and OH^- in water were limited by time resolution and could only examine the slow diffusive step of the recombination process (11, 12). Our results suggest the formation of transient species during the recombination occurring on the time scale of approximately 0.5 ps that could provide a signal for experimental detection (32, 33). The simultaneous flux of protons of the water wire results in the formation of transient species, $(\text{H}_5\text{O}_2)^+(\text{H}_3\text{O}_2)^-$ and $(\text{H}_7\text{O}_3)^+(\text{OH})^-$ illustrated in Fig. 5. The $(\text{H}_5\text{O}_2)^+(\text{H}_3\text{O}_2)^-$ state can be interpreted as the formation of a Zundel-like cation and anion simultaneously. Just like the Eigen and Zundel cationic states, these species should be viewed as limiting transient species that help categorize the intermediates. The recombination step involves a fast process occurring in approximately 0.5 ps. On this time scale, the solvent surrounding the nascent neutralized OH^- does not respond adiabatically to proton motion during neutralization, thereby forming a hypercoordinated water molecule. The distinct role of the solvent in the ionization and recombination processes may provide a signal that could be resolved experimentally.

Conclusion and Perspectives. In conclusion, we find that the neutralization step of the recombination of H_3O^+ and OH^- in bulk water is characterized by phenomena that are strikingly different from those expected within the framework of the modern view of the Grotthuss mechanism. The penultimate neutralization step involves a collective compression of all the oxygen atoms of the water wire on a time scale of approximately 0.5 ps and results in a concerted flux of three protons. The recombination mechanisms elucidated in this work combined with earlier results on the auto-ionization of liquid water (2) provide a more complete molecular picture of the most fundamental process in acid-base chemistry. The picture emerging is that when the H_3O^+ and OH^- are far apart from each other, they undergo bulk-like diffusion where proton transfer is a stepwise process involving the cooperative motion of the surrounding solvent (1, 3, 4, 17). As the ions approach contact distance at 6 Å beginning to form hydrogen-bonded wires linking the ions, the diffusion constants of the ions are enhanced relative to the bulk. Once the ions reach contact

Table 1. Various average distances of bonds along the water wire are compared with classical and quantum simulations

Method	Bond	Distance	Method	Bond	Distance
QM	O ₁ -O ₂	2.64 ± 0.13	classical	O ₁ -O ₂	2.56 ± 0.10
QM	O ₁ -H ₁	1.04 ± 0.06	classical	O ₁ -H ₁	1.04 ± 0.03
QM	O ₂ -O ₃	2.63 ± 0.11	classical	O ₂ -O ₃	2.68 ± 0.13
QM	O ₂ -H ₂	1.06 ± 0.07	classical	O ₂ -H ₂	1.03 ± 0.04
QM	O ₃ -O ₄	2.64 ± 0.15	classical	O ₃ -O ₄	2.58 ± 0.08
QM	O ₃ -H ₃	1.06 ± 0.06	classical	O ₃ -H ₃	1.07 ± 0.04

See [S/ Appendix](#) for nomenclature of the water wire.

Fig. 5. *A* illustrates the transient species $(\text{H}_5\text{O}_2^+)(\text{H}_3\text{O}_2^-)$ involving the formation of a “Zundel-like” cation and anion simultaneously. *B* shows the transient $(\text{H}_7\text{O}_3^+)(\text{OH}^-)$ which results in the proton being delocalized over three water molecules. The anionic and cationic species are highlighted with red and blue boundaries, respectively.

distance, a collective compression of the wire occurs with a concerted proton transfer which neutralizes both ions and forms two water molecules. The time-reversed process will involve similar phenomena albeit a larger activation barrier for the collective compression which is likely to be the rate-limiting step for auto-ionization. Our results qualitatively examine the transition from bulk-like diffusive motion to the regime at contact distance. These studies should motivate exploration of the intermediate regime in greater detail.

Concerted transport phenomena of protons have recently been observed in systems involving acid-base neutralization (7) as well as photoactive proteins like bacteriorhodopsin (34) and the green fluorescent protein (GFP) (35, 36). GFP consists of a high density of negatively charged residues on the surface that attracts protons and funnels them through a water wire to the active site (37). The phenomena unveiled in this report are likely to form the basic rules governing proton transport in these systems but will require further experimental and theoretical exploration.

Computational Details. Ab initio molecular dynamics simulations of the recombination of the hydronium and hydroxide ions in water were conducted by using Quickstep, which is part of the CP2K package (15). In these calculations, ab initio Born-Oppenheimer molecular dynamics is used for propagation of the classical nuclei. The electronic orbitals are converged to the Born-Oppenheimer surface at every step in the molecular dynamics simulation. A tight convergence criterion of 5×10^{-8} a.u. was used for the optimization of the wave function. By using the Gaussian and plane waves method, the wave function was expanded in the Gaussian DZVP basis set. An auxiliary basis set of plane waves was used to expand the electron density up to a plane wave cutoff of 300 Ry. We used the Perdew-Burke-Ernzerhof gradient correction (16) to the local density approximation and Goedecker-Teter-Hutter pseudopotentials for treating the core electrons (38).

The system consists of a box of side length 12.4138 Å with 64 water molecules. The hydronium and hydroxide ions were formed by constraining the geometry of two separate water molecules to exhibit the corresponding protonation state. This was achieved by constraining the number of hydrogen atoms around the hydronium and the hydroxide ion by using switching functions of the following form: $n_O(r) = \sum_{O^{OH^-} \text{ or } H_3O^+} \frac{1 - (\frac{r}{r_0})^{16}}{1 - (\frac{r}{r_0})^{56}}$, where $r_0 = 1.32$ Å. The starting configuration for generating the ion pair was begun from simulations of bulk water with the PBE functional that had

been equilibrated for approximately 200 ps (39). Deuterium masses were used for the hydrogen atoms. Equilibrium simulations to generate starting configurations for the recombination studies were conducted within the *NVT* ensemble at 300 K by using the canonical-sampling velocity-rescaling thermostat (40). Simulations with the hydronium and hydroxide ions constrained at a distance of approximately 5–7 Å were equilibrated for at least 7.5 ps, after which initial configurations for the recombination studies were taken from two ensuing trajectories of an accumulated length of approximately 30 ps. The simulations with the hydronium and hydroxide ions constrained at a distance of approximately 7–9 Å were equilibrated for at least 6 ps, after which initial configurations for the recombination studies were taken from two ensuing trajectories of an accumulated length of approximately 20 ps. The nonequilibrium recombination studies were performed within the *NVE* ensemble with initial velocities sampled from a Maxwell-Boltzmann distribution corresponding to a temperature of 300 K.

Sensitivity of results with respect to the choice of basis set and density functional is always a concern in *ab initio* simulations. We have repeated some of our recombination studies with the PBE functional and the more accurate TZV2P basis set. To test

the sensitivity of our results to the choice of density functional, we have repeated some of our recombination studies of the hydronium and hydroxide ions with the HCTH/120 density functional with a DZVP basis set. The HCTH/120 functional has recently been advocated as being a more reliable functional for both protonated and bulk water simulations (17). A simulation of length approximately 15 ps was run with the HCTH/120 functional, of which the first 6.5 ps was considered as equilibration. At contact distance, the solvation properties of the OH[−] are very similar to those seen with the PBE functional. We find that the phenomenon of the collective compression of the water wire and concerted motion of the protons appears to be independent of the choice of density functional or basis set. See *SI Appendix* for figures illustrating these details.

ACKNOWLEDGMENTS. The authors acknowledge Noam Agmon, David Chandler, and Sherwin Singer for insightful comments on the manuscript. We thank Swiss National Supercomputing Center (CSCS) and High Performance Computing Group of Eidgenössische Technische Hochschule Zurich for computational resources. Financial support from the European Union grant (ERC-2009-AdG-247075) are gratefully acknowledged.

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