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Proton transfer and the diffusion of H^+ and OH^- ions along water wires

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Hydrogen and hydroxide ion transport in narrow carbon nanotubes (CNTs) of diameter 8.1 Å and lengths up to 582 Å are investigated by molecular dynamics simulations using a dissociating water model. The diffusion coefficients of the free ions in an open chain are significantly larger than in periodically replicated wires that necessarily contain D or L end defects, and both are higher than they are in bulk water. The free hydroxide ion diffuses faster than the free hydronium ion in short CNTs, unlike diffusion in liquid water, and both coefficients increase and converge to nearly the same value with increasing tube length. The diffusion coefficients of the two ions increase further when the tubes are immersed in a water reservoir and they move easily out of the tube, suggesting an additional pathway for proton transport via OH^- ions in biological channels. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4821764]

I. INTRODUCTION

Proton transfer (PT) is the fundamental mechanism by which hydrogen and hydroxide ions are transported along water wires in narrow pores, of special relevance to proton transport in fuel cells,[1] tubular peptide structures,[2] membrane channels such as gramicidin[3,4] and bacteriorhodopsin,[5–10] and the proton transfer function of carbonic anhydrase.[12,13] It is different in many ways from PT in bulk water. In particular, there is a significant desolvation penalty for the hydronium ion (H_3O^+) to enter a narrow pore.[14] Within the pore, proton transfer is significantly faster than in bulk water[10,11,15] since confinement impedes solvation, and solvent rearrangements that modulate the transport of hydrogen and hydroxide ions in liquid water are absent in narrow pores.[16–25] Synchronized multiple proton transfers across hydrogen-bonded water wires occur in certain acid-base neutralization reactions[26] and in the recombination of H^+ and OH^- ions in liquid water[27] and water filled nanopores.[28]

We present the results of molecular dynamics simulations of proton transfer in the transport of free H^+ and OH^- ions in open chains of water molecules filling carbon nanotubes (CNTs) of diameter 8.1 Å and lengths ranging from ∼29.6 to 581.4 Å containing from 12 to 240 water molecules, using a dissociating water model.[29] The rates of diffusion of hydrogen and hydroxide ions as a function of the length of the water wire and the activation energies for proton transport from the corresponding temperature dependence of the diffusion coefficients were determined. The activation energies are nearly the same for the two ions and are lower by a factor of ten than in bulk water. The diffusion coefficients converge for long tubes, are higher by an order of magnitude along open chains than periodically replicated ones, and increase even further when the tubes are immersed in a water reservoir.

Water quickly fills a narrow CNT of diameter 8.1 Å immersed in a water reservoir to form a one dimensional hydrogen bonded chain or water wire observed in molecular dynamics simulations[30–32] and in experiments.[33,34] The dipoles of the chain are tilted slightly away from the tube axis but are otherwise oriented in the same direction reinforcing each other to form a giant dipole along the tube axis.[35–37] The charges on the projected dipole moments of the water molecules along the tube axis cancel except at the end points of the projected chains.[15,35,36]

In traversing a narrow pore, a hydronium ion (H_3O^+) donates a hydrogen-bonded proton to a chain of water molecules that are already hydrogen bonded with a string of dipoles oriented away from the ion. As the excess charge of the hydronium ion moves down the chain, through a range of Zundel-like intermediates,[10] it leaves behind in its wake, a string of water molecules with dipoles pointing in the opposite direction. The hydronium H_3O^+ ion then behaves effectively as a positively charged hydrogen bonded L-defect (Fig. 1), with two chains (or strings) of dipoles pointing away from the ion.[15] Likewise, an OH^- ion accepts a proton from a water molecule hydrogen bonded to it, leaving behind a dipole in the opposite direction to the one it just encountered, to form a negatively charged hydrogen bonded D-defect with dipoles pointing towards the negatively charged OH^- ion (Fig. 1). Hydrogen and hydroxide ion transport involve proton transfer in the same and opposite directions respectively to the directions of structural or topological diffusion of the ions.

We first study an excess charge (H_3O^+ or OH^-) in an open chain of water molecules filling (6-6) armchair type carbon nanotubes of diameter 8.1 Å and lengths ranging from 29.6 to 581.4 Å. The hydrogen bonded water wires in tubes (not immersed in a water reservoir) were restrained from leaving the tubes by applying a weak harmonic potential to the oxygen atoms at the tube ends. Periodic boundary conditions (PBC) produce defects at tube ends from opposing water dipoles oriented by the excess charge. They lower

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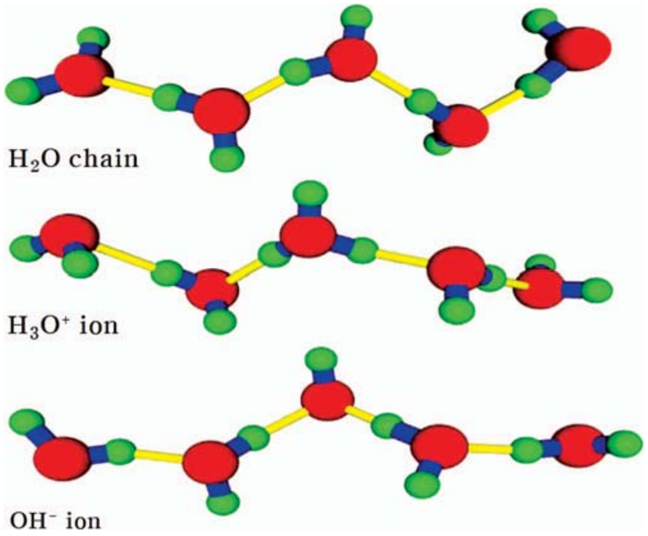

FIG. 1. Configurations of the water chain, hydronium (H_3O^+), and hydroxide ion (OH^-) in water wires similar to L- and D-defects, respectively, at the ions.

the diffusion coefficients through the coupled motion of the defect and ion,[15] but are absent in open chains. End effects from the weak harmonic potential are less critical (see below) near the central region of the tube as it elongates.

The interaction of the excess charge q on the hydronium (H_3O^+) ion with two oppositely oriented chains of dipoles forming a hydrogen bonded L-defect at the ion, is equivalent to the repulsive interaction between a charge of magnitude $(q - 2\mu_z/\Delta)$ on the ion with two charges of magnitude (μ_z/Δ) at the ends of the open chains,[15] as shown in the dipole lattice model developed by Dellago *et al.*[15] From simple electrostatic considerations it follows that the free energy of interaction of the ion with chains of dipoles is[15]

$$F(z') = (\mu_z/\Delta)(q - 2\mu_z/\Delta)[1/z' + 1/(1 - z') - 4]/L, \tag{1}$$

relative to the energy at the center. Here, $z' = z/L$, where z is the distance of the moving excess charge q from one end of the tube of length L, μ_z is the magnitude of the projected dipole moment of a water molecule along the tube axis and Δ is the average distance between the centers of the adjacent dipoles. An analogous expression must hold for the interaction energy of the negative hydroxide ion (OH^-) with the two oppositely oriented dipole chains (D-defect at the ion and negative charges at the chain ends).

II. METHODS

The dissociating water model employed in our work was obtained by scaling the potential derived by Ojamäe, Shavitt, and Singer (OSS2) from *abinitio* studies of neutral and protonated water clusters[38] at the Møller-Plesset (MP2) level, as described in our work on the mobility of hydrogen and hydroxide ions in bulk water.[29] Briefly, a scaling parameter λ for the OSS2 potential was chosen to optimize agreement between the simulations and experimental atom-atom distribution functions, diffusion coefficients, and the rotational autocorrelation functions of liquid water. The optimal λ for the scaled potential (sOSS2), determined from the experimental data for bulk water at 298 K, was 0.530.[29] The charges q_i on the hydrogen or oxygen atoms scale as $\lambda^{1/2}$ with $q_H = 0.728e$, where e is the electronic charge. Classical simulations with scaled potential produce results that agree well with the solvation structures of hydrogen and hydroxide ions, the mechanism of PT in liquid water proposed earlier in Car-Parrinello molecular dynamics (CP-MD) studies,[18,19,24,39] and the experimental mobilities of the hydrogen and hydroxide ions in aqueous solution from 0 to 50 °C.[29] The method is easily applied to PT along water wires in the short and long nanotubes described below.

We assume the same sOSS2 force field for the water chain in the nanotube as for bulk water and also for the interactions of the water molecules in the chain with hydronium and hydroxide ions in the tube modeled as a water molecule with an extra proton (H_3O^+) or a missing proton (OH^-)[29] also described as a proton hole. Nanotube-water interactions are treated as Lennard-Jones interactions between the carbon atoms of the nanotube and the oxygen atoms of the ions and water molecules.[30] The setup of the initial configurations of H_3O^+ and OH^- at the center of the nanotube is described in the supplementary material (see Figs. S1 and S2).[40] The temperature was controlled by a Nosé-Hoover thermostat.[41,42] Nuclear quantum effects are ignored in this model and tunneling is unimportant since the free energy barriers for PT are low[16]—see the supplementary material.[40] The same model was used by us to discuss the recombination of H^+ and OH^- ions along water wires.[28]

III. RESULTS AND DISCUSSION

The predictions of Eq. (1) for interactions of the excess charge on H_3O^+ or OH^- with the directed dipoles of five water wires in nanotubes with increasing numbers of water molecules N_w = 12, 24, 72, 120, and 240 are shown as solid lines in Fig. 2. They agree almost perfectly with the numerical calculations of the energy of interaction in the sOSS2 model. The parameters of Eq. (1), namely the spacing Δ between the projected dipoles along the tube axis and the

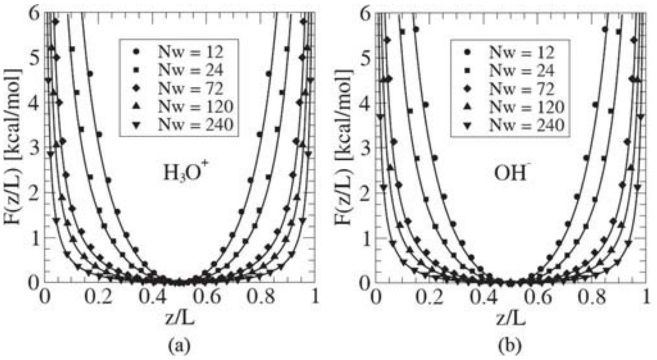

FIG. 2. (a) Numerical calculations of the energy of interaction of the H_3O^+ charge with open water chains for the sOSS2 model in an MD simulation compared with analytic lattice model of the energy Eq. (1) for the interaction between an equivalent charge $(q - 2\mu_z/\Delta)$ and charges μ_z/Δ at the tube ends. (b) Corresponding energy of interaction of the OH^- ion with open water chains are compared to Eq. (1).

projected dipole moment μ_z, were obtained from independent simulations of the water chain in the absence of either ion, For the sOSS2 model with $\lambda = 0.530$, $\Delta = 2.42$ Å, $q = q_H = 0.728e$, $\mu_z = 0.684e$ Å $= 3.29$ D, $2\mu_z/\Delta = 0.565e$, and the effective charge $(q - 2\mu_z/\Delta)$ on H_3O^+ is $\sim 0.163e$. The sign of charge q and dipole moment μ_z are reversed for the OH^- ion. Extended valence bond (EVB) calculations of just H_3O^+ in a water wire by Dellago *et al*. also showed excellent agreement with the lattice model.[15]

Within the flat horizontal regions of Fig. 2, the influence of the end charges on the dynamics of PT is minimal, and the mean square displacement (MSD) of the excess charge moving along the water wire is linear in time with a slope equal to half the diffusion coefficient of the free ions as expected for transport in one dimension, provided this time is long enough to reach the infinite-time limit to measure free diffusion. The nearly flat region in the free energy (Fig. 2) increases with the length of the tube and the MSD is linear from nearly 0.05 to 8 ps when 120 water molecules and a centrally located ion occupy a CNT (Fig. 3(a)) of length ∼291 Å. MSDs of the excess charge transported along water wires of shorter lengths from 29.6 to 174.8 Å are shown in Fig. S3 of the supplementary material.[40]

The diffusion coefficients of the H_3O^+ and OH^- ions calculated from the linear regions of the MSD are summarized in Table I; the shortest and longest tubes are of length 29.6 and 581.4 Å respectively, corresponding to water wires containing 12 and 240 water molecules. Water wires in biological systems are generally short.[43] In the absence of periodic boundary conditions, the diffusion coefficient is for the free ion and not the coupled ion-end defect that arises with periodic boundary conditions.[15] At longer times, beyond the linear region, the MSD curve dips down when the ion moves closer to the tube ends and is repelled by an effective charge at the end highlighted in the lattice model,[15,36] and in our case, repelled also by the weak harmonic potential that prevents water from leaving the tube. The shorter duration of ion transport in short wires may prevent the MSD from reaching its correct linear infinite-time limit, which contributes to errors in the calculation of the diffusion coefficient.

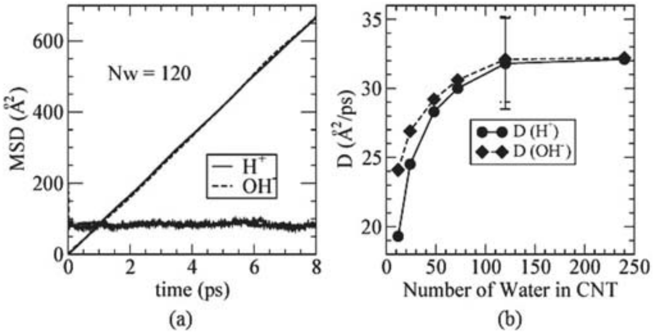

FIG. 3. (a) Mean square displacements of H^+ (solid line) and OH^-(dotted line) in CNT with $N_w = 120$ and its time derivatives. The horizontal curve is the running slope. (b) Diffusion coefficients (D in units of Å^2/ps) of H^+(solid line) and OH^-(dotted line) in CNT as a function of number of water molecules in open chains. Error bars (one standard deviation) are shown for $N_w = 120$.

TABLE I. The diffusion coefficients in units of Å^2/ps for H^+ and OH^- ions along open water chains in CNTs at 298 K calculated using the sOSS2 model ($\lambda = 0.53$).

Length *L* of CNT (Å)[a]	Time interval (ps)[b]	$D(H^+)$	$D(OH^-)$	$D(H^+)/D(OH^-)$
29.6 (12)	0.05–0.1	19.3 ± 0.5	24.1 ± 0.6	0.80
58.7 (24)	0.05–0.2	24.5 ± 1.2	26.9 ± 2.6	0.91
116.8 (48)	0.05–0.5	28.3 ± 1.3	29.2 ± 2.5	0.97
174.8 (72)	0.05–2	30.0 ± 2.8	30.6 ± 2.0	0.98
291.0 (120)	0.05–8	31.8 ± 3.3	32.1 ± 3.1	0.99
581.4 (240)	0.05–8	32.1 ± 4.4	32.2 ± 4.2	1.00

[a] Numbers of water molecules in CNTs are in parenthesis.

[b] "Time interval (ps)" is the time interval to get *D* from the slope of MSD.

The OH^- ion appears to diffuse faster than the H_3O^+ ion in short nanotubes but the difference decreases as the tube length increases converging, in the limit of long tubes ($N_w = 240$, $L = 581.4$ Å), to ∼32 Å^2/ps to within the errors (∼3 Å^2/ps) of our calculations (Fig. 3(b)), in qualitative agreement with the study by Bankura and Chandra.[11] However, their diffusion coefficients (∼3 Å^2/ps) are an order of magnitude smaller, consistent with the use of periodic boundary conditions. We estimate a diffusion coefficient $D \sim 4$ Å^2/ps for the charge-end defect pair from our calculation of 32 Å^2/ps for the free ion and 5 Å^2/ps for the free defect[15] using $D^{-1} = D^{-1}_{\text{free}} + D^{-1}_{\text{defect}}$. Dellago *et al*.[15] calculated $D = 17$ Å^2/ps using the EVB theory for the H_3O^+ ion in an open chain of 120 water molecules; which could be due to differences in the water and ion models and our explicit use of nanotubes to contain the water wires rather than an axis symmetric potential.[15] The increase in the diffusion coefficients of the hydrogen and hydroxide ions with increasing tube length in our calculations arises partly from the decreasing influence of the effective end charges on the potential of mean force (Eq. (1)) which varies inversely as the tube length *L* and the weaker effect of the harmonic potential on the ion near the center as *L* increases. Another factor is the MSD not reaching its infinite-time limit in short tubes.

Open chain calculations of the MSDs from 0 to 50 °C reveal that the diffusion coefficients increase with temperature (Fig. 4). The activation energies for diffusion, calculated from the Arrhenius equation $D = D_0 \exp(-E_{\text{trans}}/RT)$, along the wire with 72 water molecules (length $L = 174.8$ Å), are essentially the same for both ions (1.75 and 1.76 kJ/mol, respectively, for OH^- and H_3O^+) at 298 K and are much smaller than the corresponding values of 10.3 kJ/mol and 12 kJ/mol for diffusion in bulk water, where there is a significant difference between the diffusion coefficients of the two ions.[29] The higher activation energies for transport in bulk compared to channel water reflects the retarding effects of solvation and solvent rearrangement preceding and accompanying proton transfer in bulk water[17–24] that are not present in the channel.

The effects of boundary conditions and environment were further explored by calculating the diffusion coefficients of the ions in nanotubes of length 29.6 Å immersed in bath of 1024 water molecules modeled by the sOSS2 potential with the same scaling parameter $\lambda = 0.530$. The length of

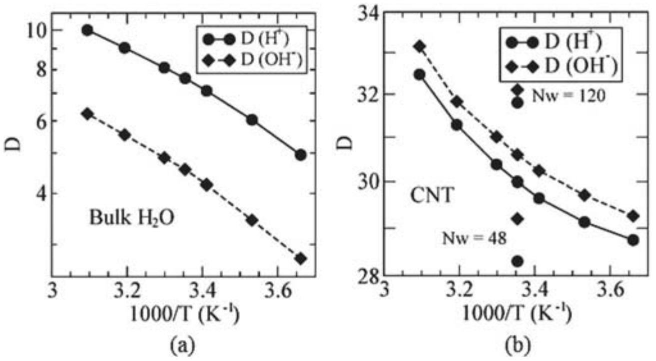

FIG. 4. Temperature dependence of the diffusion coefficients (D) of the hydrogen and hydroxide ions in the sOSS2 model plotted on a logarithmic scale as a function of the inverse temperature over the range T = 273–323 K (a) for bulk water[29] and (b) for NW = 72 ($L = 174.8$ Å) water molecules in the CNT. The values of LnD for the two ions in the water chain containing 48 ($L = 116.8$ Å) and 120 ($L = 291.0$ Å) water molecules at 298 K are also shown.

the cubic simulation box in the direction of the axis of the tube, which was held fixed at the center, was 37.0 Å. Periodic boundary conditions were applied to the whole system but the tube is not periodically replicated due to the gap between the tube end and the edge of the water bath. Ewald summations were used for the long range coulomb interactions with the parameter for $\kappa = 5.0/L$, and the real-space cut distance r_{cut} and K_{max} chosen as $0.5L$ and 7, respectively, where L is the length of the box (37.0 Å). The equations of motion for water and a single H_3O^+ or OH^- ion in both the *open* and water-immersed tubes were solved using velocity Verlet algorithm[44] with a time step of 0.2 fs with a Nosé-Hoover thermostat.[41,42] Harmonic forces were not applied to contain the water chain which was favorably coupled to the reservoir at the tube ends. The coupling diminishes the effective charge at the ends of the water chain, rendering the potential of average force less repulsive for a H_3O^+ or OH^- ion approaching the opening than in an open chain. Both ions move easily out of the tube into the reservoir, providing another pathway via OH^- ions for proton transport in channels and water wires. The proton transfer function of the enzyme carbonic anhydrase II (CAII) is thought to occur via the transport of hydroxide ions with the pK_as of the end groups of the water wire playing a role in differentiating between the two PT mechanisms.[12,13,45]

Table II summarizes our results for proton transfer in CNTs of length 29.6 Å immersed in a water reservoir. The diffusion coefficients of the hydrogen and hydroxide ions in the immersed tubes are about 1.3 to 1.5 times faster than in an open chain of water molecules of the same length shown in Table I, and nearly 34 times and 82 times faster than in bulk water using the same water model ($D = 0.762$ Å^2/ps and $D = 0.456$ Å^2/ps in 0.26 M solutions for H^+ and OH^- ions, respectively, that agree well with experimental results[29]). The hydroxide ion moves faster than the hydrogen ion in the CNT of diameter 8.1 Å and length 29.6 Å open to a reservoir, and the ratio (H^+/OH^-) for the diffusion coefficients is ~0.69 compared to ~0.80 in the open tube. Our calculations for PT along water wires in carbon nanotubes should be similar for other smooth pores (e.g., hard potential tubes) as well.

TABLE II. Comparison of diffusion coefficients (D in units of Å^2/ps) for H^+ and OH^- ions in water filled CNTs of length 29.6 Å immersed in a water reservoir at 298 K and in bulk water at 0.26 M.

D (10^{-5}cm^2/s)	CNT (MD) ($N_w = 12$)	Bulk water (MD)	Bulk water (exp)
H^+	25.8 ± 1.1	0.762[a]	0.824 (0.931)
OH^-	37.2 ± 1.1	0.456[a]	0.451 (0.530)
H^+/OH^-	0.69	1.67	1.83 (1.76)

[a] The MD results are for the scaled OSS2 model with λ = 0.530, results in bulk water are from Ref. 29. The last column shows experimental results at infinite dilution, shown in parenthesis, corrected to 0.26 M.[29]

IV. CONCLUSION

Within the pore, the mechanism of successive charge transfers between the pristine H_3O^+ or OH^- ions and a neighboring water molecule resembles the Grotthuss mechanism[46] more closely than charge migration in bulk water due to the absence of extensive solvation and solvent fluctuations, and reorganization within the channel. The hole-particle symmetry of the mechanism predicts the same diffusion coefficient for the H_3O^+ and OH^- ions,[47] and this is evident in our calculations of hydrogen and hydroxide ion transport along water wires. This symmetry is, however, imperfect. For instance, the proton affinity of the oxygen atom in a water molecule is not necessarily the same as that of oxygen in an OH^- ion. This difference may contribute to a slightly larger diffusion coefficient of the hydroxide ion relative to the hydrogen ion mitigated by greater rattling across the lower free energy barrier for proton transport towards the hydroxide ion.[40] The relative rates of diffusion along water wires in real membrane channels will depend on the membrane structure and hydrophobicity that are not discussed here.

Our study of hydrogen and hydroxide ion diffusion along water wires uses classical simulations and scaled potentials derived from *ab initio* MP2 calculations.[29,38] The energies of interaction of the ions with water wires agree nearly exactly with the lattice model of Dellago *et al.*[15,36] in which the charge defect is partially neutralized by the charges on the adjacent solvent dipoles, thereby lowering the barrier further for proton transport. The diffusion coefficients of the free ions are shown to be consistent with hole-particle symmetry of the Grotthuss mechanism for H^+ and OH^- ion transport in water wires.[46,47] An alternative pathway for proton transport in channels via diffusion of the hydroxide ion is highlighted. These conclusions are unlikely to be reversed by more accurate quantum simulations that would show the significance of neglected nuclear quantum effects and inaccuracies in the potentials used in this study.

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[1] D. E. Moilanen, D. B. Spry, and M. D. Fayer, Langmuir **24**, 3690 (2008).

[2] U. S. Raghavender, Kantharaju, S. Aravinda, N. Shamala, and P. Balaram, J. Am. Chem. Soc. **132**, 1075 (2010).

[3] R. Pomès and B. Roux, Biophys. J. **82**, 2304 (2002).

[4] A. Chernyshev and S. Cukierman, Biophys. J. **91**, 580 (2006).

[5] R. Rousseau, V. Kleinschmidt, U. W. Schmitt, and D. Marx, Phys. Chem. Chem. Phys. **6**, 1848 (2004).

[6] M. L. Brewer, U. W. Schmitt, and G. A. Voth, Biophys. J. **80**, 1691 (2001).

[7] S. A. Hassan, G. Hummer, and Y.-S. Lee, J. Chem. Phys. **124**, 204510 (2006).

[8] E. Freier, S. Wolf, and K. Gerwert, Proc. Natl. Acad. Sci. U.S.A. **108**, 11435 (2011).

[9] G. Hummer, Mol. Phys. **105**, 201 (2007).

[10] Z. Cao, Y. Peng, T. Yan, S. Li, A. Li, and G. A. Voth, J. Am. Chem. Soc. **132**, 11395 (2010).

[11] A. Bankura and A. Chandra, J. Phys. Chem. B **116**, 9744 (2012) (the diffusion coefficients reported in units of $\text{Å}^2/\text{s}$ should be corrected to $\text{Å}^2/\text{ps}$ (private communication from A. Chandra)).

[12] D. Riccardi, P. King, X. Prat-Resina, H. Yu, M. Elstner, T. Frauenheim, and Q. Cui, J. Am. Chem. Soc. **128**, 16302 (2006).

[13] D. Riccardi, S. Yang, and Q. Cui, Biochim. Biophys. Acta **1804**, 342 (2010).

[14] C. Dellago and G. Hummer, Phys. Rev. Lett. **97**, 245901 (2006).

[15] C. Dellago, M. M. Naor, and G. Hummer, Phys. Rev. Lett. **90**, 105902 (2003).

[16] D. Marx, ChemPhysChem **7**, 1848 (2006).

[17] N. Agmon, Chem. Phys. Lett. **244**, 456 (1995).

[18] M. E. Tuckerman, A. Chandra, and D. Marx, Acc. Chem. Res. **39**, 151 (2006).

[19] D. Marx, M. E. Tuckerman, J. Hütter, and M. Parrinello, Nature (London) **397**, 601 (1999).

[20] R. Vuilleumier and D. Borgis, J. Chem. Phys. **111**, 4251 (1999).

[21] D. Asthagiri, L. R. Pratt, J. D. Kress, and M. A. Gomez, Proc. Natl. Acad. Sci. U.S.A. **101**, 7229 (2004).

[22] G. A. Voth, Acc. Chem. Res. **39**, 143 (2006).

[23] A. Chandra, M. E. Tuckerman, and D. Marx, Phys. Rev. Lett. **99**, 145901 (2007).

[24] D. Marx, A. Chandra, and M. E. Tuckerman, Chem. Rev. **110**, 2174 (2010).

[25] E. S. Stoyanov, I. V. Stoyanova, and C. A. Reed, J. Am. Chem. Soc. **132**, 1484 (2010).

[26] M. J. Cox, R. L. A. Timmer, H. J. Bakker, S. Park, and N. Agmon, J. Chem. Phys. **113**, 6599 (2009).

[27] A. Hassanali, M. K. Prakrash, H. Eshet, and M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. **108**, 20410 (2011).

[28] S. H. Lee and J. C. Rasaiah, J. Chem. Phys. **139**, 036102 (2013).

[29] S. H. Lee and J. C. Rasaiah, J. Chem. Phys. **135**, 124505 (2011).

[30] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, Nature (London) **414**, 188 (2001).

[31] M. C. Gordillo and J. Marti, Chem. Phys. Lett. **329**, 341 (2000).

[32] J. Dzubiella, R. J. Allen, and J.-P. Hansen, J. Chem. Phys. **120**, 5001 (2004).

[33] J. A. Thomas and A. J. H. McGaughey, Phys. Rev. Lett. **102**, 184502 (2009).

[34] M. Majumder, N. Chopra, R. Andrews, and B. J. Hinds, Nature (London) **438**, 44 (2005).

[35] J. Köfinger, G. Hummer, and C. Dellago, Proc. Natl. Acad. Sci. U.S.A. **105**, 13218 (2008).

[36] J. Köfinger, G. Hummer, and C. Dellago, Phys. Chem. Chem. Phys. **13**, 15403 (2011).

[37] D. J. Mann and D. Halls, Phys. Rev. Lett. **90**, 195503 (2003).

[38] L. Ojamäe, I. Shavitt and S. J. Singer, J. Chem. Phys. **109**, 5547 (1998).

[39] M. E. Tuckerman, D. Marx, and M. Parrinello, Nature (London) **417**, 925 (2002).

[40] See supplementary material at http://dx.doi.org/10.1063/1.4821764 for the setup of the initial configurations of H_3O^+ and OH^- in nanotubes, the mechanism of proton transfer, the mean square displacements of H_3O^+ and OH^- along water wires of different lengths, and the free energy barriers for proton transfer.

[41] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[42] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[43] V. R. I. Kaila and G. Hummer, Phys. Chem. Chem. Phys. **13**, 13207 (2011).

[44] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982).

[45] A. Shurki and A. Warshel, Adv. Protein Chem. **66**, 249 (2003).

[46] C. J. T. Grotthuss, Ann. Chim. (Paris) **LVIII**, 54 (1806).

[47] F. H. Stillinger and T. A. Weber, Mol. Phys. **46**, 1325 (1982).