Water Alignment and Proton Conduction inside Carbon Nanotubes

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First-principles molecular dynamics simulations have been carried out to investigate the structure, electronic properties, and proton conductivity of water confined inside single-walled carbon nanotubes. The simulations predict the formation of a strongly connected one-dimensional hydrogen-bonded water wire resulting in a net electric dipole moment directed along the nanotube axis. An excess proton injected into the water wire is found to be significantly stabilized, relative to the gas phase, due to the high polarizability of the carbon nanotube.

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Filling single-walled carbon nanotubes (SWCNTs) with chosen materials could lead to one-dimensional nanostructures with exciting new applications [1]. Many experiments have already been reported that demonstrate the feasibility of filling carbon nanotubes by a variety of methods [1–4]. The incorporation of water into SWCNTs has been demonstrated both experimentally [5] and theoretically [6] under ambient conditions. Based upon results from classical molecular dynamics (MD) simulations, Hummer and co-workers found that water spontaneously fills the hydrophobic channel of SWCNTs, with periodic transitions between filled and empty states [6]. In a separate study, Koga and co-workers found that, when confined inside a SWCNT under axial pressure, water can exhibit a first-order freezing transition to hexagonal and heptagonal ice nanotubes, and a continuous phase transformation into solidlike square or pentagonal nanotubes [7]. Water-filled carbon nanotubes might be expected to play a central role in future nanoscale devices, for proton storage and transport applications. The fulfillment of this possibility will require an indepth understanding of the structure and dynamics of carbon nanotube encapsulated water wires. Proton transport through the interior of a water-filled SWCNT may be highly efficient and analogous to transport through biological channels, depending on the stability of the endohedral hydrogen-bonded water wire.

Water wires are known to exist in naturally occurring biological systems; the purple bacteria *Rhodobacter spaeroides* [8] and the protein Gramicidin A (gA) [9] are two such examples. The one-dimensional water wires formed in these systems are believed to mediate proton translocation following a Grotthuss-type mechanism involving proton hopping rather than molecular diffusion [10]. Similarities in the structure of the hydrophobic channels of transmembrane proteins with SWCNTs suggest that the transport behavior of small molecules and ions through SWCNTs may parallel that of cell membrane transport proteins. In this Letter we present results from *ab initio* simulations of a one-dimensional water wire encapsulated inside a small diameter (6,6) SWCNT and the subsequent transport of an excess proton along this water wire.

The present simulations were based on density functional theory, using a pseudopotential method, as implemented in the VASP code [11]. The generalized gradient approximation, as parametrized by Perdew and Wang, is used for the exchange-correlation energy. The one-electron wave functions are expanded in a plane wave basis with an energy cutoff of 325 eV, using the Vanderbilt pseudopotentials of Kresse and Hafner [12]. The Brillouin zone is sampled using only the Γ point, which has already been shown to be accurate for describing the properties of bulk water with an identical energy functional and plane wave cutoff [13]. The primitive cell consists of a (6,6) SWCNT segment with dimensions $(15 \times 15 \times 12.4)$ Å. In order to determine the number of water molecules that fill a nanotube segment 12.4 Å in length under ambient conditions, a classical MD simulation was carried out with the nanotube immersed in a large bath of TIP3 water [14]. The simulation indicates that a maximum of six water molecules fill the nanotube at a temperature of 298 K, similar to the findings of Hummer *et al.* [6]. The *ab initio* MD simulations performed in this study were carried out with six water molecules encapsulated inside the (6,6) SWCNT with periodic boundary conditions applied only along the nanotube axis. Results are compared with a bulk water simulation for a system consisting of 27 molecules in a 9.32 Å cubic cell. A time step of 1 fs was used for each simulation and the temperature was controlled using a Nosé thermostat.

Previous simulations of water-filled SWCNTs indicate that, as water enters the tube, one-dimensional water wires form, with each water molecule hydrogen bonded to just two other water molecules (fewer than the three to four hydrogen bonds formed in bulk liquid water) [6,15]. As a consequence, the hydrogen bonds are expected to become well oriented inside SWCNTs [6]. Our simulations reveal the formation of a preferentially aligned water wire with each water dipole oriented in the same direction parallel to the nanotube axis. This is illustrated

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in Fig. 1(a) from a snapshot of the simulation at 298 K. Deviations in the structure of this well-ordered water wire were determined both by animation of the trajectory and analysis of the angles between the individual water dipole vectors with the nanotube axis, $\theta_{\mu z}$. Shown in Fig. 1(b) is a plot of the average dipolar angle, $\langle\theta_{\mu z}\rangle$, versus the trajectory simulation time. The small fluctuations in $\theta_{\mu z}$ are representative of a strong hydrogen-bonded, preferentially aligned water wire. Exchange of the hydrogen bonds via rotation of individual water molecules about the nanotube axis is observed to take place only at the higher temperature of 598 K. In addition, the reorientation of the water dipoles along the opposite direction of the nanotube is never observed, at either of the two temperatures. This is expected as previous studies of one-dimensional water wires by Pomès and Roux [16] indicate the presence of large free energy barriers for reorienting confined water wires, suggesting that dipolar flipping is a rare event under ambient conditions. Results from these simulations are consistent with the formation of well-aligned water wires inside the hydrophobic interior of carbon nanotubes, similar to those inside biological channels.

As seen in Fig. 1(a), there are two distinct O-H bonds in the nanotube confined water wire: those contributing to the hydrogen-bonded chain and those oriented radially outward that are not involved in hydrogen bonding. Since the hydrogen bonding polarizes, and subsequently lengthens O-H bonds, these two disparate covalent bonds should be spectroscopically distinguishable. We calculated the vibrational spectrum [Fig. 2(a)] for bulk water and the water-filled nanotube by a Fourier transform of the velocity autocorrelation function. The most noticeable difference is a large splitting of the broad O-H stretching band. Although no experimental Raman or IR spectra have been reported for water-filled nanotubes, the results presented here are supported by a previous study [15]. Analysis of the oxygen-hydrogen radial distribution function, $g_{\mathrm{OH}}(r)$, reveals a bimodal peak in the region corresponding to covalent bonding [Fig. 2(b)]. The positions of these two peaks are centered at 0.973 and 1.005 Å, equivalent to the average non-hydrogen-bonded and hydrogen-bonded O-H bond lengths, respectively. Constrained dynamics simulations indicate that the higher frequency peak (4050 cm^{-1}) corresponds to the O-H stretching mode for the non-hydrogen-bonded O-H bonds. We attribute this enhanced frequency to radial compression resulting from confinement.

As a consequence of the high polarizability of carbon nanotubes [17], the electronic properties, such as electric dipole moment, of the encapsulated water wire could be significantly altered. This could inadvertently affect the orientational dynamics and proton conductivity compared to water wires confined inside nonpolarizable channels. We calculated the dipole moments, μ, of two nonperiodic water-filled nanotube segments with the water wires annealed to a local minimum energy configuration. Nonperiodic nanotube segments of length 12.4 and 24.8 Å filled with 6 and 12 water molecules,

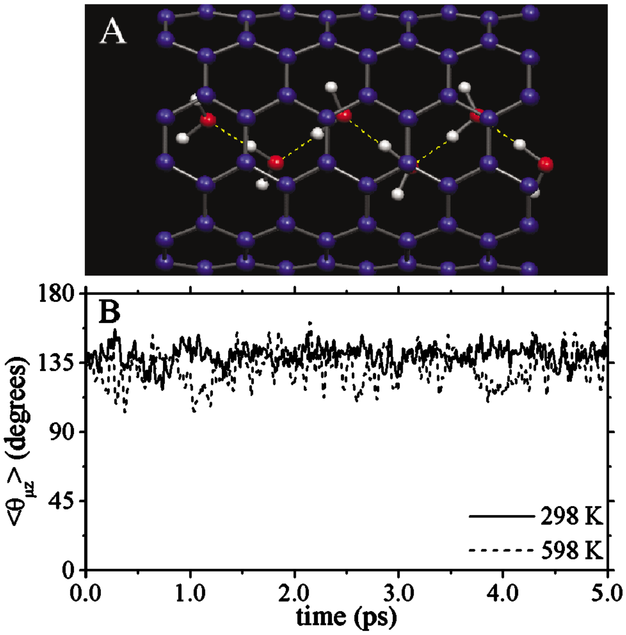

FIG. 1 (color). (a) Snapshot from the simulation at 298 K illustrating the preferential alignment of the encapsulated water wire. (b) Plots of the average dipolar angle versus simulation time at 298 and 598 K for 5 ps of simulation.

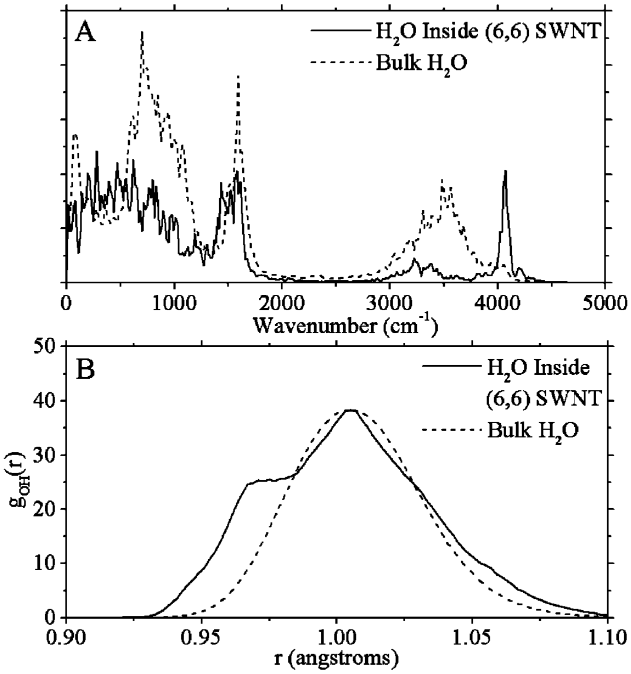

FIG. 2. Vibrational spectrum of bulk water (dashed line) and the water filled (6,6) SWCNT (solid line). (b) First peak in the oxygen-hydrogen radial distribution function, $g_{\mathrm{OH}}(r)$, corresponding to the covalent O-H bonds.

respectively, were used in the calculations, with supercell dimensions of (15 × 15 × 20) Å and (15 × 15 × 35) Å. The dipole moments were calculated from charge densities obtained from single point energy calculations on fully relaxed structures, as implemented in VASP. Listed in Table I are the components of the electric dipole vectors and the net dipole moments of the two different length water-filled nanotube segments, along with values for the water wire in the absence of the carbon nanotube. For the latter, single point energy calculations were performed on the same water wire, but with the SWCNT removed. The average dipole moment per water molecule is found to be approximately 0.75 D for the water-filled nanotubes, significantly smaller than the average of 2.7 D for water wires in the absence of the nanotube. This is the result of the water wire interacting with its image dipole induced on the carbon nanotube, effectively reducing the dipole moment of the composite system. The net result is a length dependent dipole moment of approximately 0.36 D/Å.

The efficiency for proton conduction along the encapsulated water wire is studied using a nonperiodic nanotube segment terminated with hydrogen atoms at each end. A nonperiodic model is used to avoid interactions of the excess charge with its image ion. The model used is similar to that shown in Fig. 1(a), except that the carbon atoms at each end are terminated with hydrogen atoms. The excess proton is injected through one end of the water wire and the dynamics is simulated at a temperature of 298 K, while constraining the positions of the terminal hydrogen atoms of the carbon nanotube segment. Although nuclear quantum effects are often important for proton transfer processes, path integral *ab initio* dynamics simulations of similar sized one-dimensional water wires were found to yield results nearly identical to the classical simulations [18]. The translocation of an excess proton along the water wire and the formation of extended $H_{2n+1}O_n^+$ complexes are investigated and compared for simulations in the absence and the presence of solvent end caps. For the latter, two different models are studied: one with three water molecules placed at each end of the water wire outside the nanotube, and the second consisting of a single hydroxide ion (OH^-) placed at the opposite end of the nanotube, mimicking a *p*H gradient. We have chosen as a reaction coordinate the geometric coordinate $q = \sum_{i=1}^{5}(r_{O_{i+1}H^*} - r_{O_iH^*})$ to identify the location of the excess proton along the water wire, where H^* is a hydrogen atom located between atoms O_i and O_{i+1}.

TABLE I. Dipole moments and dipole moment vectors of the water-filled (6,6) SWCNT segments.

H_2O wire length[a]	μ_x[b]	μ_y[b]	μ_z[b]	$\vert\mu\vert$[b]
6	0.05	−0.15	4.53	4.53
6(no CNT)[c]	0.49	−0.79	16.07	16.09
12	0.08	−0.22	9.00	9.00
12(no CNT)[c]	0.61	−0.79	32.63	32.65

[a] Number of molecules in the one-dimensional water wire.

[b] In units of debye.

[c] Water wire in the absence of the carbon nanotube.

Shown in Fig. 3 is the free energy profile for proton conduction through the interior of the SWCNT in the absence of end caps. The free energy profile is qualitatively similar to those obtained from previous studies of water wires in model hydrophobic channels [16], becoming flat along the region where the excess proton is located on one of the interior water molecules. This results in the excess proton becoming delocalized over the four inner water molecules of the water hexamer forming a stabilized eigen complex ($H_9O_4^+$) [19] (see the inset of Fig. 3), more extended than the Zundel ions ($H_5O_2^+$) observed inside the channel of gA [20]. Static calculations reveal that the binding energy to form the Zundel ion from H_3O^+ and H_2O decreases from −1.67 eV in vacuum to −1.35 eV inside the nanotube. The destabilization of the Zundel ion complex inside the carbon nanotube indicates an overall enhancement in the stabilization of the excess charge and a higher mobility of the proton along the nanotube confined water wire. This is further illustrated by the large stabilization of −0.84 eV for inserting the protonated water wire inside the carbon nanotube compared to −0.24 eV for the neutral water wire, suggesting that protonated water has a higher affinity to fill a carbon nanotube than neutral water. This enhanced stabilization is due to the effective dielectric of the carbon nanotube environment [17,21,22].

One would expect that when the ends of the nanotube are solvated with water molecules, this would facilitate complete conduction through the interior along the water wire. Previous *ab initio* MD studies of water wires

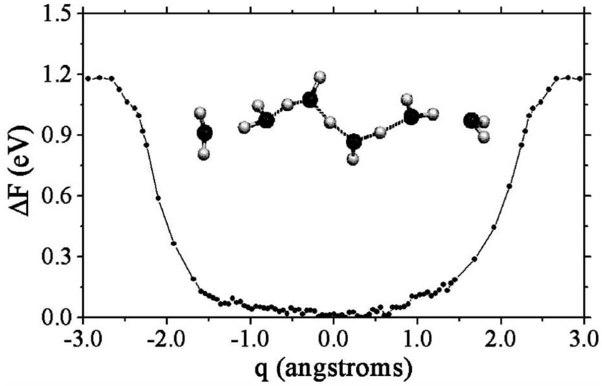

FIG. 3. Free energy along the reaction coordinate *q* for the translocation of an excess proton through the interior of the (6,6) SWCNT at 298 K. The excess proton is located on one of the end waters when $q \approx \pm 3.0$. Shown in the inset is the stabilized eigen complex formed along the encapsulated water wire.

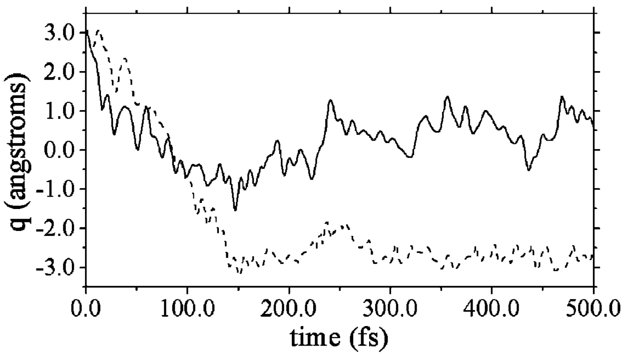

FIG. 4. Time evolution of the proton reaction coordinate at 298 K for proton conduction through the unsolvated water wire (solid line) and the water wire capped with a single hydroxide ion (dashed line). The excess proton is located on one of the end waters when $q \approx \pm 3.0$

encapsulated inside model nonpolarizable channels revealed that the excess proton became more mobile with the inclusion of capping waters, with occasional penetration into the water end caps [18]. The inclusion of three water molecules solvating each end of the nanotube was not found to significantly alter the proton transport dynamics. Although the excess proton reaches the end waters of the hexamer wire, it never penetrates the end caps during the 2 ps of dynamics. This indicates the presence of a free energy barrier for proton leakage out of the nanotube, providing further support for the charge stabilization inside the nanotube interior.

To include the effects of an electric field directed along the axis of the nanotube, we placed a single OH^- ion at the end of the nanotube opposite to the injected proton. The positions of the oxygen atom on the end water molecule and the atoms of the neighboring OH^- ion were held fixed to avoid proton transfer between the two. With the inclusion of the applied electric field, the excess proton traverses the water wire reaching the end water molecule within 150 fs at 298 K (Fig. 4). Since the end water and hydroxide ions are both fixed a distance of 3 Å apart, proton transfer to the OH^- ion does not occur and the excess proton remains on the end water molecule forming a stable hydronium ion (H_3O^+).

In summary, *ab initio* MD simulations of a water-filled (6,6) SWCNT reveal the formation of a well-aligned water wire resulting in a net electric dipole moment directed along the nanotube axis. Injection of an excess proton along this water wire leads to the formation of a stabilized $H_9O_4^+$ complex within the inner four water molecules, effectively trapping the proton inside the carbon nanotube. We find a significant stabilization of the water wire confined inside the nanotube compared to that in vacuum, with an additional stabilization of 0.6 eV for inserting a protonated water wire. This suggests that protonated water has a higher affinity towards filling a carbon nanotube than neutral water. The presence of neutral water end caps does not favor complete conduction through the nanotube interior, as the excess proton remains stabilized inside the carbon nanotube. This could result in important applications for charge (proton) storage devices. With the presence of a small applied electric field along the tube axis, the excess charge rapidly transports from end to end, reminiscent of biological proton conduction in a transmembrane environment. Future studies will focus on modeling the charge transport dynamics for SWCNT's completely immersed in a water bath along with exploring the pH dependencies.

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