# Notes

## H$^+$ Ion Migration in Water Filled Carbon Nanotube

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Extensive studies have been carried out on carbon nanotubes (CNT) since the discovery of this novel material,[1] and many of its interesting properties have been revealed. CNTs promise various technical applications, e.g., in making nanoscale electronic devices[2] or microscopic filters.[3] CNTs can be manufactured in various sizes, with diameters ranging from less than 1 nm to more than 100 nm.

Computational studies have suggested that CNTs can be designed as molecular channels to transfer water. A single-walled CNT, with a diameter of 8.1 Å, has been studied recently by molecular dynamics (MD) simulations.[4] The simulations revealed that the CNT was spontaneously filled with a single file of water molecules and that water diffused through the tube concertedly at a fast rate. Water filling is extremely sensitive to small changes of the nanotube-water interactions[4,5] imposed by chemical modification of the nanotube or electric fields created by charges and dipoles. The motion of water through CNTs can be described by a continuous-time, single-file random-work model.[6]

The mechanism of hydrogen ion migration in water filled carbon nanotubes (CNT), both naked and decorated by charges and dipoles, has been studied extensively for its intrinsic interest and as a simplified model for PT in biological channels[7-10] ever since molecular dynamics (MD) simulations[4,5] and experiments[11,12] showed that water quickly fills a narrow CNT through which it is conducted without appreciable friction. Hydrogen ion transport through a water filled CNT containing a one dimensional hydrogen bonded chain of water molecules is about forty times faster than in bulk water, but entry into the channel, from an external reservoir, is opposed by a high free energy barrier for desolvating a H$_3$O$^+$ ion. Dellago and Hummer[7] found, using the multi-state empirical valence bond model (EVB), that there is a large free energy barrier for entry and estimated a translocation rate of about 1 proton per hour at neutral pH from a reservoir. The mobility and desolvation penalty of a hydroxide ion moving in a CNT has not been studied.

In this note, we have employed a dissociation water model, the OSS2 model of Ojamäe *et al.*[13] to investigate H$^+$ ion migration in water filled CNT by classical MD simulation as a primary study. This water model is one of a family of potentials for solvated proton H$^+$(H$_2$O)$_n$ complexes in water called the OSSn potentials where n = 1 to 3 which are fitted to *ab initio* MP2 calculations.

## Molecular Models and MD Simulation Methods

In previous studies,[14] the OSS2 model of water molecule was used for MD simulations of pure water, oxonium ion monomers, protonated water clusters, and solvated H$^+$, and OH$^-$ ions in water. The induced dipole moment $\boldsymbol{\mu}_i$ at each oxygen site in the OSS2 model can be obtained self-consistently by imposing the conditions $dV_{el}/d\mu_k = 0$ (k = 1, 2, …, n$_O$):[13]

$$\mu_i = \alpha \left[ \sum_{j, j \neq i}^{n_O + n_H} \frac{r_{ij} q_j}{r_{ij}^3} S_{ij}^{cd}(r_{ij}) + \sum_{j, j \neq i}^{n_O} \frac{T_{ij} \cdot \mu_j}{r_{ij}^3} S_{ij}^{dd}(r_{ij}) \right] \tag{1}$$

where $V_{el}$ is the electrostatic energy, $n_O$ and $n_H$ are the numbers of oxygen and hydrogen atoms, $\alpha$ is the polariza bility of the induced dipole moment, and $S_{ij}^{cd}(r_{ij})$ and $S_{ij}^{dd}(r_{ij})$ are the electric field cutoff functions for charge-dipole and dipole-dipole interactions, respectively. Ewald summations were used in our simulations with the parameter for $\kappa = 5.0/L$ and the real-space cut distance $r_{cut}$ and $K_{max}$ chosen as 0.5 L and 7, respectively, where L is the length of the box. ($\sim 18.64$ Å for 216 water molecules) The equations of motion were solved using Gear's fifth order predictor-corrector algorithm[15] with a time step of $2 \times 10^{-16}$ second (0.2 fs). The simulations were first validated by checking our results against Ojamäe's work for pure water using the same OSS2 model. The calculated oxygen-hydrogen (O-H) radial distribution function and the hydration number n(r) for hydrogen in the 216 molecule pure water system are nearly identical, even though Ojamäe *et al.* used a different method[13] for the Ewald summations in the calculation of the induced dipole moment.

## Results and Discussion

To investigate the mobility of hydrogen ion in a narrow CNT by computer simulation using the OSS2 water model a single-walled uncapped 144 carbon atom (6,6) CNT of diameter 8.1 Å and length 13.4 Å is immersed in a bath of 216 water molecules. The length of the simulation cubic box in the direction of the axis of the tube which is held fixed at the center was 22.0 Å. At 298K the bath density corresponds to that of liquid water (0.60685 g/cm$^3$). The O atoms (not H
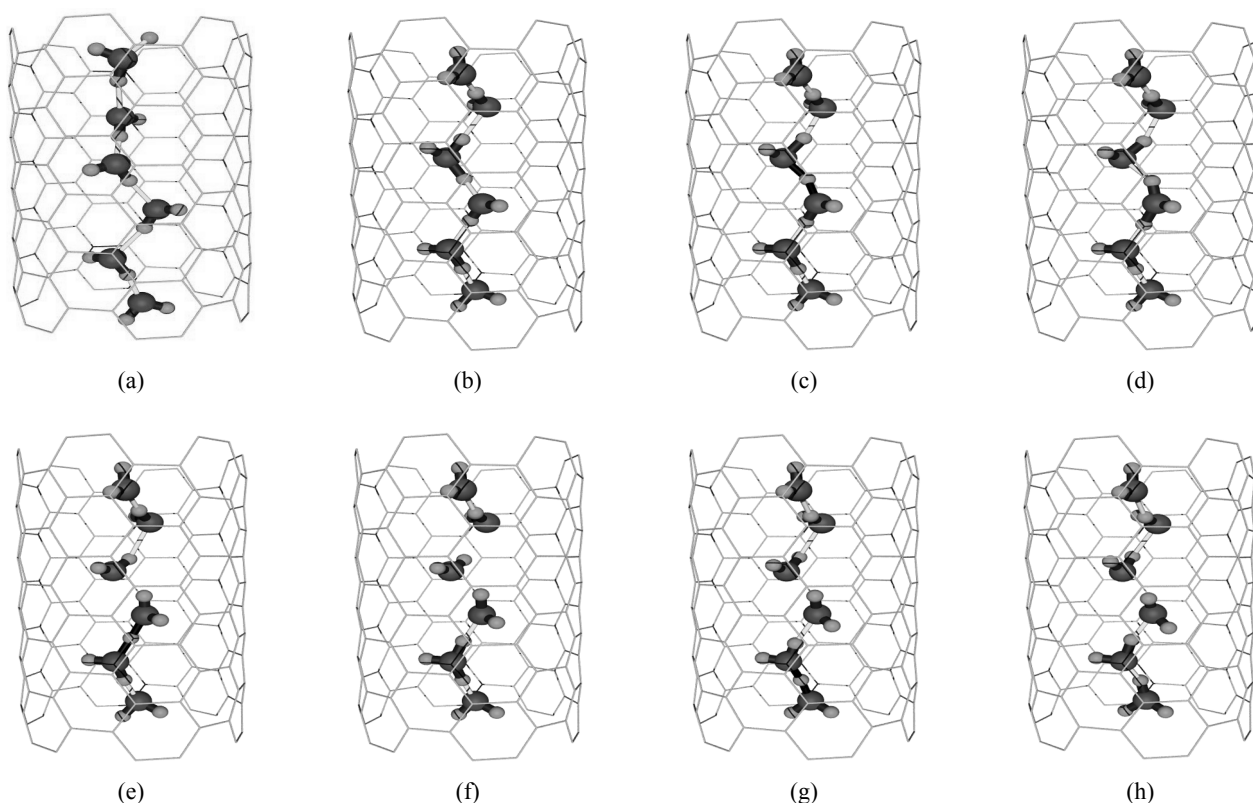
**Figure 1.** Representative configurations at intervals of 2 fs showing the mechanism of proton transfer of an $H_3O^+$ ion originally at the center a carbon nanotube (CNT) open to a water reservoir.

atoms) interact with C atoms in CNT through a simple Lennard-Jones (LJ) potential with LJ parameters of $\sigma = 3.2752$ Å and $\varepsilon = 0.11433$ kacl/mol.[4]

Despite its strongly hydrophobic character of the interaction between water and CNT, the initially empty central channel of the CNT is rapidly filled by water from the surrounding water reservoir, and remains occupied by about $6 \sim 7$ water molecules during the period of $\sim 100$ ps simulation. These water molecules form a hydrogen-bonded chain (Fig. 1(a)).

To study $H^+$ ion transport through a CNT using the OSS2 potential, an excess proton is initially inserted near a water molecule in the middle of an equilibrated quasi one-dimensional hydrogen bonded chain filling the nanotube in physical contact with the water reservoir (not shown). The inserted proton breaks the one-dimensional hydrogen-bonded chain and the water molecule in the middle of the chain immediately forms a $H_3O^+$ structure with this proton. This proton repels the H atom of the upper water molecule, which was hydrogen bonded to the O atom of the central water molecule, to form a new hydrogen bond to the O atom of the upper water molecule. This causes consecutive rotations of two upper water molecules resulted in forming new hydrogen bonds. The final structure was shown in Fig. 1(b). The one-dimensional chain has a symmetry on the central $H_3O^+$ structure flanked on either side by chains of hydrogen bonded water molecules with their dipoles oriented away from the excess charge as seen in Fig. 1(b). The central $H_3O^+$ structure is similar to an L defect[16] from which hydrogen bonds point away.

This equilibration of the excess charge takes nearly fifty time steps (10 fs) after which proton transport commences

along the chain, initiated by a thermal fluctuation. The transport of $H^+$ ion in the CNT takes place through a series of configurations that correspond to one dimensional Eigen ($H_3O^+$) and Zundel ($H_5O_2^+$) cations (Fig. 1(b) $\sim$ 1(h)). Succeeding snapshots at intervals of $\sim 2$ fs show the excess proton migrating from the center to the end of the nanotube in $\sim 60$ time steps (12 fs). Remarkably over a period of $\sim 200$ ps the proton was observed to migrate back and forth between one end of the nanotube and a defect near the center, never leaving the channel to enter the reservoir during the simulation time.
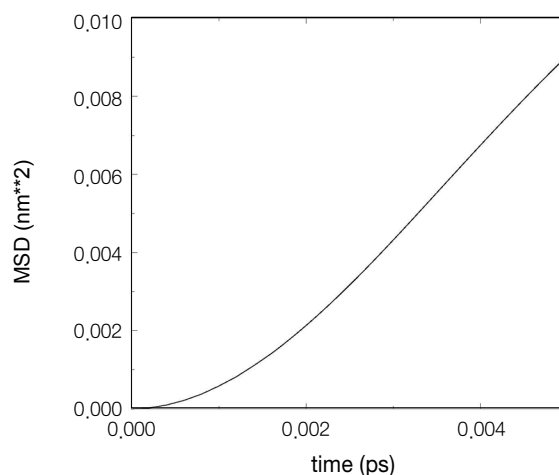


**Figure 2.** Mean square displacements (MSD) of the excess charge in carbon nanotube (CNT) for MD simulations of a $H_3O^+$ ion inside a carbon nanotube (CNT) immersed in water reservoir.

Entry as well as exit from the narrow channel of an excess proton is restricted.

We estimate the diffusion coefficient of the $H^+$ ion from the mean square displacement (MSD) of the excess charge in Fig. 2. The position of the excess charge is defined as the center of the charged cluster [Eigen ($H_3O^+$) or Zundel ($H_5O_2^+$) structure for $H^+$ transport], $\mathbf{r}(t) = \sum_k q_k \mathbf{r}_k(t)$, where $\mathbf{r}_k$ denotes the position of atom $k$ and $q_k$ is the electrostatic charge on the atom.[17] Fig. 2 shows the MSD of the excess charge of $H^+$ cluster (the below 4 O atoms and 9 H atoms in Fig.1) along the water chain for very short period (occurring $H^+$ transfer) of 0 $\sim$ 60 time steps for $H^+$ in CNT. We find D = 392 $\times$ $10^{-5}$ cm$^2$/sec, obtained from the slope between 0.002 $\sim$ 0.0045 ps, which is about 42 times the experimental diffusion coefficient of $H^+$ (D = 9.31 $\times$ $10^{-5}$ cm$^2$/sec); Dellago and Hummer[7] calculated the diffusion coefficient of the $H^+$ ion in a periodically water filled CNT to be about 40 times higher than that in bulk water.

In summary classical simulations using the OSS2 model potential derived from *ab initio* calculations can be used to understand the mechanism of $H^+$ ion transport in a narrow water filled channels which is in general agreement with previous *ab initio* and EVB studies of the same system. The diffusion coefficient of the hydrogen ion is about 40 times faster in the CNT than in bulk water. In spite of its high mobility, the $H_3O^+$ ion was never observed to leave the CNT and move into the reservoir during the time of our simulations.

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