Mechanism of Fast Proton Transport along One-Dimensional Water Chains Confined in Carbon Nanotubes

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Abstract: A reactive molecular dynamics simulation employing the multistate empirical valence bond (MS-EVB) methodology is reported for the hydration structure of an excess proton in a (6,6) carbon nanotube as well as for the mechanism of proton transport (PT) within the nanoconfined environment. The proton is found to be hydrated in a distorted Zundel cation ($H_5O_2^+$) form within the one-dimensional, confined water chain. Proton transfer events occur via a "Zundel−Zundel" mechanism through a transient $H_7O_3^+$ intermediate that differs significantly from the "Eigen−Zundel−Eigen" mechanism found in bulk water.

Proton transport (PT) in a nanoconfined environment is important, for example, in biological processes[1,2] and in fuel cell membranes.[3] Previous studies have shown that water forms a one-dimensional chain within the confines of a narrow hydrophobic carbon nanotube (CNT).[4] The rate of PT in these narrow structures[5,6] is much higher than that of bulk water, often by more than 1 order of magnitude.[5,6] The hydrophobic wall of a CNT provides an environment in which one-dimensional hydrogen bond (HB) networks replace the three-dimensional networks ordinarily present in bulk water. This difference in bonding may significantly affect excess proton hydration and transport. While the fast to slow PT transition as a function of the radius of hydrophobic nanotubes has been well discussed in our previous work,[5] we focus on this study of the mechanism of fast PT in a narrow (6,6) CNT. To understand the mechanism of fast PT in such a nanoconfined environment, we performed a third generation, multistate empirical valence bond (MS-EVB3)[7] molecular dynamics (MD) simulation in which an excess proton was hydrated in a one-dimensional, 48-water chain and confined to a narrow hydrophobic (6,6) CNT with a radius of 4.1 Å.[4−6] For details of MS-EVB methodology and simulation, we refer to our previous works.[1,5,7−10] For this system, we did not address how a proton is injected into the structure[11] or how water chain defects may influence the PT.[6] We show that (1) within a one-dimensional water chain confined to a CNT, a proton is mainly hydrated in a distorted Zundel ($H_5O_2^+$) form, unlike the distorted Eigen ($H_9O_4^+$) form seen in bulk water[8,12,13] and (2) PT in the CNT occurs via a "Zundel−Zundel" (ZZ) mechanism, in contrast with the "Eigen−Zundel−Eigen" (EZE) mechanism[12] of bulk water.

The rate of PT in bulk solution is influenced by the Grotthuss mechanism[14] in which interconversion arises between Eigen and Zundel hydration structures.[12,15,16] The superposition of EVB states in the MS-EVB methodology[7−9] describes both hydration structures
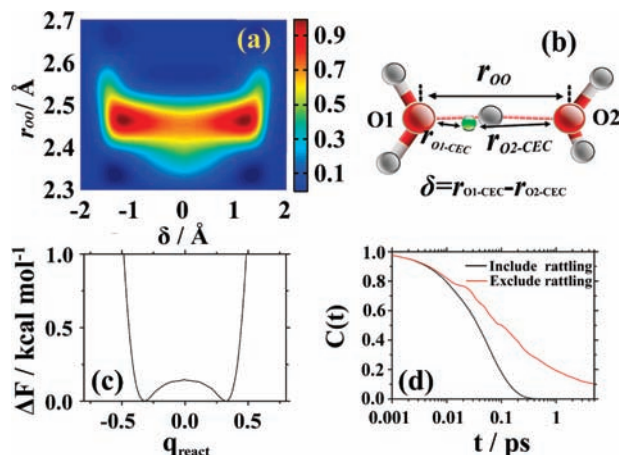
Figure 1. (a) Two-dimensional distribution function $P(\delta, r_{OO})$ in CNT. The definition of δ and r_{OO} are depicted in (b), and the green ball denotes CEC (see text). (c) Free energy profile of PT as a function of the reaction coordinate, and (d) presents the autocorrelation function of the lifetime of the hydronium cation.

and the corresponding charge defect delocalization associated with the excess proton in the hydrogen-bond network. In the MS-EVB model, the charge defect center of excess charge (CEC) is calculated from the vector $r_{CEC} = \sum_{i=1}^{N} c_i^2 r_{COC}^i$, in which c_i^2 is the probability and r_{COC}^i is the center of charge of the hydronium (H_3O^+) ion in the ith EVB state. Figure 1a shows the two-dimensional probability distribution $P(\delta, r_{OO})$ in a CNT, where δ is the difference between the distances of O1 and O2 from the CEC, as depicted in Figure 1b. Within this scheme, O1 and O2 represent the "special pair" of water oxygen atoms[12,15] that form hydronium ions with the largest and second largest probabilities, c_1^2 and c_2^2. The distance parameter $\delta = 0$ for an ideal Zundel cation and $|\delta| \approx 2.6$ Å for an ideal Eigen cation in bulk water. $P(\delta, r_{OO})$ in the simulated CNT peaks at $(\delta, r_{OO}) \approx (\pm 1.20, 2.50)$ Å, with non-negligible probability around $(\delta, r_{OO}) \approx (0.00, 2.47)$ Å. The value of $r_{OO} \approx 2.50$ Å is comparable with the 2.40 Å of an isolated gas phase Zundel species, which becomes distorted or stretched in the nanotube environment. The offset of the CEC with respect to the excess proton nucleus, as depicted in Figure 1b, highlights the associated charge defect delocalization. In this case, the shift of the CEC closer to O1 arises from an interaction with another water in the nanotube water chain via its hydrogen bonding to the hydronium ion centered on O1. The hydrated proton structures described above are in fact consistent with the presence of $H_7O_3^+$ cations, whose existence is also supported by a recent X-ray study of protons in hydrophobic nanotubes that estimated $r_{OO} \approx 2.567$ Å.[17] However, the high probability of r_{OO} around 2.5 Å within the $|\delta| < 1.5$ Å region in Figure 2a indicates that the excess proton in the filled nanotube

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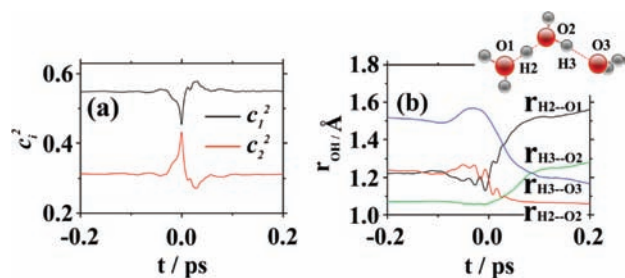
Figure 2. (a) Time evolution of the highest and the second highest EVB state probabilities, c_1^2 and c_2^2, of proton transfer reaction in a (6,6) CNT. (b) Time evolution of r_{H2O1} (black), r_{H2O2} (red), r_{H3O2} (green), and r_{H3O3} (blue) of PT reaction in CNT. The inset in (b) shows an $H_7O_3^+$ cation, with atom labels. The results are averaged over all reaction events with 0.2 ps before and after the PT instance, which is the onset of excess proton CEC transfer from the left of the hydronium centered on O2 to the right of it. The excess proton can be viewed as H2 before time origin and H3 after that.

one-dimensional water chain is usually hydrated as a distorted Zundel cation, since $|\delta| \approx 2.567$ Å for an ideal $H_7O_3^+$ cation in the nanotube.

Figure 1c shows the free energy, $\Delta F = -k_B T \ln P(q_{react})$, in which the reaction coordinate is defined by $q_{react} = c_1^2 - c_2^2$.[8] The central point, $q_{react} = 0$, corresponds to a symmetric Zundel cation in the CNT. The free energy barrier along this coordinate in the CNT is relatively small, in good agreement with a previous study of PT in hydrophobic nanotubes.[5] This thermodynamic measure supports that PT in a CNT should be much faster than PT in bulk water. Figure 1d shows the continuous time correlation function (TCF)[18,19] $C_c(t) = \langle h_i(0)H_i(t)\rangle/\langle h_i(0)h_i(0)\rangle$, as well as the pseudocontinuous TCF $C(t) = \langle h_i(0)h_i(t)\rangle/\langle h_i(0)h_i(0)\rangle$. In the former, $H_i(t) = 1$ if the ith oxygen atom is the hydronium oxygen from 0 to t, and zero otherwise. For the pseudocontinuous case, $h_i(t) = 1$ if the ith oxygen atom is the hydronium oxygen, and zero otherwise. $C_c(t)$ decays much faster in CNT than in bulk water,[19] while $C(t)$ decays much slower in CNT than in bulk water.[19] The bumps in the curves may be the result of frequent proton transfer events causing the proton to "rattle" back and forth between two oxygens (red line). The one-dimensional water chain hardly changes its structure in this nanoconfined environment, so it is reasonable to presume that slow $C(t)$ decay is symptomatic of sluggish water reorganization within the solvation structure.

We further examined the mechanism of PT by averaging over selected pair distances before and after the proton transfer event. The proton transfer event moment is defined by the switch of the EVB state identity with the largest probability. Figure 2a plots the time evolution of c_1^2 and c_2^2 over the interval extending from 0.2 ps before to 0.2 ps after the time origin, averaged over all observed events. Generally, in the confined nanotube environment $c_1^2 \geq 0.6$ shows that the excess proton CEC is located on a given $H_7O_3^+$ structure, while $c_1^2 < 0.6$ corresponds to a distorted Zundel cation. The scenario shown in Figure 2a is quite different from that of the EZE mechanism in bulk water. Note that c_1^2 is slightly smaller than 0.6 and c_2^2 is slightly larger than 0.3 over a wide time window, again indicating that the proton in the present simulation is mostly hydrated in a distorted Zundel state. At $t = 0.03$ ps, c_1^2 increases to 0.58 while c_2^2 decreases to 0.28, indicating that a distorted $H_7O_3^+$ forms at that instant. However, the evolution of c_1^2 and c_2^2 also indicates that another Zundel cation is rapidly restored after $t = 0.03$ ps. These observations further support the notion that PT in a confined CNT occurs by a mechanism that differs substantially from that observed for bulk water.
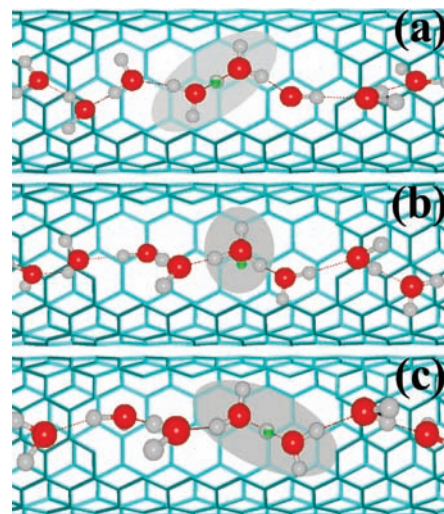
Figure 3. Snapshots for a PT event of an excess proton in one-dimensional water chain confined in a (6,6) CNT. (a) Zundel at $t = -0.17$ ps; (b) $H_3O_7^+$ at $t = 0.03$ ps; and (c) Zundel at $t = 0.05$ ps. The green ball denotes CEC.

To characterize proton transfer events from a geometrical standpoint, we analyzed the evolution of selected H---O distances. A proton transfer event is defined as transference of the excess proton CEC from the O1---O2 interval to the O2---O3 interval, as depicted in the insets of Figure 2b. The same definition is used in one of our previous studies.[20] The time dependent curves of r_{H2O1}, r_{H2O2}, r_{H3O2}, and r_{H3O3} are shown in Figure 2b. At $t = -0.2$ ps, $(r_{H2O1}, r_{H2O2}) = (1.21, 1.23)$ Å in the CNT. The distances in this illustration highlight the distorted Zundel structure of the hydrated proton. The crossover of r_{H2O2} and r_{H3O2} at 1.10 Å and $t = 0.03$ ps in Figure 2b occurs at the same time as the bump in Figure 2a, demonstrating that the intermediate structure $H_7O_3^+$ is briefly formed. The transport of the CEC from the O1---O2 interval to the O2---O3 interval corresponds to a hop (from a classical mechanical point of view) of the excess proton nucleus from H2 to H3. At $t = 0.20$ ps, the values become $(r_{H3O2}, r_{H3O3}) = (1.28, 1.18)$ Å in the CNT, which corresponds to a new Zundel-like structure. Therefore, geometrical considerations of the proton transfer events in a one-dimensional, CNT-confined water chain support the presence of a new ZZ mechanism that differs from that of bulk water due to the nanotube confinement effects. Figure 3 shows successive snapshots of a single proton transfer event in a CNT, along with the CEC position at each time as the green ball. The ZZ mechanism is apparent, as is the intermediate $H_7O_3^+$ ion between the successive Zundel cations.

In summary, we have presented the hydration structure and corresponding PT behavior of an excess hydrated proton in a one-dimensional water chain contained within a (6,6) CNT. The formation of a three-dimensional, coordinated hydronium cation is suppressed due to the confinement of the hydrophobic CNT, and the existence of a distorted Zundel hydrated proton structure instead results. We also show that proton transfer events occur in CNTs via a "Zundel−Zundel" (ZZ) mechanism, which is quite different and more efficient than the "Eigen−Zundel−Eigen" (EZE) mechanism present in bulk water. This study therefore provides important new insights into the possible existence and mechanism of fast PT in narrow hydrophobic channels.

Supporting Information Available: Computational method of the MS-EVB MD simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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