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## One dimensional confinement inhibits water dissociation in carbon nanotubes

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# One dimensional confinement inhibits water dissociation in carbon nanotubes

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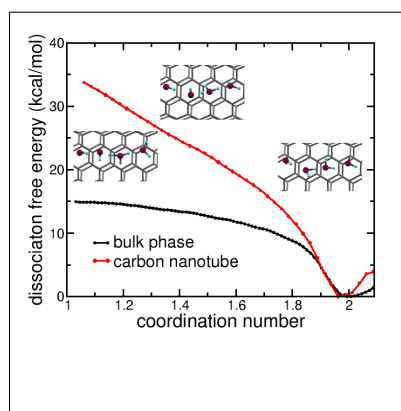
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## Abstract

The effect of nanoconfinement on the self-dissociation of water constitutes an open problem whose elucidation poses a serious challenge to experiments and simulations alike. In slit pores of width  $\approx 1$  nm, recent first-principles calculations have predicted that the dissociation constant of  $\text{H}_2\text{O}$  increases by almost two orders of magnitude [*Phys. Rev. Lett.* **2017**, *119*, 056002]. In the present study, QM-MM molecular dynamics combined with a biased sampling strategy, are employed to compute the dissociation free-energy profile of water in a (6,6) carbon nanotube. According to our results, the equilibrium constant  $K_w$  drops by 3 orders of magnitude with respect to the bulk phase value, at variance with the trend predicted for confinement in two dimensions. The higher barrier to dissociation can be ascribed to the undercoordination of the hydroxide and hydronium ions in the nanotube, and underscores that chemical reactivity does not exhibit a monotonical behavior with respect to pore size, but may vary substantially with the characteristic length-scale and dimensionality of the confining media.

## Graphical TOC Entry



First-principles free energy calculations reveal that the self-dissociation constant of water confined in a carbon nanotube drops by 3 orders of magnitude with respect to its value in bulk.

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Following the study by Hummer and collaborators reporting the spontaneous filling and transport of water through a carbon nanotube (CNT),<sup>1</sup> many experimental and theoretical investigations have sought to characterize the structure, the diffusivity, and the phase behavior of H<sub>2</sub>O confined in these carbon nanostructures.<sup>2–16</sup> A wealth of unexpected properties have been postulated arising from one-dimensional confinement in these systems, including fast proton transport,<sup>2,3,10–14</sup> superpermittivity,<sup>17</sup> high-polarization and ferroelectricity.<sup>3,8</sup> Based on these findings, CNTs have been considered as model structures for hydrophobic channels in membranes or proton-transferring proteins,<sup>1,18</sup> as well as candidates for nanotechnological applications as dielectric materials<sup>8,17</sup> and nanovalves.<sup>5</sup>

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Despite all these significant advances in the physical characterization of water in small-diameter CNTs, a fundamental question still remains unanswered: how is self-dissociation of H<sub>2</sub>O affected by 1D confinement? In (6,6) carbon nanotubes, with a diameter of 8.1 Å, water molecules organize in one-dimensional ordered chains, where the diffusion of protons was found to be several times faster than in bulk.<sup>2,3,10–14</sup> This surprising behavior has been attributed to a proper molecular alignment that makes proton transport possible with almost no reorganization of the hydrogen bonds, at variance with the corresponding process in solution,<sup>19–22</sup> and to a highly polarized structure that stabilizes the proton in low coordination states. At the same time, molecular simulations indicate that the static dielectric constant of water in small CNTs is an order of magnitude higher than in bulk.<sup>17</sup> It has recently been argued that the rise in permittivity resulting from confinement in slit nanopores is responsible for an increase in the dissociation constant  $K_w$  by a factor of 55.<sup>23</sup> In principle, a highly dielectric medium would favor dissociation through the stabilization of the hydronium and hydroxide ions. The question we address in this letter is whether this effect is also operative in a carbon nanotube, where the confining conditions are more extreme.

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From a more general standpoint, the way in which the dissociation of water changes in situations that are different from the bulk such as near interfaces or in secluded porous media, remains a very relevant, open and rather challenging problem for both experimentalists and

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3 theoreticians.<sup>24</sup> How the pK<sub>w</sub> depends on pore radius and on the nature of the interface, is  
4 a central—but essentially unresolved—question. An exception is a recent study by Muñoz-  
5 Santiburcio and Marx mentioned above,<sup>23</sup> where first-principles simulations were employed  
6 to estimate the self-dissociation of water confined between FeS layers at high temperature and  
7 pressure. The authors found that in this environment, the dissociation free-energy decreases  
8 by more than 15%, an effect that was explained in terms of the increase in the dielectric  
9 constant that results from confinement.<sup>23</sup>

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11 In the present letter we investigate the self-dissociation of water in (6,6) carbon nan-  
12 otubes and show that confinement in this case results in a decrease in the  $K_w$ . Dissociation  
13 free-energies were obtained from QM-MM Car-Parrinello molecular dynamics simulations  
14 combined with the umbrella sampling scheme, adopting as the reaction coordinate, the pro-  
15 ton coordination  $n_H$  introduced by Sprik:<sup>25</sup>

$$n_H(j) = \sum_i^{N_H} \frac{1}{\exp[\kappa(r_i - r_c)] + 1} \quad (1)$$

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17 where  $N_H$  is the number of H atoms in the system,  $r_i$  the distance from oxygen atom  $j$  to pro-  
18 ton  $i$ , and the parameters  $\kappa$  and  $r_c$  are chosen to produce a continuous coordination index.<sup>25</sup>  
19 The bias in the umbrella sampling protocol drives  $n_H$  from 2 to 1, forcing the separation of a  
20 proton from a given water molecule. Molecular dynamics simulations at 300 K were carried  
21 out with a DFT QM-MM periodic approach<sup>26</sup> implemented in the Quantum-Espresso pro-  
22 gram.<sup>27</sup> Water molecules were modeled quantum-mechanically, whereas the carbon atoms  
23 were represented classically (further details are provided in the SI). A snapshot illustrating  
24 the model system is presented in Figure 1. The image corresponds to a configuration ex-  
25 tracted from the umbrella sampling trajectory with  $n_H=1.4$  where it is possible to see the  
26 hydroxide-hydronium ion pair.

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28 Figure 2 shows the free-energy profiles for the self-dissociation reaction  $2H_2O \rightarrow H_3O^+ + OH^-$ ,  
29 expressed in terms of the coordination number defined in equation 1. The minima at  $n_H \approx 2$   
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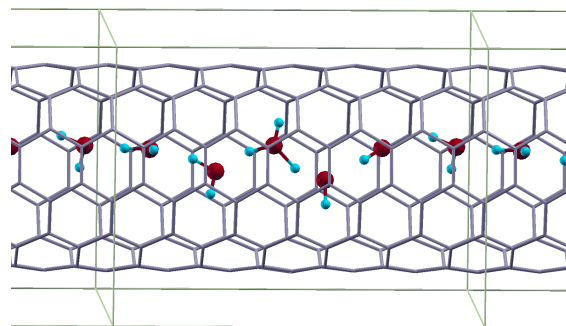


Figure 1: Model structure of water confined in a (6,6) carbon nanotube, displaying the boundaries of the periodic cell. The image corresponds to a configuration extracted from the Umbrella sampling simulation with  $n_H=1.4$ .

correspond to the reactant; as the reaction coordinate evolves from 2 to 1, a proton is transferred to a neighboring water molecule to produce a hydronium and leaving behind a hydroxide anion. At this point it is important to notice that, in order to extract  $K_w$ , it is necessary to establish what value of  $n_H$  corresponds to the product state. A reasonable criterion is to consider that the reaction is complete when  $n_H$  is equal to the coordination number corresponding to aqueous  $\text{OH}^-$ . This limit is indicated by the black vertical dotted line in Figure 2, computed as the average  $n_H$  value for a single hydroxide in a supercell of 64 water molecules. It is certainly larger than 1.0 due to the hydrogen-bonds that make fractional contributions. Thus, this line is used to define the end of the reaction. The free-energy barrier  $\Delta G_{bulk}$  obtained in this way for the bulk phase with a model system of 64 water molecules in periodic conditions, turns out to be nearly 30% below the corresponding experimental value at 300 K. This underestimation, similar to that reported by Muñoz-Santiburcio and Marx,<sup>23</sup> can be ascribed to the exchange-correlation functional, and possibly also to the fact that the limited system sizes and timescales do not allow for the ions to separate from each other forming a solvent separated product state. The biased sampling scheme drives the system to a dissociated state in which the hydronium and hydroxide species are in contact, or separated by at most two bonds. Presumably, a further delocalization of the ions would yield a marginal additional enthalpic cost together with an entropic stabilization that might account for part of the difference between the experimental and the computed values.

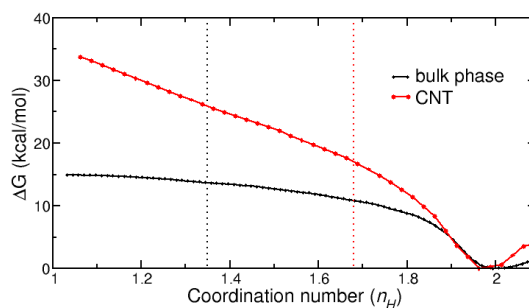


Figure 2: Free energy profiles computed for the dissociation of water in the bulk phase and in a (6,6) carbon nanotube. The dotted vertical lines indicate the value of  $n_H$  corresponding to the final product state in each environment.

In the same Figure the free-energy corresponding to water dissociation inside the nanotube,  $\Delta G_{CNT}$ , is depicted in red. It scales up much faster with the decrease in coordination number than does  $\Delta G_{bulk}$ . Therefore, the value of  $K_w$  is extremely sensitive to the election of the reaction end-point. If the same criterion as in bulk is adopted here to mark the end of the reaction, the final  $n_H$  turns out to be 1.68. This value, signalled in Figure 2 by the red vertical line, corresponds to the coordination of a hydroxide anion in a water-filled nanotube. Such a large value is explained by the proton-avidity of the undercoordinated  $\text{OH}^-$  in the nanopore, which tends to abstract the hydrogen atoms from neighboring water molecules, yielding very short  $\text{H} \cdots \text{OH}^-$  distances. In fact, inspection of the trajectories shows that these protons are essentially shared between the hydroxide and the two surrounding water molecules intermittently resembling  $\text{H}_3\text{O}_2^-$  or  $\text{H}_5\text{O}_3^-$  anions, resulting in strong fluctuations in  $n_H$  between 1.1 and 1.9 and producing an unexpectedly high mean value for the coordination number of the anion, much larger than the one in bulk.

In any case, regardless of the gauge adopted to specify the ending point, Figure 2 reveals that self-dissociation will be severely inhibited in this nanotube. In particular, assuming that the final state coincides with the vertical line implies an increase in the free-energy barrier by a factor of 1.25 and a value of  $K_w$  of  $\sim 3 \times 10^{-17}$  in the CNT. Noticeably, this result appears to be independent of the nature of the pore but is essentially the outcome of

confinement. Figure 3 shows that the alteration of the nanopore properties does not have a significant impact on the computed  $\Delta G_{CNT}$ . This Figure presents the effect on the free-energy profiles of: (i) a change in the water-carbon interactions, where the C-O  $\sigma$  and  $\epsilon$  QM-MM parameters have been adjusted to reproduce the DFT forces; (ii) the suppression of nanopore thermal vibrations; and (iii) the doubling of the supercell. All these modifications have a marginal effect on  $\Delta G_{CNT}$ , indicating that this behavior of  $K_w$  originates from the quasi one-dimensional alignment exerted by confinement within hydrophobic or weakly interacting walls.

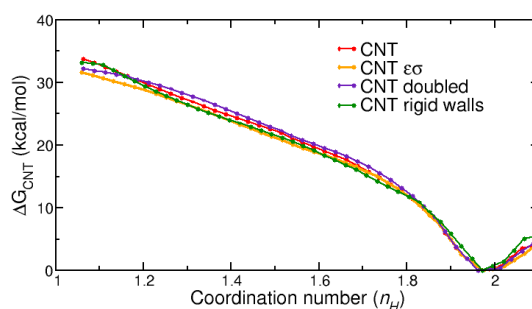


Figure 3: Free energy profiles computed in the (6,6) carbon nanotube altering the simulation conditions. The labels “ $\epsilon\sigma$ ”, “doubled”, and “rigid walls”, represent, respectively, a change in the QM-MM Lennard-Jones parameters, the duplication of the supercell size, and the freezing of the carbon atoms.

How can this drastic drop in the dissociation constant be explained? As mentioned earlier, in a recent study of the  $pK_w$  in slit pores, the reason for an enhanced dissociation was attributed to the high dielectric constant of confined water.<sup>23</sup> These authors have suggested that this phenomenon could be also relevant in carbon nanotubes,<sup>28</sup> but our simulations have shown the opposite, pinpointing that in the present case the trend reverts to a non-dissociative behavior. Importantly, in the slit pore, the solvation structure of aqueous  $H^+$  and  $OH^-$  was found to be essentially the same as in the bulk limit.<sup>23</sup> In the (6,6) CNT environment, instead, the solvation structures of the hydroxide and hydronium ions are significantly affected, exhibiting a number of hydrogen bonds always smaller than in bulk. Figure 4 depicts the oxygen-oxygen radial distribution function and the running coordination



number for each species, reflecting a considerable undercoordination in the nanotube with respect to the bulk phase. There have been numerous studies investigating the solvation structure of aqueous hydronium and hydroxide ions in the bulk, at interfaces and also in water clusters.<sup>20,29–34</sup> In the bulk phase, the hydronium ion donates 3 strong and accepts one weak hydrogen bond, while the hydroxide accepts 4 strong and donates one weak hydrogen bond. In the nanopore, however, both ions form only two hydrogen bonds with the surrounding water molecules, evinced in both Figures 4 and 5, where the later displays the distribution of the number of hydrogen bonds for each ion in the bulk and in the pore. Clearly, the decay of the dissociation constant in the CNT results from the destabilization of the hydroxide and hydronium species, which cannot be surrounded by a solvation shell. The dissociation free-energy is seemingly much more sensitive to solvation than to the dielectric or the polarization effects arising from confinement, which may modulate the value of  $\Delta G$  only by a small fraction.

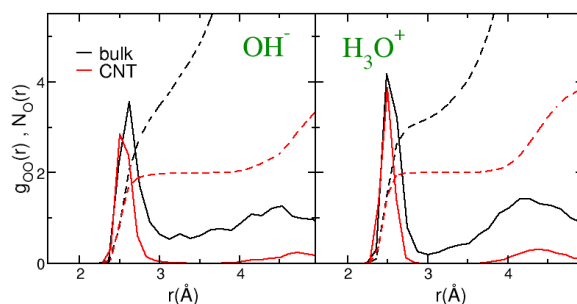


Figure 4: Oxygen-oxygen radial distribution functions (solid lines) and running coordination numbers (dashed lines) for  $\text{OH}^-$  (left panel) and  $\text{H}_3\text{O}^+$  (right panel). Results in the bulk and in the CNT are depicted in black and in red respectively.

In conclusion, these results highlight that the effect of confinement on the  $\text{pK}_w$  cannot be generalized from previous results, because it may vary substantially depending on the size and dimensionality of the confining media. With the evidence at hand, it seems plausible to conclude that under nanometric confinement, a rise in the self-dissociation constant can be expected due to the increase in the permittivity of the confined fluid, pro-

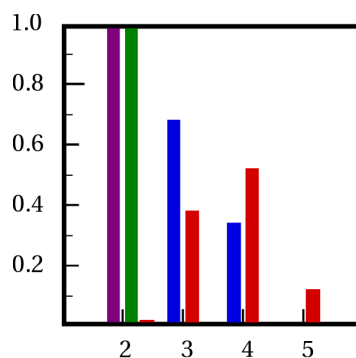


Figure 5: Distribution of the number of hydrogen bonds formed by the hydronium and the hydroxide ions. Blue: hydronium in the bulk phase. Red: Hydroxide in the bulk phase. Green: hydronium in the CNT. Indigo: hydroxide in the CNT.

viding that the solvation structure of the dissociation products  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  are preserved. At subnanometer confinement, however, or in low-dimensional geometries that restrain the hydrogen-bond network around the ions, undercoordination will strongly dominate the chemical equilibrium. All in all, the dependence of  $\text{pK}_w$  with pore size is not a monotonical function with a previsible trend, but may vary in sharp and unexpected ways in severely confined environments.

## Supporting Information Available

Methodological details and an analysis of the QM-MM forces. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

## Acknowledgement

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