

Supporting Information:

**“One dimensional confinement inhibits water
dissociation in carbon nanotubes”**

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Methodology

All calculations were performed using DFT in periodic boundary conditions employing the Quantum-Espresso code.¹ Water molecules were modeled with the BLYP exchange-correlation functional^{2,3} including Grimme’s Van der Waals corrections.⁴ The Kohn-Sham orbitals and the charge density were expanded in plane-waves basis sets up to a kinetic energy cutoff of 20 and 160 Ry, respectively. Vanderbilt ultrasoft pseudopotentials⁵ were adopted to compute the total energies and forces. Molecular dynamics simulations were carried out with the Car-Parrinello method⁶ with an effective electron mass of 400 a.u., coupled to a Nosé-Hoover thermostat at 300 K and a time step of 0.145 fs. Reciprocal space sampling was restricted to the Γ -point.

Water in carbon nanotubes was modelled using hybrid QM-MM simulations, employing our implementation embedded within the Quantum-espresso package.⁷ The carbon nanotube was described according to the force-field optimized by Kaukonen and co-authors.⁸ The supercell dimensions were $11.11 \text{ \AA} \times 11.11 \text{ \AA} \times 14.76 \text{ \AA}$, containing six water molecules and a (6,6) carbon nanotube of 144 atoms aligned with the z -axis in periodic boundary conditions.

Dissociation free-energies were obtained from Car-Parrinello molecular dynamics simulations combined with the umbrella sampling scheme,⁹ adopting as the reaction coordinate the proton coordination n_H introduced by Sprik:¹⁰

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

where N_H is the number of H atoms in the system, r_i the distance from oxygen atom j to proton i , and the parameters κ and r_c are chosen to produce a continuous coordination index.¹⁰ All protons lying closer than $r_c - \kappa^{-1}$ add one to this sum, those further than $r_c + \kappa^{-1}$ are excluded, and those protons located in between contribute with a fractional weight, thus providing a continuous measure of the number of H atoms bound to the oxygen j that is suitable as a reaction coordinate. For κ and r_c we employed respectively the values of 10

\AA^{-1} and 1.38 \AA , as proposed in reference [10].

The major limitation of the present reaction coordinate seems to be the inability to completely separate the proton from the parent H_2O molecule, driving the system to a dissociated state in which the hydronium and hydroxide species are in contact, or separated by at most two bonds. This weakness is more manifest in the nanotube, where the ion pair $\text{H}_3\text{O}^+ \cdots \text{OH}^-$ remains in contact along the full trajectory even for values of n_H very close to 1. Presumably, the diffusion of the hydronium away from the hydroxide might be responsible for an additional free-energy amount, which would have a negative entropic plus a positive enthalpic contributions, and that may account for part of the difference between the experimental and computed values. A proper determination of this contribution would entail a multi-dimensional sampling scheme capable to map the free-energy surface as a function of at least two reaction coordinates (e.g., n_H and H-O distance), using system sizes beyond the current computational possibilities. However, our educated guess with the evidence at hand is that this contribution should be marginal. On the one hand, our free-energy profile appears converged with respect to system size: the curve corresponding to a model of 32 water molecules does not differ significantly from that of 64 molecules. On the other hand, the bulk dissociation profiles obtained from those trajectories that end up in a separation of a couple of bonds between the hydronium and the hydroxide, are indistinguishable from those profiles derived from trajectories where the ions remain in contact. Moreover, preliminary results from our group involving classical molecular dynamics simulations indicate that the $\text{H}_3\text{O}^+ \cdots \text{OH}^-$ interaction falls in the order of kT . In view of this, we deem the magnitude of this missing contribution not significant in comparison with that of the barrier, and hence the proton coordination a good reaction coordinate for this process.

The thermodynamic integration was carried out according to the Umbrella sampling protocol, in which the total energy was modified by adding a harmonic potential of the form

$$V_u(t) = \frac{1}{2}k_u(n_H(t) - n_H^0)^2$$

where $n_H(t)$ is the instantaneous proton coordination introduced in equation (1), and n_H^0 , the reaction coordinate, was kept constant throughout the dynamics. Aside from this potential, no other constraint was applied during the simulation. To compute a single free-energy profile, around 10 molecular dynamics trajectories were performed, each one for a different value of n_H^0 . This parameter was varied between 1.0 and 2.0, corresponding to the dissociated and molecular states, respectively. The force constant k_u was adjusted to achieve an appropriate sampling. Its optimal value depends on n_H^0 , and must be large enough to constrain the dynamics around the desired reaction coordinate, but not as large as to deteriorate the overlap between adjacent windows. In the present case the optimized values fell between 0.3 and 1.8 a.u. A histogram was produced for each value of n_H^0 , reflecting the (logarithmic) probability distribution around that value of the reaction coordinate. The Figure below illustrates these histograms for the case of bulk water at room temperature. For each n_H^0 , initial configurations were extracted from thermalized classical molecular dynamics, and thereafter, QM-MM trajectories were run for 17.4 ps, of which the initial 5.8 ps were discarded. These time-lengths were checked to provide converged free-energy curves. Every histogram was then weighted by the exponential factor $\exp[-\frac{1}{2}k_u(n_H - n_H^0)^2]$, to extract a piece of curve representing the free energy around n_H^0 . Finally, the free energy profile was constructed by matching these pieces corresponding to adjacent values of n_H^0 , according to the Weighted Histogram Analysis Method.^{11,12}

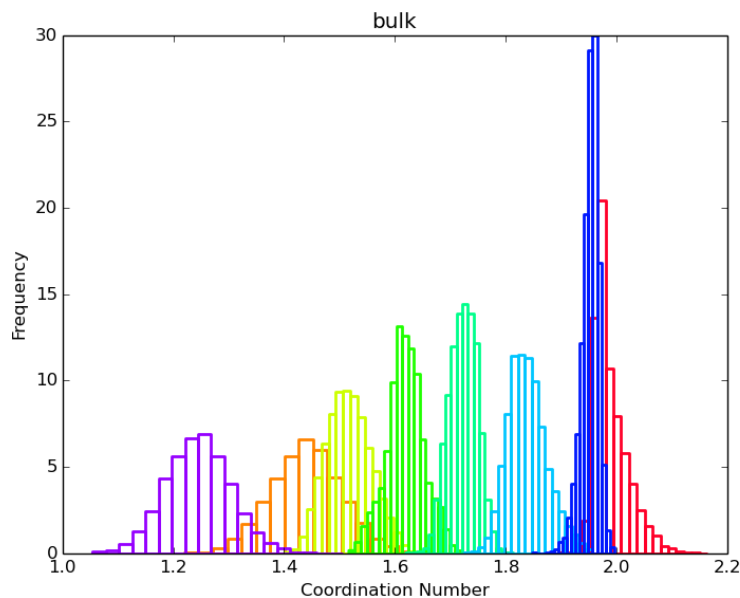


FIG. S1

QM-MM forces

Interactions between the QM water molecules and the MM carbon atoms were modeled using the Lennard-Jones parameters published in reference [8]. Figure S1 displays the water-CNT forces as a function of the O-C distance for different situations. In these calculations the plane of the H_2O molecule was oriented perpendicular to the z -axis. The dotted curves depict results from pure DFT calculations, in which either the oxygen (black curve) or one hydrogen (red curve) atom is facing the CNT inner surface. The green line corresponds to the parameters proposed in the literature⁸ ($\sigma=5.756$ a.u., $\varepsilon=0.3845$ kcal/mol), whereas the indigo and brown lines were obtained by modifying one or both of these parameters to 6.5 a.u. and 0.1 kcal/mol.

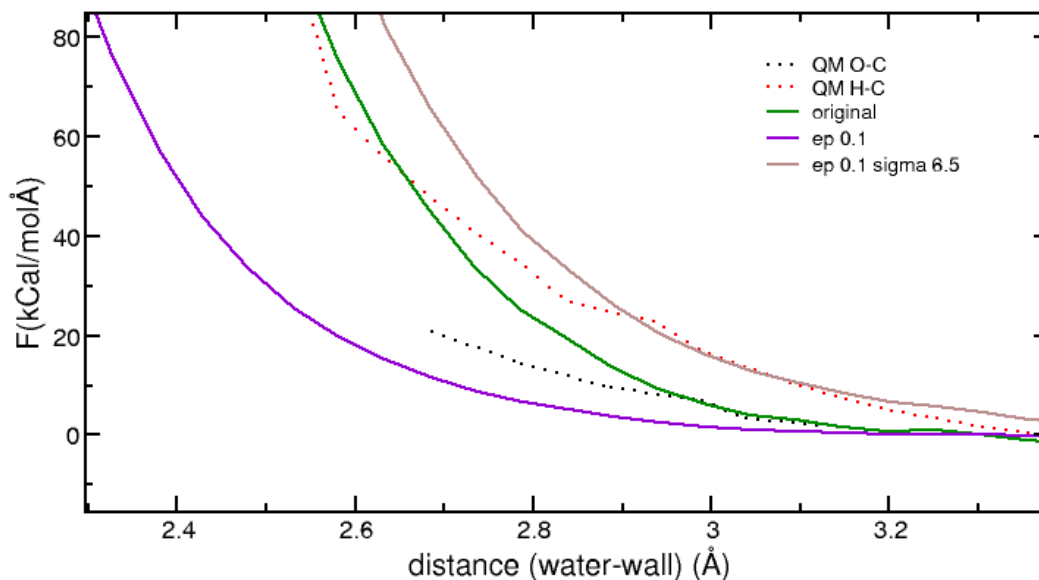


FIG. S2

It must be noticed that for distances below ~ 2.9 Å the potential becomes too repulsive, so that such region is hardly accessible during the dynamics and it is therefore irrelevant. On the other hand, in the QM-MM calculations the potential is independent from the orientation of the H_2O molecule (because it is a function of the C-O distance only), and thus it is not possible to faithfully reproduce the orientation-dependent DFT forces with this QM-MM model. However, this limitation does not seem to play an important role in determining the pKw, as shown by Figure 3 of the main manuscript.

The effect of temperature

DFT molecular dynamics have been shown to produce an overstructured phase with exacerbated melting temperatures, more representative of a glassy state than of a liquid.¹³ The adoption of van der Waals corrections should largely correct this flaw.¹³ In any case, we have explored the effect of temperature on the free-energy profiles, to find that the barrier to dissociation becomes higher with T. Note that in spite of this, the pKw diminishes with increasing

temperature because of its exponential dependence with T^{-1} , i.e, $K_w = \exp[-\Delta G/RT]$. Our results are depicted in Figure S3. The relative increase of nearly 25% in the free-energy obtained for the bulk phase at 500 K with respect to the value at room temperature reasonably reproduces the experimental behavior and is comparable to the ab-initio results reported by Muñoz-Santiburcio and Marx.¹⁴ This effect was attributed to the decrease of the permittivity of the liquid phase, which disfavors the stability of the ionized species. The same trend, though more moderately, is found in confinement. In particular, the differences between the profiles corresponding to 300 K and 350 K appear to fall within the precision of our methodology, which can not resolve the curves.

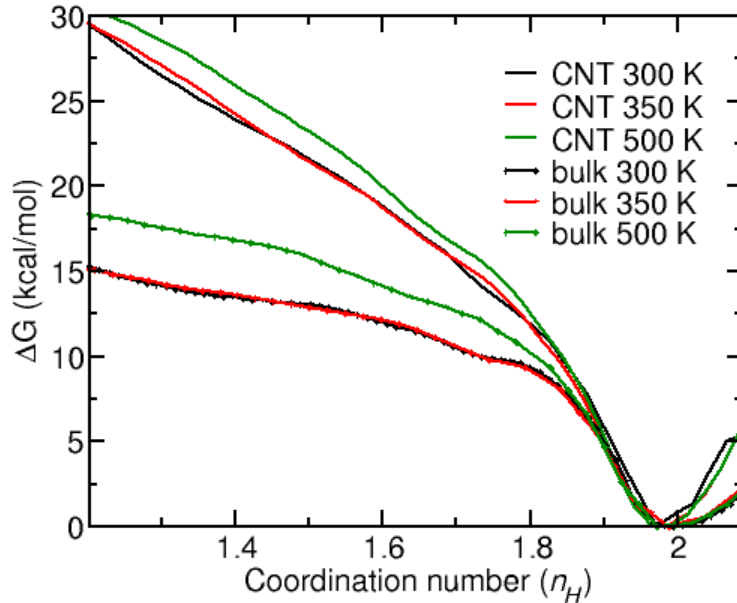


FIG. S3

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