

Abstract

We describe molecular dynamics (MD) simulations of a dissociating water model based on a scaled interatomic potential (s-OSS2) derived by Ojāme, Shavitt and Singer from *ab-initio* calculations at the MP2 level. We calculate the equilibrium and transport properties and diffusion coefficients of water and H⁺ and OH⁻ ions. The mobility of H⁺ > OH⁻ ions by nearly a factor of two, in excellent agreement (after correction to infinite dilution) with experiments between 0 to 50C. The same force field applied to ion transport along an open single-water wire agrees with the more demanding CP/MD and EVB quantum calculations, and with the dipole-lattice model of Dellago et al. Unlike bulk water, the diffusion coefficients of OH⁻ > H⁺ for short wires, but nearly the same for long wires, a classic manifestation of the Grothaus mechanism found also by Bankura and Chandra in QM/MM simulations of water-filled nanotubes. Recombination (neutralization) of H⁺ and OH⁻ in an open wire is accompanied by compression and the synchronized jump of three H-bonded protons at the final stages of neutralization, observed in the bulk by Hassanali et al in QM/MM simulations. Our semi-classical method is simpler though inexact and captures essential features of PT

Simulation of sOSS2 dissociating model for water

- **OSS2 model Ojāme, Sherwin and Singer JCP 1093547,(1998)**
- Ionic (H⁺ and O²⁻(Polarizable) dissociable water model
- Electrostatic potential with self consistency of polarizability of O²⁻
- Analytical fit of Interaction between H⁺, O²⁻ and 3-body (H-O-H) from *ab initio* MP2 level calculations of H⁺ transfer between water dimer and clusters
- Ewald sum for water interactions
- Original OSS2 behaves like a glass at ambient conditions (300K) Fig1 (a) **solid** line for T = 300,450 and 540K
- On Increasing temperature to 640K, MSD, diffusion coefficient D ~ 2.00 x 10⁻⁵ cm² s⁻¹ near exptal Da 298.15 K, d = 0.998 g cm⁻³. (**long-dashed** line)-
- Suggests total OSS2 potential V_{OSS2} too strong for liquid water
- Remedy scale V to get correct D at 298K without changing
- **Scaled OSS2 model (sOSS2)(SHL and JCR JCP 138,124505,2011**
- In the partition function (PF), and (TPT), Z ~ exp(-βV), where β = 1/k_BT, V are like "two peas in a pod"
- To rescale potential, let V_{sOSS2} = λ V_{OSS2}, where
- λ = (T(reqd)/ T(closest, that gives the required D)
For water T (closest) = 540K, T (required) = 298K. (λ ~ 0.551)
With Further tweekiing - λ = 0.530 for D at 298K.
Excellent agreement with experiment between 298 and 345K (fig 2) even with same λ at required temp T and density d

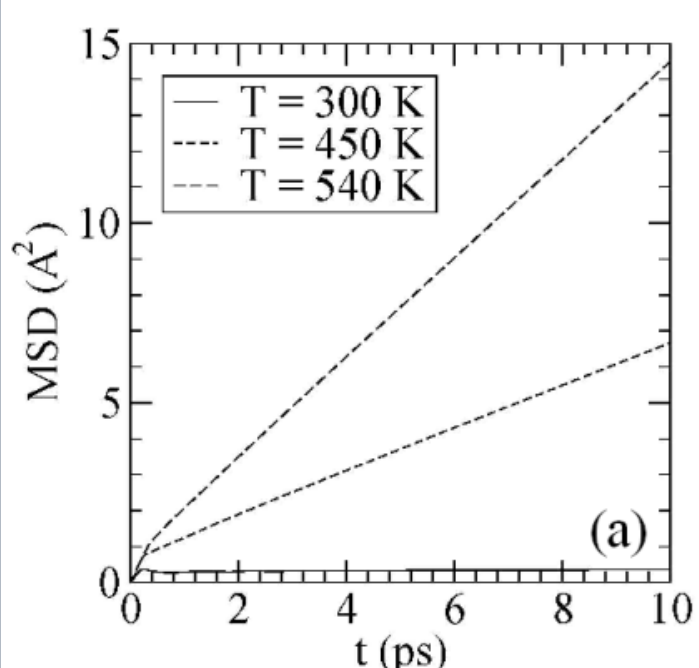


Figure 1. OSS2 model-Mean Square disp at different temp.

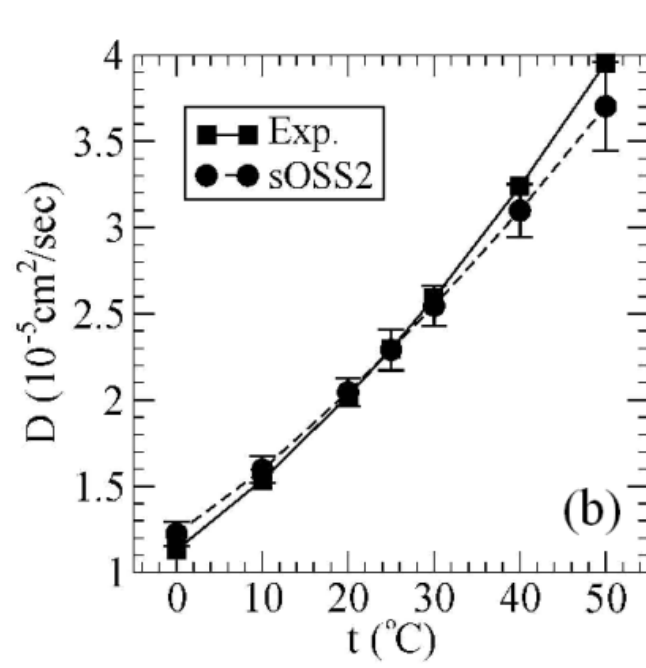


Figure 2. sOSS2 model. λ = 0.530 Comparison of D vs T with experiment. Activation energy E=16kj/mol(18kj/mol).

Equilibrium Distribution functions (λ = 0.530)

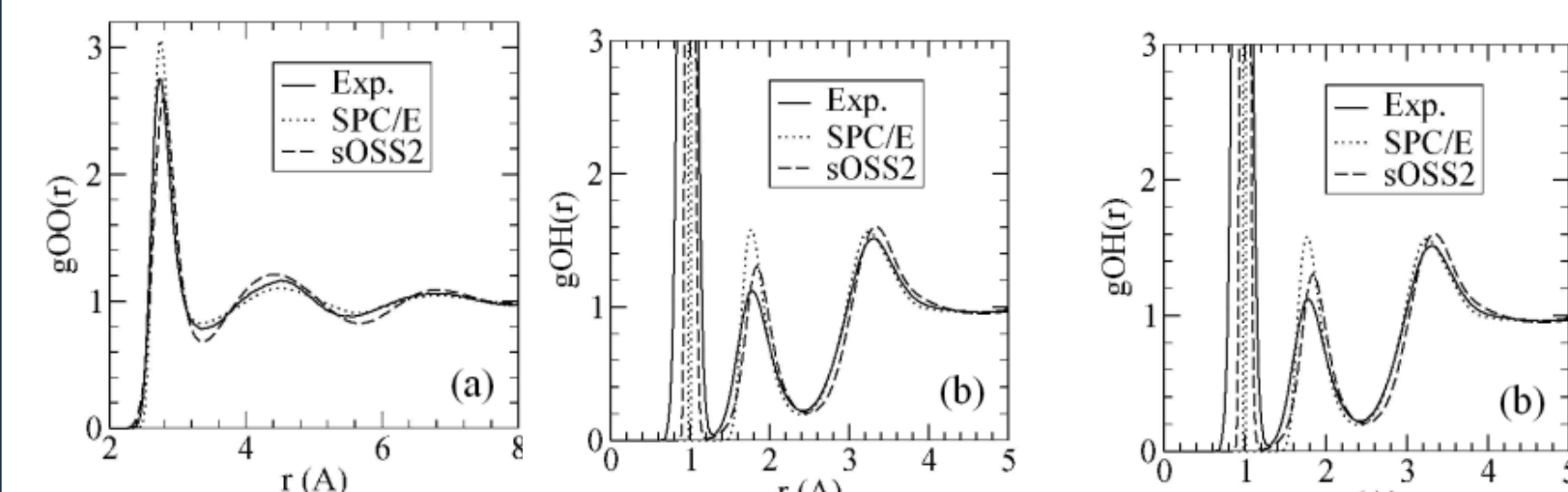


Figure 3. Comparison of experimental radial distribution functions (A. Soper Chem. Phys. 258, 121,2000 with sOSS2 (S.H. Lee and J.C.Rasaiah, JCP 138,124505, 2011) and SPC/E (Berendsen, Grigera and Straasma JPC J. Phys. Chem. 91: 6269) models,

Simulating structural diffusion of H⁺ and OH⁻ ion using the sOSS2 model for water (λ = 0.530)

Same force field λ =0.530 as for sOSS2 water.
Add or remove proton from 215 water molecules and counter-ion-Models HCl solution H₃O⁺ and Cl⁻ ion (fixed) in 215 OSS2 water (215 O₂⁻ and 430 H⁺ - 0.26M solution) Model NaOH solution OH⁻ and Na⁺ ion (fixed) in 215 OSS2 water (215 O₂⁻ and 430 H⁺ - 0.26M solution)

Classical MD- velocity-Verlet algorithm, Δt = 1 fs
NVT ensemble, Nose-Hoover thermostat, switch to MCE if needed
Box length L = 18.64Å (216 water, molecules d = 0.9970 g/cm³),
Periodic BC, Ewald summation κ = 5.0/L

Single and multiple-step proton transfer of H⁺ and OH⁻ ions

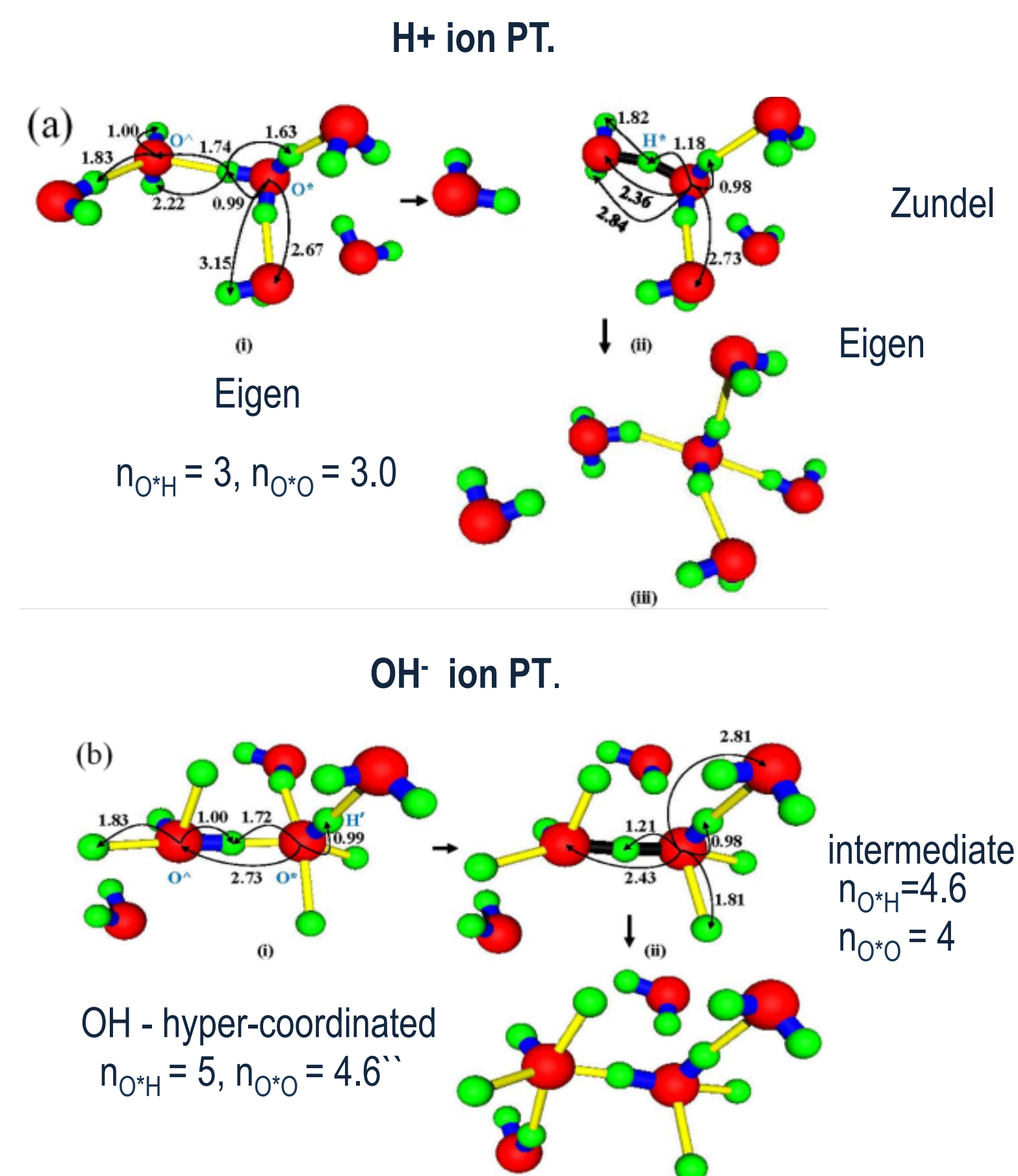
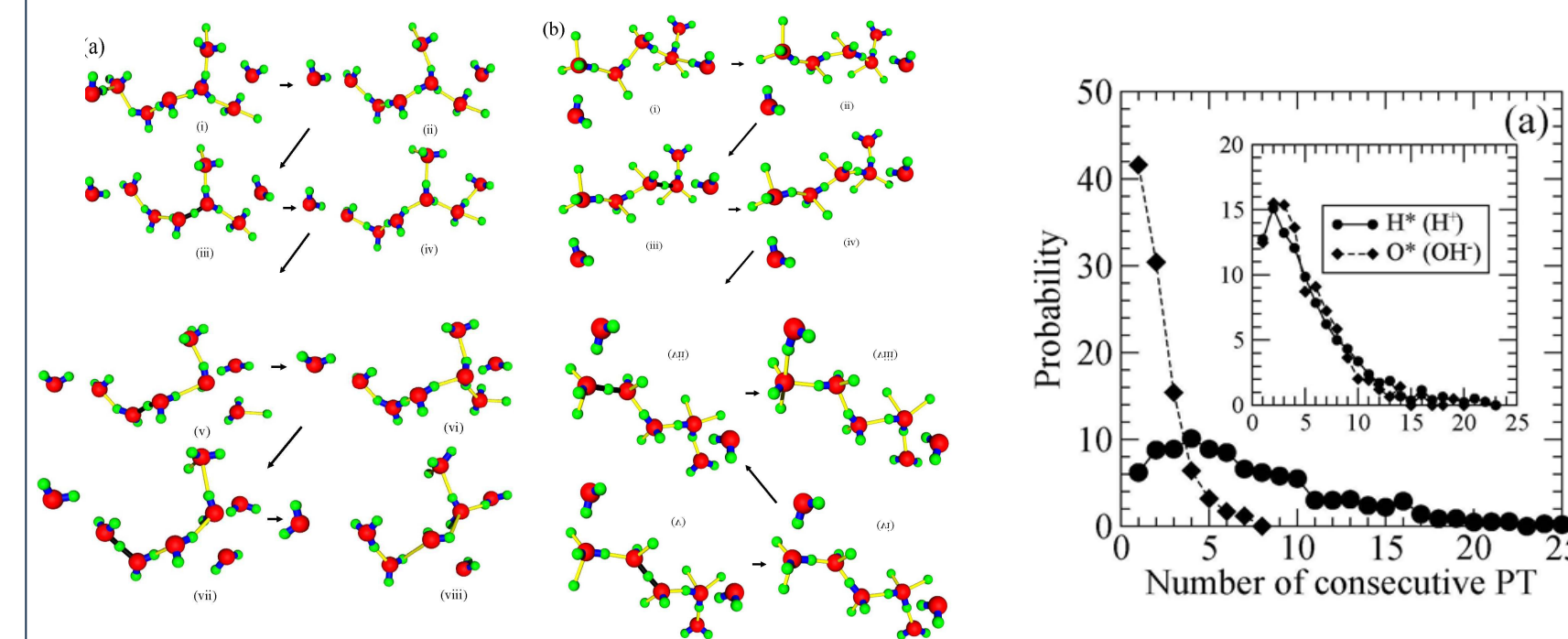


Figure4. Representative mechanisms of single proton transfer for (a) H⁺ and (b) OH⁻ structural ion diffusion- results similar to QM/MM calculations using CP/MD with DFT BLYP3 and EVB calculations (References M.Tuckerman, R.Laksoonen, M.Sprk and M.Parrinello JCP,103,150(1995), D.Marx, M Tuckerman J.,Hutter and M.Parrinello, Nature(Lond) 3097,6011 (1999), D.Marx,A.Chandra and M.Tuckerman, Chem.Rev110, 2174 (2010) D. Marx ChemPhysChem 7,1848,(2006) (G.A.Voth Acc.Chem. Research, 39, 143 (2006))

Multiple PT jumps for H⁺ and OH⁻ ions. Jump distributions within 1ps and (in insert) within average time between consecutive jumps (0.7s ps, H⁺ and 2.52 ps OH⁻ ion) for structural diffusion at 298K



Comparison of experiment with Diffusion coefficients of H⁺ and OH⁻ ions in bulk water for sOSS2 dissociation model

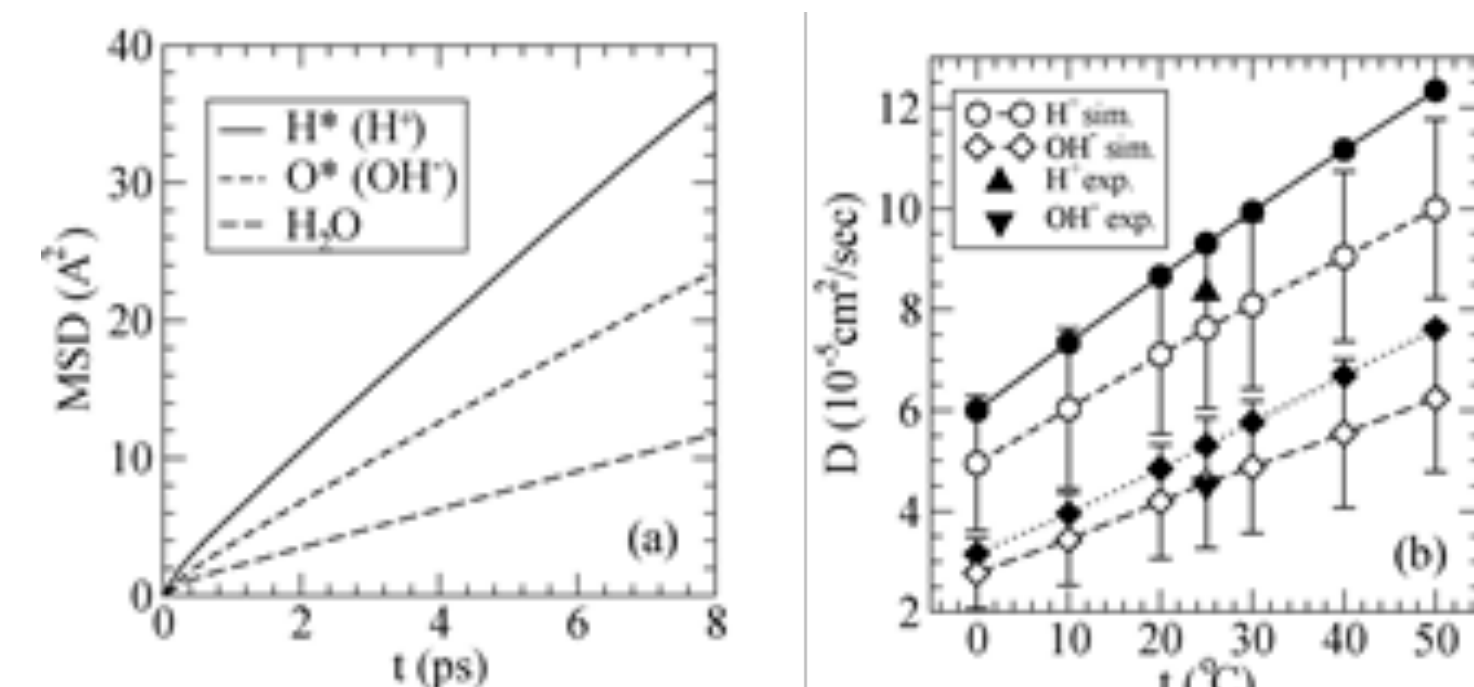


Figure 5. (Left) Mean square displacement (MSD) of H⁺ of H⁺, O²⁻ of OH⁻ ion and water at 298.15K. Slope H⁺ > OH⁻ > H₂O and (right) comparison with experiment. Differences due to different solvation, desolvation and pre-solvation in PT mechanisms for ions seen in CP/MD, EVB and sOSS2 in bulk water. Activation energies for H⁺, OH⁻ and H₂O: 10.3 (10.6), 12.0 (13.0), 16 (18) kJ/mol. - expt numbers in parenthesis.

PT in one dimensional water wires

Desolvation penalty for ion to enter water wire in carbon nanotube of 8.3Å diameter immersed in water reservoir. Avoid by Inserting charge defect directly in open water wire in CNTs of different lengths with 12 to 250 water molecules - weak harmonic potential at ends prevents escape.

Dellago et al electrostatic lattice model

Free energy of interaction of excess charge with oppositely oriented dipoles, relative to the center. Equivalent to interaction between (q - 2μ_z/Δ) excess charge and two charges at tube ends.

$$F(z') = (q - 2\mu_z/\Delta)(\mu_z/\Delta) [1/z' + 1/(1-z') - 4]/L$$

where z is the distance of the excess charge q from one end of the tube of length L, μ_z is the magnitude of the projected dipole moment of a water molecule along wire axis, and Δ is the average distance between the centers of the adjacent dipoles. model.

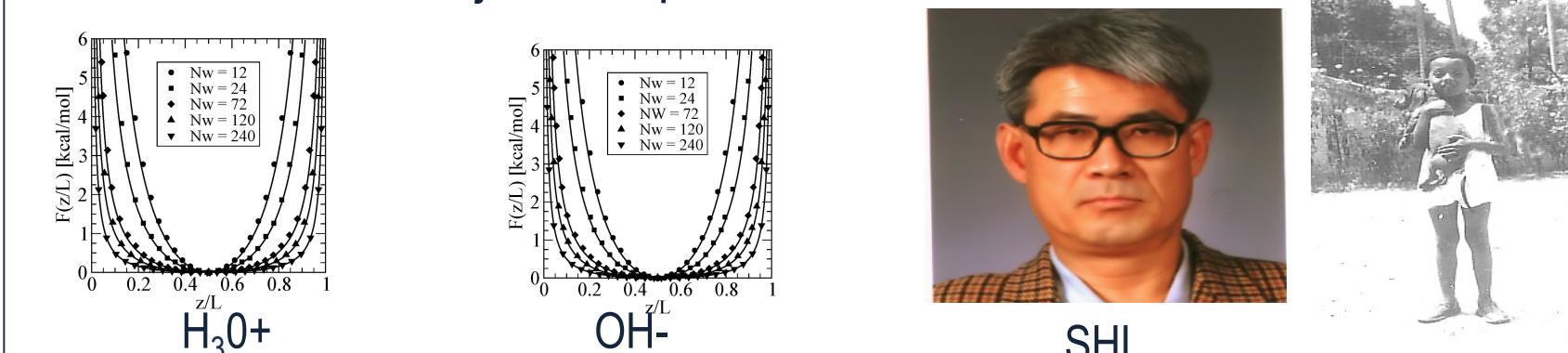
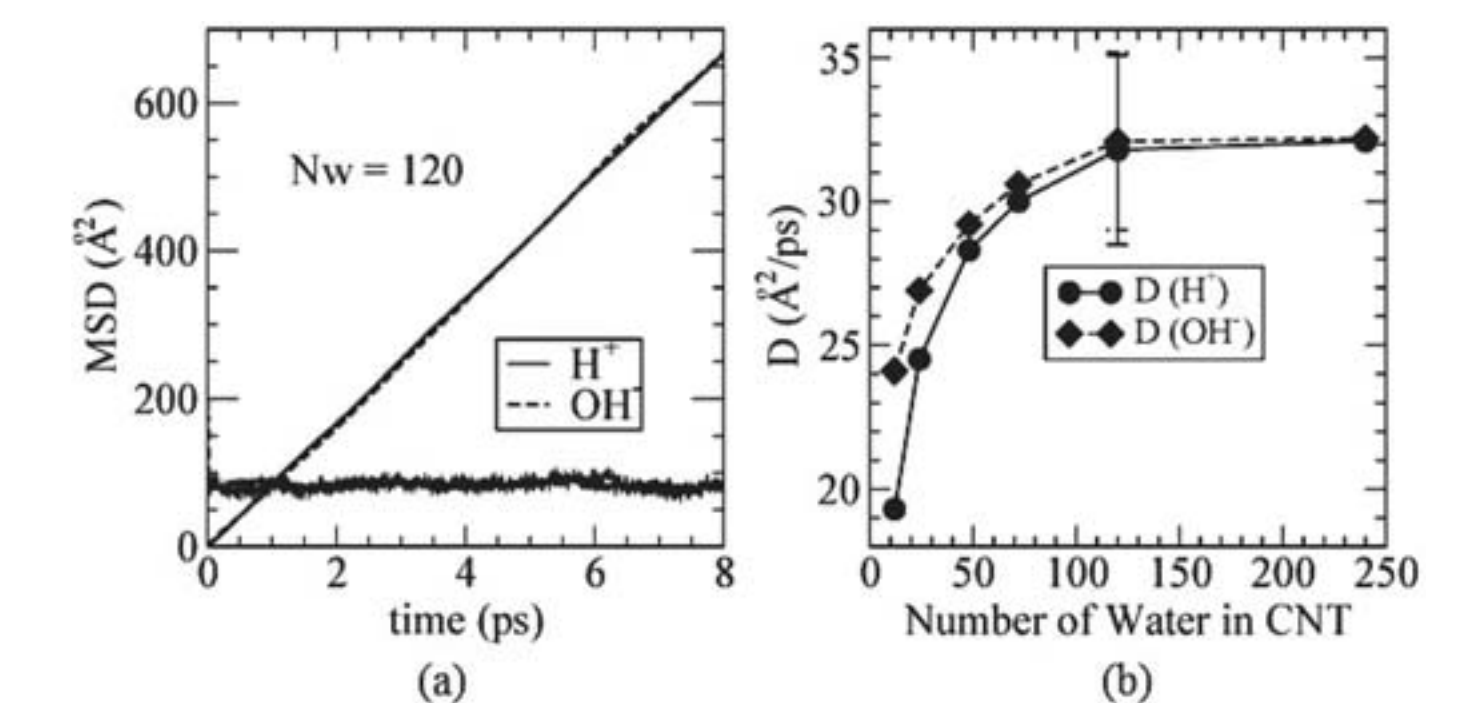


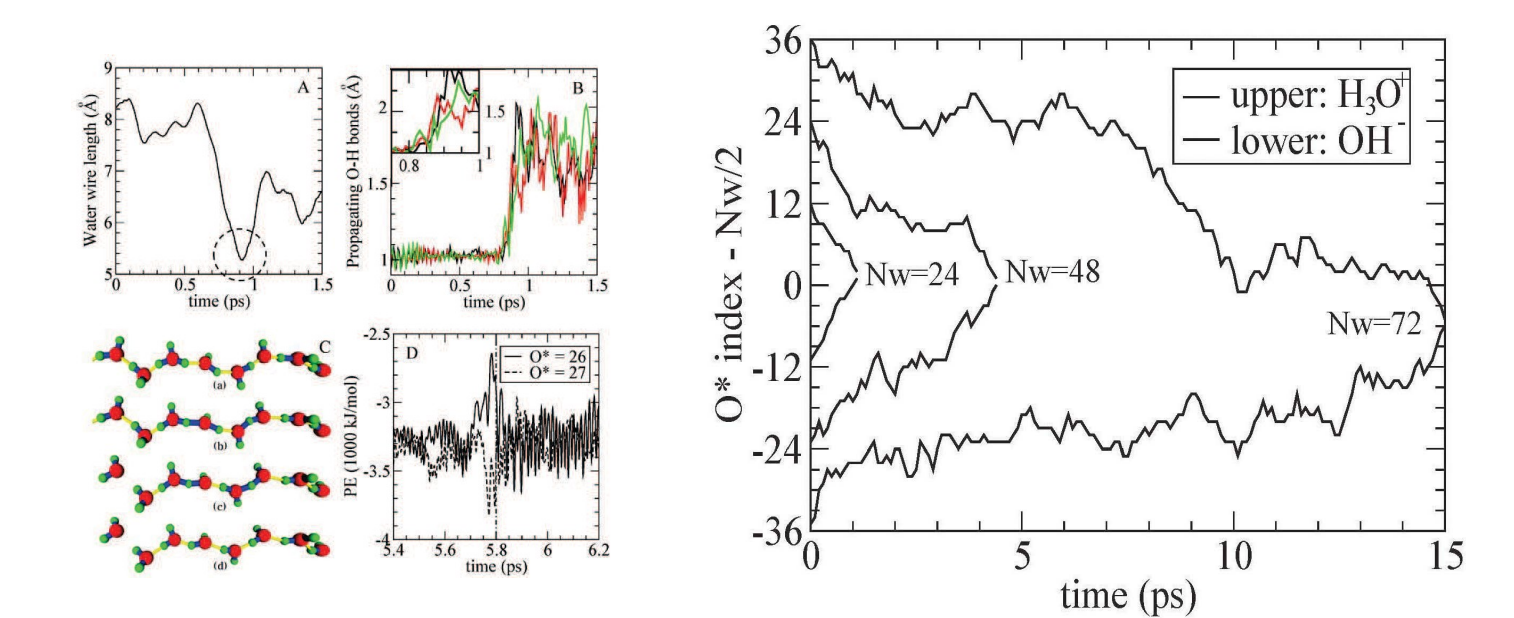
Figure 6. Interaction free energy of H₃O⁺ and OH⁻ charge centers in open water chains compared with lattice model of Dellago et al. Verified for H⁺ with CP/MD and EVB models (Dellago, Naor and Hummer) and both H⁺ and OH⁻ in sOSS2 model (SHL and JCR) .

Diffusion coefficient D of OH⁻ and H⁺ ion vs chain length (a) .equal for long chains -Grothaus mechanism (b)OH⁻ > H⁺ for short wires



Recombination of H⁺ and OH⁻ ions along water wires

Neutralize H₃O⁺ and OH⁻ ions in quasi-1 dimensional water wires after placing at opposite ends of open chain of water-filled nanotubes of lengths 29.6, 58.7, 116.8 and 174.8 Å with 12, 24, 48, and 72 water molecules respectively. Temperature controlled at 298K by a Nose-Hoover thermostat. Equilibration with ions fixed for 20 ps. Switch of for last steps. Each ion coordinates with single water molecule pointing towards or away on each side. Ions move towards the center in the attractive coulomb force field of the other ion, modulated by electrostatic shielding of dipole chains. Small effect for turning off thermostat near last steps or neutralization and energy dissipation..



Proton transfers occur in same direction - ions H⁺ and OH⁻ move in opposite. Hydrogens on hydronium ion jumps to a neighboring H-bonded water molecule, and another from a water molecule to adjacent hydroxide ion. Neutralization occurs in three steps; (a)ion transport, (b)compression of the water wire between ions (c)recombination. Ions move faster in channel (~100 fs) than in bulk water until separated by two water molecules at ~7Å distance followed by compression and synchronized transfer of three hydrogen-bonded protons along a water chain between ions in both bulk and water wire. Compression occurs in wire over a slightly longer time than in bulk and energy dissipates along wire.

Acknowledgement

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References

- D. Marx, M Tuckerman, J.Hutter and M. Parrinello, Nature(Lond) 3097,6011 (1999); L. Ojāme, I. Shavitt, and S. Singer, JCP. 109, 5547-5564 (1998); C. Dellago, M. M. Naor, and G. Hummer, PRL 90, 105902 (2003); A. Bankura and A. Chandra J.Phys.Chem.B,116,9744 (2012); A. Hassanali, M.K. Prakash, H. Eshet and M. Parrinello PNAS (2011), S. H. Lee and J. C. Rasaiah, JCP,135,124505,(2012); ibid 139 12450, ibid036102 (2013) and references therein.