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Abstract

Molecular dynamics (MD) simulations of a dissociating water model based on a rescaled interatomic potential (s-OSS2) derived by Ojåme, Shavitt and Singer from *ab-initio* calculations at the MP2 level were used to calculate the ion mobilities of H⁺ and OH⁻ ions in bulk water. The diffusion coefficient of the H⁺ ion is greater than that of OH⁻ ions by nearly a factor of two, and in excellent agreement (after correction to infinite dilution) with experimental values from 0 to 50°C. The same model applied to ion transport along an open single-chain water wire agrees CP/MD and EVB calculations and with the energy of the theoretical dipole-lattice model of Dellago et al. Unlike bulk water, the diffusion coefficients of OH⁻ is > H⁺ for short wires and nearly the same for a long wire as found by Bankura and Chandra in QM/MM simulations in water-filled nanotubes. Recombination (neutralization) of H⁺ and OH⁻ in the open chain wire is accompanied by compression and a synchronized jump of three hydrogen bonded protons at the final stages of neutralization, similar to bulk water observed by Hassanali et al in QM/MM simulations.

Simulation of sOSS2 dissociating water model

- OSS2 model Ojåme, 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 gives expt diffusion coefficient $D \sim 2.00 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 298.15 K, $d = 0.998 \text{ g cm}^{-3}$. (long-dashed line)-
- Suggests total OSS2 potential V_{OSS2} too strong for liquid water
- Can we modify V to get correct D without changing T?

- Scaled OSS2 model (sOSS2)(S.L and JCR JCP 138,124505,2011
- In partition function (PF), and thermodynamic perturbation theory TPT $Z \sim \exp(-\beta V)$, where $\beta = 1/k_B T$, and V are like "two peas in a pod" Rescale potential $V_{\text{sOSS2}} = \lambda V_{\text{OSS2}}$, where $\lambda = (T(\text{reqd})/T(\text{closest}))$ that gives required D

For water at 298K, $T(\lambda \sim 298/540 = 0.551)$

Further tweekiing -. $\lambda = 0.530$ for D at 298K.

Good agreement with expt between 298 and 345K (fig 2) with λ nearly constant at reqd temp T and density d

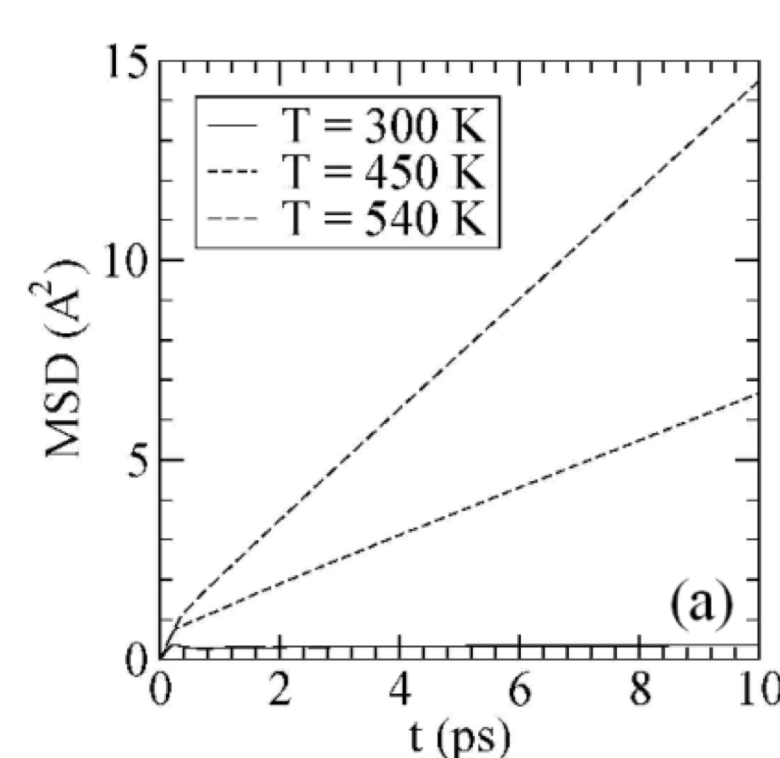


Figure 1. OSS2 model-. Mean square displacement (MSD) at different temperatures.

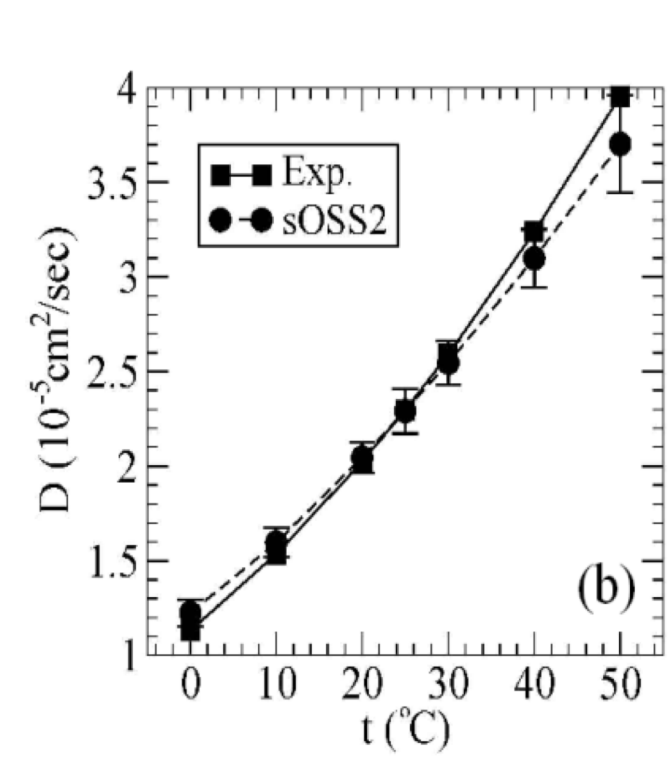


Figure 2. sOSS2 model. $\lambda = 0.530$. Comparison of D vs T with experiment. Activation energy $E = 16 \text{ kJ/mol}$ (18 kJ/mol).

Distribution functions

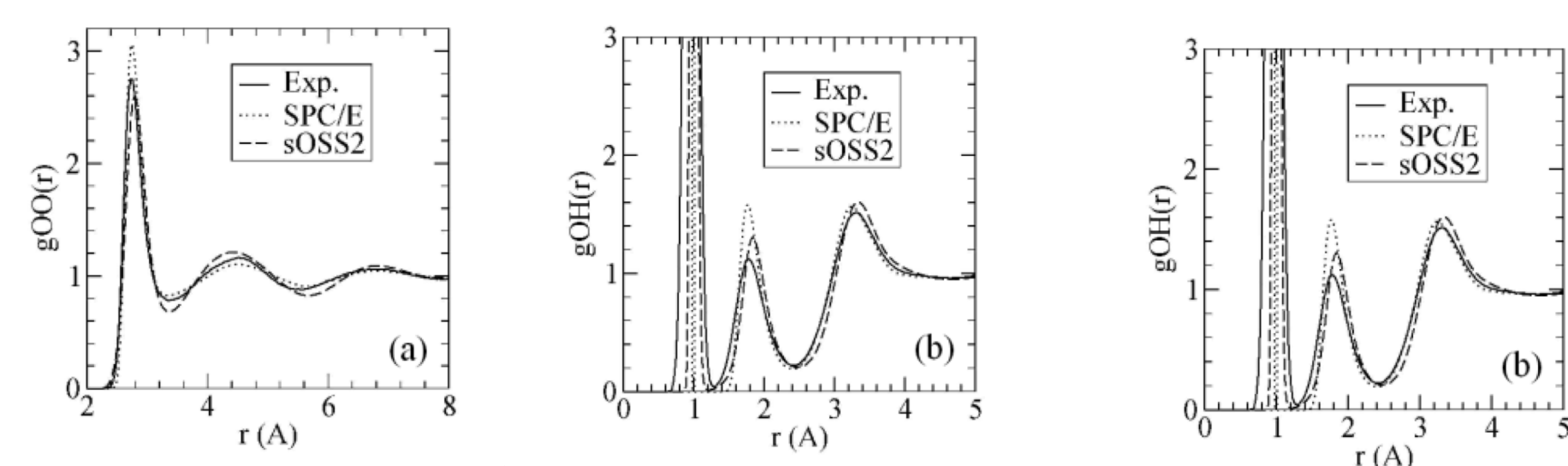


Figure 3. Comparison of expt radial distribution functions (A. Soper Chem. Phys. 258, 121,2000 with sOSS2 (S Lee and J C Rasaiah, JCP 138,124505, 2011) and SPC/E (Berendsen, Grigera and Straasma JPC J. Phys. Chem. 91: 6269) models,

Simulating structural diffusion of H⁺ and OH⁻ ion using sOSS2 model for water ($\lambda = 0.530$)

Add or remove proton. Same force field $\lambda = 0.530$ as for sOSS2 water. Model 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, $\Delta t = 1 \text{ fs}$ NVT ensemble, Nose-Hoover thermostat, switch to MCE if needed Box length $L = 18.64 \text{ \AA}$ (216 water, $d = 0.9970 \text{ g/cm}^3$), Periodic BC, Ewald summation $\kappa = 5.0/L$

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

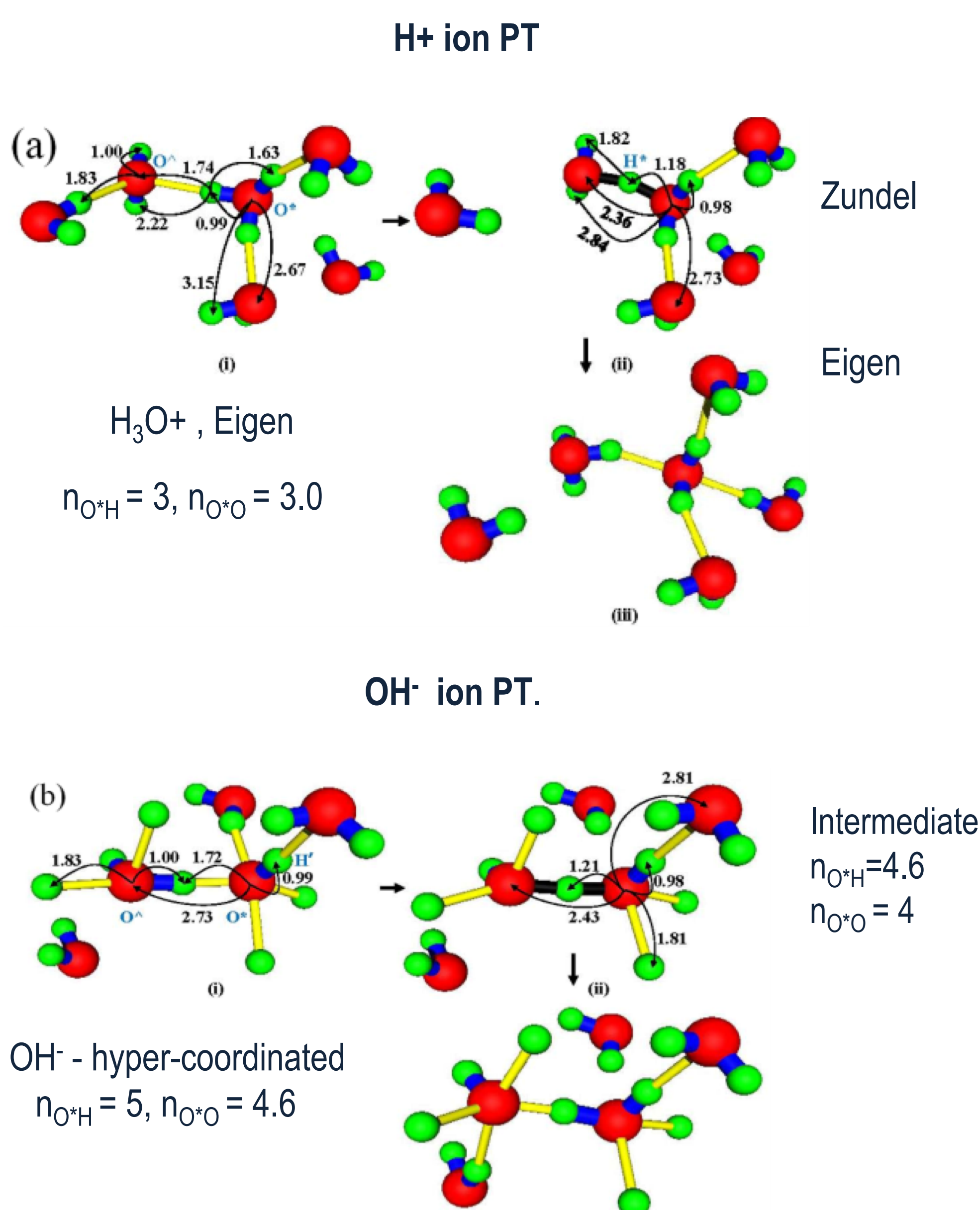
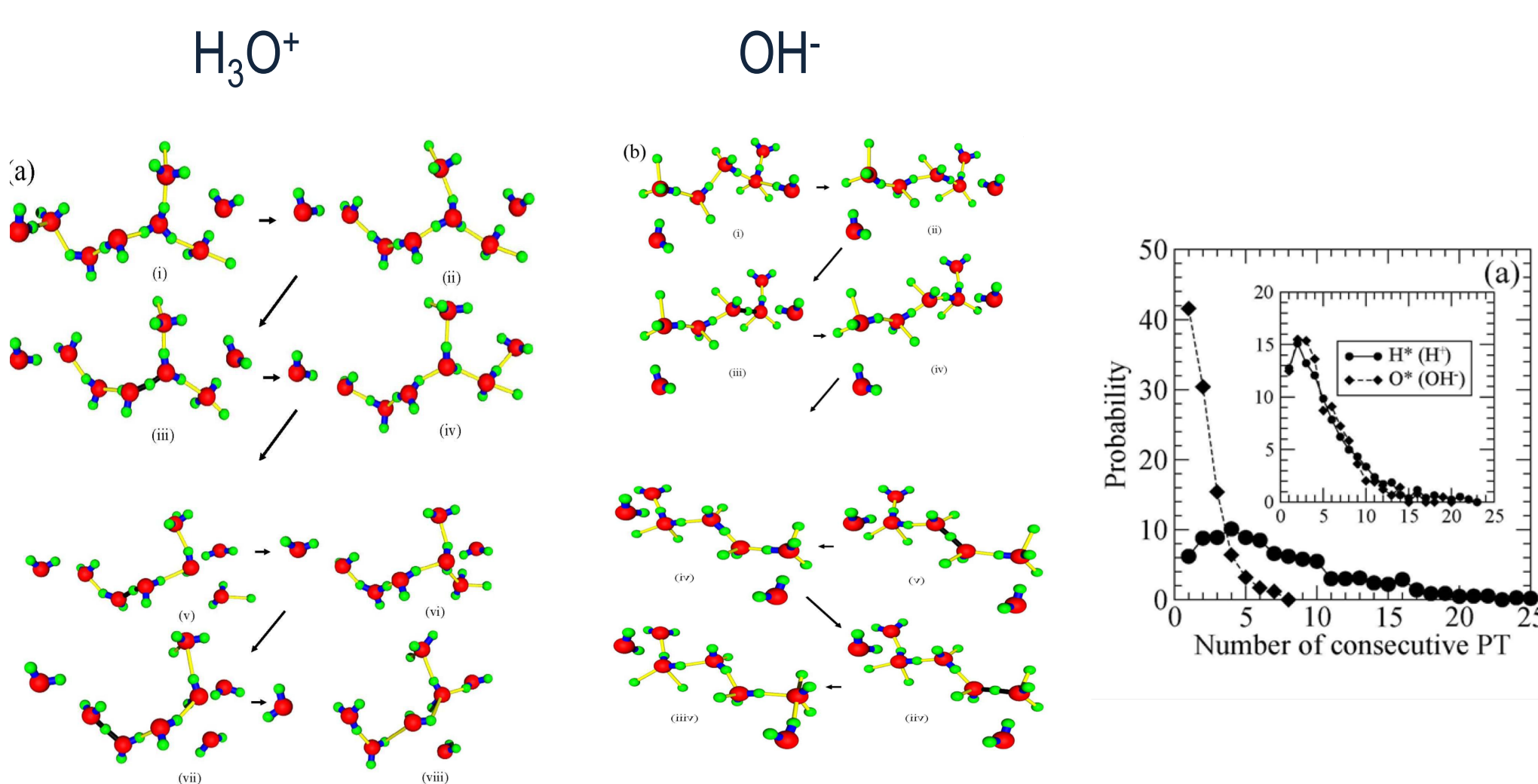


Figure 4. Representative mechanisms of single proton transfer for (a) H⁺ and (b) OH⁻ structural ion diffusion- results similar to QM/MM calculations using CP/MD with DFT BLYP3 and EVB calculations (References M.Tuckermann, R.Laksoonen, M.Sprink and M. Parrinello JCP,103, 150 (1995), D.Marx, M Tuckermann J.Hutter and M. Parrinello, Nature(Lond) 3097,6011 (1999), D.Marx, A.Chandra and M.Tuckermann, Chem.Rev, 110, 2174 (2010), D.Marx ChemPhysChem 7,1848,(2006) (G.A.Voth Acc.Chem. Research, 39, 143 (2006))

Multiple time distributions for H⁺ and OH⁻ ions

Jump distributions within 1 ps and (in insert) within average time for 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 dissociating model

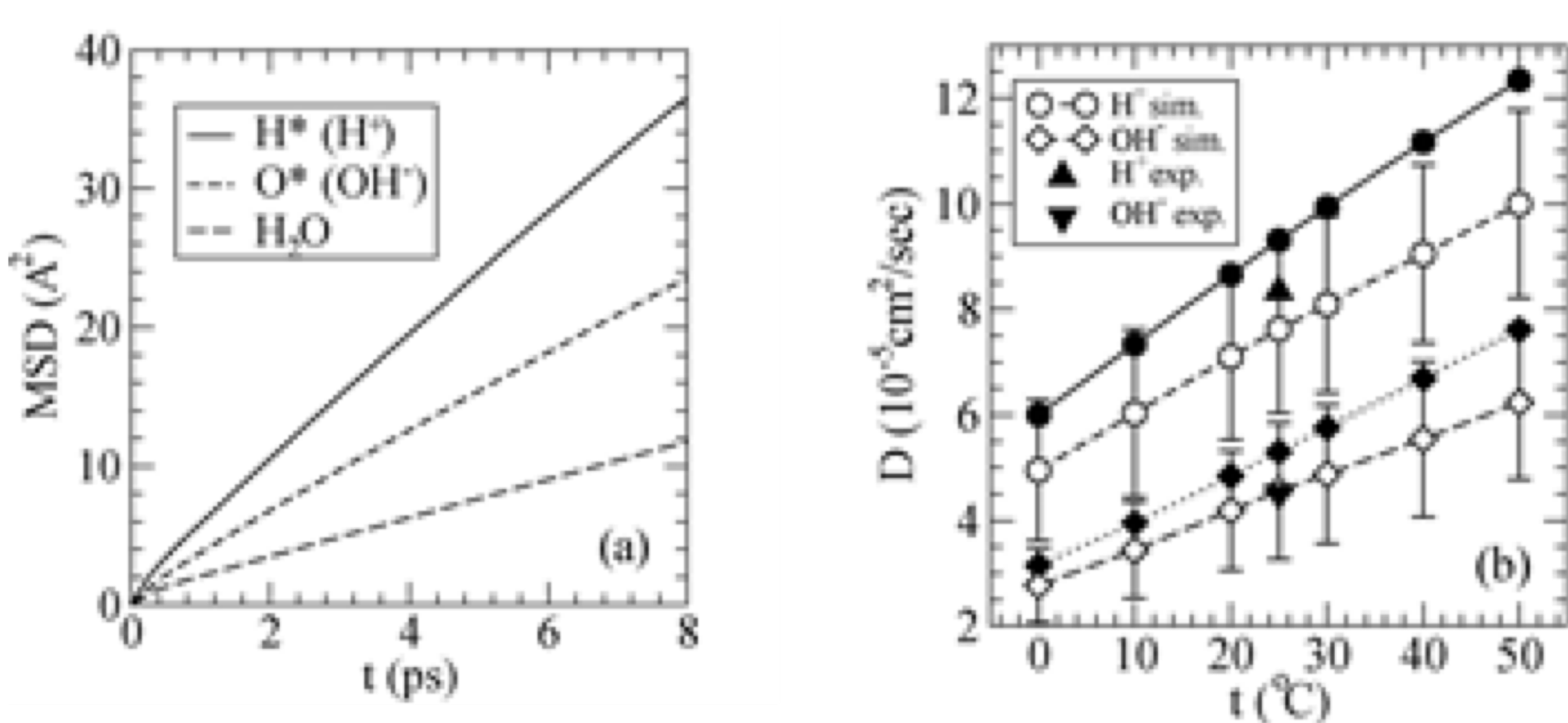
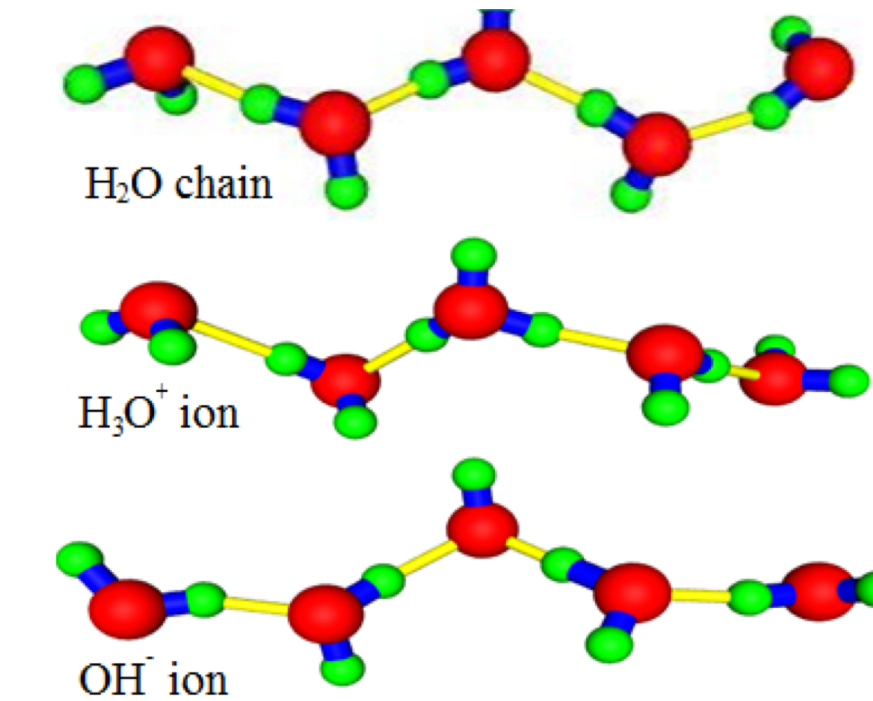


Figure 5. (Left) MSD of H⁺ of H⁺ and O* of OH⁻ ion and water at 298.15K. H⁺ > OH⁻ > H₂O and (right) comparison with experiment. Differences due to different solvation, desolvation and presolvation PT mechanisms seen in CP/MD, EVB and sOSS2 in bulk water. Activation energies for H⁺, OH⁻ and H₂O: 10.3 (10.6), 12.0 (13.0), 16 (18) kJ/mol.

One dimensional water wires



Desolvation penalty water wire in carbon nanotube of 8.3Å diameter for ion to immersed in water reservoir. Insert H⁺ or OH⁻ charge defect directly in open water wire in CNTs of different lengths with 12 to 250 water molecules - weak harmonic potential at ends prevent escape

Dellago et al electrostatic Lattice model

Energy of interaction of excess charge with oppositely oriented dipoles relative to center, is equivalent to interaction between charge $(q-2\mu_z/\Delta)$ at center and two charges at the ends that remain after cancellation!!

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

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.

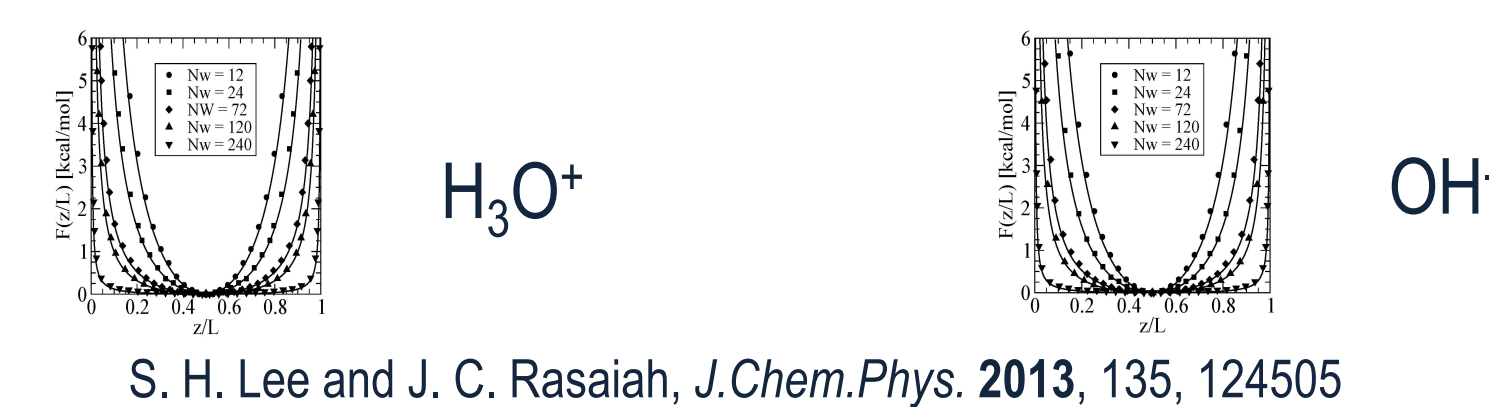
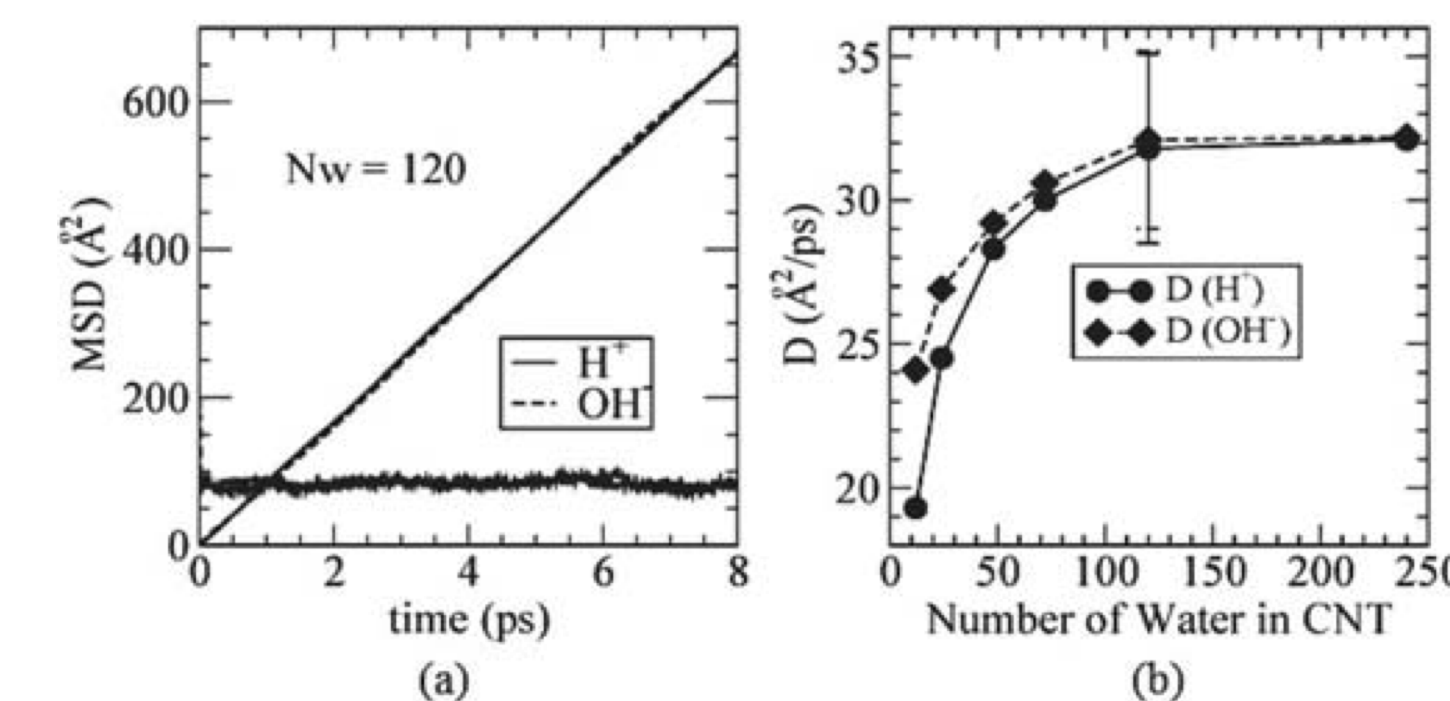
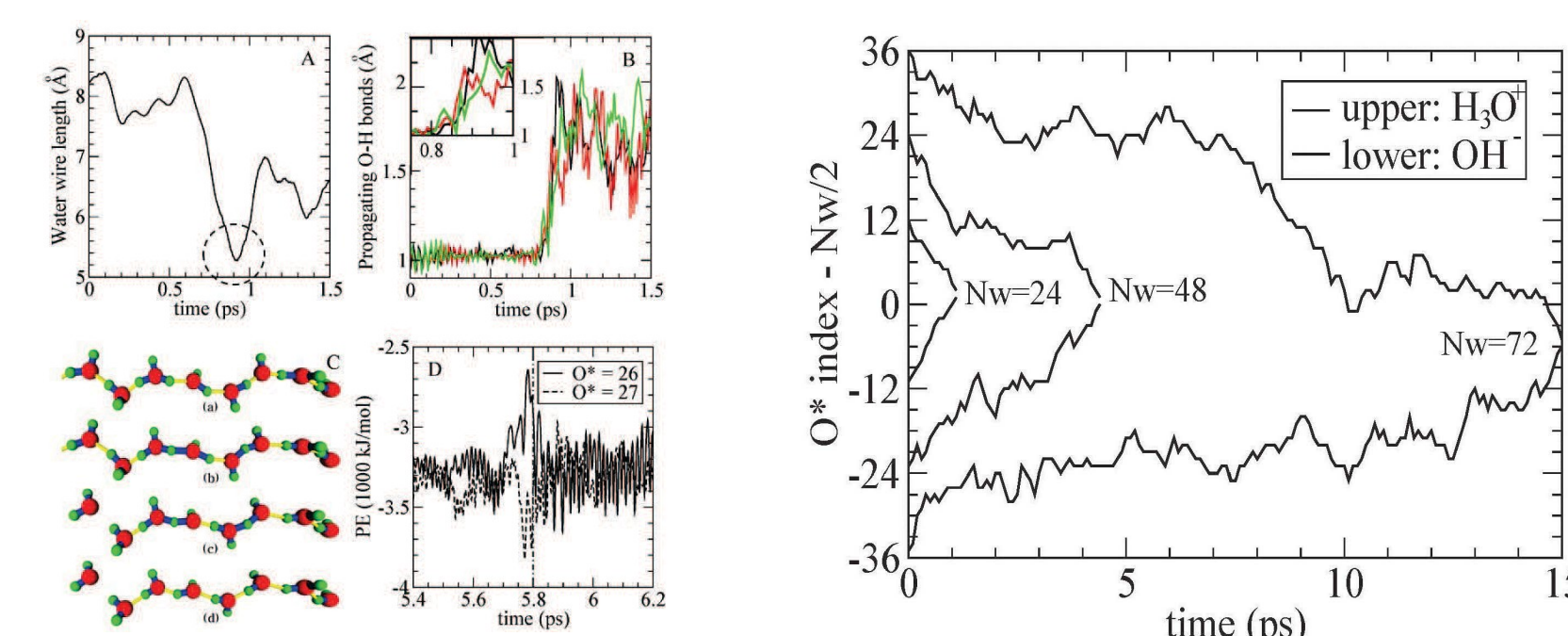


Figure 6. Numerical calculations of interaction energy of H₃O⁺ and OH⁻ charge centers in open water chains for the sOSS2 mode compared with lattice model of Dellago et al. Verified for H⁺ with CP/MD and EVB models (Dellago) and for both H⁺ and OH⁻ in sOSS2 model (SHL and JCR). Diffusion coefficient D of OH⁻ and H⁺ ion vs chain length. (a) equal for long chains (b) OH⁻ > H⁺ for short wires



Recombination of H⁺ and OH⁻ ions

Neutralize H₃O⁺ and OH⁻ ions in quasi-1 dimensional water wires after placing them at opposite ends of open chain of water-filled nanotubes lengths 29.6, 58.7, 116.8 and 174.8 Å with 12, 24, 48, and 72 water molecules. Temperature controlled at 298K by a Nose-Hoover thermostat. 20ps Equilibration. Single water molecule coordinates ion on each side which moves towards the center of water wire in the attractive coulomb force field of the other ion, modulated by electrostatic shielding of dipole chains. Turning off thermostat for neutralization steps run had small effect.



Proton transfers occur in same and ions move in opposite direction - Hydrogen on hydronium ion jumps to a neighboring hydrogen-bonded water molecule, and another H jumps from a water molecule to adjacent hydrogen-bonded hydroxide ion. Neutralization occurs in three steps; ion transport, compression of the water wire between the ions, and recombination (neutralization)

Ions move faster in channel (~100 fs) than in bulk water (Hassan Ali et al) until separated by two water molecules at ~7Å distance followed by compression and synchronized transfer of three hydrogen-bonded protons along the water chain between ions. Compression occurs over a slightly longer time than in bulk. Recombination energy dissipates along the water wire.

References

- D. Marx, M Tuckermann, J.Hutter and M.Parrinello, Nature(Lond) 3097,6011 (1999); L. Ojåme, 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. Eset and M.Parrinello PNAS (2011), S. H. Lee and J. C. Rasaiah, JCP.,135,124505,(2012); 139 12450, 036102 (2013) and references therein.