Behavior of the Eigen form of hydronium at the air/water interface

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Abstract

Surface affinity of hydronium was explored using umbrella sampling molecular dynamics simulations with a refined polarizable potential. The polarizable interaction potential of H_3O^+ was reparameterized against accurate ab initio calculations for geometries including a water molecule approaching the Eigen cation from its oxygen side. Although there is no true hydrogen bonding with H_3O^+ acting as an acceptor, respecting in the force field the very shallow ab initio minimum corresponding to this interaction leads to a decrease in surface propensity of hydronium compared to previous results. Qualitatively, the mild surface affinity and strong surface orientation of hydronium is, nevertheless, robustly predicted by various computational approaches, as well as by spectroscopic experiments.

1. Introduction

Protons in an aqueous environment chemically react with water forming hydronium cations. The species resulting from proton hydration is very dynamical and susceptible to frequent proton hops, in between which it oscillates between two limiting structures. The first one is the Eigen cation, i.e., H_3O^+ strongly solvated by three additional water molecules, which accept hydrogen bonds from the cation.[1] The second one is the Zundel cation, i.e., $H_5O_2^+$, where the proton is equally shared by two water molecules.[2] The structural and dynamical aspects of protons in bulk water and aqueous solutions have been calculated at the molecular level extensively in the last decades.[3-5]

Recently, a lot of emphasis has been also devoted to computational and experimental investigations of the behavior of protons at the water/vapor interface.[6-16] Since surface affinity of ions correlates with their size and softness (polarizability), one could naively assume that proton as the smallest ion with exactly zero polarizability should be strongly repelled from water surface. However, due to its reactivity with water one has to consider surface propensity of the hydronium cation rather than that of the bare proton. A rigorous theoretical approach thus requires a quantum mechanical description of the electronic structure of the whole proton-water system.[16] Moreover, proton hopping involves motion of a relatively light particle, therefore, quantum nuclear effects play a role in the description of the proton dynamics.[4]

At this advanced level of theoretical description it is still not possible to obtain statistically converged data, therefore, approximation are inevitable. *Ab initio* molecular dynamics is becoming feasible for the description of a classical proton on aqueous surfaces of a limited size.[16] An approach which allows for capturing the proton hopping process, including quantum nuclear effects, in a semiempirical way is the effective valence bond (EVB) method.[4,17] If one is

only interested in thermodynamical observables, such as distribution of hydronium cations between the aqueous bulk and the water/vapor interface, one can even resort to a classical force field molecular dynamics (MD), which in principle does not allow for proton hopping.[6,8,12,14,18] Both EVB and classical MD with polarizable potentials showed, in agreement with experimental observations, that hydronium exhibits an appreciable affinity for the water/vapor interface.[7,8,12,14] A simple (likely oversimplified) rationalization of this behavior is based on the fact that H_3O^+ is an excellent hydrogen bond donor but a very bad hydrogen bond acceptor due to a too low electronegativity of its oxygen. Therefore, hydronium prefers to "sit" at the water-vapor interface with its oxygen pointing into the gas phase over being in the bulk and disrupting the hydrogen bonding network there.[7-9]

Due to its inability to describe bond making/breaking, empirical force fields can only describe separately the two limiting structures, Eigen or Zundel, of hydronium.[19] Both have been investigated previously and were shown to exhibit surface affinity.[19] It can hardly be overemphasized, that the quality of a classical MD simulation can be only as good as that of the underlying force field. In this study we focus on the quality of the force field for the most often considered limiting structure - the Eigen cation and consequences thereof on the surface behavior of aqueous hydronium. Our previous polarizable force field for H_3O^+ was parameterized against *ab initio* calculations in clusters where hydronium acted as hydrogen bond donor,[12] which is the dominant interaction pattern of this ion with water molecules.[7,9] Here, we develop a refined force field for H_3O^+ based on *ab initio* calculations newly including cluster geometries, where the cation could potentially act as a hydrogen bond acceptor. For this model we then describe in detail the behavior of hydronium at the water/vapor interface and compare it to previous results.

2. Computational Methods

Ab initio calculations of the interaction energy in clusters containing H_3O^+ with four water molecules were performed at the coupled cluster CCSD(T) level of theory with the aug-cc-pVDZ basis set.[20,21] The calculated interaction energy was corrected for the basis set superposition error using the counterpoise method.[22] The $H_3O^+(H_2O)_4$ cluster was prepared by first performing a geometry optimization at the MP2/ aug-cc-pVDZ level of a smaller cluster, namely the Eigen cation $H_3O^+(H_2O)_3$, which contained three water molecules each donating one hydrogen bond to the hydronium ion. One additional water molecule, acting as a hydrogen bond donor, was then added to the $H_3O^+(H_2O)_3$ in such a way that the oxygen atom of hydronium and the atoms of one of O-H bonds of this water molecule were collinear (see Fig. 1). Then a series of $H_3O^+(H_2O)_4$ clusters was produced by varying the oxygen-oxygen distance (r_{OO}) between the hydronium ion and this hydrogen-bond-donating water molecule without any other change in the cluster geometry. Interaction energy between the hydrogen-bond-donating water molecule and the cluster was calculated for this series of structures. All *ab initio* calculations were performed with the Gaussian03 software.[23]

The above series of $H_3O^+(H_2O)_4$ cluster relative energies was used for refining the classical force field. Namely, interaction energy between the hydrogen bond donating water molecule and the rest of the cluster was calculated as the energy of the system with respect to its energy at $r_{OO} = 5$ Å, which was taken as reference. A polarizable force field was employed, with the POL3 model for water molecules[24] and the starting parameters for the Eigen ion taken from

Ref. 25. We denote these parameters as the Eigen force field I. The shell-particle model of polarization was employed.[26] An additional Lennard-Jones interaction acting exclusively between the oxygen atom of the hydronium ion and hydrogen atoms of water molecules was introduced in order to better describe the hydrogen bond accepting side of the Eigen cation with the very shallow minimum on the calculated *ab initio* curve (Figure 1). The Lennard-Jones parameters of this interaction were tuned to match as close as possible the *ab initio* interaction energies. We refer to this parameterization as Eigen force field II. Both sets of force field parameters are given in Table 1.

Surface preference of hydronium was studied by calculating the free energy profile as a function the distance of the Eigen ion from the water/vapor interface. Free energy was obtained from calculations employing the umbrella sampling method.[27] Slab geometry was used for the system of 1574 water molecules and a single hydronium ion in the Eigen form. In order to neutralize the charge of the system one chloride anion was added to the water phase far from hydronium; we checked that during simulations this anion was never directly interacting with hydronium. The water slab was simulated in a periodic box of $29 \times 29 \times 287$ Å^3 size. A cutoff of 11 Å was employed for van der Waals interactions, and the long-range electrostatic forces were accounted for using the Particle Mesh Ewald method.[28] The constant volume canonical ensemble was simulated with the temperature of 300 K controlled by the Nose-Hoover algorithm.[29] Bond lengths in the hydronium ion were constrained using the SHAKE algorithm, while the Settle method was employed for constraining bonds in water molecules.[30,31] Calculations were performed employing Gromacs 4.0.7 software suite.[32]

In order to generate initial configurations for umbrella sampling windows the hydronium ion was pulled in the direction perpendicular to the surface of water from the bulk region of the water slab toward the gas phase. To this end we used an umbrella potential with a force constant of 1000 kJ mol^{-1} nm^{-2} and employed a pulling rate of 0.02 nm ps^{-1}. Based on this simulation, 17 initial configurations were selected with positions of hydronium ion center of mass with respect to the interface spaced by 1 Å. For each of these 17 umbrella sampling windows the position of the hydronium ion in the z-direction, i.e., with respect to the surface of water was restrained with a force constant of 1000 kJ mol^{-1} nm^{-2} and a 50 ps equilibration run was performed, followed by a 150 ps production run. Consequently, the weighted histogram analysis method[33] was employed to calculate the potential of mean force acting on the hydronium ion and thus the changes of the free energy.

3.   Results and Discussion

The potential energy curves for a series of $H_3O^+(H_2O)_4$ cluster geometries with varying distance between the Eigen cation and the hydrogen bond donating water molecule are depicted in Figure 1. *Ab initio* coupled cluster calculations show a very shallow minimum of about -0.3 kcal/mol at a O-O distance of about 3.4 Å. This marginal attraction is too weak to be classified as a hydrogen bond accepted by H_3O^+ on its oxygen side, however, it is interesting to note that it exists at al. Potential energy curve calculated employing the classical force field I exhibits no such minimum, predicting a purely repulsive interactions between the Eigen cation and a hydrogen bond donating water molecule. To account for the very weak attraction predicted by *ab initio* calculations we introduced an additional interaction in the form of a Lennard-Jones potential acting between the oxygen atom of the hydronium ion and hydrogen atoms of water

molecules. The optimized Lennard-Jones parameters of this additional term are presented in Table 1. This parametrization leads to a potential energy minimum of about -0.3 kcal/mol located at the O-O distance of about 3.2 Å, in a good agreement with the *ab initio* results (Figure 1).

In order to investigate the surface affinity of H_3O^+ we calculated using the umbrella sampling method free energy profiles as a function of the distance of the center of mass of the ion from the surface of water. Figure 2 compares free energy profiles obtained with versions I and II of the force field. For version I, a free-energy minimum of about -1.8 ± 0.5 kcal/mol is present in the interfacial region. This is consistent, within the error margins, with the surface preference of -3 ± 1 kcal/mol previously reported for this force field from calculations based on the free energy perturbation method.[25] From the present calculations it follows that the force field II also leads to an interfacial free-energy minimum for hydronium, however, its depth is reduced to -0.2 ± 0.5 kcal/mol. This reduction in surface preference can be traced back to differences in hydrogen bond accepting properties of the Eigen ion in the two force fields. The purely repulsive interaction between the oxygen of the Eigen cation and water hydrogens in force field I leads to destabilization of hydronium in the bulk phase where water molecules are placed all around the ion. While at the surface, the Eigen cation orients with its oxygen atom pointing toward the gas phase,[25] minimizing thus repulsive interactions with water molecules. Since force field II has a shallow minimum for water approaching the oxygen of the Eigen cation, its destabilization in the aqueous bulk and, consequently, stabilization at the surface is weaker than for force field I. It should be noted, however, that effects neglected in the present treatment, such as electronic delocalization may lead to further surface stabilization of hydronium.[16]

Orientation of the Eigen cation with respect to the normal to the water/vapor interface is depicted in Figure 3. As expected, the orientation is isotropic in the bulk, however, in the

interfacial region a significant orientational preference can be observed. In particular, the Eigen ion tends to point with its oxygen atom towards the gas phase, which is consistent with a previously established picture of the Eigen ion at the surface of water.[25] Little difference between the two investigated force field is observed for the orientational preference of the Eigen cation.

Figure 4 shows radial distribution functions between oxygen and hydrogen atoms of both hydronium and water molecules, which follow from simulations with force field II. Functions corresponding to the different location of hydronium with respect to the water/vapor interface are depicted, based on calculations performed for the individual umbrella sampling windows. The rather broad peaks located around 3.1 Å in Figure 4A correspond to the preferred oxygen-hydrogen distances between hydronium and the three tightly bound water molecules which accept hydrogen bonds from the ion, as well as to signal from more distant water molecules on the oxygen side of H_3O^+. A weak feature corresponding to neighboring water molecules on the oxygen side of hydronium is visible around 2.2 Å (see the inset in Figure 4A). Close to the surface this feature disappears and the peak at 3.1 Å decreases due to the fact that in this region the oxygen atom of Eigen is predominantly oriented towards the vapor phase. The peaks located around 1.6 Å in Figure 4B reflect the three tightly bound water molecules to H_3O^+, while the peaks located around 3 Å in this plot correspond to preferred distances between each of the hydrogen atom of H_3O^+ and the two oxygen atoms accepting hydrogen bonds from the two other hydrogens of the hydronium ion. It is worth noting that the first peak of the radial distribution functions in Figure 4B practically does not change with the distance of Eigen ion from the interface, indicating that H_3O^+ takes with itself the three tightly bound water molecules all the way to the surface.

The number of donating and accepting hydrogen bonds of H_3O^+ as a function of the position of the ion in the slab is quantified in Figure 5. A cutoff of 2.0 Å was assumed for evaluating the number of contacts between hydrogen atoms of H_3O^+ and oxygen atoms of water molecules (see Figure 4B). The number of donating hydrogen bonds of H_3O^+ is exactly equal to three, independent of both its location with respect to the water/vapor interface and the choice of the force field (i.e., variant I or II). The number of contacts between the oxygen atom of H_3O^+ and hydrogen atoms of water molecules is calculated within the distance of 2.5 Å employing both force fields (see Figure 4A). The number of Eigen oxygen-water hydrogen contacts is more than an order of magnitude smaller than the number of donating hydrogen bonds and it also exhibits more a complex interfacial behavior. First, these contacts virtually disappear when H_3O^+ is located close to the interface, which is consistent with the previous results concerning orientation of the hydronium ion at the surface of water with oxygen atom exposed into the gas phase. Second, in bulk of water the average number of Eigen oxygen-water hydrogen contacts increases by a factor of three (while still remaining less than 0.2) upon moving from force field I to II. This is a consequence of the weak attraction between water hydrogen atoms by the oxygen atom of Eigen introduced in the force field II.

4. Conclusions

Using umbrella sampling MD we quantified the surface affinity of the Eigen cation and the sensitivity of the result to the employed force field for H_3O^+. Respecting the very shallow minimum on the potential curve corresponding to a water molecule approaching the Eigen cation from its oxygen side, which is revealed by high quality ab initio calculations, lead us to a reparameterization of the force field H_3O^+. Qualitatively, the surface orientation and preference

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of the Eigen cation is preserved, albeit quantitatively it is reduced from -1.8 to -0.2 kcal/mol. It is likely that effects neglected in the present classical MD with polarizable potentials, such as electronic delocalization, further increase the surface stabilization of the hydrated proton.[16] In summary, albeit the exact value of the surface free energy of hydronium depends to some extent on the particular method employed, the experimental observation[9,10,15] that this ion is present at the water/vapor interface exhibiting a modest surface affinity, is robustly reproduced by computer simulations.

Table 1. Parameters (i.e., partial charges e, polarizabilities α, and Lennard-Jones parameters σ and ε) of the force field II employed for hydronium ion in water. O-H bonds in H_3O^+ were constrained to 0.98 Å, and H-H the distances were constrained to 1.63 Å. Note that for the force field I the same parameters were used, however, without the extra interaction between the oxygen atom of hydronium and water hydrogens.

	e	α (Å^3)	σ (Å)	ε (kJ/mol)
O (H_3O^+)	-0.4166	0.97	3.214	0.1560
H (H_3O^+)	+0.4722	0.0	0.0	0.0
O (H_3O^+) – H (H_2O)	–	–	1.9	1.077

Figure captions

Figure 1

Potential energy calculated with both *ab initio* methods and empirical force-fields for

$H_3O^+(H_2O)_4$ clusters as a function of the distance between O-atom of Eigen and O-atom of the

water molecule nearest neighboring oxygen of hydronium ion. The cluster is schematically

depicted in the inset and the O-O distance is defined.

Figure 2

Potential of mean-force for Eigen ion in water as a function of the distance of hydronium oxygen

from the slab surface calculated employing three different force-fields. The water density profile

is also shown.

Figure 3

Distribution of the values of cosine of the angle between the normal to the surface and the

prinicipal molecular axis of H_3O^+. The color scale reflects the occurrence of a given cosine value

in arbitrary units. The value of cosine equal to 1 corresponds to the molecular axis of H_3O^+

parallel to the normal with the oxygen atom of hydronium pointing towards the gas phase.

Figure 4

Radial distribution functions calculated between O-atom of Eigen ion and H-atoms of water (A),

and between H-atoms of hydronium and O-atoms of water (B) for the new force field. In each

case the distribution corresponding to different location of hydronium in the slab are depicted (z

is the distance between the hydrogen oxygen atom and the slab surface). The inset in the upper

panel shows a zoomed view in the region corresponding to the H-bond accepted by Eigen.

Figure 5

Number of contacts between atoms of the Eigen ion and water as a function of the location of hydronium in the slab calculated employing both the old and the new empirical force-field. The density profile of water is depicted for comparison.
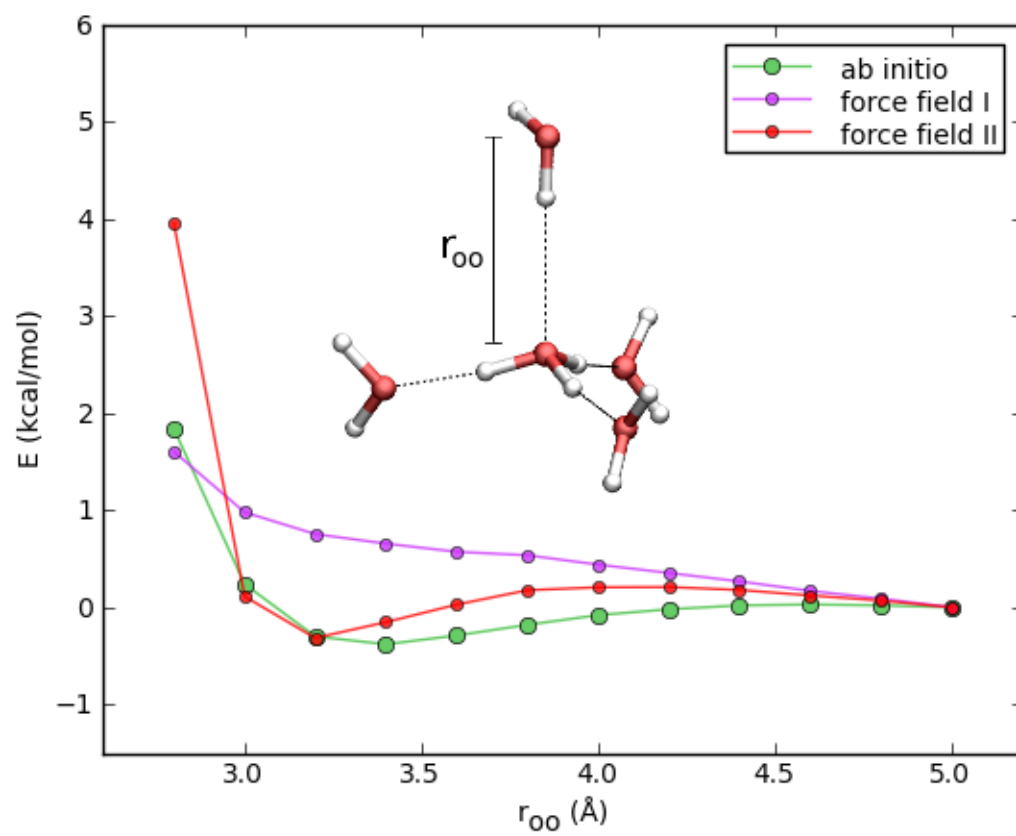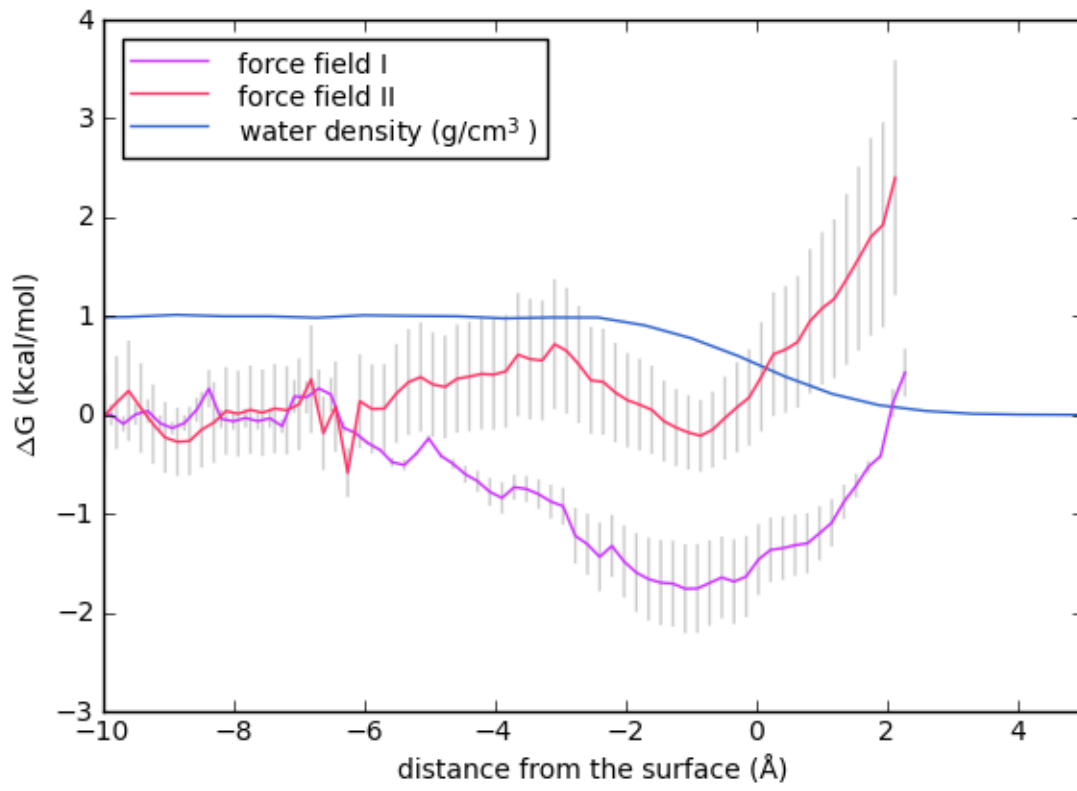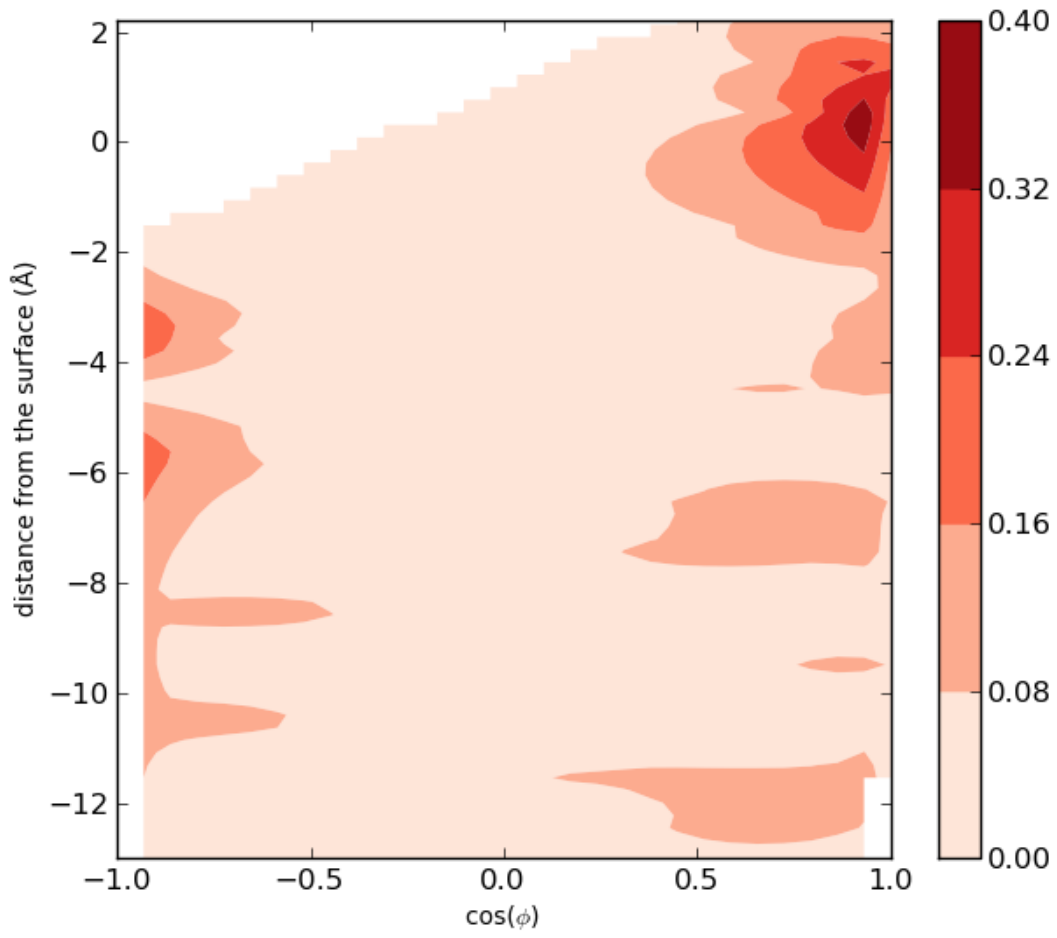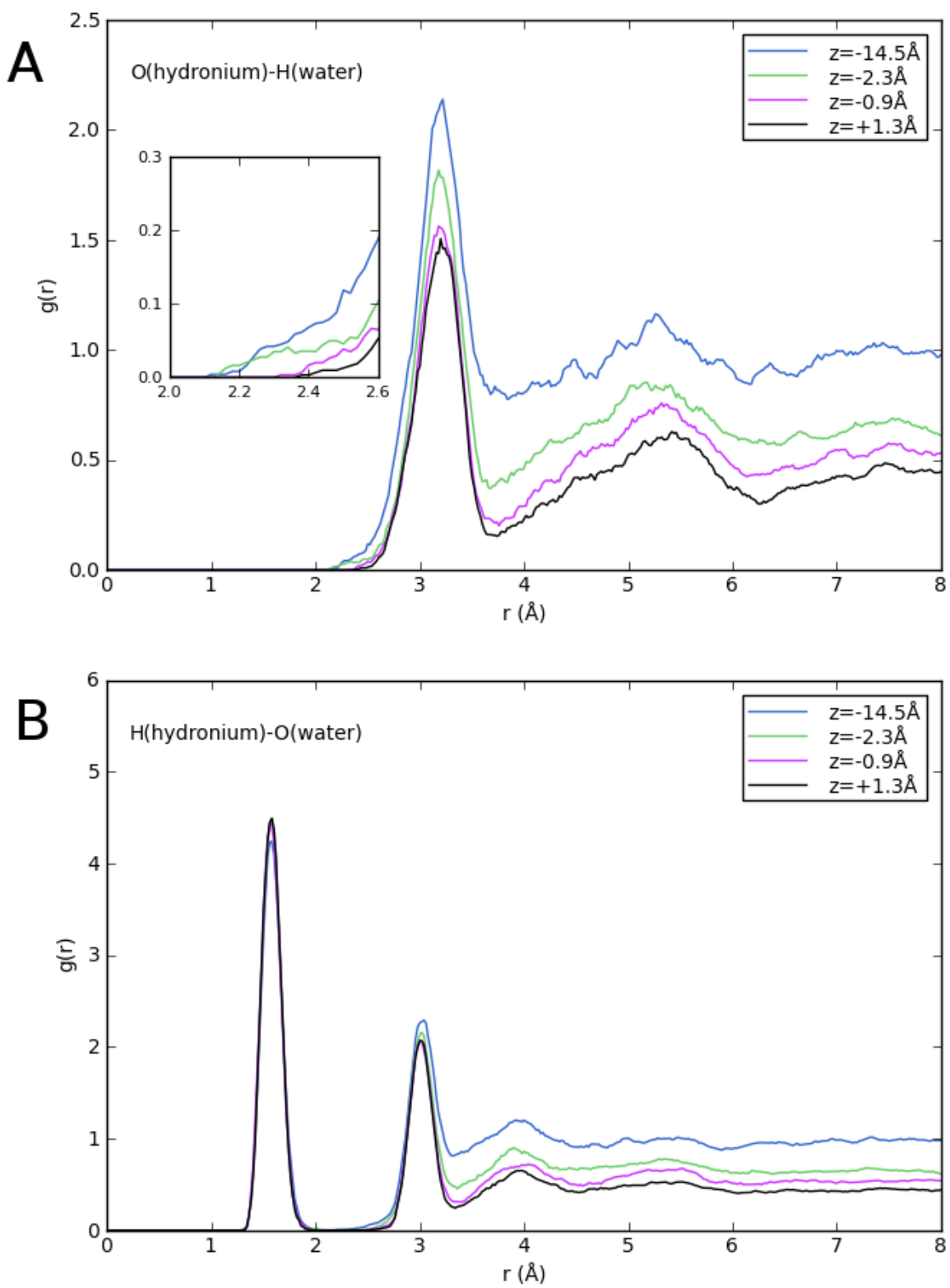
Figure 1

Figure 2

Figure 3
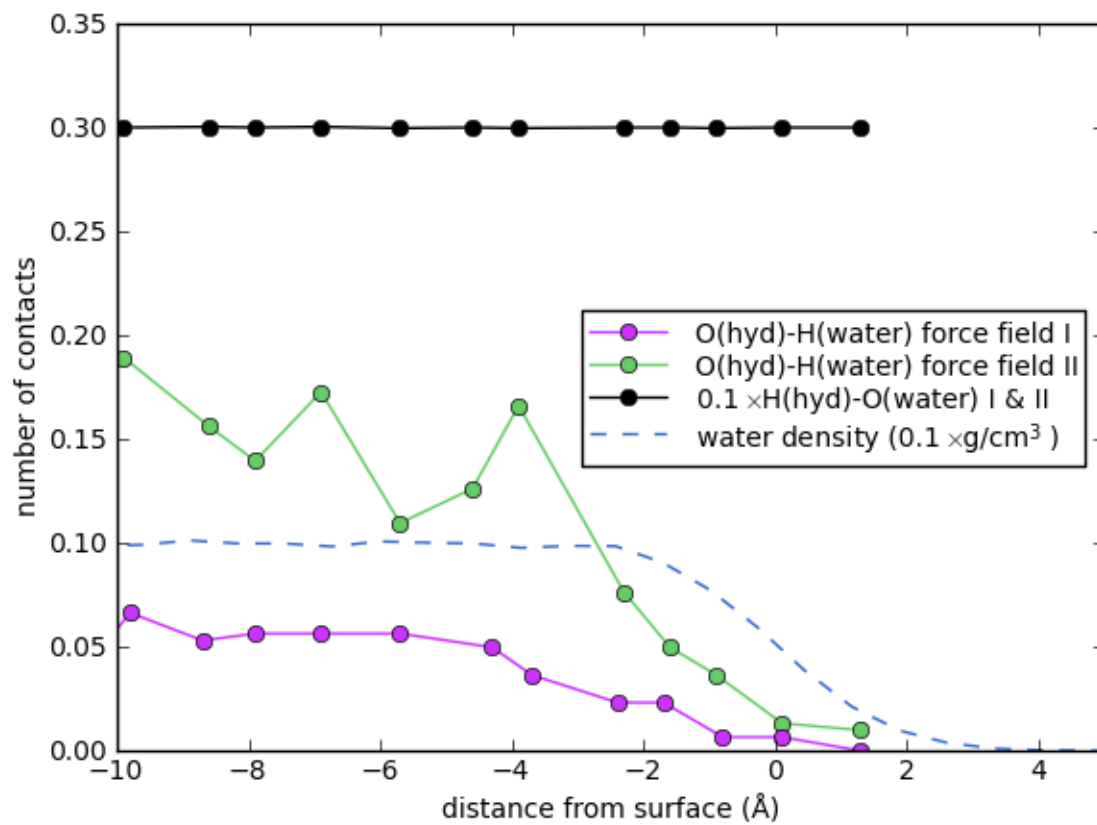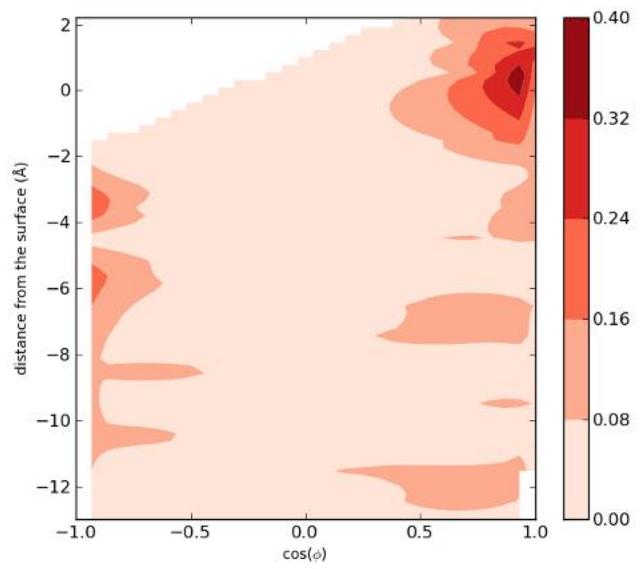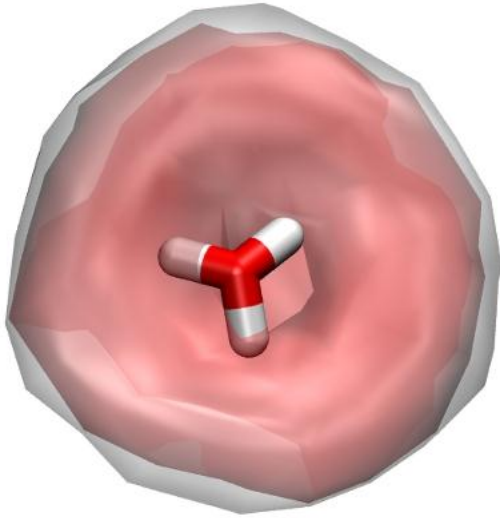
Figure 4

Figure 5

TOC Graphics

References

(1)   Eigen, M. *Angewandte Chemie, International Edition* **1964**, *3*, 1.

(2)   Zundel, G. *Advances in Chemical Physics* **2000**, *111*, 1.

(3)   Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601.

(4)   Schmitt, U. W.; Voth, G. A. *Journal of Chemical Physics* **1999**, *111*, 9361.

(5)   Chen, H. N.; Voth, G. A.; Agmon, N. *Journal of Physical Chemistry B*, *114*, 333.

(6)   Dang, L. X. *Journal of Chemical Physics* **2003**, *119*, 6351.

(7)   Petersen, M. K.; Iyengar, S. S.; Day, T. J. F.; Voth, G. A. *Journal of Physical Chemistry B* **2004**, *108*, 14804.

(8)   Mucha, M.; Frigato, T.; Levering, L. M.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. *Journal of Physical Chemistry B* **2005**, *109*, 7617.

(9)   Petersen, P. B.; Saykally, R. J. *Journal of Physical Chemistry B* **2005**, *109*, 7976.

(10)   Tarbuck, T. L.; Ota, S. T.; Richmond, G. L. *Journal of the American Chemical Society* **2006**, *128*, 14519.

(11)   Iyengar, S. S.; Day, T. J. F.; Voth, G. A. *International Journal of Mass Spectrometry* **2005**, *241*, 197.

(12)   Buch, V.; Milet, A.; Vacha, R.; Jungwirth, P.; Devlin, J. P. *Proceedings of the National Academy of Sciences of the United States of America* **2007**, *104*, 7342.

(13)   Voth, G. A. *Accounts of Chemical Research* **2006**, *39*, 143.

(14)   Wick, C. D.; Kuo, I. F. W.; Mundy, C. J.; Dang, L. X. *Journal of Chemical Theory and Computation* **2007**, *3*, 2002.

(15)   Tian, C. S.; Shen, Y. R. *Proceedings of the National Academy of Sciences of the United States of America* **2009**, *106*, 15148.

(16)   Lee, H. S.; Tuckerman, M. E. *Journal of Physical Chemistry A* **2009**, *113*, 2144.

(17)   Wu, Y. J.; Chen, H. N.; Wang, F.; Paesani, F.; Voth, G. A. *Journal of Physical Chemistry B* **2008**, *112*, 467.

(18)   Vacha, R.; Horinek, D.; Berkowitz, M. L.; Jungwirth, P. *Physical Chemistry Chemical Physics* **2008**, *10*, 4975.

(19)   Vacha, R.; Buch, V.; Milet, A.; Devlin, P.; Jungwirth, P. *Journal of Chemical Physics* **2007**, *9*, 4736.

(20) Purvis, G. D. III; Bartlett, R. J. *Journal of Chemical Physics* **1982**, *76*, 1910.

(21) Dunning, T. H. Jr. *Journal of Chemical Physics* **1989**, *90*, 1007.

(22) Simon, S.; Duran, M.; Dannenberg, J. J. *Journal of Chemical Physics* **1996**, 105 11024.

(23) Frisch, M. J. et al. *Gaussian 03* (Gaussian, Inc., Wallingford, CT, 2003).

(24) Caldwell, J. W.; Kollman, P. A. *J. Phys. Chem.* 1995, 99, 6208

(25) Vacha, R.; Buch, V.; Milet, A.; Devlin, J. P.; Jungwirth, P. *Journal of Chemical Physics* 2007, 9, 4736-4747.

(26) Lamoureux, G., Roux, B. *Journal of Physical Chemistry A* **2004**, *119*, 3025.

(27) Torrie, G. M.; Valleau, J. *Journal of Computational Physics* **1977**, *23*, 187

(28) Darden, T.; York, D.; Petersen, L. *Journal of Chemical Physics* **1993**, *98*, 10089.

(29) Hoover, W. G. *Phyycal Reviews A* **1985**, *31*, 1695.

(30) Ryckaert, J. P., Ciccotti, G., Berendsen, H. J. C. *Journal of Computational Physics* **1977**, *23*, 327.

(31) Miyamoto, S., Kollman, P. A. *Journal of Computational Chemistry* **1992**, *13*, 952.

(32) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *Journal of Chemical Theory and Computation* **2008**, *4*, 435.

(33) Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. *Journal of Computational Chemistry* **1992**, *13*, 1011.