Surface Affinity of the Hydronium Ion: The Effective Fragment Potential and Umbrella Sampling

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Abstract
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Surface Affinity of the Hydronium Ion: The Effective Fragment Potential and Umbrella Sampling

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ABSTRACT: The surface affinity of the hydronium ion in water is investigated with umbrella sampling and classical molecular dynamics simulations, in which the system is described with the effective fragment potential (EFP). The solvated hydronium ion is also explored using second order perturbation theory for the hydronium ion and the empirical TIPSP potential for the waters. Umbrella sampling is used to analyze the surface affinity of the hydronium ion, varying the number of solvent water molecules from 32 to 256. Umbrella sampling with the EFP method predicts the hydronium ion to most probably lie about halfway between the center and edge of the water cluster, independent of the cluster size. Umbrella sampling using MP2 for the hydronium ion and TIPSP for the solvating waters predicts that the solvated proton most probably lies about 0.5–2.0 Å from the edge of the water cluster independent of the cluster size.

1. INTRODUCTION

The solvated proton is of great importance in chemistry, occurring in a wide variety of natural settings, such as biological phenomena, surface science, and interstellar chemistry and has been widely studied experimentally and computationally. 1–18 Of particular interest is the surface affinity of the solvated proton, since if the proton demonstrates a surface affinity, the proton could catalyze acid–base reactions at the interface. A general consensus has emerged that the solvated proton demonstrates a surface affinity, though there is conflicting evidence regarding the cause of the surface affinity.

Ideally, computational studies of the solvated proton should be performed with ab initio molecular dynamics (AIMD) simulations. 19 The solvated proton is shared and transported among many different water molecules over the course of molecular dynamics (MD) simulations through the Groththus shuttling mechanism, 20,21 and AIMD can account for the changing bonding topology of the solvated proton. However, AIMD simulations of the solvated proton are difficult due to their computational expense and are therefore limited to smaller system sizes and shorter simulations, compared with classical MD simulations. While there has been some success with AIMD simulations on larger systems using Car–Parrinello density functional theory, 8,9 most MD simulations of the solvated proton have used either a classical molecular mechanics (MM) force field or a QM/MM description of the system.

Classical or QM/MM MD simulations of the solvated proton can be broadly separated into two groups: simulations that account for the Groththus shuttling mechanism through the use of the multistate empirical valence bond method (MS-EVB) or other similar methods and simulations that treat the solvated proton as existing in either the limiting form of the Eigen 24 (H₃O⁺) or Zundel 25 (H₅O₂⁺) cation. Although methods that include the Groththus shuttling mechanism are more physically correct in the way they account for proton transport, classical or QM/MM simulations in which the Groththus shuttling mechanism is not included have described the surface affinity of the solvated proton in water reasonably well. A previous study 3 using classical MD and the Eigen cation found no significant change in the surface affinity of the solvated proton when the proton was allowed to stochastically hop between water molecules, although another study 6 found that classical MD simulations using the Eigen and Zundel cations were consistent with Born–Oppenheimer DFT MD calculations on smaller clusters. More recently, 13 QM/MM MD calculations that used a limiting Eigen cation showed a surface affinity for the solvated proton. The limiting form of the Eigen cation, the hydronium ion, is the focus of the present study. Both a model potential and a QM/MM approach are used.

The effective fragment potential 26,27 (EFP) is a one-electron model potential with fixed internal geometry. EFP calculations compute the interaction energy between fragments. In a typical EFP calculation, each molecule is treated as a fragment. The EFP interaction parameters are derived from a preparatory ab initio calculation. For neutral water clusters, the EFP method correctly reproduces the relative energies and geometries of second order Møller–Plesset (MP2) perturbation theory at orders of magnitude lower computational cost. 27–29 The EFP method has also been used successfully to model ion...
For the protonated water cluster, one would expect that the EFP method will provide a level of accuracy similar to that of correlated electronic structure theory at a significantly smaller computational cost. The present study employs the general EFP2 method for both the solute hydronium ion and the solvent water, in combination with umbrella sampling to calculate the probability distribution function of the hydronium ion as a function of the distance of the center of mass of the hydronium ion from the center of the cluster. A previous study used umbrella sampling to calculate the surface affinity of the hydronium ion using a polarizable force field. Umbrella sampling has also been combined with the EFP2 method to accurately compute the hydration structures of salts and absolute $pK_a$ values.

### 2. COMPUTATIONAL METHODS

The surface affinity of the hydronium ion was calculated using NVT MD simulations with umbrella sampling. To systematically investigate the $H_3O^+$ surface affinity as a function of cluster size, simulations were performed with one $H_3O^+$ and 32, 64, 128, or 256 solvating water molecules. All MD simulations were performed using the electronic structure program GAMESS.

In addition to the EFP2 simulations, an analogous set of calculations were performed in which the $H_3O^+$ is represented with second order perturbation theory (MP2) and the aug-cc-pVDZ basis set, and the waters are described with the TIPSP potential (MP2/TIP5P).

For each umbrella sampling calculation, a harmonic spherical boundary potential centered at the origin was used to prevent evaporation. The force constant for the spherical boundary potential was set to 3.0 kcal/mol/Å$^2$, and the edge of the spherical boundary potential was set such that the density of each cluster would be equal to the density of water at 300 K if all molecules were inside the spherical boundary potential. For 32, 64, 128, and 256 solvating waters, the edge of the spherical boundary was set to 6.2, 7.8, 9.7, and 12.2 Å from the origin, respectively. For the umbrella sampling, windows were selected every 0.5 Å, starting at the origin and ending at the edge of the spherical boundary potential. For 32, 64, 128, and 256 solvating waters there were 13, 16, 20, and 26 windows, respectively. The force constant for the umbrella sampling constraint was set to 2.0 kcal/mol/Å$^2$. The force constants for the spherical boundary potential and umbrella sampling constraint were chosen to ensure adequate sampling and overlap among the umbrella sampling simulations.

For each combination of cluster size, level of theory, and window, initial NVT equilibrations were performed for 20 ps at 300 K. The final configurations of the equilibration were then used for NVT production simulations for 100 ps at 300 K. The NVT simulations all used the velocity-Verlet integration and a step size of 1.0 fs.
To improve the convergence of the probability distribution function for the EFP2 simulations with 256 solvating water molecules, two additional MD simulations with umbrella sampling were performed with windows at 9.5 and 10.5 Å from the center of the cluster. The additional calculations used the same MD, spherical boundary potential, and umbrella sampling protocol as the other MD simulations with umbrella sampling.

The probability distribution function and potential of mean force (PMF) for each cluster size and level of theory was then obtained from the production simulations by the weighted histogram analysis method (WHAM).39,40

To investigate the solvent−solute local structure, the average number of hydrogen bonds to the hydronium ion was computed for the EFP2 and MP2/TIP5P umbrella sampling simulations with 256 waters where the hydronium ion was restrained to be in the middle and on the surface of the cluster. The calculation was performed using the hbond analysis tool in VMD41 with the default parameters.

Results and Discussion

The probability distribution functions and PMFs for each cluster size and combination of theory are presented in Figure 1 and Figure 2 respectively. To better indicate the surface of the water cluster, Figure 1 and Figure 2 include the integrated radial distribution function ($g(r)$) calculated from the EFP2 umbrella sampling simulation where the hydronium ion was constrained to lie on the surface. For all cluster sizes, EFP2 predicts the hydronium ion to lie closer to the center of the water cluster than does MP2/TIP5P.

For the hydronium ion solvated by 32 waters, EFP2 and MP2/TIP5P predict that the hydronium ion most probably lies about 1/2 and 3/4 of the way between the center and the edge of the water cluster respectively, where the edge of the water cluster is defined as the start of the spherical boundary potential. The greatest probability for finding H$_3$O$^+$ corresponds to a distance from the edge of the water cluster of about 2.5−3.5 Å for EFP2 and about 0.5−2.0 Å for MP2/TIP5P. The EFP2 and MP2/TIP5P probability density functions maintain common features as the water cluster size is increased. MP2/TIP5P predicts that the hydronium ion most probably lies at a distance of about 0.5−2.0 Å from the surface of the water cluster independent of the water cluster size. EFP2 predicts that the hydronium ion most probably lies about 1/2 of the way from the center to the surface of the water cluster independent of water cluster size.

For all cluster sizes, the peaks in the MP2/TIP5P probability distribution functions are sharper and higher than the corresponding EFP2 probability distribution functions. The sharp MP2/TIP5P probability distribution function indicates that for MP2/TIP5P the hydronium ion is unlikely to be found outside the most probable region of space of 0.5−2.0 Å from...
the edge of the water cluster. The more diffuse EFP2 probability distribution function indicates that while the hydronium ion is most likely to be found at a distance of about 1/2 of the way from the center to the surface of the water cluster, the hydronium ion is predicted to be much less constrained to one region of space than is the case with MP2/TIP5P. That is, there are significant probabilities that the $\text{H}_3\text{O}^+$ lies closer to the surface.

Both the MP2/TIP5P and EFP2 probability distribution functions show smaller propensities for the hydronium ion to be near the center of the water cluster than in other regions of the water cluster. There is a stronger surface affinity for MP2/TIP5P than there is for EFP2, so MP2/TIP5P predicts a lower probability for the hydronium ion to be at the center of the water cluster. It is important to stress that unlike the potential of mean force, the probability distribution function does not need to be corrected with the inclusion of a volume-entropy term.\(^{42}\)

As the PMFs can be calculated directly from the probabilities, the trends in the PMFs are similar to the probabilities. The PMFs for the EFP2 simulations show a large increase at the edge of the cluster, while the PMFs for the MP2/TIP5P simulations are much flatter than the EFP2 PMFs with a small decrease in the PMF at the edge of the water cluster. The PMFs for both the EFP2 and MP2/TIP5P simulations are less flat than the PMFs computed from ab initio MD simulations for the interfacial region of bulk water of a recent study.\(^{18}\) One possible reason for the difference is that the present study is performed using water clusters and not the interfacial region of bulk water. In the present study, the simulation with 256 waters is the closest approximation to bulk water and the MP2/TIP5P simulation with 256 waters has the flattest PMF.

To investigate the solvent−solute local structure, the average number of hydrogen bonds to the hydronium ion has been computed for the EFP2 and MP2/TIP5P methods for the umbrella sampling simulations with 256 waters where the hydronium ion was constrained to be in the middle and on the surface of the cluster. The average number of hydrogen bonds when the hydronium ion was constrained to be in the middle of the cluster was 2.81 for both the EFP2 and MP2/TIP5P methods. The average number of hydrogen bonds where the hydronium ion was restrained to be on the surface of the cluster was 2.88 and 0.80 for the EFP2 and MP2/TIP5P method, respectively.

The difference in the solvent−solute local structure is proposed to arise because the EFP2 fragments have fixed internal geometries. The hydronium ion $\text{H}−\text{O}−\text{H}$ bond angle distribution changes for MP2/TIP5P with 32 solvent waters as the umbrella potential is moved from the center to the surface of the cluster (Supplemental Figures 1 and 2). The distribution of the hydronium ion $\text{H}−\text{O}−\text{H}$ bond angles for MP2/TIP5P with 32 solvent waters indicates that the hydronium ion is flatter when the hydronium ion is in the interior compared to when the hydronium ion is on the exterior of the water cluster. The EFP2 hydronium ion is constrained to be flat on both the surface and the interior of the cluster. When the hydronium ion is in the interior of the cluster, the EFP2 and MP2/TIP5P hydronium ion bond angles are similar, and the average number of hydrogen bonds agrees. But because of the fixed EFP2 internal geometry, when the hydronium ion is near the surface of the cluster, the EFP2 system is prevented from relaxing to a structure in which the hydronium ion would form fewer hydrogen bonds.

The MP2/TIP5P results agree with much of the recent literature\(^{11−18}\) by predicting that the hydronium ion demonstrates a modest surface affinity. The EFP2 predicts a weaker surface affinity than does MP2/TIP5P. The EFP2 method predicts that it is most probable to find the hydronium ion halfway between the center and edge of the cluster independent of the water cluster size. However, as noted above, the EFP2 probability distribution is rather broad and indistinct.

There are two possible origins of the differences between the EFP2 and MP2/TIP5P surface affinities. The first possibility is similar to the proposed reason for the difference in the EFP2 and MP2/TIP5P solvent−solute local structures. Since EFP2 uses fragments with fixed internal geometries, the system is prevented from relaxing to a lower energy structure in which the hydronium ion might lie closer to the surface of the cluster.

The MP2/TIP5P results presented here use a solvent with frozen internal geometry, and since the MP2 hydronium ion does lie closer to the surface than does the EFP2 hydronium ion, it may be that only internal relaxation in the solute is needed for EFP2. If this is indeed the case, QM/MM MP2/EFP2 MD simulations should allow the system to relax sufficiently. Ab initio-EFP2 MD simulations are not currently possible, since the QM-EFP2 gradient is not yet fully implemented. Once this implementation is complete, QM-EFP2 MD simulations will be performed on solvated $\text{H}_3\text{O}^+$.

Because the EFP2 method generally predicts intermolecular interactions with an accuracy that is equivalent to that of MP2, a second possible reason that EFP2 MD simulations predict that $\text{H}_3\text{O}^+$ lies further from the surface than is predicted by most methods is that an MP2 MD simulation would predict such a result as well. That is, the EFP2 prediction could be the correct one. At present, performing MP2 AIMD simulations with no approximations is computationally infeasible for the system sizes and simulation times required. However, with fragmentation methods\(^{43}\) such as the fragment molecular orbital (FMO) method,\(^{41}\) or related methods,\(^{45−47}\) MP2 AIMD simulations will be possible.

4. CONCLUSIONS

The surface affinity of the hydronium ion was investigated using umbrella sampling based on MD simulations with both the EFP2 method and the combined MP2/TIP5P methods. The EFP2 and MP2/TIP5P probability density functions maintain common features independent of the number of solvating waters. According to the EFP2 method, the hydronium ion most probably lies ~halfway between the center and the edge of the cluster, while the MP2/TIP5P simulations predict that the $\text{H}_3\text{O}^+$ is most likely to be found ~0.5−2.0 Å from the edge of the cluster. Both of these predictions are independent of the cluster size. The origin of the different predictions by the two methods will be investigated in future calculations.

ASSOCIATED CONTENT

Supporting Information

Graphs of the frequency and the difference in the frequency of the $\text{H}−\text{O}−\text{H}$ bond angle of the hydronium ion solvated by 32 waters at the MP2/TIP5P level of theory with the umbrella potential centered at the edge of the water cluster and at the center of the water cluster. This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes

The authors declare no competing financial interest.

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