Ab initio molecular dynamics and quasichemical study of H\(^+\) (aq)

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The excess proton in water, H\(^+\) (aq), plays a fundamental role in aqueous solution chemistry. Its solution thermodynamic properties are essential to molecular descriptions of that chemistry and for validation of dynamical calculations. Within the quasichemical theory of solutions those thermodynamic properties are conditional on recognizing underlying solution structures. The quasichemical treatment identifies H\(_2\)O\(^{+}\) and H\(_2\)O\(^{2+}\) as natural inner-shell complexes, corresponding to the cases of \(n = 1, 2\) water molecule ligands, respectively, of a distinguished H\(^+\) ion. A quantum-mechanical treatment of the inner-shell complex with both a dielectric continuum and a classical molecular dynamics treatment of the outer-shell contribution identifies the latter case (the Zundel complex) as the more numerous species. Ab initio molecular dynamics simulations, with two different electron density functionals, suggest a preponderance of Zundel-like structures, but a symmetrical ideal Zundel cation is not observed.

Eigen cation | Zundel cation

The hydrated proton, H\(^+\) (aq), plays a fundamental role in aqueous phase chemistry. Here, we address two related issues of the molecular theory of H\(^+\) (aq) that haven’t been resolved: the structural categorization of the local environment of H\(^+\) (aq) and hydration free energy of this ion under standard conditions.

The difficulty of treating H\(^+\) (aq) on the basis of molecular theory is principally that the interactions are fundamentally chemical, and therefore complicated when viewed on a thermal energy scale. This is also true of other aqueous ions (1, 2), but H\(^+\) (aq) is an extreme example. In addressing this complexity, computations of thermodynamic properties of these solutions and comparisons with experimental results give the clearest assessment of theory and simulation work (3–8).

Structural and thermodynamic issues are connected, of course, and particularly directly by the quasi-chemical theory (9–17). A primitive quasi-chemical approximation has been developed for the hydration free energy of H\(^+\) (aq) (4, 7). The conclusion of that work was that the H-centered Zundel complex ion H\(_2\)O\(^+\) provided a simple and valid structural description of the local environment of H\(^+\) (aq); that theory identifies the Eigen complex ion H\(_2\)O\(^{+}\) (i.e., hydrated oxonium) as a structural specification of outer-shell hydration of a distinguished H\(^+\), and therefore assigns the Eigen cation less significance.

A distinguishing feature of the Zundel complex is an O–O distance of 2.4 Å, shorter than O–O distances between water molecules, or within the hydrated oxonium ion. The latter case (the Eigen structure) might be taken as an O-center basis of a quasichemical model of the solution thermodynamics. But a subsequent observation obtained from ab initio molecular dynamics (AIMD) simulation of HO\(^−\) (aq) then becomes relevant (1). AIMD results showed that the nearest coordinating O atom to a HO\(^−\) oxygen has the 2.45-Å displacement distinctive of the H\(_2\)O\(^{2+}\) complex. This separation is analogous to the case of the Zundel possibility here and shorter than the O–O distance to the oxygens within the inner shell of the corresponding ideal O-centered structures for HO\(^−\) (aq) complexes. The H\(_2\)O\(^{2+}\) complex appeared then as a subgrouping in the dynamical simulations (1). It is natural to ask the corresponding questions for H\(^+\) (aq), particularly because quasichemical models for H\(^+\) (aq) might be based on either H-centered or O-centered definitions.

With a liquid material composed of \(n\) O atoms, 2H atoms, and one H\(^+\) ion, and with a specific spatial configuration of those nuclei sampled from an AIMD calculation, it is conceptually nontrivial to identify one H nucleus as locating the H\(^+\) (aq) species. We might assign each H nucleus to its closest O nucleus. On physical grounds, for the conditions studied here, we expect that such a procedure would identify one H\(_3\)O\(^+\) ion, although that expectation is not a guarantee. Alternatively, we could find the shortest third nearest OH distance, and regard that O nucleus as the center of an H\(_3\)O\(^+\) ion. These procedures give the same results for the present study. The latter procedure emphasizes that both an O center and an H center are identified. These two procedures are similar to ones discussed by Stillinger (18) and avoid “unnecessary commitment to specific chemical structures” (18) such as H\(_2\)O\(^{+}\) or H\(_2\)O\(^{2+}\).

AIMD is well suited to consider chemical transformations in a dynamical setting. Small system sizes and short simulation times are the most severe limitations of these methods. An early AIMD study of H\(^+\) (aq) used the method of ref. 19. In that work, which was based on classical statistical mechanics, all protons were associated with a single water oxygen in ~60% of the configurations, as in the ideal H\(_2\)O\(^+\) structure. In the other 40% of the configurations the proton was not assigned to a single oxygen atom, but was found midway between the O atoms of two water molecules, as happens in the ideal H\(_2\)O\(^{2+}\) structure. In a subsequent study (20), heavy particle quantum effects were included in the simulations. That study concluded that the H\(^+\) (aq) proton exists as a “fluxional” defect, i.e., it is uncategorizable. The classical barrier for proton transfer between two adjoining oxygen centers was studied there, too. Inclusion of quantum mechanical effects on the atomic motion was found to wash out the barrier observed for the classical case.

Alternative computational studies of H\(^+\) (aq) have been based on the empirical valence bond (EVB) approach, progressively refined by Voth and coworkers (21–23). Vuilleumier and Borgis (24) and Kornyshev et al. (25) have also considered H\(^+\) (aq) by using EVB approaches. The EVB method can access long simulation times, but it requires a serious parametrization. The results of those studies are not unanimous, and thermodynamic characteristics of H\(^+\) (aq) have not been sought. It is the intertwined issues of structure and molecular thermodynamics associated with H\(^+\) (aq) that are the focus of the present investigation.

Quasichemical Theory

The quasichemical theory is founded on partitioning the system into an inner-shell region and an outer-shell region (15, 26) on a distinguished solute of interest, here H\(^+\). This partitioning...
permits detailed treatment of the chemically important interactions within the inner shell while exploiting a simpler model to describe the interaction of inner-shell material with the rest of the system. A variational check is available to confirm the appropriateness of the partitioning (17, 27), although this point has not been pursued in this work.

The inner-shell reactions pertinent to the hydration of H* are

\[ H^+ + nH_2O \rightarrow [H_2O]^n_+ \]

As discussed earlier (4), \( n = 1, 2 \) are the only relevant inner-shell hydration numbers from an H-centered point of view. The free energy change for these reactions were calculated by using the Gaussian programs (28).

For estimating the outer-shell contribution, the ChelpG method (29) was used to obtain partial atomic charges. Then the electronic energy was obtained by using B3LYP/aug-cc-pVTZ (30). The statistical uncertainties in the molecular dynamics values are of the order of 1.5 kcal/mole (it is half that for water). The partial charges are calculated by using GAUSSIAN programs (28).

For the PW91 run a total of 22.3 ps of simulation was performed, of which the first 13.9 ps were for equilibration and the last 8.6 ps were for data collection. The mean temperature in the production phase was 301 \( \pm 2 \) K. The relative energy fluctuation, \( \sqrt{\langle E^2 \rangle / \langle E \rangle} \), was 6.5 \( \times 10^{-5} \). The relative drift in the energy was about \( -3 \times 10^{-5} \) ps\(^{-1} \).

For the PW91 run a total of 22.3 ps of simulation was performed, of which the first 13.9 ps were for equilibration and the last 8.4 ps were for production. The mean temperature in the production run was 334 \( \pm 20 \) K. The relative energy fluctuation, \( \sqrt{\langle E^2 \rangle / \langle E \rangle} \), was 6.4 \( \times 10^{-5} \), and the relative drift was about \( -2.0 \times 10^{-5} \) ps\(^{-1} \). For both the rPBE and PW91 runs, the metrics quantifying energy conservation are reasonable (1, 39).

In the present results the excess proton was identified as follows. For each oxygen in turn, the nearest two protons are found and assigned to that oxygen atom as water hydrogens. This approach leaves one proton unassigned, which is regarded as the excess proton, H* of Fig. 1.

Results

Quasichemical Theory. From Table 1 and Eq. 1, using the SPC/E values, we calculate the free energy of H* (aq) to be \(-244.1 \pm 10\) kcal/mole. A detailed discussion on standard states and this replacement contribution can be found in Astagiri et al. (4). Note that it is in forming Eq. 2 that approximations enter the theory; but all these approximations are available for scrutiny and improvement. Table 1 collects the relevant energies. For the dielectric continuum calculations, the molecular volumes of the H\(_2\)O ligands and the complex ion were defined by atom-centered spheres by using conventional, empirical radii (31). The radius assigned to H atoms was 1.172 Å, for example. Changes of these free energies with increases in these radii by 10% are not significant (7). This insensitivity is a manifestation of the variational character alluded to above.

Simulation Methodology

The initial system was obtained from the last snapshot of an AIMD simulation of K\(^+\) (aq) (8): the K\(^+\) was replaced by H\(^+\), and cubical cell edge length was adjusted to be consistent with the experimental partial specific volume. The system was 32 water molecules and a single H\(^+\) in a cubic box of length 9.8432 Å. All of the hydrogen atoms have the deuterium mass; hence our \(ab\ initio\) simulation corresponds to classical statistical mechanics of D\(^+\) in D\(_2\)O.

The AIMD simulations were carried out with VASP (32, 33) by using a generalized gradient approximation to the electron density functional theory. The core–valence interactions were described by using the projector augmented-wave (PAW) method (34, 35) adopting a kinetic energy cutoff of 400 eV for the plane wave orbitals. The PAW treatment is thought to handle difficult cases with large electronegativity differences with “exceptional precision” (35).

For the PW91 run a total of 22.1 ps of simulation was performed, of which the first 13.5 ps were for equilibration and the last 8.6 ps were for data collection. The mean temperature in the production phase was 301 \( \pm 20 \) K. The relative energy fluctuation, \( \sqrt{\langle E^2 \rangle / \langle E \rangle} \), was 6.5 \( \times 10^{-5} \). The relative drift in the energy was about \( -3 \times 10^{-5} \) ps\(^{-1} \).

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with the earlier determined free energy of components can be found in ref. 7.

estimates of the excess free energy of the charged quasicomponent. With the dielectric models these values are

kcal/mole. It is interesting that a more refined outer-shell model increases the balance in favor of Zundel. The reasons for the difference between classical molecular dynamics and dielectric continuum estimates of the excess free energy of the charged quasicomponent can be found in ref. 7.

Solvation free energy of neutral pairs can be considered as further checks. With the earlier determined free energy of HO\(^{+}\) (aq) of \(-123.8\) kcal/mole, the Zundel component gives the free energy of the pair HOH(aq) to be \(-367.9\) kcal/mole, compared with an experimental value of \(-366.6\) (7). The hydronium component gives \(-360.1\) kcal/mole.

AIMD. Figs. 2 and 3 provide the density distributions around O* and H* (Fig. 1) for the PW91 and rPBE runs.

Figs. 2 and 3 and Table 2 show that oxygens that are close neighbors to O* are somewhat asymmetric. In fact, O(1) is typically positioned \(\approx 2.45\) Å from O*. This separation is roughly the O–O separation expected in the Zundel complex (Table 2).

In contrast to the ideal Zundel structure, however, the two oxygen atoms coordinating the H* are not symmetrically disposed around H*. On the other hand, the shortest H*–O* bond lengths, \(\approx 1.12\) Å (Table 2), are significantly larger than the corresponding distances in the ideal Eigen structure (1.01 Å).

These results are qualitatively similar for the two functionals, PW91 and rPBE, considered here. For the case of pure liquid water these functionals give significantly different results for the most accessible properties such as radial distribution functions, and the rPBE functional seems to give the better results (17). Nevertheless, for ionic solutes, for example HO\(^{+}\) (aq) (1), the results are insensitive to this choice and highlight the importance of local chemistry for these strong interactions.

We reiterate that the small system sizes and observation times are a foremost limitation of AIMD simulations. This limitation might not have been a problem for inner-shell structures of metals ions in water in previous work, but it is still a point of reservation. Increasing the system size by less than a factor of 10 is not expected to be illuminating. Simulations longer by a factor of 10 might be marginally helpful. In that case, the concern isn’t statistical uncertainties with the structures that are observed, but that limited equilibration might preclude access to structures that would require an activated process. This limitation hasn’t been a problem in earlier work on hydrated ions (40).

Table 2. Statistical characterization of relevant bond lengths around H* and O* (Fig. 1)

<table>
<thead>
<tr>
<th></th>
<th>PW91</th>
<th>rPBE</th>
<th>Ideal Zundel</th>
<th>Ideal Eigen</th>
</tr>
</thead>
<tbody>
<tr>
<td>H*–O*</td>
<td>1.13 ± 0.05</td>
<td>1.12 ± 0.05</td>
<td>1.20</td>
<td>1.01</td>
</tr>
<tr>
<td>H*–O(1)</td>
<td>1.35 ± 0.10</td>
<td>1.37 ± 0.10</td>
<td>1.20</td>
<td>1.54</td>
</tr>
<tr>
<td>O*–O(1)</td>
<td>2.44 ± 0.05</td>
<td>2.45 ± 0.05</td>
<td>2.40</td>
<td>2.55</td>
</tr>
<tr>
<td>O*–O(2)</td>
<td>2.52 ± 0.06</td>
<td>2.56 ± 0.07</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O*–O(3)</td>
<td>2.63 ± 0.09</td>
<td>2.68 ± 0.11</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

O(n) indicates the nth closest neighbor of O*, and O(1) was invariably the second closest neighbor of H* in the present data. The statistical uncertainties are at 1σ level. The results of the H\(_5\)O\(_2\)* and H\(_2\)O\(_4\)* clusters, labeled ideal Zundel and ideal Eigen, respectively, are shown. The values for the optimized clusters are from B3LYP/6-31 + G(d,p) calculations. All lengths are in Å.
Discussion

The long nearest-neighbor $H^+\text{---}O^-$ distances are probably the most telling observations here. Also, the probable shortest $O\text{---}O$ distances are <2.5 Å. These results taken together then suggest the view that the H-centered ideal Zundel structure is the more appropriate simple characterization of the environment of $H^+$ (aq). The quasichemical thermodynamic model is consistent with this view.

Nevertheless, the principal peak of $g(H^+\text{---}O^-)$ is structured so as to be inconsistent with chemical equivalency of the two O atoms nearest to the distinguished $H^+$. The natural view is then that hydration induces a symmetry-breaking effect on ideal inner-shell structures. The electrical asymmetry associated with displacement of the centering H atom in a Zundel complex leads to stronger stabilizing interactions with the solution external to the complex, and consequently to asymmetric distribution of that H atom in this simulation. Because the two contributions to the composite first peak are well overlapped, we view this symmetry breaking as a secondary physical effect.

The asymmetric placement of the proton in $H_2O_2^{+}$ was noted earlier (21, 22, 24) and associated with the classical description of proton motion. Incorporating quantum effects for the atomic motion, either explicitly (21, 22) or implicitly in terms of effective potentials (24), was found sufficient to wash out a hydration-induced barrier.

Concentrated HCl(aq) solutions have been studied by x-ray and neutron diffraction methods (41, 42). Comparison of our results to those works is problematic because the interpretations are not uniform, and the assumptions imposed on the interpretations seem to preclude some of the questions we address. For example, the interpretations assume rigid $H_2O^+$ molecular units for $H^+$ (aq).

The mobility of $H^+$ (aq) is also of great interest and deserves more specific study. A primitive initial characterization can be obtained by identifying the exchange events as shown in Fig. 4. The shuttling of the excess proton between adjacent pairs of hydrogen-bonded oxygen atoms, for example, $O^-(\text{--}O(1))$ or $O^-(\text{--}O(2))$ in Fig. 1, is more frequent than for the analogous case for $HO^-$ (aq), also shown in Fig. 1 for similar circumstances (1).

In this way, the present simulation data are qualitatively consistent with the experimental results that mobilities of $HO^-$ (aq) are not as high as those of $H^+$ (aq).

Fig. 4. Exchange events involving $H^+$ and $HO^-$ motion in water. The vertical bars flag hydrogen exchange events, those times at which the identity of the excess proton and the hydroxide oxygen changes. (Upper) The rPBE run. (Lower) The PW91 run. The data for the hydroxide exchange are from an earlier paper (1), and note particularly the previous hydroxide PW91 calculation was for the hydrogenated, not deuterated, case. The hydroxide PW91 and rPBE production runs were for 8.2 and 5.9 ps, respectively. For a similar length of time, $HO^-$ (aq) switches identity less frequently than $H^+$ (aq).

Conclusions

A primitive quasichemical theory suggests that the preponderant state of $H^+$ (aq) is the Zundel cation, $H_2O_2^{+}$. AIMD simulations of the classical statistical mechanics of $D_2O$ appear to support this conclusion, but the results display additional subtlety. In particular, the excess proton is asymmetrically positioned between its two coordinating oxygen atoms. Those oxygen atoms, however, are well separated to form the Zundel cation.

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