Comparative Proton Transfer Efficiencies of Hydronium and Hydroxide in Aqueous Solution: Proton Transfer vs Brownian Motion

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ABSTRACT: With the help of QM/EFP-MD with modern correlated quantum theories, distinctly different proton transport dynamics for hydronium and hydroxide ions was revealed. The efficiency of proton transfer for hydronium was found to be significantly higher than that for hydroxide, and the difference in efficiency increased as the temperature was lowered. This difference in dynamics suggests that molecular Brownian diffusion may play an important role in hydroxide transport. Our theoretical findings are consistent with recent experimental observations of proton transfer in amorphous solid water.

I. INTRODUCTION

Hydronium (H₃O⁺) and hydroxide (OH⁻) transport in aqueous solutions has been a subject of intense research in recent years due to its fundamental significance in many chemical and biochemical processes ranging from simple acid–base reactions to enzymatic functions.¹–²³ It is well-known that the diffusion coefficients of hydronium and hydroxide ions are anomalously large and that the mobility of a hydronium ion is nearly twice that of a hydroxide ion at room temperature, which led to Grotthuss’ concept of proton transfer via structural diffusion.

Extensive theoretical studies using Car–Parrinello molecular dynamics (CPMD),¹⁴,²⁴–²⁷ extended valence bond (EVB) theory,²⁸–³⁰ reactive molecular dynamics,³¹ and the dissociating model³² have been performed to illuminate the intriguing transport features of these ions. Accordingly, it has been well established that the proton transfer mechanism of hydronium involves an intricate interplay between the Eigen cation, H₃O⁺(H₂O)₃, and Zundel cation, [H₂O···H···OH₂]⁺.¹–⁷ It has been presumed that hydroxides also undergo such proton transfer,⁸–¹² although their critical solvation structures and related proton transfer mechanisms are quite controversial.¹,⁷,¹³–¹⁶ A recent comprehensive review by Marx et al.¹³ proposed three possible hydroxide mechanisms via proton transfer: mirror image, dynamical hypercoordination, and static hypercoordination mechanisms. However, the mechanism determined from theoretical investigations strongly depends on the choice of exchange-correlation functionals used in the CPMD simulations.

Following the terminology of Hynes, Borgis, and others,³³–³⁶ proton transfer in aqueous solutions is in general associated with a separating reaction barrier within the Born–Oppenheimer approximation. Depending on barrier heights,³⁴–³⁹ proton transfer can be classified as either adiabatic or nonadiabatic due to the quantum tunnel splitting effect. In the limit of adiabatic proton transfer,³⁵,⁴⁰ the energy separation of ground and excited proton transfer vibrational states is large enough to prevent a significant population of excited states, as is the case when the potential energy barrier is small or nonexistent. On the other hand, nonadiabatic proton transfer becomes especially important at low temperatures, where the proton transfer barrier is much higher than the thermal energy. Therefore, obtaining an accurate potential energy or free energy barrier of proton transfer in solution is critical. Contrasting to its importance, traditional high level ab initio correlation theories have not been well adopted for the study of hydronium and hydroxide dynamics in solution.

Diffusion coefficients represent collectively the dynamics of various transport events such as proton hopping, molecular diffusion, thermal rattling, hydrogen bonding, rotational relaxations, and solvation shell dynamics. To model various transport events with energetically reliable accuracies, long-time quantum mechanical molecular dynamics simulations with high level correlation theories are desirable. Recently, a hybrid quantum mechanical/effective fragment potential (QM/EFP)
scheme within the Born–Oppenheimer approximation has been suggested for practical quantum mechanical MD simulations. The EFP is a fully ab initio force field composed of sophisticated Coulomb, polarization, exchange repulsion, dispersion, and charge transfer terms. Detailed descriptions of the EFP and pertinent references can be found in a recent paper by Gordon et al. The hybrid QM/EFP-MD method has been successfully utilized in various solution dynamics studies, including proton transfer.

Experimental studies of the microscopic dynamics of hydroxide ion diffusion in an aqueous solution have been relatively scarce due to the difficulty in identifying the transitory structures of hydroxide ion diffusion through spectroscopic methods. Using femtosecond spectroscopy, Thøgersen et al. showed that the reorientation time of OH⁻ ions in water has a drastic temperature dependence, especially at low temperatures, implying that structural diffusion events are significantly suppressed. Later, Ma and Tuckerman suggested an explanation for this observation using CPMD simulations by showing that proton transfer events were suppressed by a pronounced population change of the dominant aqueous OH⁻ solvation complexes at low temperatures. Recently, the diffusion of hydronium and hydroxide ions has been studied experimentally in amorphous solid water (ASW) at low temperatures, which showed that the ions move via intrinsically different mechanisms in ASW. Although hydronium ions hop via an efficient proton transfer, hydroxide ions move via Brownian molecular diffusion. This new experimental finding strongly suggests the importance of the molecular diffusion mechanism, especially in the case of hydroxide transport, which has been neglected thus far. Since ASW and liquid water have certain similarities in molecular packing structures and thermodynamic properties, an intriguing question is to what extent the different transport mechanisms are transferable to hydronium and hydroxide ions in aqueous solution at room temperature. Hence, the present report explores the comparative proton transfer efficiencies of hydronium and hydroxide ions in aqueous solution using both ab initio quantum calculations on molecular clusters and QM/EFP-MD simulations. The consequent competition between proton transfer and molecular Brownian motion in the two ion transport systems is also discussed.

II. COMPUTATIONAL DETAILS

Density functional theory using BLYP and the exact exchange-incorporated B3LYP functional was adopted using 6-31G(d) basis sets to estimate proton transfer barriers for H₅O⁺ and H₃O⁻ model clusters. In addition, traditional correlated theories such as MP2 and CCSD(T) were also adopted using cc-pVDZ, cc-pVTZ, and cc-pVQZ correlation consistent basis sets. Quantum mechanical/molecular dynamics simulations were also performed for hydronium and hydroxide diffusion by employing our quantum mechanical/effective fragment potential molecular dynamics (QM/EFP-MD) method. The advantages of QM/EFP-MD are as follows: (i) the hybrid QM-EFP method can significantly reduce computational overhead, (ii) the ab initio driven EFP offers a high computational accuracy, and (iii) the calculation of the QM region can be improved by utilizing various advanced quantum chemical theories in combination with traditional
atom-center Gaussian basis sets. In the present work, canonical QM/EFP-MD simulations were performed for excess hydronium and hydroxide ions in a condensed water model. Spherical QM/EFP models of $\text{O}_2\text{H}_{13}^+$ and $\text{O}_2\text{H}_{13}^-$ QM regions were prepared with 286 and 285 explicit EFP water molecules, respectively. MD simulations were performed at 160 and 300 K, where the former condition possibly represents supercooled water or ASW. In order to prevent the evaporation of water during long-time simulations, a harmonic restraint potential for the solvent boundary was applied. Spherical boundary models with $\sim$300 EFP waters have been verified as a good model for condensed phase simulation in our previous papers, in which we have shown that the results of our spherical boundary models are nearly identical to those of periodic boundary models. The size of the QM region was designed by explicitly adding water molecules one at a time near the charged ion (hydronium or hydroxide) until the radial distribution functions (RDFs or $g(r)$) and potential of mean force (PMF) converged. Since we were using fixed QM boundary for the QM/EFP, it is possible that the chances of proton transfer to EFP are discouraged. However, the convergence of the radial distribution functions as well as potential of mean forces as a function of QM water ensures that the proton transfer occurs within QM region during our simulation time. We employed the BLYP/6-31G(d), B3LYP/6-31G(d), and MP2/cc-pVDZ levels of theory for the QM region during the MD simulations. Since the comparisons against earlier CPMD studies are important parts of current studies, we adopt the same BLYP functional. In addition, B3LYP was also chosen for its exact exchange functional. Canonical NVT simulations were performed for more than 100 ps in addition to the initial NVE equilibrations with 1 fs time steps. A Nose–Hoover thermostat was employed during the NVT simulations. All calculations were performed with a modified version of GAMESS.$^{53}$

III. RESULTS AND DISCUSSION

A. Quantum Mechanical Calculations on Small Ion Clusters. The proton transfer barriers of $\text{H}_2\text{O}_2^+$ and $\text{H}_2\text{O}_2^-$ were investigated by calculating the single point energy as a function of the location of the proton transferring between the two O atoms. In the proton transfer mechanism, the H$^+$ of $\text{H}_2\text{O}^+$ is transferred to $\text{H}_2\text{O}$ while the H$^+$ of $\text{H}_2\text{O}$ is transferred to OH$^-$. The geometries of $\text{H}_2\text{O}_2^+$ and $\text{H}_2\text{O}_2^-$ at each location were first optimized at the MP2/cc-pVDZ level of theory. In order to introduce solvation effects to the transferring proton, the calculations were performed at O–O distances of 2.54 and 2.60 Å. The shared proton was displaced along the line joining the two O atoms while keeping all other degrees of freedom fixed. Figure 1 shows the potential energy curves of proton transfer as calculated with BLYP, B3LYP, MP2, and CCSD(T), where the curves of CCSD(T) serve as references. Basis set convergence is seen from the values of CCSD(T) with the cc-pVTZ and cc-pVQZ basis sets. The proton transfer barriers of $\text{H}_2\text{O}_2^+$ are consistently lower than those of $\text{H}_2\text{O}_2^-$ for all theories. Among the results, the BLYP functional, which does not include exact exchange, yielded negligible barriers, irrespective of ion type and O–O distance. These results are especially distinct when the BLYP values are compared against the CCSD(T) results. The underestimation of reaction barriers by density functional theory without exact exchange has been well documented in the literature. In contrast, the B3LYP values are closer to those of MP2, indicating that the inclusion of exact exchange improves the accuracy in calculations of reaction barriers. The predicted barrier heights of hydronium and hydroxide are comparable to the average thermal energy of 0.59 kcal/mol at 300 K, indicating relatively small tunneling effects.

As compared with potential energy surfaces found by static quantum mechanical calculations, free energy surfaces obtained from molecular dynamics simulations involve various dynamical effects. Therefore, it is not straightforward to assume that the same dependency on computational theory can be applied to the free energy barriers of proton transfer. Therefore, QM/EFP-MD simulations were also performed on hydronium and hydroxide transport dynamics, and the results are discussed in the following section.

B. QM/EFP-MD Simulations on Hydronium and Hydroxide Transport in Solution. We performed canonical QM/EFP-MD simulations for excess hydronium and hydroxide ions in water at 160 and 300 K as described in the Computational Details section using three different quantum theories for the QM region: BLYP/6-31G(d), B3LYP/6-31G(d), and MP2/cc-pVDZ. The resulting PMFs for hydronium and hydroxide along the proton transfer paths at 300 K are shown in Figure 2. The proton transfer coordinate is represented by $\delta = \min|\text{O}^{\delta} - \text{H}^{\delta} - \text{O}_{w}^{\delta}|$, where $\text{O}^\delta$ is the oxygen atom of either hydronium or hydroxide and $\text{O}_{w}$ represents the oxygen atom of water. When we compare our QM/EFP-MD simulations based on BLYP/6-31G(d) with previous BLYP-based CPMD simulations, we found that the two methods produce similar PMFs for hydronium and hydroxide transfer. This shows that the QM/EFP-MD and CPMD simulations are consistent when the same exchange-correlation functionals are used, even though the two methods have significantly different computational procedures. On the other hand, the QM/EFP-MD simulations using both B3LYP/
6-31G(d) and MP2/cc-pVDZ predicted consistently higher free energy barriers than BLYP/6-31G(d) and CPMD. The difference is especially large in the case of hydroxide (0.7–0.9 kcal/mol). The discrepancy between these two groups of calculations (B3LYP and MP2 versus BLYP) was also seen in the potential energy barriers in the previous section (Figure 1). Therefore, the potential energy barriers of proton transfer have a determining effect on the free energy barriers. Consequently, it is reasonable to expect that CCSD(T) could yield even higher free energy barriers. Therefore, our results contradict the previous fluxional idea of negligible barrier,14 especially in the case of hydroxide.

Clearly different free energy barriers for hydronium and hydroxide were observed from the QM/EFP-MD simulations only with B3LYP and MP2. According to these results, hydronium diffusion has a lower free energy barrier (by ∼1.3 kcal/mol) and a narrower barrier width (by 0.2 Å) than hydroxide, which makes proton transfer with hydronium much easier. After adding nuclear quantum effect corrections to the CPMD simulations, the barriers for proton transfer with hydronium and hydroxide reduced to 0.1 and 0.3 kcal/mol, respectively,13 making the difference between the free energy barriers of the two ions negligible. Similar nuclear quantum effect corrections would certainly reduce the free energy barriers of our B3LYP and MP2 computations. However, the effects would not be significant, since the barrier heights are near the average thermal energy at 300 K. It should also be noted that the potential energy barriers of proton transfer were even higher with the more accurate CCSD(T) theory, implying free energy barriers as obtained with CCSD(T) would be higher than those found with B3LYP and MP2. The effect of the difference in the free energy barrier heights on the transport dynamics is discussed in the next section.

C. Space-Time Correlation Functions for Multiple Transport Paths. While previous theoretical studies focused on structural and thermodynamic aspects of proton transfer mechanisms, they often do not include dynamic information. We calculated the van Hove space-time correlation functions, \( G_s(r,t) \equiv \langle \delta[r - r_O(t) + r_O(0)] \rangle \), of the oxygen atoms in hydronium and hydroxide to determine the space-time correlation of the target oxygen. Here, \( r_O(t) \) denotes the position vector of the target oxygen, where \( r \) is the size of vector \( r \). The term \( 4\pi r^2 G_s(r,t) \equiv P(r,t) \) is the probability that an oxygen atom is at position \( r \) at time \( t \) given that the oxygen atom was at the origin at \( t = 0 \). Note that unlike the conventional estimation of the \( G_s(r,t) \) of single molecules, we keep track of the ion charges and calculate \( G_s(r,t) \) from the position vectors of charged molecules. For example, when a proton transfers from molecule 1 to molecule 2, we record the position vector of molecule 2 instead of molecule 1. For Brownian particles, \( G_s(r,t) \) takes a simple Gaussian function. Otherwise, \( G_s(r,t) \) shows non-Gaussian behavior often with additional peaks, indicating the presence of spatially heterogeneous dynamics or multiple transport mechanisms. Figure 3 shows the \( P(r,t) \)'s of the oxygen atoms in hydronium and hydroxide as a function of \( r \) for various times \( t \) obtained from the QM/EFP-MD simulations using BLYP, B3LYP, and MP2 for the QM region.

![Figure 3](https://example.com/figure3.png)
proton transfer. The large intensity of the second peak when $t < 0.2$ ps indicates the occurrence of fast proton transfer, whose time scale is consistent with recent experimental results. After $t = 0.5$ ps, hydronium may diffuse longer distances via thermal motion, causing an overlap of the two peaks. In the case of hydroxide, the $P(r,t)$s show different behaviors depending on the quantum theory employed in the QM/EFP-MD simulations. When BLYP is employed (Figure 3b), the second $P(r,t)$ peak is still observed even though its height is smaller than that of hydronium. This suggests that proton transfer still occurs readily for hydroxide, though the process is not as efficient as it is for hydronium. More interesting is that the second $P(r,t)$ peak is hardly observed when B3LYP and MP2 are employed. This alternatively suggests that proton transfer would hardly occur within a time scale of 1 ps even at 300 K, which is very different from the current view of efficient proton transfer mechanism in hydronium diffusion. Consequently, it is clear that 1 kcal/mol barrier height difference between hydronium and hydroxide in free energy scale dramatically changes the dynamics of proton transfer. Although we adopted relatively low levels of theory (B3LYP and MP2) for QM region, the fact that they exhibited consistent results justifies their validity.

**D. Dynamic Properties of the Temperature Dependency of Proton Transfer.** To gain insight into the proton transfer mechanism, the identities of the hydronium and hydroxide oxygen were tracked during the MD simulations. Figure 4 shows the time profiles of the indices ($I^*$), the identities of the $\text{H}_3\text{O}^+$ or $\text{OH}^-\text{O}^*$. The 100 ps trajectories were calculated with (a) BLYP, B3LYP, and MP2 at 300 K and (b) B3LYP at 160 K.

![Figure 4. Time dependence of the indices ($I^*$) of the $\text{H}_3\text{O}^+$ and $\text{OH}^-\text{O}^*$. The 100 ps trajectories were calculated with (a) BLYP, B3LYP, and MP2 at 300 K and (b) B3LYP at 160 K.](image-url)
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Figure 5. (a) Survival probability \( \langle C(t) \rangle \) of hydronium and hydroxide as a function of time at 300 and 160 K obtained from QM/EFP-MD simulations using B3LYP/6-31G(d) for the QM region. (b) \( \langle C(t) \rangle \) of hydronium and hydroxide at 300 K obtained using BLYP/6-31G(d) (blue), B3LYP/6-31G(d) (red), and MP2/cc-pVDZ (black). \( \langle C(t) \rangle \) denotes the fraction of protons that stay with the original molecules without hopping until time \( t \).

\( \langle C(t) \rangle \) does not decay for hydroxide, indicating that hydroxide hardly undergoes proton transfer within 100 ps. Conversely, proton transfer occurs for about 80% of the hydronium ions at \( t = 1 \) ps, i.e., \( \langle C(t = 1 \text{ ps}) \rangle \approx 0.2 \). This result is in good agreement with the experimental studies of ASW, which did not show proton transfer during hydroxide diffusion through an ASW film at 155–175 K, in contrast to the efficient proton transfer of hydronium. As the temperature increases to 300 K, both hydronium and hydroxide are more likely to undergo proton transfer. However, proton transfer for hydronium is much more efficient than that for hydroxide. For example, when \( t = 0.1 \) ps, about 80% of the hydronium ions experience proton transfer whereas only a small fraction of the hydroxide ions undergo proton transfer.

Figure 5b compares the \( \langle C(t) \rangle \)s obtained using different levels of quantum theories. Regardless of the quantum theory used, \( \langle C(t) \rangle \) decays faster for hydronium than for hydroxide, indicating that proton transfer occurs more readily for hydronium ions. According to simulations using B3LYP and MP2, the \( \langle C(t) \rangle \) of hydronium decays more slowly than that of hydronium, which is consistent with the simulation results for \( P(r,t) \). On the other hand, the \( \langle C(t) \rangle \) of hydroxide obtained using BLYP in the QM/EFP-MD simulations decays relatively quickly, implying spuriously fast proton transfer.

E. Statistical Analysis of Solvation Structures. It is helpful to investigate the solvation structure around proton transfer events. Figure 6 shows the radial distribution functions (RDFs), \( g_{O^* - Ow}(r) \), for hydronium and hydroxide generated with QM/EFP-MD simulations using three different quantum theories: BLYP, B3LYP, and MP2. The first peaks in the solvation of hydronium calculated with the three different QM theories are nearly identical and agree well with that found by CPMD. In the solvation of hydroxide, the first peaks calculated with QM/EFP-MD using the BLYP functional and previous CPMD simulations were slightly shifted to the left (Ow is held closer to O*) compared with those calculated at the B3LYP and MP2 levels of theory. This is in agreement with observations from the PMF analysis shown in Figure 2b. Although the first peak found by CPMD for hydroxide is slightly broader than those found by QM/EFP-MD, the overall shapes and heights are similar, which indicates a close correspondence between our QM/EFP-MD results and the CPMD simulations for at least the first solvation structure.

To investigate the solvation pattern in detail, the coordination number (CN) of the proton-receiving oxygen (Ow) was analyzed. Figure 7 shows the probability distribution of the CNs in the first solvation shell, which indicates the number of hydrogen bonds accepted by O*. Hydronium ions mostly accept three hydrogen bonds in all QM/EFP-MD simulations. However, the most probable CN for hydroxide in simulations with B3LYP and MP2 is four, whereas simulations with BLYP still favor 3-fold coordination. When proton transfer occurs (\( \delta \leq 0.1 \text{ Å} \), corresponding to a nearly symmetric Zundel-like structure), as shown in Figure 7c, the most probable CN changes from four to three. Thus, the hydroxide ion becomes less solvated near a proton transfer event. The reduced CN during proton transfer is consistent with the dynamical hypercoordination suggested by previous CPMD simulations.

IV. CONCLUSION

The quantum mechanical theories of BLYP, B3LYP, MP2, and CCSD(T) were adopted to estimate the proton transfer barriers of \( H_2O_2^+ \) and \( H_2O_2^- \) model clusters. Compared with CCSD(T)/cc-pVQZ, BLYP/6-31G(d), which does not include exact exchange functional, significantly underestimate the proton transfer barriers. On the other hand, the results of B3LYP are consistent with those of MP2, indicating the...
importance of including exact exchange functional. Similar to the model cluster calculations, the transport dynamics depended on the computational theory. Specifically, MD simulation with the BLYP functional largely underestimated the proton transfer free energy barrier of hydroxide as compared with the other theories, which resulted in a spuriously efficient proton transfer for hydroxide. In contrast, the MD simulations with B3LYP and MP2 clearly showed the importance of Brownian motion in hydroxide transport.

In brief, contrasting to the previous assumptions, the present comparative study shows that the proton transfer efficiency of hydroxide is significantly lower than that of hydronium. Consequently, at room temperature, Brownian molecular diffusion may have an important contribution to the transport and reaction of hydroxide ions. Furthermore, at a low temperature (160 K), hydroxide migrates exclusively via Brownian motion without proton transfer, which is consistent with recent experimental studies of hydroxide diffusion in ASW at 155−175 K.69 This is in stark contrast to the proton-transfer-dominated hydronium transport, which shows rapid proton oscillation on the picosecond time scale at both 300 and 160 K. The present findings imply that acids and bases may have quite different acting mechanisms and ranges in aqueous solutions due to their different diffusion mechanisms.

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