Water exchange dynamics around H_3O^+ and OH^- ions

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ABSTRACT: In this letter, we report the first computer simulation of the dynamics of water exchanging between the first and second solvation shells of H_3O^+ . Employing different rate theories for chemical reactions such as the transition state theory, the Grote-Hynes theory, the reactive flux method, and the Impey-Madden-McDonald method, we calculate the solvent exchange rates from molecular dynamics simulations that account for explicit polarization effects. In addition, we also study water exchanges around OH^- and find that the corresponding time scale is much smaller than that for H_3O^+ .

I. INTRODUCTION

The amphiprotic nature of water leads to its autoionization. A water molecule as an acid donates a proton to a neighboring water molecule acting as a base, creating two molecular ions H_3O^+ and OH^- . [1] However, this event is rare, and recombination occurs quickly because of the strong acidic and basic nature of H_3O^+ and OH^- ions, respectively. [2] The dynamics of these ions in water have indispensable roles in many chemical and biological processes related to proton transfer. [3-5] A proton in water is known to form two structures. [6-7] In the first structure, H_3O^+ forms strong hydrogen bonds with three neighboring water molecules, resulting in the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ structure. In the second structure, one of the protons of H_3O^+ migrates along the hydrogen bond and is shared between two water molecules ($\text{H}_2\text{O}\dots\text{H}\dots\text{H}_2\text{O}$). This structure is called the Zundel structure. [8] Hydration of OH^- leads to tri-coordinated $\text{OH}^-(\text{H}_2\text{O})_3$ and hyper-coordinated $\text{OH}^-(\text{H}_2\text{O})_4$ structures. [9]

Although the hydration structure around a proton and a hydroxide ion is understood, the dynamics of water hydrating them is less clear. It is essential to understand the dynamics of water exchanging between different solvation shells of a proton or a hydroxide ion, as that can be an influencing factor in proton or hydroxide diffusion in water and other biological systems. [10-14] To this end, we wish to reveal the water exchange dynamics around these ions by employing molecular dynamics (MD) simulations. However, simulating a proton in water is complicated and requires accurate but computationally expensive (i.e., time consuming) semiclassical and quantum mechanical (SC & QM) methods such as Empirical Valence Bond, [15-16] Car-Parrinello MD, [17] Centroid MD, [18] Path Integral MD, [19] and Ring Polymer MD. [20] A classical MD simulation can minimize this computational cost, but with a lesser accuracy of the ion-water interaction. This accuracy can be improved by explicitly accounting for polarization effects on this interaction. In this letter, we treat a proton in the H_3O^+ form and investigate water

exchange dynamics between its first and second solvation shells using classical MD simulation with a polarizable potential model.[21-24] We follow a similar protocol in our investigation of the OH^- ion.[23, 25] In this study, we assumed that the proton-hopping rate is much faster than the water exchange rate between the solvation shells of these ions; therefore, these time scales are can be separated. If the proton-hopping mechanism were taken into account in our molecular model, we would expect that the water exchange rate between the solvation shells of these ions would be increased and the corresponding residence times would be decreased. The reason for this expectation is the solvation structures around these ions are more flexible and more mobile.

We combine rate theories of chemical reactions with MD simulations. Here, the reactants are H_3O^+ (OH^-) and water molecules bound to it through electrostatics and hydrogen-bonding in the first solvation shell. Exchange of bound water with a water molecule from the second solvation shell leads to the products, which simply can be described by the following equation:

where, X is either H_3O^+ or OH^- . H_2O^{1st} and H_2O^{2nd} are the water molecules in the first and second solvation shells. Experimental techniques such nuclear magnetic resonance,[26-27] quasi-elastic neutron scattering spectroscopy,[28-29] and the ligand substitution approach are used to measure solvent exchange rates around ions.[30] However, as the reactants and products are identical, it is challenging to examine the solvent exchange process experimentally. On the other hand, MD simulations enable identification of each individual molecule and provide an atomic-level description of molecular structure and dynamics. We employ transition state theory (TST),[31-33] Grote-Hynes (GH) theory,[33-36] the reactive-flux (RF) method,[31, 34, 37] and the Impey-Madden-McDonald (IMM) method[38] to compute time scales of H_2O^{1st} and

H_2O^{2nd} exchange (Equation 1) around H_3O^+ (OH^-) from MD simulations. Examining this exchange dynamics with four different methods will not only allow us to gain a deep insight into the problem, but also will help us to determine the quality and applicability of these methods.

II. METHODS & SIMULATIONS

To employ the TST, GH, RF, and IMM methods, we require having prior knowledge of potential of mean force (PMF) between H_3O^+ (OH^-) and a water molecule in the presence of the solvent water. Water exchange reaction pathways can be multidimensional and different for different ions. Assuming that the ion-water center of mass (COM) separation is a suitable reaction coordinate, we obtained the PMF along this coordinate from MD simulations as discussed below.

To perform MD simulations of the H_3O^+ -water and OH^- -water systems, a modified version of AMBER was used, incorporating the polarizable force field parameters (Table 1).[21-25] The H_3O^+ -water (OH^- -water) system comprised of a cubic box of 600 water molecules and one H_3O^+ (OH^-) ion. The MD time step of 2 femtosecond (fs) was chosen and the long-range electrostatic interactions were treated with the Ewald summation technique.[39] The internal geometry of molecules was kept constrained in the simulations using the SHAKE algorithm.[40] The H_3O^+ -water and OH^- -water systems were equilibrated in the NPT ensemble at room temperature ($T = 298$ K) and a pressure of 1 atmosphere ($P = 1$ bar). The H_3O^+ -water and OH^- -water systems have the same equilibrated average cubic box length (26.3 Å).

For PMF calculations,[31-33] we performed MD simulations in the NVT ensemble using equilibrated cubic boxes, fixing COM separation ($r = |\vec{r}|$) between H_3O^+ (OH^-) and a selected water molecule, and sampling other degrees of freedom. A series of such simulations (each for

5 nanoseconds [ns]) with different r -values were carried out, and the $\text{H}_3\text{O}^+(\text{OH}^-)$ -water mean force was calculated using Equation 2.

$$F(r) = \frac{1}{2} \langle \hat{r} \cdot (\vec{F}_{\text{ion}} - \vec{F}_{\text{wat}}) \rangle \quad (2)$$

Here, $\vec{F}_{\text{ion}}$ and $\vec{F}_{\text{wat}}$ are the forces acting on the $\text{H}_3\text{O}^+(\text{OH}^-)$ ion and the selected water molecule, respectively, and $\hat{r} (= \vec{r}/|\vec{r}|)$ is the unit vector pointing from the ion to the water molecule. The PMF, $W(r)$, was obtained by numerically integrating the mean force as given below:

$$W(r) = - \int_{r_0}^r F(r') dr'. \quad (3)$$

Water exchange rate between the first and second solvation shells was obtained by applying TST to the PMF as follows:[31-33]

$$k_{\text{tst}} = \frac{1}{\sqrt{2\pi\beta\mu}} \frac{(r^\ddagger)^2 e^{-\beta W(r^\ddagger)}}{\int_{r_0}^{r^\ddagger} dr r^2 e^{-\beta W(r)}}. \quad (4)$$

Here, $r^\ddagger$ represents the position of the barrier top (transition state) of the PMF. β and μ are the inverse of thermal energy ($1/k_B T$) and the ion-water reduced mass, respectively. The shortcoming of TST is that it overestimates the water exchange rate (k_{tst}) because of the assumption that, once the ion-water system reaches the barrier top of its PMF from the reactant state, it goes immediately to the product state. However, it is likely that barrier recrossing can occur. The probability of actually getting to the product state is the transmission coefficient κ , and therefore, the actual water exchange rate is $k = \kappa k_{\text{tst}}$. We used the GH and RF theories to determine the transmission coefficient. The GH theory,[33-36] assumes that the dynamics along the reaction coordinate r in the barrier top region can be modeled with a generalized Langevin equation as given below:

$$\mu \frac{dv}{dt}(t) = F_b(t) - \int_0^t dt' \xi(t') v(t-t') + F^\ddagger(t). \quad (5)$$

The static potential at the barrier region is modeled with the inverted parabola; therefore, the corresponding force has the form $F_b = \mu\omega_b^2 r$. The term ω_b is the barrier frequency, and $v(t) = \dot{r}(t)$. The friction $\xi(t)$, the time correlation function of fluctuating forces ($\Delta F^\dagger(t) = F^\dagger(t) - \langle F^\dagger(t) \rangle$) exerted by the fluctuating solvent on the effective particle of mass μ (ion-water reduced mass), can be expressed as:

$$\xi(t) = \frac{1}{\mu k_B T} \langle \Delta F^\dagger(0) \Delta F^\dagger(t) \rangle. \quad (6)$$

Now, the transmission coefficient employing the GH theory (κ_{GH}) can be determined iteratively as follows:

$$\kappa_{\text{GH}} = 1 / (\kappa_{\text{GH}} + \frac{1}{\omega_b} \int_0^\infty dt \xi(t) e^{-\omega_b \kappa_{\text{GH}} t}). \quad (7)$$

To obtain $\xi(t)$ and κ_{GH} , we performed MD simulations of the H_3O^+ -water and OH^- -water systems fixed in their transition states for 10 ns in the NVT ensemble, saving the force $F^\dagger(t)$ every 2 fs.

The RF method is very useful for extracting the exact value of transmission coefficient from MD trajectories.[26, 32, 34] From the 10-ns MD trajectory in the NVT ensembles of the H_3O^+ -water and OH^- -water systems constrained at the transition state, 2500 conformations were collected to perform RF calculations. Using these conformations as the starting ones and releasing the constraint, MD simulations at the NVE ensemble were performed in both backward and forward directions for 2 ps. Then the transmission coefficient $\kappa_{\text{RF}}(t)$ was obtained using the following expression:[34]

$$\kappa_{\text{RF}}(t) = \frac{\langle (v \cdot \hat{r}) \theta(v \cdot \hat{r}) \delta(r - r^\dagger) [\theta(r(t) - r_-^\dagger) - \theta(r(-t) - r_+^\dagger)] \rangle}{\langle (v \cdot \hat{r}) \theta(v \cdot \hat{r}) \delta(r - r^\dagger) \rangle}. \quad (8)$$

Here, $v \cdot \hat{r}$ is the initial ion-water velocity projected along the reaction coordinate and $\theta(v \cdot \hat{r})$ is the Heaviside function to select MD trajectories starting with positive velocities. The term

$\delta(r - r^\ddagger)$ makes sure that the starting conformation is in the transition state. The terms $r(t)$ and $r(-t)$ are obtained from the forward and backward MD trajectories, respectively. The term $r_\pm^\ddagger = r^\ddagger \pm \partial r$, where ∂r is a positive infinitesimal quantity, ensures that $\kappa_{\text{RF}}(t)$ has the initial value (at $t = 0$) of 1. $\kappa_{\text{RF}}(t)$ reaches a plateau at a long time; the actual transmission coefficient is obtained by averaging over the last 0.5 ps.

For the IMM method, we performed MD simulations of the H_3O^+ -water and OH^- -water systems for 5 ns in NVT ensemble, saving snapshots every 100 fs. A normalized time correlation function for the population of water molecules in the first solvation shell of H_3O^+ (OH^-) was calculated from the MD trajectory (Equation 9).[38]

$$C_p(t; t^*) = \langle p_\alpha(t_i, t_f, t^*) \rangle / \langle p_\alpha(t_i, t_i, t^*) \rangle_{\alpha, t_i} \quad (9)$$

If a water molecule is located in the first solvation shell at both initial (t_i) and final (t_f) times, p_α is assigned to 1, provided that, within this time interval, the water molecule does not leave the shell for a continuous period of time longer than $t^* = 2$ ps. The term t^* is introduced to account for the barrier recrossing (i.e., to ignore the transient escapes from the first solvation shell). The term $\langle \dots \rangle$ in Equation 9 represents averaging over water molecules and initial times. $C_p(t; t^*)$ is assumed to have the exponential form $\exp(-t/\tau_p)$, where τ_p is the residence time of a water molecule obtained as follows:

$$\tau_p = \int_0^\infty C_p(t; t^*) dt = \int_0^\infty \exp(-t/\tau_p) dt. \quad (10)$$

III. RESULTS & DISCUSSION

The PMFs computed for the H_3O^+ -water and OH^- -water systems are depicted in Figure 1. We find three distinct features in the PMFs, corresponding to three different states of the systems. The first minimum represents the contact-ion-water-pair (CIWP) state, the barrier top at $r = r^\ddagger$ represents the transition state, and the third feature is the solvent-separated-ion-water-

pair (SSIWP) state. In the CIWP state, the ion and the water are held in close contact by the electrostatic forces; whereas, in the SSIWP state, the solvent screens these forces. A couple of differences are observed in the PMFs for the H_3O^+ -water and OH^- -water systems. First, the barrier height is larger for the H_3O^+ -water system than for the OH^- -water system, and second, the COM separation corresponding to the transition state for the OH^- -water system is larger than that for the H_3O^+ -water system. In Table 2, we report these differences quantitatively and conclude that H_3O^+ - H_2O binding is stronger than OH^- - H_2O binding. We found that the coordination number for the H_3O^+ -water system (the number of water molecules that bind to H_3O^+ on the average in the CIWP state) is 3, which is consistent with the previously found $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ structure.[6, 7] The Zundel structure ($\text{H}_2\text{O}\dots\text{H}\dots\text{H}_2\text{O}$) was not observed as our model did not account for proton transfer.[8] The coordination number for the OH^- -water system is 5, which is overestimated in comparison with the previous studies ($\text{OH}^-(\text{H}_2\text{O})_4$ and $\text{OH}^-(\text{H}_2\text{O})_3$).[9] In Figure 2, we have pictorially represented the CIWP and SSIWP states to clarify the distribution of water molecules around H_3O^+ and OH^- ions. Using the TST method (Equation 4), the transition rate between these two states turns out to be slower for the H_3O^+ -water system than for the OH^- -water system. The corresponding time scales ($\tau_{\text{tst}} = 1/k_{\text{tst}}$) are reported in Table 2.

As mentioned earlier, these TST rates do not display the complete picture of water exchange dynamics. Therefore, we corrected these rates by multiplying with transmission coefficients obtained from the GH and RF calculations. In the GH method, we required to obtain the friction $\zeta(t)$ to determine the transmission coefficient. $\zeta(t)$, as depicted in Figure 3, has two distinguishable components for both the H_3O^+ -water and OH^- -water systems: 1) a rapid initial drop around 50 to 60 fs and 2) a slow decay on the picosecond time scale. However, it is clear that the H_3O^+ -water system experiences larger friction than the OH^- -water system. We also

found that the barrier frequency for the H_3O^+ -water system (39 ps^{-1}) is larger than that for the OH^- -water system (21 ps^{-1}). The transmission coefficients (κ_{GH}) are 2.0×10^{-3} and 3.0×10^{-2} , respectively, for the H_3O^+ -water and OH^- -water systems. These values are too low, which means that the CIWP state is extremely stable and transition to the SSIWP state rarely occurs. The term τ_{GH} in Table 2 is the water exchange time scale obtained using the GH theory, which is sub-nanosecond for the H_3O^+ -water system and is an order of magnitude smaller for the OH^- -water system.

The time-dependent transmission coefficient obtained using the RF method $\kappa_{\text{RF}}(t)$ rapidly decays to a plateau for both the H_3O^+ -water and OH^- -water systems (Figure 4). By averaging over the last 0.5 ps, we find the actual transmission coefficient: 1.5×10^{-2} for the H_3O^+ -water system and 2.4×10^{-2} for the OH^- -water system. Again, these transmission coefficients are very small, resulting in slow water-exchange time scales (τ_{RF} in Table 2) and the exchanges occur faster around OH^- than around H_3O^+ .

Finally, using the IMM method we calculated the residence time τ_p of a water molecule in the first solvation shell of H_3O^+ and OH^- from the normalized time correlation function $C_p(t; t^*)$ (Equation 9 and 10). As depicted in Figure 5, the approximation that $C_p(t; t^*)$ has an exponential form turns out to be valid for both the systems. $C_p(t; t^*)$ decays much faster for the OH^- -water system (gets close to zero at $t \sim 500 \text{ ps}$) than for the H_3O^+ -water system (gets close to zero at $t > 1 \text{ ns}$). We find from Equation 10 that, τ_p (given in Table 2) is one order of magnitude smaller for the OH^- -water system than for the H_3O^+ -water system. IMM is qualitatively consistent with other methods.

From the quantitative comparison between τ_{GH} , τ_{RF} , and τ_p (Table 2), we find significant discrepancies between them. The RF method provides with the exact and correct value for the

water exchange time scale, therefore, τ_{GH} , and τ_{p} are overestimated for the H_3O^+ -water system and are underestimated for the OH^- -water system. The errors for the GH results may arise from the assumption that the barrier top of a PMF is an inverted parabola. In the case of the IMM method, the choice of t^* may introduce artifacts in the results. However, all the results qualitatively agree that the water exchange dynamics between the first and the second solvation shells is faster for the OH^- -water system than for the H_3O^+ -water system.

IV. CONCLUSION

We demonstrated the first computer simulation of the exchange dynamics of hydrating water around H_3O^+ and OH^- ions. Using polarizable force field parameters in MD simulation and employing classical rate theories of chemical reactions, we examined water exchange process between the first and second solvation shells. We calculated the water exchange rates using TST and weighted them with the transmission coefficients determined by the GH and RF methods. We found that the water exchange dynamics around H_3O^+ (time scale of ~ 100 ps) is much slower than OH^- (time scale of ~ 50 ps). We also calculated the residence time of a water molecule in the first solvation shell of H_3O^+ and OH^- using the IMM method; these results are qualitatively in agreement with the GH and RF results.

We kept our investigation simple, classical, and at the fundamental level. Due to lower computational costs, we were able to explore most of the configuration space of water molecules distributed around H_3O^+ and OH^- ions (for example, see Figure 2), determining the water exchange time scales around these ions. Using this information as a reference, in the future, it will be interesting to employ CM & QM methods for more accurate understanding of the water exchange process. These methods will allow one to simulate a proton in water and examine proton transfer from H_3O^+ to a neighboring water molecule. Then, one can gain insights into

how proton transfer can influence the water exchange dynamics between the solvation shells of a proton. Exploring multi-dimensional reaction coordinates will be necessary for such an investigation. In this letter, we focus only on the kinetics of water exchange between the first and second solvation shells of H_3O^+ and OH^- and defer other calculations of other properties such that the relative mobility and structure of the two ions in water. Our future work will include the comparison between the relative mobility of hydronium and hydroxide with the water exchange dynamics around these ions.

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Table 1: Polarizable force field parameters for water, H_3O^+ , and OH^- . The terms σ and ϵ are the Lennard-Jones parameters, q is the atomic charge, and α is the molecular polarizability.

Atom type	σ ($\text{\AA}$)	ϵ (kcal/mol)	q (e)	α ($\text{\AA}^3$)
OW	3.2340	0.1825	0.0000	0.0000
HW	0.0000	0.0000	0.5190	0.0000
MW	0.0000	0.0000	-1.0380	1.4400
O (H_3O^+)	3.2340	0.1475	-0.4166	0.9800
H (H_3O^+)	0.0000	0.0000	0.4722	0.0000
O (OH^-)	3.2215	0.1825	-1.2000	2.3000
H (OH^-)	0.0000	0.0000	0.2000	0.0000

Table 2: Barrier positions and heights of the PMFs (Figure 1) for the H_3O^+ -water and OH^- -water systems and time scales of water exchange around H_3O^+ and OH^- ions.

Systems	Barrier height (kcal/mol)	$r^\ddagger$ ($\text{\AA}$)	τ_{ist} (ps)	τ_{GH} (ps)	τ_{RF} (ps)	τ_{p} (ps)
H_3O^+ -water	1.7	2.9	1.4	658	95	206
OH^- -water	1.1	3.2	0.9	39	61	35

Figure Captions

Figure 1. PMFs for the H_3O^+ - H_2O and OH^- - H_2O interactions in water as the solvent.

Figure 2. A MD snapshot to show the distribution of water molecules around H_3O^+ and OH^- ions in the CIWP and SSIWP states.

Figure 3. Time-dependent friction for the H_3O^+ -water and OH^- -water systems computed using the GH theory.

Figure 4. Time-dependent transmission coefficient for the H_3O^+ -water and OH^- -water systems obtained from the RF method.

Figure 5. Normalized time-correlation function to determine the residence time of a water molecule in the first hydration shell of H_3O^+ and OH^- ions.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Graphical Abstract