Mechanisms of proton transfer in Nafion®: elementary reactions at the sulfonic acid groups

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Proton transfer reactions at the sulfonic acid groups in Nafion® were theoretically studied, using complexes formed from trillic acid (CF$_3$SO$_2$H), H$_2$O$^+$ and H$_2$O, as model systems. The investigations began with searching for potential precursors and transition states at low hydration levels, using the test-particle model (T-model), density functional theory (DFT) and ab initio calculations. They were employed as starting configurations in Born–Oppenheimer molecular dynamics (BOMD) simulations at 298 K, from which elementary reactions were analyzed and categorized. For the H$_3$O$^+$.H$_2$O complexes, BOMD simulations suggested that a quasi-dynamic equilibrium could be established between the Eigen and Zundel complexes, and that was considered to be one of the most important elementary reactions in the proton transfer process. The average lifetime of H$_3$O$^+$ obtained from BOMD simulations is close to the lowest limit, estimated from low-frequency vibrational spectroscopy. It was demonstrated that proton transfer reactions at −SO$_3$H are not concerted, due to the thermal energy fluctuation and the existence of various quasi-dynamic equilibria, and −SO$_3$H could directly and indirectly mediate proton transfer reactions through the formation of proton defects, as well as the −SO$_3$$^-$ and −SO$_3$H$^+$ transition states.

1. Introduction

An energy crisis and environmental concerns about global warming, as well as the need to reduce CO$_2$ emissions, have provided strong motivation to seek ways of improving energy conversion technology. The proton exchange membrane fuel cell (PEMFC) has received much attention as one of the most promising energy suppliers for the future world. The polymer electrolyte membrane which has been widely used in PEMFCs is Nafion®, introduced by Dupont in 1967. Nafion® is a perfluorinated polymer with hydrophobic Teflon backbone and randomly attached hydrophilic side chains. The backbones and the side chains of Nafion® are terminated by trifluoromethanesulfonic (trillic) acid, which is known to be one of the strongest acids. The trillic acid functional groups (−CF$_3$SO$_2$H) are preferentially hydrated and play important roles in proton transfer reactions in PEMFCs. Experiments have shown that hydrated −CF$_3$SO$_2$H form aggregates, resulting in large interconnected hydrophilic domains. Since the hydrophilic and hydrophobic domains are quite well separated, theoretical and experimental investigations could emphasize only the hydrophilic domains, in which proton conduction takes place. It was observed in general that the degree of hydration at −CF$_3$SO$_2$H, the morphology of PEM and the size of the hydrophilic domains are directly related to the efficiency of proton conduction in Nafion®. Although some theoretical and experimental information has been accumulated, the complete mechanisms of proton conduction in Nafion® seem not available, especially at the molecular level. Since basic chemistry of Nafion® has been discussed in details in many review articles, only some information relevant to the present study will be briefly summarized.

Three basic molecular fragments, potentially involved in proton transfer reactions at the hydrophilic side chains in Nafion®, are −(CF$_3$OCF$_2$)$_n$−, −CF$_3$SO$_2$H and −CF$_3$SO$_3$$^−$. Density functional theory (DFT) at B3LYP/6-31G(d,p) level suggested that, the hydrogen-bond (H-bond) between CF$_3$OCF$_3$ and H$_2$O is rather weak, due to the strong electron withdrawing effects from the two CF$_3$ groups. Therefore, −(CF$_3$OCF$_2$)$_n$− might not be directly involved in proton transfer reactions in Nafion®, which is in accordance with IR experiment and molecular dynamic (MD) simulations. Experimental evidence has shown that when sufficiently hydrated, the −CF$_3$SO$_2$H groups in Nafion® are highly dissociated. Spectroscopic measurements in which the assignment and comparison of IR and Raman spectra of individual species in Nafion® were made revealed that −CF$_3$SO$_2$H could be completely dissociated, depending upon the experimental conditions. Dielectric spectroscopy also showed a strong dependence of the dielectric constant and the specific conductivity of Nafion® with water content. Whereas $^{19}$F NMR experiment indicated that there is a range of temperatures over which the −CF$_3$SO$_2$H groups in

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In the present study, a theoretical method was employed to study the electronic properties of proton transfer processes in liquid water. It was found that the proton transfer is not only a direct process but also involves the formation of hydrogen bonds. The theoretical investigations focused on the interaction of two water molecules, and the results showed that the proton transfer is facilitated by the formation of a hydrogen bond.

2. Computational methods

For hydration of a single proton, according to experimental and theoretical investigations, there are at least three important H-bond structures involved in proton transfer reactions, namely, H-bond complexes (H-O-H), H-bond complexes (H-O-H), and H-bond complexes (H-O-H). Based on the results of the calculations, the proton transfer process in liquid water is facilitated by the formation of hydrogen bonds.

Similar theoretical studies were carried out using the semi-empirical methods and density functional theory. The results showed that the proton transfer is facilitated by the formation of hydrogen bonds, and the proton transfer occurs via a H-bond complex (H-O-H). The theoretical investigations confirmed that the proton transfer process is facilitated by the formation of hydrogen bonds.
the complexes formed from CF₂SO₂H, H₂O⁺ and H₂O as model systems; including H₂O⁺ in the model systems could promote proton transfer reactions by creating proton defects which involve the formation of H₂O⁻, as in the case of water and triflic acid monohydrate solid. 21 Because the size of the model systems must be reasonable and manageable by our computer resources, the CF₂SO₂H/H₂O⁻−H₂O 1:1:n complexes, 1 ≤ n ≤ 3, were adopted. It should be added that previous theoretical investigations considered CF₂SO₂H as a primary source of proton, from which H₂O⁺ and CF₂SO₂⁻ are generated. Therefore, proton transfer reactions among CF₂SO₂H, H₂O⁺ and H₂O have not been emphasized.

2.1 T-model

Since proton transfer reactions have been pointed out to be sensitive to structures and dynamics of the H-bond,36 all important H-bond structures in the model systems had to be identified, characterized and analyzed. Attention was focused on H-bond structures, which could be precursors or transition states in proton transfer pathways. In order to effectively and systematically scan the potential energy surfaces, T-model potentials were constructed and employed in the calculations of the equilibrium structures of the H₂O⁺−H₂O and CF₂SO₂H−H₂O⁺−H₂O complexes. Since the T-model had been discussed in details in our previous studies, only some important aspects of geometry optimizations will be briefly summarized.

For the H₂O⁺−H₂O complexes, a rigid H₂O⁺ was placed at the origin of the Cartesian coordinate system. The coordinates of water molecules were randomly generated in the vicinity of H₂O⁺. Based on the T-model potentials, equilibrium structures of the H₂O⁺−H₂O complexes were searched, using a minimization technique. Similar methods were applied on the CF₂SO₂H−H₂O⁺−H₂O complexes, in which CF₂SO₂H was placed at the origin of the Cartesian coordinate system, and the positions and orientations of H₂O⁺ and H₂O were randomly assigned in its vicinity. For each H-bond complex, one-hundred starting configurations were generated and employed as starting configurations in the T-model geometry optimizations.

2.2 DFT and ab initio calculations

Since the T-model potentials are based on rigid molecules, in which cooperative effects are neglected, further structural refinements had to be made using appropriate quantum chemical methods. As it is known in general that sophisticated theoretical methods require more computer resources, and especially in the present case, MD simulations with thousands of timesteps must be performed, it was necessary to compromise between the accuracy of theoretical methods and the available computer resources. A literature survey showed that DFT methods have been frequently chosen due to the ability to treat molecules of relatively large sizes with a reasonable degree of accuracy, compared to other nonempirical methods. Especially for similar H-bond systems,7,10,11,19,20,23 the DFT method at B3LYP/6-31G(d,p) level represents one of the most popular choices. Therefore, it was adopted as a primary candidate in the refinement of the T-model results. It should be noted, however, that the performance of DFT methods can be poor or fairly good, depending upon the chemical systems considered. As in the present case, the existence of three fluorine atoms in CF₂SO₂H could bring about strong electron correlation effects, and thus made it necessary to examine the applicability of B3LYP/6-31G(d,p) in details. Our experience on strong H-bond systems30,33,39 suggested that ab initio calculations at MP2/6-311++G(d,p) or MP2/6-311++G(2d,2p) level could serve as a benchmark in this case. The absolute and some local minimum energy geometries of the H-bond complexes, predicted from the T-model potentials, were employed as starting configurations in DFT and ab initio geometry optimizations. Both partial and full geometry optimizations were performed, using the Berny algorithm in Gaussian 03.42 In partial geometry optimizations, monomer geometries were kept constant and only the intermolecular geometrical parameters were optimized. The purpose of the partial geometry optimizations was to verify the T-model optimized geometries, whereas the full geometry optimizations were aimed at structural refinements. In the present study, the partial and full geometry optimizations were denoted by OPT1 and OPT2, respectively. Since forces in MD simulations are computed from energy gradients, which are determined by structures of potential energy surface, and in order to compare the performance among candidate theoretical methods, the potential energy profiles for a single proton transfer event were constructed for selected H-bond complexes, using both DFT and ab initio calculations; by moving a proton within a fixed H-bond distance. In the present case, B3LYP/6-31G(d,p), HF/6-311++G(d,p) and MP2/6-311++G(d,p) calculations were employed in the calculations of the potential energy profiles. For the DFT method, additional calculations at B3LYP/6-31++G(d,p) level were made to examine the effects of diffuse functions.

2.3 MD simulations

The dynamics of rapid covalent and H-bond formation and cleavage could be studied reasonably well using theoretical approaches that incorporate quantum chemical methods into MD simulations,43 among which DFT-MD simulations have been widely used in recent years.44,45

In the present work, the precursors and transition states, as well as elementary reactions, in proton transfer processes at CF₂SO₂H were studied using Born–Oppenheimer MD (BOMD) simulations.46,47 Within the framework of BOMD simulations, classical equations of motions of nuclei on the Born–Oppenheimer surfaces are integrated, whereas forces on nuclei are calculated in each MD step from quantum energy gradients, with the molecular orbitals (MOs) updated by solving Schroedinger equations in the Born–Oppenheimer approximation. This makes BOMD simulations more accurate, as well as considerably CPU time consuming, compared to conventional classical MD simulations, in which forces on nuclei are determined from predefined empirical or quantum pair potentials. It should be noted that the high mobility of the excess proton was initially attributed to QM tunneling.48 This has been challenged, for example, by the results obtained from ab initio BOMD simulations49 and conductivity
The table below provides a detailed comparison of the different complexes formed between water and hydroxide ions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>H₂O⁻</th>
<th>H⁺</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.125</td>
<td>0.125</td>
<td>0.75</td>
</tr>
<tr>
<td>2:1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>3:1</td>
<td>0.375</td>
<td>0.375</td>
<td>0.25</td>
</tr>
</tbody>
</table>

3 Results and Discussion

3.1 Theoretical Modeling

The theoretical modeling of the complexes was performed using density functional theory (DFT) calculations. The results indicated that the 1:1 complex is the most stable, followed by the 2:1 and 3:1 complexes.

3.2 Comparison with Experiment

The calculated binding energies for the 1:1, 2:1, and 3:1 complexes were -3.4, -2.8, and -2.2 kcal/mol, respectively. These values are in good agreement with experimental data, which also suggested that the 1:1 complex is the most stable.

3.3 Implications for Reaction Mechanisms

The stability of the 1:1 complex suggests that this is the preferred binding mode for water and hydroxide ions in aqueous solutions. This has important implications for reaction mechanisms, as it is likely that this complex will be the dominant species in these systems.

4 Conclusion

In conclusion, the results of this study provide a comprehensive understanding of the binding modes of water and hydroxide ions, which will be useful for the development of new reaction mechanisms and materials.

References

Table 2 Structures of the CF₃SO₂H+H₂O and CF₃SO₂H−H₂O −1 : 1 complexes, obtained from the T-model, DFT and ab initio geometry optimizations. (a) CF₃SO₂H−H₂O −1 : 1 complex. (d) CF₃SO₂H−H₂O −1 : 1 complex complex

<table>
<thead>
<tr>
<th>Method</th>
<th>ΔE/kmol⁻¹</th>
<th>H-bond</th>
<th>Distance/Å</th>
<th>Angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-model</td>
<td>−51.9</td>
<td>(1) OH−· · · Ow</td>
<td>2.71</td>
<td>158.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) Ow−· · · O</td>
<td>2.79</td>
<td>111.6</td>
</tr>
<tr>
<td>MP2-OPT1</td>
<td>−51.9</td>
<td></td>
<td>2.68</td>
<td>166.2</td>
</tr>
<tr>
<td>B3LYP-OPT2</td>
<td></td>
<td></td>
<td>2.93</td>
<td>133.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.60</td>
<td>166.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.84</td>
<td>127.2</td>
</tr>
</tbody>
</table>

(b) T-model     | −15.7     | (1) Ow−· · · O   | 2.95        | 122.8   |
| MP2-OPT1    | −13.2     |                 | 3.05        | 127.6   |
| B3LYP-OPT2  |           |                 | 3.18        | 134.5   |
|             |           |                 | 3.20        | 136.3   |
|             |           |                 | 3.01        | 138.9   |
|             |           |                 | 3.22        | 102.3   |

(c) T-model     | −15.7     | (1) Ow−· · · O   | 2.95        | 122.8   |
| MP2-OPT1    | −13.2     |                 | 3.05        | 127.6   |
| B3LYP-OPT2  |           |                 | 3.21        | 127.5   |
|             |           |                 | 3.24        | 123.6   |
|             |           |                 | 3.10        | 120.7   |
|             |           |                 | 3.08        | 120.1   |

(d) T-model     | −68.1     | Oh−· · · O      | 2.60        | 141.3   |
| MP2-OPT1    | −114.6    |                 | 2.48        | 177.3   |
| B3LYP-OPT2  |           |                 | 2.40        | 177.4   |

MP2-OPT1 = MP2/6.31++G(d,p) with partial geometry optimizations. B3LYP-OPT2 = B3LYP/6-31G(d,p) with full geometry optimizations.

equivalent linear Oh−· · · Ow H-bonds to be the most stable. Only slightly shorter Oh−· · · Ow H-bond distances were observed when MP2-OPT2 and B3LYP-OPT2 were applied on the T-model results. All theoretical methods predicted longer Oh−· · · Ow H-bond distances when the number of water molecule was gradually increased from one to three. For the H₂O₃−· · · H₂O 1 : 3 complex, the T-model suggested the Oh−· · · Ow H-bond distance to be 2.58 Å, whereas the values obtained from MP2-OPT1 and B3LYP-OPT1 are 2.57 and 2.54 Å, respectively. MP2-OPT2 and B3LYP-OPT2 showed the same trend, with slightly shorter Oh−· · Hh covalent bonds in H₂O⁺.

3.1.2 The CF₃SO₂H−H₂O and CF₃SO₂H−H₂O⁻ complexes. For the CF₃SO₂H−H₂O 1 : 1 complex, T-model, MP2-OPT1 and B3LYP-OPT2 predicted a cyclic H-bond structure in which CF₃SO₂H acts simultaneously as proton donor and acceptor, to be the global minimum energy geometry, structure a in Table 2; whereas other cyclic H-bond structures, in which CF₃SO₂H acts only as proton acceptor, structures b and c, possess considerably lower stability. For the CF₃SO₂H−H₂O⁻ 1 : 1 complex, both the T-model and MP2-OPT1 predicted H₂O⁻ to be a stronger proton donor than CF₃SO₂H, structure d in Table 2. The linear H-bond in structure d did not change substantially when B3LYP-OPT2 was applied. However, small but not negligible change was observed at the Oh−· · · Ow H-bond. It becomes shorter and comparable with the Ow−· · · Ow H-bond distance in the Zundel complex. The decrease in the H-bond distance is accompanied by an increase in the Oh−· · Hh covalent bond distance. This reflects a tendency for proton transfer from H₂O⁺ to CF₃SO₂H, leading to a Zundel-like structure (CF₃SO₂H⁻· · · H₂O) as proposed in ref. 26.

3.1.3 CF₃SO₂H−H₂O⁻· · · H₂O complexes. For the CF₃SO₂H−H₂O⁻· · · H₂O 1 : 1 complexes, the T-model generated three important minimum energy geometries, namely, structures a, b and c in Fig. 1. All of them adopt compact cyclic H-bond structures. The most stable one, structure a,
Fig. 1: Equilibrium structures of the CFSiOH-...H₂O (CFSiOH-...H₂O) complexes obtained from the T-model MP2 and BLYP-DFT calculations, BLYP-DFT calculations. BLYP-DFT calculations with full geometry optimizations. The CFSiOH-...H₂O complexes are shown in different colors, with the CFSiOH molecule shown in green, the H₂O molecule in blue, and the H₂O...H₂O hydrogen bond in purple. The figure shows the relative positions of the complexes in the gas phase, with the CFSiOH molecule placed at the origin of the coordinate system. The CFSiOH-...H₂O complexes are characterized by a significant distortion of the SiOH group, with the Si-O bond length being significantly shorter than in the isolated CFSiOH molecule. The H₂O molecule is hydrogen-bonded to the CFSiOH molecule, with the O-H bond length being significantly shorter than in the isolated H₂O molecule. The H₂O...H₂O hydrogen bond is also significantly shorter than in the isolated H₂O molecule.
Fig. 2  Equilibrium structures of the CF₃SO₂H-H₂O⁺⁻-H₂O 1:1:2 and 1:1:3 complexes, obtained from the T-model, DFT and ab initio calculations. Interaction energy in kJ mol⁻¹ and distance in Å. (a) (d) CF₃SO₂H-H₂O⁺⁻-H₂O 1:1:2 complexes. (e) CF₃SO₂H-H₂O⁺⁻-H₂O 1:1:3 complex. MP2-OPT2 = MP2/6-311++G(d,p) with full geometry optimizations. B3LYP-OPT2 = B3LYP/6-31G(d,p) with full geometry optimizations.

- SO₃⁻, H₂O⁺ and H₂O₂⁺ within the CF₃SO₂H-H₂O⁺⁻-H₂O 1:1:3 complex. The appearance of -SO₃⁻ and the ion-pair complex when n = 3 is in good agreement with the theoretical results in ref. 26.

Comparison of the size and shape of the potential energy profiles for proton transfer in Fig. 3a to 3d revealed that B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p) and MP2/6-311++G(d,p) show different results, e.g. the minima are seen systematically at shorter distances. The discrepancies are quite obvious in Fig. 3b to 3e; double-well potential is seen in the case of large cyclic H-bond of water; shoulders are seen in the case of CF₃SO₂H-H₂O⁺⁻-H₂O 1:1:1 complexes. Based on the above discussions and the fact that DFT requires lowest computational resources, we concluded that B3LYP/6-31G(d,p) is the most appropriate choice for our MD simulations.

3.2 Dynamics and elementary reactions

3.2.1 The H₂O⁺⁻⁻H₂O complexes. Since H-bond structures can vary in a rather wide range, care must be exercised in the discussion of proton transfer profiles. In order to study dynamics and elementary reactions in proton transfer processes, some characteristic structures in proton transfer profiles have to be interpreted, using BOMD results on the H₂O⁺⁻⁻H₂O 1:1 complex in Fig. 4 and 5 as examples. It appeared, in general, that the proton transfer in H₂O₂⁺
Fig. 4  Examples of characteristic proton transfer profiles for the H$_2$O$^-$–H$_2$O 1 : 1 complex, with snapshots of H-bond structures obtained in the course of BOMD simulations. (a) Large-amplitude vibrations. (b) Small-amplitude vibrations (c) Snapshots of H-bond structures.

O–O and O–H vibrations. Since, for large-amplitude vibration, $\tau_{H_2O^L}$ and $\tau_{H_2O^{LLPT\max}}$ are nearly the same, $\tau_{H_2O^L}/\tau_{H_2O^{LLPT\max}}$ could be adopted as a criterium to measure the degree of coherence ($\xi_{H_2O^L}$). Therefore, in Fig. 4a, $\xi_{H_2O^L}$ ≈ 1 is attributed to the highest degree of coherence, whereas in Fig. 4b, the short lifetimes of the precursor H$_2$O$^-$ ($\tau_{H_2O^{L}}$ and $\tau_{H_2O^{LLC}}$) compared to $\tau_{H_2O^{LLPT\max}}$ reflect a lower degree of coherence and higher frequency of proton transfer.

Proton transfer elementary reactions in the H$_2$O$^-$–H$_2$O 1 : n complexes, 1 ≤ n ≤ 3, are listed in Fig. 5. BOMD simulations predicted the average lifetimes of the quasi-dynamic equilibria in H$_2$O$^-$ ($\tau_{H_2O^{LAB}}$), $\tau_{H_2O^{LBC}}$ and $\tau_{H_2O^{LAC}}$, to be 20.5, 19.4 and 15.5 fs, respectively, whereas the average lifetimes of the precursor and product H$_2$O$^+$, $\xi_{H_2O^{L}}$ and $\tau_{H_2O^{LC}}$, are nearly the same, 12.4 and 10.7 fs, respectively. The average maximum proton transfer cycle time ($\tau_{H_2O^{LLPT\max}}$) in this case amounts to 69.9 fs, with $\xi_{H_2O^{L}}$ = 0.2. This confirms that, on average, small-amplitude vibration with a low degree of coherence dominates in H$_2$O$^+$.

Due to the fact that BOMD simulations were started from minimum energy geometries, it was not straightforward to predict the preferential proton transfer directions. However, for each proton transfer elementary reaction, the probability

Fig. 5  Important elementary reactions in proton transfer in the H$_2$O$^-$–H$_2$O complexes obtained from BOMD simulations. The symbols are explained in details in the text.
for proton transfer in the forward direction \( \langle P_{H,O_2}^{low} \rangle \) could be conceivably associated with the average lifetime of the product, which becomes a precursor in the next proton transfer step. Therefore, \( P_{H,O_2}^{low} \) was approximated as \( \langle t_{H,O_2}^{LA} \rangle / \langle t_{H,O_2}^{LA} \rangle \). Since the product and precursor are the same in \( H_2O_2^{+} \), \( P_{H,O_2}^{low} = 1 \) represents the upper limit of the relative probability for proton transfer in the forward direction.

The characteristics of proton transfer profiles for the \( H_2O^{+} - H_2O \) 1:2 complex (\( H_2O_2^{+} \)) are not substantially different from \( H_2O_2^{+} \). The presence of another strong \( OH - Hh - OH \)-bonds in \( H_2O_2^{+} \) tends to increase the stability of the central \( H_2O^+ \). Since BOMD results in Fig. 5 suggested that \( \langle t_{H,O_2}^{LA} \rangle \) and \( \langle t_{H,O_2}^{ILP_{low}} \rangle \) are comparable, one could conclude that the elementary reaction II favors large-amplitude vibration, with \( \langle t_{H,O_2}^{LA} \rangle \approx 1 \), compared to 0.2 in \( H_2O_2^{+} \); \( \langle t_{H,O_2}^{ILP_{low}} \rangle \) is 81.1 and 77.8 fs, respectively. In this case, the relative probability for proton transfer in the forward direction \( \langle P_{H,O_2}^{ILP_{low}} \rangle = \langle t_{H,O_2}^{ILP_{low}} \rangle / \langle t_{H,O_2}^{ILP_{low}} \rangle \approx 0.2 \) is considerably lower than \( H_2O_2^{+} \). The increase in the stability of the central \( H_2O_2^{+} \) is accompanied by shorter average lifetimes of the quasi-dynamic equilibrium; \( \langle t_{H,O_2}^{ILP_{low}} \rangle \) and \( \langle t_{H,O_2}^{ILP_{low}} \rangle \) are 12.5 and 11.8 fs, respectively.

Due to coupled motions among the three strong \( OH - Hh - OH \)-bonds, as well as some \( H_2O \)-bond structure reorganizations, proton transfer profiles for the \( H_2O^{+} - H_2O \) 1:3 complex are more complicated than \( H_2O_2^{+} \) and \( H_2O_2^{+} \). Although the central \( H_2O_2^{+} \) in the Eigen complex (\( H_2O_2^{+} \)) is more stabilized than in \( H_2O_2^{+} \), the fluctuations of the surrounding water dipoles seem to help promote proton transfer reactions; similar to an extended local dynamic disorder which leads to a compression and breaking of \( H_2O_2^{+} \), as discussed in ref. 56. BOMD results suggested two important precursors for proton transfer elementary reactions in the \( H_2O^{+} - H_2O \) 1:3 complex, namely, the Eigen complex and a linear \( H_2O \)-bond structure. Since the proton transfer profiles for the linear \( H_2O_2^{+} \) structure are similar to those in \( H_2O_2^{+} \), attention was focused on the Eigen complex. For elementary reaction III in Fig. 5, both large- and small-amplitude vibrations were observed in the course of BOMD simulations. Analyses of proton transfer profiles revealed that, due to the coupled vibrational motions, the average lifetime of the central \( H_2O_2^{+} \) (\( \langle t_{H,O_2}^{ILP_{low}} \rangle \)) is shorter than \( H_2O_2^{+} \) (\( \langle t_{H,O_2}^{ILP_{low}} \rangle \)), but still considerably longer than \( H_2O_2^{+} \) (\( \langle t_{H,O_2}^{ILP_{low}} \rangle \)), 68.2, 77.8 and 12.4 fs, respectively. For the Eigen complex, the average maximum proton transfer cycle time (\( \langle t_{H,O_2}^{ILP_{low}} \rangle \)) = 122.0 fs) is nearly twice longer than the average lifetime of the precursor (\( \langle t_{H,O_2}^{ILP_{low}} \rangle \) = 68.2 fs). This implies that, on average, the probabilities for proton transfers through small- and large-amplitude vibrations are comparable; \( \langle t_{H,O_2}^{ILP_{low}} \rangle = 0.6 \) and \( \langle t_{H,O_2}^{ILP_{low}} \rangle = 0.4 \) and \( \langle t_{H,O_2}^{ILP_{low}} \rangle = 0.4 \). The former is lower than \( H_2O_2^{+} \), but still higher than \( H_2O_2^{+} \), whereas the latter could support the previous investigation that the proton transfer rate is about one order of magnitude lower than the O-O vibration rate.58 Since small-amplitude vibration is a characteristic of the Zundel complex, one could conclude that, due to the thermal energy fluctuation and the coupled motions among \( H_2O_2^{+} \), a quasi-dynamic equilibrium between the Eigen and Zundel complexes could be established in the course of BOMD simulations, and considered as the most fundamental elementary reaction in proton transfer process.

The most important property of \( H_2O^{+} \), which could be obtained from experiments, is the average lifetime. Based on an approximate Eigen's relationship, the average lifetime of \( H_2O^{+} \) was demonstrated to be sensitive to the concentration of acid;57 as the concentration of the acid increases, so does the average lifetime. This could be one of the reasons why the average lifetime of \( H_2O^{+} \) reported in literatures varies in a rather wide range.51 For example, through the measurements of proton conductance,49 the average lifetime was estimated to be 240 fs, whereas a higher value, by about one order of magnitude, was derived from dielectric relaxation data.58 While the measurement of the low frequency (1200 cm\(^{-1}\)) in the vibrational spectrum of \( H_2O^{+} \) requires a minimum lifetime of only 30 fs,51 the one obtained from the measurement of \( ^{17}O \)-induced proton relaxation in water and very dilute acids amounts to 2.2 ps.59,60 In the present study, the average lifetime of \( H_2O^{+} \) in the Eigen complex is within this range. It should be added that, in our model systems, the lack of continuous \( H_2O \)-bond network connecting the first and second hydration shells could restrict the mobility of proton, whereas the inclusion of strong interaction between proton and polar environment could lead to a retardation of proton transfer events.58,60 Our \( \langle t_{H,O_2}^{ILP_{low}} \rangle \) = 68.2 fs is, however, closer to the lowest limit, estimated from the low-frequency vibrational spectroscopy.51

3.2.2 The CF\(_2\)SO\(_2\)H–H\(_2\)O–H\(_2\)O complexes. Fig. 6 shows examples of proton transfer profiles for the CF\(_2\)SO\(_2\)H–H\(_2\)O–H\(_2\)O 1:1 complexes, with snapshots of H-bond structures observed in the course of BOMD simulations. Three important elementary reactions were extracted from BOMD results and illustrated in Fig. 7 with all other results. For the CF\(_2\)SO\(_2\)H–H\(_2\)O–H\(_2\)O 1:1 complex, both large- and small-amplitude vibrations exist in the proton transfer profiles. In Fig. 6b, large-amplitude vibrations are seen, for example, between \( \tau_1 = 27 \) fs and \( \tau_2 = 420 \) fs, within which quasi-dynamic equilibria, followed by actual proton transfers in the reverse direction are seen in general. Small-amplitude vibrations are, for example, from \( \tau_3 = 420 \) fs to \( \tau_4 = 647 \) fs. Starting from structure \( a \) in Fig. 1, the \( H_2O \)-bond proton (\( H_2O \) in Fig. 6c) moved in the course of BOMD simulations from \( O_2 \) to \( O_3 \), resulting in structure \( a \) in Fig. 6c. The proton transfer profile in Fig. 6a and the snapshots in Fig. 6c reveal an example of the H-bond structure reorganization from cyclic to linear. At \( \tau_5 = 750 \) fs, \( H_2O \)-forms H-bond with an oxygen atom of \( \text{SO}_2 \)H, then structure \( C \) changes to structure \( D \). Structures \( D \), \( E \) and \( F \) show a possibility for proton transfer away from \( \text{SO}_2 \)H, whereas structure \( G \) for proton transfer in the reverse direction; forming \( \text{SO}_2 \)H\(_2\)\( ^+ \) at \( \tau_6 = 1335 \) fs and \( \tau_9 = 1416 \) fs. The probability for proton transfer through the formation of \( \text{SO}_2 \)H\(_2\)\( ^+ \) is higher for structure \( C \) in Fig. 3. Starting from structure \( C \), \( \text{SO}_2 \)H\(_2\)\( ^+ \) was generated right at the beginning of BOMD simulations. Snapshots in Fig. 6d reveal that structure \( A \) acts as a precursor and the proton transfer could be mediated by \( \text{SO}_2 \)H\(_2\)\( ^+ \) in both directions; from structures \( A \) to \( B \) to \( C \), as well as from structures \( A \) to \( D \) to \( E \). Since there is no water molecule to stabilize the product.
(H\textsubscript{2}O\textsuperscript{+}), both structures C and E return to structure A, as also recognized in the case of H\textsubscript{2}O\textsuperscript{+}.

The results in Fig. 7 show that, due to a limited number of water molecules, the products in elementary reactions I and II were observed in short times. \((\tau\textsuperscript{1A}_{\text{III}}\textsuperscript{1})\) and \((\tau\textsuperscript{II}_{\text{III}}\textsuperscript{1})\) are 10.1 and 9.3 fs, respectively, compared to the lifetimes of the precursors, \((\tau\textsuperscript{A}_{\text{III}}\textsuperscript{1})\) and \((\tau\textsuperscript{II}_{\text{III}}\textsuperscript{1})\), of 51.0 and 54.6 fs, respectively. For elementary reaction I, the quasi-dynamic equilibrium between the precursor and the transition state \((\tau\textsuperscript{AB}_{\text{III}}\textsuperscript{1})\) is 38.8 fs, with the average maximum proton transfer cycle time \((\tau\textsuperscript{PT\text{max}}\textsuperscript{1})\) of 79.9 fs; whereas those of elementary reaction II are 25.3 and 95.8 fs, respectively. The values of \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) and \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) in Fig. 7, indicate that the degrees of coherence in elementary reactions I and II are comparable with H\textsubscript{2}O\textsuperscript{+}, with a lower probability for proton transfer in the forward direction; \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) and \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) are only 0.2. Elementary reaction III in Fig. 7 involves proton transfer through \(-\text{SO}_{2}\text{H}\textsuperscript{+}. Although elementary reaction III possesses the highest degree of coherence, \((\tau\textsuperscript{III}_{\text{III}}\textsuperscript{1})\) is 0.8, the probability for proton transfer from \(-\text{SO}_{2}\text{H}\textsuperscript{+} and the lifetime of the product are the highest; \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) is 0.4 and \((\tau\textsuperscript{III}_{\text{III}}\textsuperscript{1})\) is 23.9 fs. These confirm the possibility that \(-\text{SO}_{2}\text{H}\textsuperscript{+} could represent an effective transition state in proton transfer pathway at low hydration levels.

For the CF\textsubscript{3}SO\textsubscript{3}H-H\textsubscript{2}O\textsuperscript{+}-H\textsubscript{2}O 1:1:2 complexes, five important proton transfer elementary reactions could be extracted from BOMD results. The extension of the H-bond network in the vicinity of \(-\text{SO}_{2}\text{H} could bring about both stabilization and destabilization effects to H\textsubscript{2}O\textsuperscript{+}, depending upon the H-bond structures. Comparison of the results in Fig. 7 and 8 shows that, for elementary reaction I, the average lifetimes of the precursor \((\tau\textsuperscript{I}_{\text{III}}\textsuperscript{1})\), as well as the quasi-dynamic equilibrium \((\tau\textsuperscript{I}_{\text{III}}\textsuperscript{1})\), are increased when H\textsubscript{2}O\textsuperscript{+} is triply H-bonded; the former is 73.7 fs, and the latter is 29.0 fs. These are accompanied by an increase in the degree of coherence and a decrease in the average lifetime of the product, \((\tau\textsuperscript{I}_{\text{III}}\textsuperscript{1})\) 8.3 fs, and \((\tau\textsuperscript{I}_{\text{III}}\textsuperscript{1})\) 7.8 fs, as well as a decrease in the probability for proton transfer in the forward direction, \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) 0.1.

Elementary reactions II, III, and IV in Fig. 8 represent three possibilities for proton transfers along the linear H-bonds at \(-\text{SO}_{2}\text{H}. For elementary reaction II, the extension of the H-bond network, through the formation of the O-H-O-H-O bond, brings about higher stability to H\textsubscript{2}O\textsuperscript{+}. This makes it difficult for H\textsubscript{2}O\textsuperscript{+} to transfer a proton to the adjacent water. Comparison of \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) and \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) in Fig. 7 and 8 shows that, due to an increase in the stability of H\textsubscript{2}O\textsuperscript{+} in elementary reaction II, the probability for proton transfer away from \(-\text{SO}_{2}\text{H} is considerably decreased; structure C which is the product was rarely found in the course of BOMD simulations.

Comparison of elementary reaction III in Fig. 7 and 8 reveals a similar trend, namely, the probability for H\textsubscript{2}O\textsuperscript{+} to protonate at \(-\text{SO}_{2}\text{H} is reduced upon the Oh-H-O bond formation, with a shorter average lifetime of \(-\text{SO}_{2}\text{H}\textsuperscript{+} (\tau\textsuperscript{III}_{\text{III}}\textsuperscript{1})\) 11.7 fs, compared to \((\tau\textsuperscript{III}_{\text{III}}\textsuperscript{1})\) 66.2 fs. The elementary reaction IV shows a small probability to detect \(-\text{SO}_{2}\text{H} in the course of BOMD simulations, with \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) 0.03. In this case, large-amplitude vibration with \((\tau\textsuperscript{IV}_{\text{III}}\textsuperscript{1})\) 4.7 fs. The stability of H\textsubscript{2}O\textsuperscript{+} and the degree of coherence in the H-bond are substantially reduced upon larger cyclic H-bond network formation; \((\tau\textsuperscript{V}_{\text{III}}\textsuperscript{1})\) and \((\tau\textsuperscript{V}_{\text{III}}\textsuperscript{1})\) for elementary reaction V are 10.2 fs and 0.14, respectively. The values of \((\tau\textsuperscript{V}_{\text{III}}\textsuperscript{1})\) are close to those in H\textsubscript{2}O\textsuperscript{+}. Since the average lifetimes of both precursor and product are small, the probability for proton transfer in the forward direction is the highest among the CF\textsubscript{3}SO\textsubscript{3}H-H\textsubscript{2}O\textsuperscript{+}-H\textsubscript{2}O 1:1:2 complexes, with \(p\textsuperscript{1}_{\text{III}}\textsuperscript{1}\) 0.6.

Due to a high degree of freedom in the CF\textsubscript{3}SO\textsubscript{3}H-H\textsubscript{2}O\textsuperscript{+}-H\textsubscript{2}O 1:1:3 complexes, only linear H-bonds were observed in the course of BOMD simulations. The elementary reactions I, II, and III in Fig. 9 represent three possibilities for proton transfer along the H-bond network.
Fig. 7. Important elementary reactions in proton transfer in the H3O+/H2O+ complexes obtained from B3LYP/6-31G(d,p) calculations.

1. SOH is predicted to be the most important reactive species, with H3O+/H2O+ forming SOH, and the reverse reaction having a very high barrier.

2. The reaction H3O+/H2O+ + H2O → H3O+ + H2O + H2O has a low barrier and is predicted to be a significant channel for proton transfer.

3. The reaction H3O+/H2O+ + H2O → H2O + H2O+ + H2O is predicted to be less important than the first reaction.

4. The reaction H2O+ + H2O → H3O+ + H2O has a high barrier and is not predicted to be a significant channel for proton transfer.

5. The reaction H3O+ + H2O → H3O+ + H2O is predicted to be a minor channel for proton transfer.

6. The reaction H3O+ + H2O → H3O+ + H2O + H2O is predicted to be a minor channel for proton transfer.

7. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

8. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

9. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

10. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

11. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

12. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

13. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

14. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

15. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

16. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

17. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

18. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

19. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

20. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.

21. The reaction H3O+ + H2O → H3O+ + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O + H2O is predicted to be a minor channel for proton transfer.
Fig. 8 Important elementary reactions in proton transfer in the CF$_3$SO$_3$H–H$_2$O$^+$–H$_2$O 1 : 1 : 2 complexes, obtained from BOMD simulations. The symbols are explained in details in the text.

quasi-dynamic equilibria. These prohibit proton transfer reactions from being concerted, and confirm the observations that the proton motion is too fast to be a rate-determining step. Due to large- and small-amplitude vibrations in H-bond separations, the internal conversions between covalent and H-bonds, similar to the Grothuss mechanism, were concluded to form the general basis for proton transfer processes at –SO$_3$H. Attempt was also made to describe these proton-relay type mechanisms in terms of coherence and incoherence effects. BOMD simulations showed that the proton-relay type mechanisms could take place among –SO$_3$H, H$_2$O$^+$, and H$_2$O, providing some effective proton transfer pathways, through the formations of the –SO$_3$H–SO$_3$H$^+$ and H$_2$O$^+$ transition states. The analyses of the average lifetimes of the precursors and elementary reactions suggested that when the H-bond structures are right, in order that –SO$_3$H could effectively function as a mediator in proton transfer reactions, the probabilities for the elementary reactions to proceed in the forward and reverse directions should be somewhat equivalent, otherwise the proton would be trapped at –SO$_3$H.

Finally, it should be emphasized that the present BOMD simulations focused on proton transfer processes at and in the proximity of a single –SO$_3$H group, and within a narrow timescale. Therefore, H-bond structure reorganizations and molecular diffusions, which could contribute to proton conduction in different timescales, were not taken into account. It should be also added that the present theoretical investigations were performed at low hydration levels, in which the H-bond networks are not as extensive as in aqueous solutions, and strong interaction between proton and the polar environment could lead to a retardation of proton transfer. Therefore, direct comparisons between our model calculations and experiments seem not appropriate. However, some important insights, especially the interplays between local H-bond structures and dynamics, as well as the potential precursors and the proton transfer elementary reactions in an excess proton
condition could be obtained. The present BOMD results also allowed the equilibrium structures and energies obtained from MM or ab initio geometry optimizations could not be validated, and only the reaction pathways were predicted. It appeared that the theoretical methods and the analyses adopted in the present work could provide the practical basis for study of proton-tranfer reactions provided in our laboratory to include more hydrophilic functional groups and appropriate solvent effects in models of Nafion.

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