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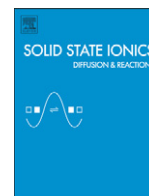


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An *ab initio* study of the primary hydration and proton transfer of $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$: Effects of the hybrid functional and inclusion of diffuse functions

Chen Wang, Jeffrey K. Clark II, Milan Kumar, Stephen J. Paddison *

Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

Electronic structures calculations were undertaken on two perfluorosulfonic acids ($\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$) with varying number of hydrating water molecules to assess the effects of the enhanced electron withdrawing afforded by an additional CF_2 group: the side chain of the short-side-chain (SSC) PFSA membrane. Both Becke's 3-parameter hybrid functional (B3LYP) and the extended hybrid functional (X3LYP) employing the 6-311G** split valence Gaussian basis set with and without the inclusion of diffuse functions were performed to determine the impact on proton dissociation and separation as a function of the degree of the hydration of the acids. The calculations underscore the increased acidity of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ due to the enhanced electron withdrawing of the β $-\text{CF}_2-$ but did not reveal any differences in the strength of the binding of the water molecules over that computed for $\text{CF}_3\text{SO}_3\text{H}$. The calculated structural parameters obtained from optimized geometries of both acids with from 1 to 4 water molecules revealed that the inclusion of diffuse functions has negligible effects. Furthermore, the results obtained with the X3LYP functional were nearly identical to those obtained with the B3LYP functional.

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1. Introduction

Over the past two decades, considerable interest in eliminating the overwhelming dependence on fossil fuels as an energy source has steadily increased. This has led to an intense search for clean, renewable sources of energy. One promising solution lies in the utilization of proton exchange membrane (PEM) fuel cells as efficient energy conversion devices due to their wide range of applicability and minimal environmental impact [1,2]. The PEM is critical to the operation of a fuel cell as it functions as the separator of the electrodes and reactant gases, the electrolyte, and the internal ion conductor [3]. Efficient operation of these devices thus strongly depends on the properties and functionality of the membrane electrolyte. Furthermore, the employment of PEM fuel cells in various applications (vehicular, stationary, portable) places explicit demands on the PEM, including: long-time chemical and thermal stability at temperatures up to 120 °C and good proton conductivity ($\geq 10^{-1} \text{ Scm}^{-1}$) under low humidity conditions (25–50% relative humidity) [4].

Perfluorosulfonic acid (PFSA) ionomers, such as Nafion®, are currently the most commonly used fuel cell electrolytes. PFSA membranes consist of a polytetrafluoroethylene (PTFE) backbone functionalized with pendant side chains each terminated with a single sulfonic acid (SO_3H) group. The chemical structure, properties, and functionality in PFSA and other PEMs are an ongoing area of research

[3,5–14]. This work has contributed to the fundamental understanding of existing materials, as well as the development of novel materials, such as, polymers with structural and chemical variations to the polymer backbone and/or side chains and protogenic groups [15–17]. Extensive experimental testing of PEM fuel cells under relatively dry conditions will undoubtedly assist in the improvement of these materials but a molecular-level understanding of the mechanisms of proton transport is needed for the overall success of these materials. Specifically, investigation of the effects of hydration and side chain functionality on proton dissociation through the formation of contact ion pairs and separation of the proton into a solvent separated state will provide fundamental understanding that should lead to advances in the field.

Efforts using various multi-scale modeling techniques have contributed to a better understanding of morphological phenomena and chemical functionalities of PFSA membranes, as well as, molecular-level structural properties and local interactions [3,10,18]. Coarse-grained modeling methods are utilized to examine systems at long time and length scales to be representative of multiple hydrophilic domains of the material [19–23]. The morphology evolution and eventual phase separation has been examined for a variety of ionomer systems with mesoscale modeling using dissipative particle dynamics (DPD) simulations [20,24–26]. Of additional interest in mesoscale modeling is the application of self-consistent mean-field (SCMF) simulations to investigate the affect temperature and water content have on phase separation and morphology in PFSA membranes [23]. Classical molecular dynamics (MD) simulations have been utilized to study hydration and transport properties of proton exchange membranes [27–36] but on systems considerably smaller in size. Empirical valence

* Corresponding author. Tel.: +1 865 974 2026; fax: +1 865 974 7076.
E-mail address: spaddison@utk.edu (S.J. Paddison).

bond (EVB) schemes have been employed to include the structural diffusion of protons (i.e., Grotthuss hopping) and has been used for simulating solvation and transport of hydrated protons in PEMs [37,38]. On an even smaller scale, *ab initio* molecular dynamics (AIMD) simulations have been utilized to investigate proton transfer and dynamics in model systems where the positions of all the atoms are either known or set a priori [39–43].

Although various molecular mechanics methods are used to understand macroscopic properties of PEM membranes, they fail to provide a complete description of proton transport at a molecular level. Electronic structure calculations may not only be used to generate force-field parameters for molecular mechanics methods, but also help in understanding fundamental aspects in polymeric membrane materials such as structural and chemical properties of the polymeric backbone and/or side chains, and proton transfer mechanisms under minimal hydration conditions. Some of the earliest work in this area focused solely on the primary hydration in single fluorinated sulfonic acid systems [44,45]. In addition to triflic acid [46–49], other single functional acid groups were studied with electronic structure calculations, including aromatic sulfonic acids [50], sulfonyl imides [51], carboxylic acid [52], imidazole [53], phosphoric acid [54], and phosphonic acid [55]. Investigations were also undertaken on systems involving more than one acidic group including oligomeric fragments of the short side chain (SSC) PFSA membranes [56–59]. These results elucidated the important correlation between conformational changes (i.e. flexibility) of side chains and the transfer and stabilization of dissociated protons as a function of the degree of hydration and separation of the protogenic groups. For the polymeric fragments involving two pendant side chains, backbone conformation [57,58], and separation of side chains [56] are important factors impacting the dissociation and transfer of the protons. These studies of oligomeric fragments of the SSC PFSA membrane showed that the formation of a connected hydrogen bond network among the water molecules is largely dependent upon the separation of the sulfonic acid groups. It was also observed that the Zundel ion plays an important role in facilitating proton transfer in these systems. In order to simulate larger polymeric systems with multiple pendant side chains, the ONIOM method was employed [59]. This study provided insight into the effects of the conformations of the side chain and backbones have on the dissociation and separation of the protons. In an investigation of single perfluoro and aromatic (*p*-toluene) sulfonic acid systems [50], it was observed that the stability of the conjugate base (i.e. the sulfonate anion in these systems) did affect proton dissociation and separation. Recently, a computational study focusing on the consequence of introducing different functional groups on the alpha site of single phosphonic acid molecules confirmed that the trifluoromethyl acid tend to bind water molecules tighter than other substituent acids due to the stronger electron withdrawing effect [60]. However, the effect of the electron withdrawing group at the beta site to the sulfonic acid is still unclear.

In the present study, we report a quantitative comparison of proton hydration and transfer in two different PFSA acids: triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) and its beta-site substituent acid ($\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$) (the side chain of the SSC PFSA ionomer), with from 1 to 6 hydrating water molecules. The structural parameters and binding energies per water molecule for both systems are calculated. In addition, the partial charge distribution is obtained and compared. We also assess the influence resulting from the use of different hybrid density functional theory and inclusion of augmented diffuse function basis set.

2. Computational methods

All electronic structure calculations of the ionomeric fragments were performed using the GAUSSIAN 03 suite of programs [61]. Full geometry optimizations, using conjugate gradient methods [62], were performed on both $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ initially using Hartree Fock theory with the 6-31G** split valence basis set [63] without symmetry constraints.

The resulting structures were then refined through optimizations performed with density functional theory (DFT) with both Becke's 3-parameter hybrid functional (B3LYP) [64,65] and the extended hybrid functional (X3LYP) [66]. Additional optimizations were then carried out at the B3LYP/6-311G** and X3LYP/6-311G** levels of theory [67]. Finally, optimizations were performed with the inclusion of diffuse basis functions [68] at the B3LYP/6-311G**++ and X3LYP/6-311G**++ levels of theory. Subsequent to the optimization of 'dry' systems (i.e. without addition of any water molecules), water molecules were incrementally added to the optimized HF/6-31G** system at a variety of initial positions, typically four after primary hydration, and full optimization was performed using the protocol described above. It should be noted, that only the data from the optimized global minimum energy structures determined are included. Vibrational frequencies and zero point energies (ZPEs) were determined for the systems at the B3LYP/6-311G**/(6-311G**++) and the X3LYP/6-311G**/(6-311G**++) levels. The binding energies of water molecules to the ionomeric fragments were computed using both uncorrected and ZPE corrected minimum electronic energies. Additionally, partial charges distributions and electrostatic potentials for each of multi-hydrated systems were obtained according to the CHelpG scheme at these levels of theory [69]. All calculations were performed by employing the above described scheme without including the effect of a dielectric medium or solvent.

3. Results and discussion

3.1. 1–3 Water molecules

Optimized structures of both the $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ (SSC side chain) acids were obtained with the addition of water molecules as described above. Structural parameters including the O—H bond length (i.e. the distance between the oxygen of the sulfonic acid/sulfonate and the acidic proton) and the $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distance (i.e. the distance between the oxygen of the sulfonic acid/sulfonate and the oxygen of the water molecule/hydronium ion) are presented in Tables 1 and 2 for the triflic acid and the SSC side chain systems, respectively. Uncorrected and ZPE corrected binding energies are presented in Tables 3 and 4 for the triflic acid and SSC side chain, respectively. The equilibrium structures of both acids without the addition of any water molecules exhibits a nearly uniform O—H bond length of 0.97 Å irrespective of the level of theory and basis set used. Upon addition of a single water molecule, this O—H bond length increased to ~1.01 Å at the B3LYP and X3LYP levels of theory with and without the implementation of the diffuse functions. A negligible difference between the results obtained for the $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distance was also observed when diffuse functions were added to the basis set. The resultant fully optimized structures, shown in Figs. 1a ($\text{CF}_3\text{SO}_3\text{H}$) and 2a ($\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$) at the X3LYP/6-311G**++ level, exhibit the water molecule acting as both a hydrogen bond acceptor and

Table 1
Structural parameters of $\text{CF}_3\text{SO}_3\text{H} + n\text{H}_2\text{O}^a$.

<i>n</i> H ₂ O	B3LYP		X3LYP	
	<i>r</i> (–SO ₂ O···H)	<i>r</i> (–SO ₂ O···H···OH ₂)	<i>r</i> (–SO ₂ O···H)	<i>r</i> (–SO ₂ O···H···OH ₂)
0	0.97 (0.97) ^b	–	0.97 (0.97) ^b	–
1	1.01 (1.00)	2.61 (2.64) ^b	1.01 (1.00)	2.60 (2.63) ^b
2	1.05 (1.04)	2.53 (2.54)	1.05 (1.04)	2.50 (2.53)
3	1.57 (1.55)	2.56 (2.55)	1.58 (1.55)	2.55 ₅ (2.55)
4	1.56 (1.54)	2.56 (2.55)	1.56 (1.54)	2.56 (2.55)
4*	3.66 (3.70)	3.90 (3.93)	3.65 (3.70)	3.89 (3.92)
5	3.68 (3.70)	3.97 (3.98)	3.67 (3.69)	3.96 (3.97)
6	3.91 (3.87)	4.32 (4.23)	3.91 (3.87)	4.30 ₅ (4.22)

^a All reported values are in Å and were obtained with the 6-311G** basis set.

^b Values in parenthesis were obtained with inclusion of diffuse functions, i.e. /6-311G**++.

Table 2
Structural parameters of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H} + n\text{H}_2\text{O}^{\text{a}}$.

$n \text{ H}_2\text{O}$	B3LYP		X3LYP	
	r ($-\text{SO}_2\text{O}\cdots\text{H}$)	r ($-\text{SO}_2\text{O}\cdots\text{H}\cdots\text{OH}_2$)	r ($-\text{SO}_2\text{O}\cdots\text{H}$)	r ($-\text{SO}_2\text{O}\cdots\text{H}\cdots\text{OH}_2$)
0	0.97 (0.97) ^b	–	0.97 (0.97) ^b	–
1	1.02 (1.00)	2.60 (2.64) ^b	1.02 (1.01)	2.60 (2.63) ^b
2	1.06 (1.03)	2.50 (2.54)	1.06 (1.04)	2.49 (2.53)
3	1.58 (1.57)	2.57 (2.56)	1.58 (1.57)	2.56 (2.56)
4	1.56 (1.55)	2.56 (2.55)	1.65 (1.56)	2.62 (2.57)
4*	3.39 (3.71)	3.61 (3.93)	3.36 (3.71)	3.58 (3.92)
5	3.69 (3.81)	3.93 (4.07)	3.64 (3.74)	3.92 (4.06)
6	3.72 (3.89)	4.06 (4.20)	3.70 (3.88)	4.02 (4.19)

^a All reported values are in Å and were obtained with the 6-311G** basis set.^b Values in parenthesis were obtained with inclusion of diffuse functions, i.e. /6-311G**++.

donor to the acid moiety in a ‘ring-like’ hydrogen bond network. The values for the triflic acid system are in complete agreement with prior calculations performed at the B3LYP/6-31G** level [50].

The addition of a second water molecule also resulted in nearly identical structural parameters between the two acid systems at each level of theory and basis set. Again, there was negligible difference in the structural parameters obtained with either functional, and the inclusion of diffuse functions on the basis set changes resulted in structural parameters that differed by ≤ 0.1 Å, a negligible amount. The fully optimized structures obtained at all levels again reveal a ‘ring-like’ hydrogen bond network with one water molecule accepting the hydrogen bond from the O—H of the sulfonic acid and acting as a hydrogen bond donor to the other water molecule which is also a hydrogen bond donor to a different oxygen atom of the acid group. These structures are shown in Figs. 1b and 2b for the triflic acid and SSC side chain systems at the X3LYP/6-311G**++ level, respectively. Proton dissociation was not observed to occur with either acid at this level of hydration, but the O—H bond length of the sulfonic acid group has increased to approximately 1.05 Å.

Proton dissociation is first observed, at all levels of theory tested, upon addition of a third water molecule in both the $\text{CF}_3\text{SO}_3\text{H}$ and the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ systems, as shown in Figs. 1c and 2c at the X3LYP/6-311G**++ level, respectively. The optimized structures of each system continue to show similar geometries in the region containing the sulfonate group and the water molecules/hydronium ion. Again, no differences in the structural parameters were observed with the diffuse

Table 3
Binding energies of $\text{CF}_3\text{SO}_3\text{H}^{\text{a}}$.

$n \text{ H}_2\text{O}$	B3LYP		X3LYP	
	ΔE^{b}	$\Delta E_{\text{ZPE}}^{\text{c}}$	ΔE^{b}	$\Delta E_{\text{ZPE}}^{\text{c}}$
1	–16.98 (–13.11) ^d	–14.61 (–10.89) ^d	–17.79 (–13.84) ^d	–15.40 (–11.61) ^d
2	–16.75 (–13.16)	–14.44 (–10.89)	–17.53 (–13.88)	–15.22 (–11.62)
3	–17.54 (–13.13)	–14.85 (–10.53)	–18.41 (–13.92)	–15.71 (–11.33)
4	–17.38 (–13.43)	–14.77 (–10.90)	–18.19 (–14.17)	–15.57 (–11.64)
4*	–17.61 (–13.65)	–14.99 (–11.13)	–18.43 (–14.42)	–15.82 (–11.90)
5	–17.99 ₅ (–13.15)	–15.11 (–10.39)	–18.90 (–13.95)	–15.98 (–11.18)
6	–17.88 (–13.42)	–14.98 (–10.73)	–18.75 (–14.19)	–15.84 (–11.50)

^a All values reported in kcal/mol obtained using the 6-311G** basis set.^b Binding energy based on uncorrected total electronic energies.^c Binding energy based on ZPE corrected total electronic energies.^d Values in parenthesis were obtained with the inclusion of diffuse functions, i.e. /6-311G**++.**Table 4**
Binding energies of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ (kcal/mol)^a.

$n \text{ H}_2\text{O}$	B3LYP		X3LYP	
	ΔE^{b}	$\Delta E_{\text{ZPE}}^{\text{c}}$	ΔE^{b}	$\Delta E_{\text{ZPE}}^{\text{c}}$
1	–16.85 (–12.99) ^d	–14.49 (–10.87) ^d	–17.70 (–13.74) ^d	–15.32 (–11.60) ^d
2	–16.38 (–12.88)	–14.08 (–10.73)	–17.18 (–13.61)	–14.87 (–11.47)
3	–17.46 (–13.04)	–14.78 (–10.48)	–18.34 (–13.84)	–15.65 (–11.28)
4	–17.24 (–13.46)	–14.51 (–10.96)	–18.56 (–13.84)	–15.66 (–11.10)
4*	–17.78 (–13.69)	–15.14 (–11.18)	–18.61 (–14.46)	–15.97 (–11.95)
5	–17.99 (–13.34)	–15.12 (–10.58)	–18.88 (–14.13)	–15.99 (–11.37)
6	–17.72 (–13.44)	–14.95 (–10.77)	–18.58 (–14.21)	–15.80 (–11.54)

^a All values reported in kcal/mol obtained using the 6-311G** basis set.^b Binding energy based on uncorrected total electronic energies.^c Binding energy based on ZPE corrected total electronic energies.^d Values in parenthesis were obtained with the inclusion of diffuse functions, i.e. /6-311G**++.

functions or in the change of functionals. Furthermore, these parameters maintain nearly the exact same results when comparing the SSC side chain and the triflic acid systems. It is shown that two of the oxygen atoms of the sulfonate group are now involved in a hydrogen bond with two individual water molecules, and the remaining oxygen and, now, hydronium ion are involved in a contact ion pair. Furthermore, the hydronium ion is also hydrogen bonded to the two water molecules maintaining a ‘ring-like’ network of hydrogen bonds. Dissociation results from stabilization of excess positive charge through the hydrogen bonds and the delocalization of excess electron density due to the electron withdrawing groups attached to the sulfonate group.

Of additional interest are the results obtained for the total charge residing on the oxygen atoms in both systems (see Figs. 9 and 10). Each level of theory tested resulted in a nearly perfect agreement for this parameter upon proton dissociation. This differs from the results obtained for the fragments with the addition of one and two molecules, as well as at increasing hydration, where a noticeable difference between the charges obtained with and without the inclusion of diffuse functions was observed. The total charge on the sulfonate oxygen atoms in the SSC side chain was calculated to be less than that on the (now) triflate anion. This is actually the case for the results obtained at each level of hydration tested (excluding the ‘dry’ fragment); however, upon addition of three water molecules the difference becomes more apparent and continues as additional water molecules are added. This suggests that the presence of the additional electron withdrawing groups located in the beta position with respect to the sulfonate group have a nontrivial effect on the delocalization of excess electron density. Thus, the SSC side chain is presumably the stronger of the two acid moieties at least in the gas phase. It should be noted that the inclusion of diffuse functions does appear to have an effect on the ZPE corrected binding energies reported in Tables 3 and 4 for the triflic acid system and the SSC side chain system (as graphically depicted Figs. 7 and 8), respectively, upon proton dissociation. The observed trend in binding energies at this point showed little change for both systems at all levels of theory (albeit the triflic acid system with the addition of two water molecules does not exactly obey the trend, but the difference is insignificant). However, the addition of a third water molecule demonstrates a noticeable difference between calculations performed with and without diffuse functions, but no change in the trend between the two different functionals. Calculations performed with inclusion of diffuse functions showed a small decrease in the binding energy, while those without diffuse functions result in a slight increase.

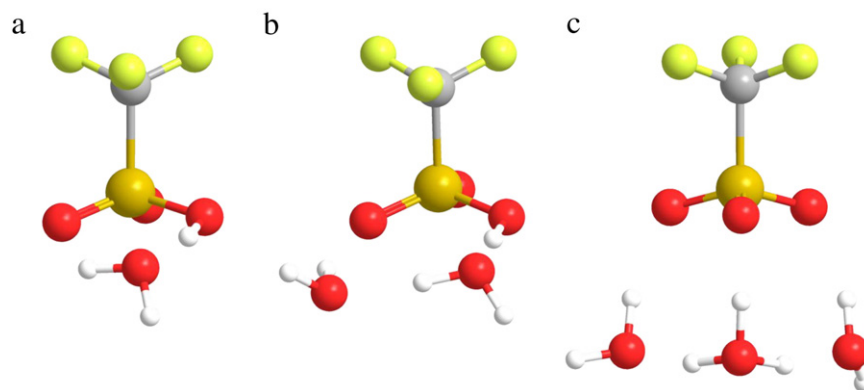


Fig. 1. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{SO}_3\text{H}$ with: (a) the addition of a single water molecule which acts as both a hydrogen bond acceptor and donor to the sulfonic acid; (b) the addition of two water molecules which further extends the 'ring-like' hydrogen bond network; and (c) the addition of three water molecules where dissociation of the proton is first observed upon formation of a contact ion pair between the hydronium ion and the triflate. The colored spheres represent different atom types in the structures where: grey—carbon, red—oxygen, yellow—fluorine, orange—sulfur, and white—hydrogen.

3.2. 4 Water molecules

The results presented for each system with the addition of four water molecules was obtained in two distinct ways. The first (designated in the data as $n=4$) follows the protocol outlined in [Computational methods](#) by simply adding an additional water molecule to the systems optimized with three water molecules. The second set (designated in the data as $n=4^*$) was obtained by completing the optimizations up to six water molecules and then removing two water molecules and then re-optimizing the structures. The 4^* triflic acid system was favored by ~ 1 kcal/mol at each level of theory tested. This system was also favored for the SSC side chain by: 2.36 kcal/mol at the B3LYP/6-311G** level; 0.78 kcal/mol at the B3LYP/6-311G**++ level; 2.23 kcal/mol at the X3LYP/6-311G** level; and 0.88 kcal/mol at the X3LYP/6-311G**++ level (Fig. 5). The fully optimized structures for each system obtained by the two methods result are very similar. The structures obtained via the method described in [Computational methods](#) (4) are shown for the $\text{CF}_3\text{SO}_3\text{H}$ and the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ systems in Figs. 3a and 4a, while the 4^* systems are shown in Figs. 3b and 4b, respectively. The structural parameters obtained in the systematic approach remain extremely similar between the systems, with little change observed between the B3LYP and X3LYP functionals with or without diffuse functions. The ZPE corrected energies calculated for these results, however, diverge from the typical trend that has been observed (see Fig. 8) in the larger SSC side chain system. The results obtained with diffuse functions

appear to converge at this hydration, while those calculated in systems without diffuse functions diverge. The structural parameters in the 4^* system, alternatively, vary between the SSC side chain and triflic acid systems. The parameters in the 4^* SSC side chain system results in significant differences upon addition of the diffuse functions, but the differences in these values for the 4^* triflic acid system remain essentially negligible. However, each level of theory tested gave qualitatively similar results. As shown, the systematically obtained structures contain a hydronium ion hydrogen bonded to two water molecules and an oxygen atom of the sulfonate group maintaining a contact ion pair. One of these water molecules is not directly hydrogen bonded to the sulfonate group; but interacts with another water molecule via a hydrogen bond creating an additional link in the 'ring-like' hydrogen bond network. The 4^* system resulted in the removal of the contact ion pair as the excess proton is fully separated; the hydronium ion forms an Eigen cation as it is hydrogen bonded to three water molecules with an average $\text{O} \cdots \text{O}$ distance of 2.54 Å in both systems. The water molecules are also individually hydrogen bonded to different oxygen atoms of the sulfonate group. Examination of the total excess negative charge residing on the sulfonate oxygen atoms in the hypothetical system reveals a noticeable difference between the systems, as well as, differences in the levels of theories at which they are tested. As mentioned before, less total negative charge resides on the oxygen atoms of the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ system than in the $\text{CF}_3\text{SO}_3\text{H}$ system at all levels of hydration. This difference is seen to a greater extent in the 4^* system.

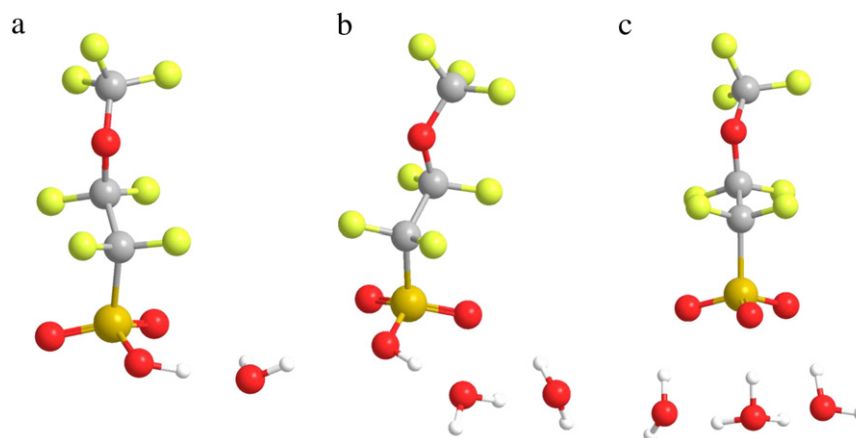


Fig. 2. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ with: (a) the addition of a single water molecule resulting in a hydrogen bond acceptor and donor as seen in the triflic acid system; (b) the addition of two water molecules continuing a 'ring-like' hydrogen bond network; (c) the addition of three water molecules where dissociation of the acidic proton is observed as a contact ion pair is formed.

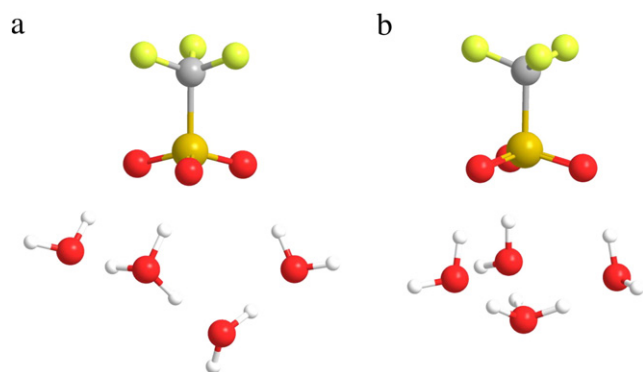


Fig. 3. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{SO}_3\text{H}$ with the addition of four explicit water molecules: (a) obtained via systematic addition of water molecules where the hydrogen bond network is expanded; (b) the 4^* system was obtained by removing water molecules from a system with five water molecules (see text for explanation) where the acidic proton is in a solvent-separated state.

The calculations performed with the inclusion of diffuse functions all resulted in the 4^* system representing the maximum value of excess charge on the sulfonate oxygen atoms. Not surprisingly, the 4^* system also gives the maximum ZPE corrected binding energy calculated with diffuse functions as the excess negative charge results in more tightly bound water molecules to the sulfonate group. Different results are observed when diffuse functions are omitted. The total excess negative charge on the sulfonate group of the 4^* system is still the maximum value found in the triflic acid system (with respect to other calculations at the same level of theory), but it does not correspond to the maximum ZPE corrected binding energy for calculations performed with either the B3LYP or the X3LYP functionals. Furthermore, calculations performed without diffuse functions on the SSC side chain for the 4^* system did not result in the maximum value for the total excess negative charge on the sulfonate oxygen atoms. This suggests that the presence of the longer chain in the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ system is more sensitive to the effect of diffuse functions than that observed in the $\text{CF}_3\text{SO}_3\text{H}$ system after proton dissociation has occurred. It is known that the addition of diffuse function does not affect the neutral systems but may have a noticeable effect on ion pairs [68,70,71]. This effect can also be seen from the energetic data presented in Tables 3 and 4. The maximum binding energy difference

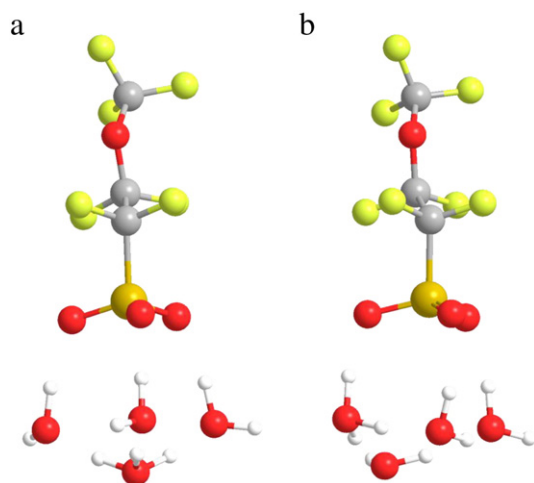


Fig. 4. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$: (a) obtained via systematic addition of water molecules where the hydrogen bond network expands similarly to the triflate system; (b) the 4^* system was obtained by removing water molecules from a system with five water molecules (see text for explanation) forming a contact ion pair again in a similar manner to the triflate system.

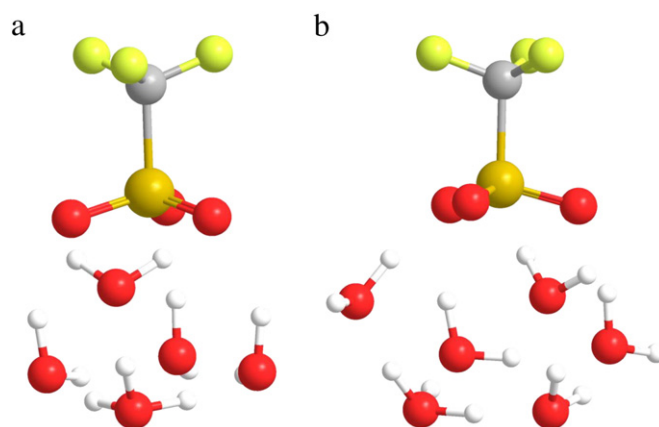


Fig. 5. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{SO}_3\text{H}$ with: (a) the addition of five water molecules where the acidic proton is no longer exists as a contact ion pair but is completely separated now as an Eigen cation as the additional water molecules fill the first hydration shell; (b) the addition of six water molecules reveals further separation of the hydrated proton from the $-\text{SO}_3^-$.

(~4.7 kcal/mol) is observed in systems where the dissociated proton moves to the next hydration shell and is stabilized by forming an Eigen cation (i.e. $n=5$). The CHelpG calculations performed at the 6-311G**++ level always gives less negative total charges of oxygen atoms for multi-hydrated systems except for systems with four water molecules (i.e. $n=4$, 4^*). It is also noticed that this discrepancy observed with inclusion of diffuse functions becomes negligible for the systems with no more than three water molecules (as seen in Figs. 9 and 10).

3.3. 5 and 6 Water molecules

The addition of a fifth water molecule brings about a significant change in each system. Namely, the hydronium ion no longer exists as a contact ion pair with the sulfonate anion. Instead, an Eigen cation forms hydrogen bonded to three separate water molecules. The resultant optimized geometries at the X3LYP/6-311G**++ level for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ are shown in Figs. 3a and 6a, respectively. This is similar to the results obtained previously with four water molecules ($n=4^*$). The greater increase in the $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distance indicates the complete separation of the dissociated proton from the $-\text{SO}_3^-$ due to the addition of an excess water molecule. The protonated water molecule binds slightly stronger to $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3^-$ than to CF_3SO_3^- , which is confirmed by the smaller $\text{O}\cdots\text{H}\cdots\text{OH}_2$ separation and greater binding energies of the former (see Tables 1–4). Not surprisingly, the atomic charge distributions computed for both systems at all levels of theory encounter a noticeable increase when a fifth water molecule is added. The excess positive charge is delocalized on water molecules forming the Eigen cation. As discussed previously, the addition of electron withdrawing groups at beta positions leads to less negative charge residing on the oxygen atoms of SO_3^- (see Figs. 9 and 10). The calculations with the B3LYP and X3LYP functionals give practically identical geometries in the triflic acid systems. Specifically, both $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distances are decreased by merely 0.01 Å with the X3LYP functional in above systems. For the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ molecule, however, the $\text{O}\cdots\text{H}$ distance is shortened by over 0.05 Å when the X3LYP functional is utilized. Moreover, the addition of diffuse functions has made a significant change to $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$, by increasing the $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distances 0.11 Å and 0.14 Å with X3LYP, respectively. Similar to the systems with one, two, and four water molecules, the variation in the charge distribution among the different calculations becomes more pronounced with the presence of an additional electron withdrawing group.

Finally, after adding a sixth water molecule, the protonated water molecule is further separated from the sulfonate anion. Similarly, CF_3O

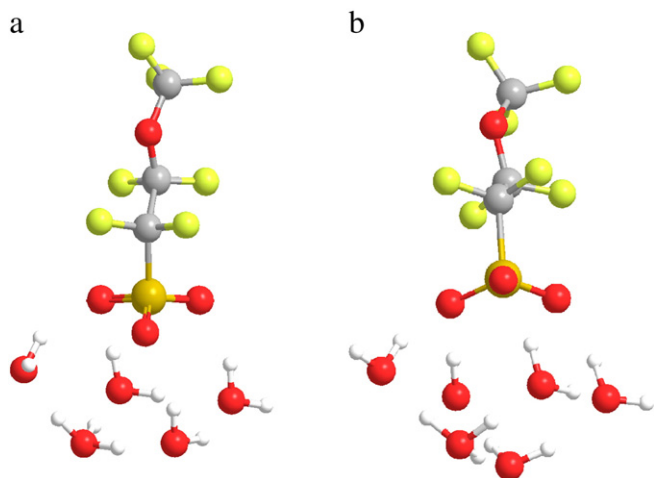


Fig. 6. Fully optimized (X3LYP/6-311G**++) global minimum energy structures of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ with: (a) the addition of five water molecules showing the formation of a contact ion pair with the proton existing as an Eigen cation as the additional water molecules fill the first hydration shell; (b) the addition of six water molecules reveals further separation of the hydrated proton from the $-\text{SO}_3^-$.

$(\text{CF}_2)_2\text{SO}_3^-$ brings the hydronium ion closer than CF_3SO_3^- as revealed by the separation of Eigen/sulfonate ion pair listed in Tables 1 and 2. For triflic acid systems, again, the different functional methods with same basis sets give the almost indistinguishable equilibrium geometries and similar charge distributions. Nevertheless, the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ molecule seems to be more sensitive to the augmented diffuse function as the $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{H}\cdots\text{OH}_2$ distances are both lengthened by $\sim 0.15 \text{ \AA}$ as opposed to $\sim 0.05 \text{ \AA}$ for triflic acid. The trends in the computed binding energy are found to be independent of the type of functional used. However, with the inclusion of diffuse functions in the basis set, the reverse trend occurs: the binding energy calculated without the diffuse functions increases after adding the sixth water molecule and decreases when diffuse functions are included.

It is important to realize that our calculations on the primary hydration of the two PFSA acids only assessed the differences of the presence of a $-\text{CF}_2-$ group located β to the sulfonic acid. Presently

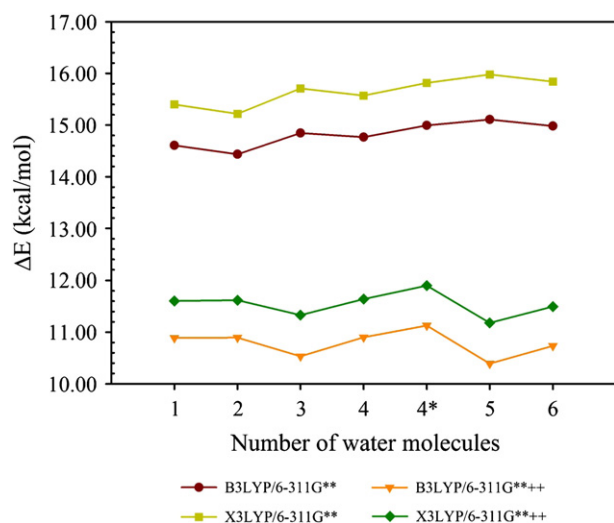


Fig. 7. ZPE corrected binding energies as a function of the number of added water molecules to $\text{CF}_3\text{SO}_3\text{H}$. The inclusion of the diffuse functions always results in a lower magnitude of the binding energy. Also, the energy gap between systems calculated using different functionals remains relatively constant for systems both with and without diffuse functions.

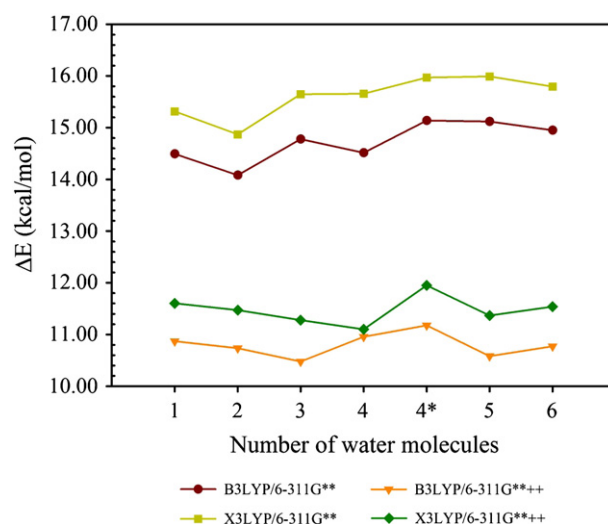


Fig. 8. ZPE corrected binding energies against the number of water molecules added for the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ system. The inclusion of the diffuse functions always results in a lower magnitude of the binding energy. Also, the energy gap between systems calculated using different functionals remains relatively constant for systems both with and without diffuse functions, but this trend does deviate to a greater extent than the triflic acid system.

available PFSA membranes typically have an ether group in the side chain positioned γ to $-\text{SO}_3\text{H}$. Although we have not specifically elucidated the effects of this $-\text{O}-$ linkage on proton hydration and transfer we can infer that this would be negligible in comparison to the electron withdrawing effects of the α and β $-\text{CF}_2-$ groups.

The present results are completely consistent with the majority of prior work examining the primary hydration and proton transfer of perfluorosulfonic acids with electronic structure calculations and BOMD simulations [44,46,47,49,50]. It should be also noted that all these theoretical results of proton dissociation with 2 or 3 water molecules and separation of the dissociated proton with a cluster consisting of 5 to 6 water molecules are in agreement with early FT-IR spectroscopy [71]. It is therefore surprising that a very recent set of electronic structure calculations of triflic acid reported qualitatively different results with dissociation and subsequent separation of the proton not occurring until after 4 and 10 water molecules were added

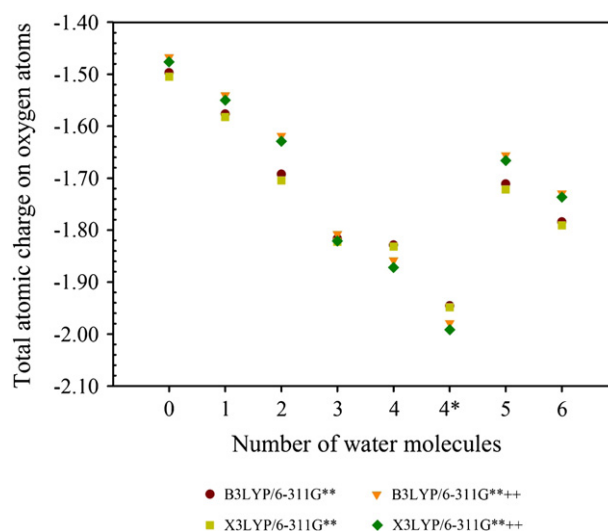


Fig. 9. Total atomic charge on the oxygen atoms of the sulfonate/sulfonic acid group in the $\text{CF}_3\text{SO}_3\text{H}$ system as a function of water molecules added computed with the CHelpG routine of Gaussian 09.

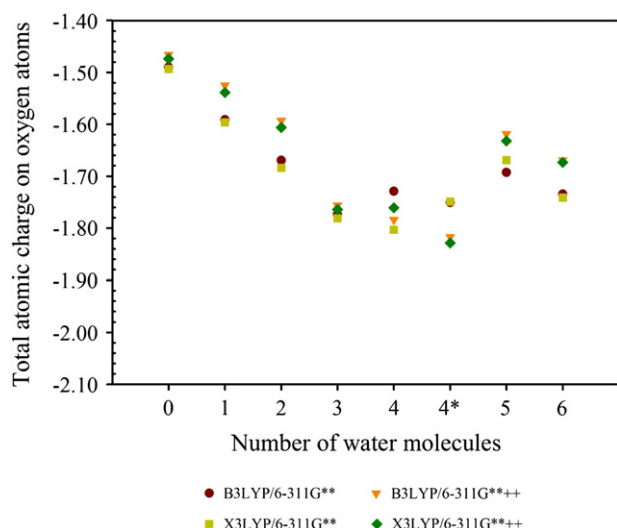


Fig. 10. Total atomic charge on the oxygen atoms of the sulfonate/sulfonic acid group in the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ as a function of water molecules added system computed with the CHeLP routine of Gaussian 09.

[48]. These authors attributed this to the use of the X3LYP functional and inclusion of the diffuse functions. However, the present work clearly indicates that the difference in their results to those of others is not due to the choice of methodology.

4. Conclusions

Our study of two PFSA molecules ($\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$) indicates that the effects of introducing electron withdrawing groups on the beta position of the sulfonic acid is relatively minor when compared to the effects resulting from substitution at the alpha position. These effects become somewhat more significant after the self-dissociation of the proton (i.e., after three water molecules are added). The enhanced electron withdrawing group of $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ increases the acidity of the molecule through stabilization of the corresponding conjugate base, but does not result in significant changes to the binding of the water molecules. A comparison of the structural parameters obtained from optimized geometries of both $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ with from 1 to 4 added water molecules indicates that the inclusion of diffuse functions has negligible effects. The only discernible structural difference, however, occurs subsequent to the formation of the first hydration shell around the conjugate base (SO_3^-) where the proton was stabilized as an Eigen ion bonded to three water molecules. For both systems, the structural data obtained with the X3LYP functional is nearly identical to that with B3LYP. The X3LYP ZPE corrected binding energies indicate are approximately 0.8 kcal/mol higher than obtained with B3LYP. The slightly lower negative charge residing on the oxygen atoms of the sulfonate ion in $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ indicates the enhanced acidity due to the electron withdrawing effects of the $-\text{CF}_2-$ group. Thus, the acidic proton on $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ is more likely to dissociate from the sulfonic acid and form an Eigen ion, at least in isolated systems. The calculations for the $\text{CF}_3\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ systems reveal that they are more sensitive to the presence of diffuse functions.

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