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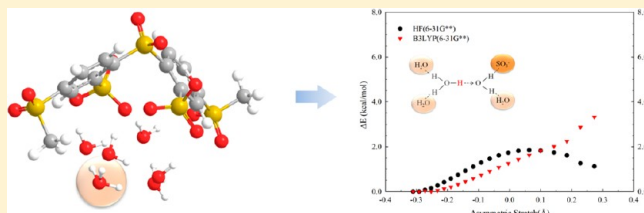
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Hydration and Proton Transfer in Highly Sulfonated Poly(phenylene sulfone) Ionomers: An Ab Initio Study

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ABSTRACT: The need to operate proton exchange membrane fuel cells under hot and dry conditions has driven the synthesis and testing of sulfonated poly(phenylene) sulfone (sPSO₂) ionomers. The primary hydration and energetics associated with the transfer of protons in oligomeric fragments of two sPSO₂ ionomers were evaluated through first-principles electronic structures calculations. Our results indicate that the interaction between neighboring sulfonic acid groups affect both the conformation and stability of the fragments. The number of water molecules required to affect the transfer of a proton in the first hydration shell was observed to be a function of the hydrogen bonding in proximity of the sulfonic acid groups: three H₂O for the meta- and four H₂O for the ortho-conformations. Calculations of the rotational energy surfaces indicate that the aromatic backbones of sPSO₂ are much stiffer than the polytetrafluoroethylene (PTFE) backbones in perfluorosulfonic acid (PFSA) ionomers: the largest energy penalty for rotating phenylene rings (i.e., 15.5 kcal/mol for *ortho*–*ortho*-sPSO₂) is nearly twice that computed for the rotation of a CF₂ unit in a PTFE backbone. The energetics for the transfer of various protons in proximity to one or two sulfonate groups (–SO₃[–]) was also determined. The computed energy barrier for proton transfer when only one sulfonic acid group is present is approximately 1.9 kcal/mol, which is 2.1 kcal/mol lower than similar calculations for PFSA systems. When two sulfonic acid groups are bridged by water molecules, a symmetric bidirectional transfer occurs, which gives a substantially small energy barrier of only 0.7 kcal/mol.



■ INTRODUCTION

As power generating devices both highly efficient and environmentally friendly, polymer electrolyte membrane fuel cells (PEMFCs) are considered to be promising candidates for automobiles and portable device applications.^{1,2} Since operational efficiency of PEM fuel cells greatly relies on the rate of proton transport through the electrolyte, it is crucial to use membrane materials possessing high proton conductivity ($\geq 0.1 \text{ S cm}^{-1}$) over a range of operating conditions.^{3,4} Thus, membrane is an important component that impacts the efficiency of a PEMFC, and consequently, numerous studies have been undertaken to develop highly proton conductive membrane materials.^{5–16} Perfluorosulfonic acid (PFSA) ionomers, such as Nafion, are commonly used as the electrolyte materials that exhibit high proton conductivity only in a fully hydrated (i.e., 100% relative humidity) environment.^{17–19}

The limitations associated with the use of Nafion have propelled the search for alternative materials, which can function as the electrolyte in fuel cells operating at higher temperatures ($>100^\circ\text{C}$) and without humidification. A novel class of sulfonated poly(phenylene) ionomers consisting of aromatic rings and sulfone units (–SO₂–) have recently been synthesized and characterized.^{20–22} These ionomers show considerable thermooxidative and hydrolytic stability due to the highly electron-deficient phenyl rings and electron-accepting sulfone units in the backbone. At high temperatures (110–160 °C) and under 100% relative humidity atmosphere ($p(\text{H}_2\text{O}) = 1 \text{ atm}$), sulfonated poly(phenylene) sulfone (sPSO₂) ionomers exhibit from 5 to 7 times higher proton conductivity than observed in Nafion. The highly sulfonated sPSO₂ ionomers, in contrast to Nafion with the crystallinity

exhibited by the hydrophobic PTFE backbones, are water-soluble due to the hydrophilic phenylene backbone. Water diffusion is greatly affected by the microstructure of the highly sulfonated phenylene rings, where the formation of hydrophilic domains upon hydration are quite narrow due to the high concentration of the protogenic groups (–SO₃H). In addition, sulfone units (–SO₂–) offer the capability of forming intermolecular hydrogen bonding with the –SO₃H groups.

Various modeling and simulation investigations over a range of scales have been utilized to understand morphological phenomena and chemical functionalities of PEMs. For instance, the morphologies associated with phase separation have recently been examined for a variety of copolymer systems via mesoscale modeling using coarse-grained modeling^{23–26} and dissipative particle dynamics (DPD) simulations.^{27–34} In addition, classical molecular dynamics (MD)^{35–44} and ab initio molecular dynamics (AIMD)^{45–49} have been employed to investigate proton mobility as a function of hydration conditions and the effects of the sulfonated functional groups. Empirical valence bond (EVB) schemes such as MS-EVB⁵⁰ and SCI-MS-EVB⁵¹ models have been employed to investigate the hydration and structural diffusion of protons (i.e., Grothuss hopping) in PEMs.^{52–55} However, extensive electronic structure calculations have been performed to investigate a number of fundamental aspects in polymeric membrane materials such as structural and chemical properties of backbone and side chains. Moreover, these small scale

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simulations are capable of providing the basis of understanding the proton transfer in various protogenic systems with minimal hydration conditions. Much of the early work^{56,57} in this field focused solely on the primary hydration of single fluorinated sulfonic acid systems. In addition to triflic acid,^{58,59} other single functional acid groups were studied including aromatic sulfonic acids;⁶⁰ sulfonyl imide;^{61,62} carboxylic acids;⁶³ imidazoles;⁶⁴ phosphoric acid;⁶⁵ and phosphonic acid.⁶⁶ In other extended systems, the conformation of PFSA side chains has also been investigated.^{67–71} These results indicate the important correlation between conformational changes (i.e., flexibility) of the side chains and/or backbones with proton transfer and transport. For the polymeric fragments of two pendant side chains, the conformation of backbones, the separation of side chains have been determined to be two factors governing the dissociation and diffusion of protons. Investigations of fragments of the SSC PFSA membrane revealed that the formation of hydrogen bonding among the water molecules is largely dependent upon the connectivity of acid groups (i.e., degrees of separation or aggregation of side chain groups). It was also observed that the Zundel ion (H_5O_2^+) plays a central role in facilitating proton transfer in systems under minimal hydration conditions. These studies provide meaningful insights into the effects of arrangement of side chain and backbones upon the dissociation and separation of the protons.

We have undertaken *ab initio* electronic structure calculations in the present study to understand the local hydration and proton transfer characteristics of sPSO₂ polymers. Specifically, the structures of sPSO₂ dimers with various numbers of water molecules were examined. Two cases where sulfonic acid groups are either *ortho* or *meta* to the sulfone units are considered. The rotational energies were computed to investigate backbone rigidity as well as intermolecular hydrogen bonding among the sulfone units and sulfonated phenylene rings. Global minimum energy structures of dimers with multiple water molecules were obtained from various plausible starting configurations of the dimers with the water molecules. The energetics and associated structures were determined for the transfer of several distinct protons in close proximity to the acid groups of the sPSO₂ fragments.

Our article is organized as follows: the first section contains a short description of the computational methods used to determine the structure and energetics for all sPSO₂ ionomers. This is followed with a discussion about equilibrium structures and backbone rigidity of two different sPSO₂ fragments without the addition of any water molecules. The next section describes the microsolvation and associated proton dissociation in the two systems. Energetics for the transfer of different protons in various hydrogen bonding environments near protogenic groups is then presented. Finally, the article finishes with concluding remarks.

■ COMPUTATIONAL METHODS

The Gaussian03 suite of programs⁷² was used to perform all electronic structure calculations. Fully optimized geometries of sPSO₂ dimer molecules, using conjugate gradient methods without symmetry constraints, were initially obtained using Hartree–Fock theory with the 6-31G** split valence basis set.^{73–76} Subsequently, refined structures were determined by employing hybrid density functional theory (DFT) with Becke's 3 parameter functional (B3LYP) initially with the same basis set and then subsequently with the larger 6-311G** basis set.^{77–79} Potential energies associated with rotating the sulfonated phenylene ring on the backbones were computed at the B3LYP/6-31G** level. The rotational energy barriers were then determined and compared for each polysulfone system. Minimum energy structures for each dimer with incrementally

added water molecules (i.e., $+n\text{H}_2\text{O}$, where $n = 1–6$) were determined at the B3LYP/6-311G** level. The zero-point energies (ZPEs) for each system were obtained from the vibrational frequencies, which were calculated at the same level of theory. Molecular binding energies for the water molecules and sPSO₂ dimers were determined from both the uncorrected and ZPE corrected total electronic energies. The counterpoise (CP) method of Boys and Bernardi was employed to compute the effect of basis set superposition error (BSSE) on all the computed binding energies.^{80–83} For the systems at high levels of hydration (i.e., 5–6 water molecules in close proximity to the sulfonic acid groups), three proton transfers were examined with different neighboring conditions near the acidic group. The profiles of the energy corresponding to each of the above proton transfers were obtained by performing potential energy surface (PES) scans at both the HF/6-31G** and the B3LYP/6-31G** levels. These scans were based on optimized static structures and as such only reveal the relative tendencies in the proton transfer energetics, not absolute values. All calculations in this study were performed without consideration of solvent effects.

It is known that dispersion interactions are important for the systems containing aromatic groups and hydrogen bonding network.⁸⁴ We performed sample calculations using two types of density functionals including empirical corrections dispersion interactions (i.e., Grimme's B97D⁸⁵ functional and long-range corrected (LC) hybrid density functionals wB97XD⁸⁶). The structures of anhydrous and hydrated systems optimized at the B3LYP/6-31G** level were reoptimized using these two methods with the same basis set. The dry sPSO₂ fragments exhibited nearly identical hydrogen bonding lengths between neighboring sulfonate groups when compared to the structures obtained with the B3LYP functional. The water binding energies obtained with B97D and wB97XD were slightly higher, but the same trend was observed as determined with B3LYP.

■ RESULTS AND DISCUSSION

Global Minimum Energy Structures. In contrast to the PTFE backbone of PFSA polymers, sPSO₂ polymers possess aromatic phenylene backbones that are highly sulfonated and bridged with sulfone units. It is believed that these unique structures may potentially affect the local hydration and proton transfer properties. Fully-optimized (B3LYP) conformations of the two different sPSO₂ dimer molecules: *meta*–*meta*-sPSO₂ and *ortho*–*ortho*-sPSO₂ (i.e., distinguished by the substituent positions of the sulfonic acid groups relative to the central sulfone unit) are shown in Figure 1. The global minimum energy structures for both fragments both exhibiting a *cis* conformation where two sulfonic acid groups reside on the same side of the backbone are displayed in Figure 1a,b. Figure 1c,d shows minimum energy conformations for the same sPSO₂ fragments but with the sulfonic acid groups on opposite sides of the backbones (i.e., in a *trans* conformation). For all conformations shown in Figure 1, intermolecular hydrogen bonding is observed either between the $-\text{SO}_3\text{H}$ groups or between a $-\text{SO}_3\text{H}$ group and a central $-\text{SO}_2-$ unit. The corresponding O...O distances and O–H bond lengths are also shown in Figure 1. Structural parameters, including the dihedral angle for rotation of each aromatic ring about the C–S bonds ($D_{\text{O-S-C-C}}$), separation of the sulfonic acid groups ($\text{S}\cdots\text{S}$), and the O–H bond length ($\text{SO}_2\text{O}\cdots\text{H}$), are reported in Table 1. The total electronic energy and zero-point energy are collected in the first and second rows of Tables 2 and 3 for the *meta*- and *ortho*-sPSO₂ dimers, including those for the corresponding *cis* and *trans* conformations.

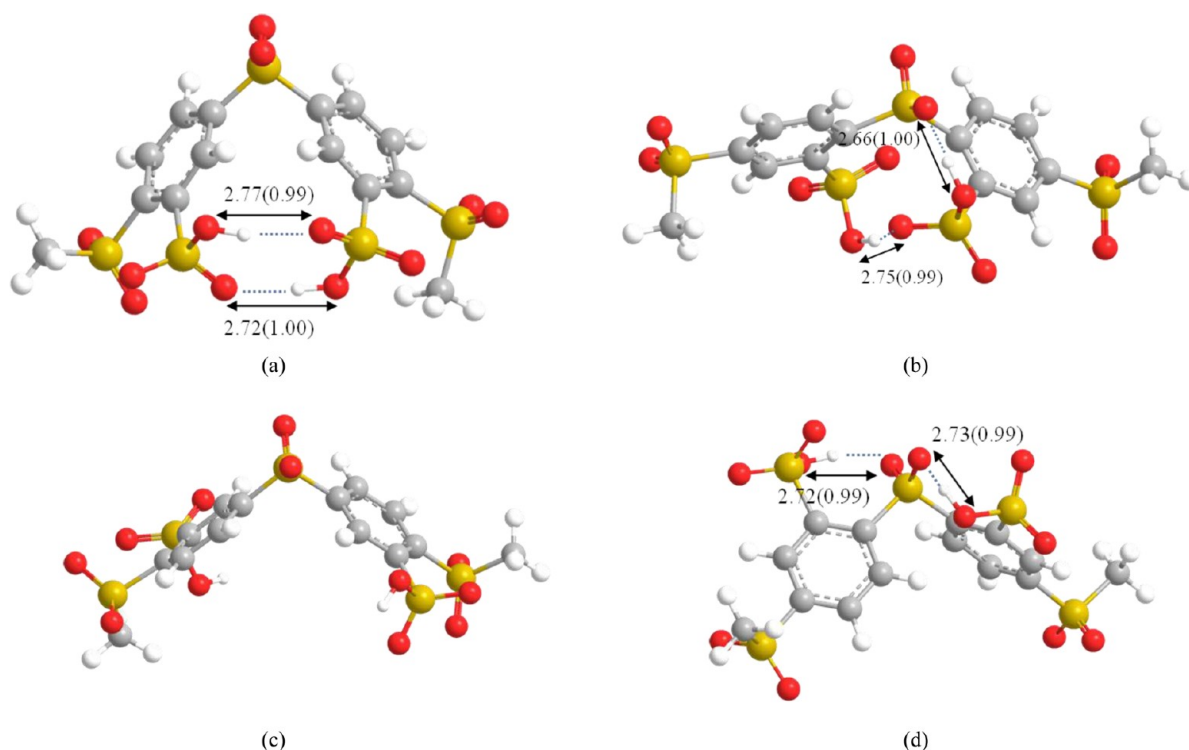


Figure 1. Fully-optimized (B3LYP/6-311G**) global minimum energy structures of sPSO₂ dimer distinguished by the positions of sulfonic acid groups corresponding to the central sulfone are listed: (a) *meta*–*meta*-sPSO₂ and (b) *ortho*–*ortho*-sPSO₂. The corresponding trans conformation of above sPSO₂ dimers are displayed in panels c and d. The total electronic energies (with ZPE corrected) of the *meta*–*meta* structure are 2.78 kcal/mol less than those of the *ortho*–*ortho* dimer.

As observed in Figure 1a, the relatively small separation of neighboring sulfonic acid groups (approximately 4.42 Å of S...S distance) in the *meta*–*meta* structure brings about the formation of double hydrogen bonds between two –SO₃H groups. Similar results were found in prior investigation of the short side chain (SSC) PFSA fragments with kinked backbone structures and nearly the same separation of the sulfonic acid groups.⁸⁷ Comparison of the energies for the equilibrium structures reveals that the *cis* conformations are 5.41 and 2.91 kcal/mol lower in energy for the *meta*–*meta* and *ortho*–*ortho* fragments, respectively. These results are in contrast to those observed for the SSC PFSA fragments, where the sulfonic acid groups doubly hydrogen bonded in the *cis* conformation would lower total energies about 12.3 kcal/mol.⁶⁷ Clearly, the presence of such interactions between two neighboring protogenic groups greatly affects the conformation and stability of these fragments.

Backbone Conformation. In addition to an intermolecular interaction between the sulfonic acid groups, the interaction arising from neighboring rings is also considered to be an important factor affecting the conformation. As discussed previously, each sulfonic acid group in a sPSO₂ dimer is expected to interact with a neighboring sulfonic acid group or a sulfone unit. As a result, two neighboring phenylene rings tend to rotate about the C–S bond to minimize steric effects. Determination of global minimum energy structures (i.e., Figure 1a,b) of the dimers indicates that two rings tend to be arranged in an energetically favorable open book configuration. Potential energy surface scans were performed (at the B3LYP/6-31G** level) for rotation of the phenylene rings about the C–S bond at 5° increments in order to assess the flexibility of the backbones. The torsional energy profiles associated with *meta*–*meta*- and *ortho*–*ortho*-sPSO₂ dimers are displayed in Figures 2 and 3, respectively. It is worth noting that the hydrogen bonding in both global minimum energy structures (the *cis* conformations

Table 1. Structural Data from Optimized *meta*–*meta*- and *ortho*–*ortho*-sPSO₂^a

| <i>n</i> H ₂ O | <i>D</i> _{O–S–C–C} ^b | <i>D</i> _{O–S–C–C} ^b | S...S ^c | SO ₂ O...H ^d |
|---------------------------|--|--|--------------------|------------------------------------|
| 0 | –7.67(80.43) ^e | 9.29(0.79) | 4.42(4.55) | 0.99 1.00 (0.99 1.00) |
| 1 | 12.65(60.62) | 21.68(2.10) | 4.93(5.22) | 0.99 1.08 (1.02 1.00) |
| 2 | 7.77(66.10) | 29.56(–4.91) | 5.51(5.03) | 1.03 1.08 (1.04 1.00) |
| 3 | 10.32(68.30) | 29.93(–5.70) | 5.27(5.04) | 1.48 1.41 (1.06 1.00) |
| 4 | 5.07(71.60) | 33.37(–6.63) | 5.53(5.01) | 1.59 1.30 (1.58 1.00) |
| 5 | 8.62(76.55) | 30.72(–8.72) | 5.49(4.92) | 1.76 1.36 (1.76 1.00) |
| 6 | 9.82(75.11) | 31.97(–7.94) | 5.61(4.88) | 1.81 1.45 (1.83 1.00) |

^aFor structures optimized at the B3LYP/6-31G** level. ^bDihedral angles (deg) for rotation of each aromatic ring about the C–S bonds. ^cSeparation distance (Å) of two acidic groups. ^dBond distances of O...H (Å) for each sulfonate group. ^eValues in parentheses are for *ortho*–*ortho*-sPSO₂.

shown in Figure 1a,b) make it difficult to obtain continuous rotational energy profiles. This is in contrast to the corresponding trans conformations (Figure 1c,d), where the effects of intermolecular hydrogen bonding are minimized. Despite performing multiple scans starting from different structures to smooth out the surfaces, these surfaces are still relatively rough and appear to be discontinuous.

As displayed in Figure 2, doubly degenerate energy barriers occur when the plane of the phenylene ring rotates into the plane that is perpendicular to the second phenylene ring. Not surprisingly, two minimum energies structures were determined with open-book orientations. Specifically, the average energy barrier in the *meta*–*meta*-sPSO₂ dimer is about 3.3 kcal/mol. Considerably larger rotational energy barriers (i.e., 15.5 and 8.2 kcal/mol) are observed in the trans conformation

Table 2. Binding Energies for *meta*–*meta*-sPSO₂ + *n*H₂O^a

| + <i>n</i> H ₂ O | <i>E</i> _{elec} ^b | <i>E</i> _{ZPE} ^c | Δ <i>E</i> ^d (kcal/mol) | Δ <i>E</i> _{ZPE} ^e (kcal/mol) | Δ <i>E</i> _{BSSSE} ^f (kcal/mol) |
|-----------------------------|---------------------------------------|--------------------------------------|------------------------------------|---|---|
| 0(cis) | −3435.22 | 0.30 | | | |
| 0(trans) | −3435.20 | 0.30 | | | |
| 1 | −3511.67 | 0.32 | 20.14 | 18.08 | 12.61 |
| 2 | −3588.12 | 0.35 | 40.34(20.17 ^g) | 36.35(18.17) | 25.62(12.81) |
| 3 | −3664.57 | 0.37 | 59.97(19.99) | 53.00(17.67) | 42.12(14.04) |
| 4 | −3741.02 | 0.40 | 79.90(19.98) | 71.01(17.75) | 55.66(13.92) |
| 5 | −3817.47 | 0.42 | 95.26(19.05) | 84.01(16.80) | 68.60(13.72) |
| 6 | −3893.92 | 0.45 | 112.32(18.72) | 97.39(16.23) | 74.88(12.48) |

^aFor structures optimized at the B3LYP/6-31G** level. ^bTotal electronic energy in Hartrees. ^cZero-point energy (ZPE) in Hartrees. ^dBinding energy based on (uncorrected) total electronic energies. ^eBinding energy based on ZPE-corrected *E*_{elec}. ^fBinding energy based on the CP correction to BSSE of optimized structure. ^gValues in parentheses are per water molecule.

Table 3. Binding Energies for *ortho*–*ortho*-sPSO₂ + *n*H₂O^a

| + <i>n</i> H ₂ O | <i>E</i> _{elec} ^b | <i>E</i> _{ZPE} ^c | Δ <i>E</i> ^d (kcal/mol) | Δ <i>E</i> _{ZPE} ^e (kcal/mol) | Δ <i>E</i> _{BSSSE} ^f (kcal/mol) |
|-----------------------------|---------------------------------------|--------------------------------------|------------------------------------|---|---|
| 0(cis) | −3435.22 | 0.30 | | | |
| 0(trans) | −3435.22 | 0.30 | | | |
| 1 | −3511.67 | 0.32 | 16.25 | 14.03 | 9.75 |
| 2 | −3588.12 | 0.35 | 34.17(17.09 ^g) | 28.91(14.45) | 19.01(9.51) |
| 3 | −3664.56 | 0.37 | 49.94(16.65) | 42.53(14.18) | 29.35(9.78) |
| 4 | −3741.01 | 0.40 | 67.54(16.88) | 57.13(14.28) | 40.81(10.20) |
| 5 | −3817.46 | 0.42 | 89.81(17.96) | 76.15(15.23) | 52.08(10.42) |
| 6 | −3893.92 | 0.45 | 110.34(18.39) | 93.11(15.52) | 64.61(10.77) |

^aFor structures optimized at the B3LYP/6-31G** level. ^bTotal electronic energy in Hartrees. ^cZero-point energy (ZPE) in Hartrees. ^dBinding energy based on (uncorrected) total electronic energies. ^eBinding energy based on ZPE-corrected *E*_{elec}. ^fBinding energy based on the CP correction to BSSE of optimized structure. ^gValues in parentheses are per water molecule.

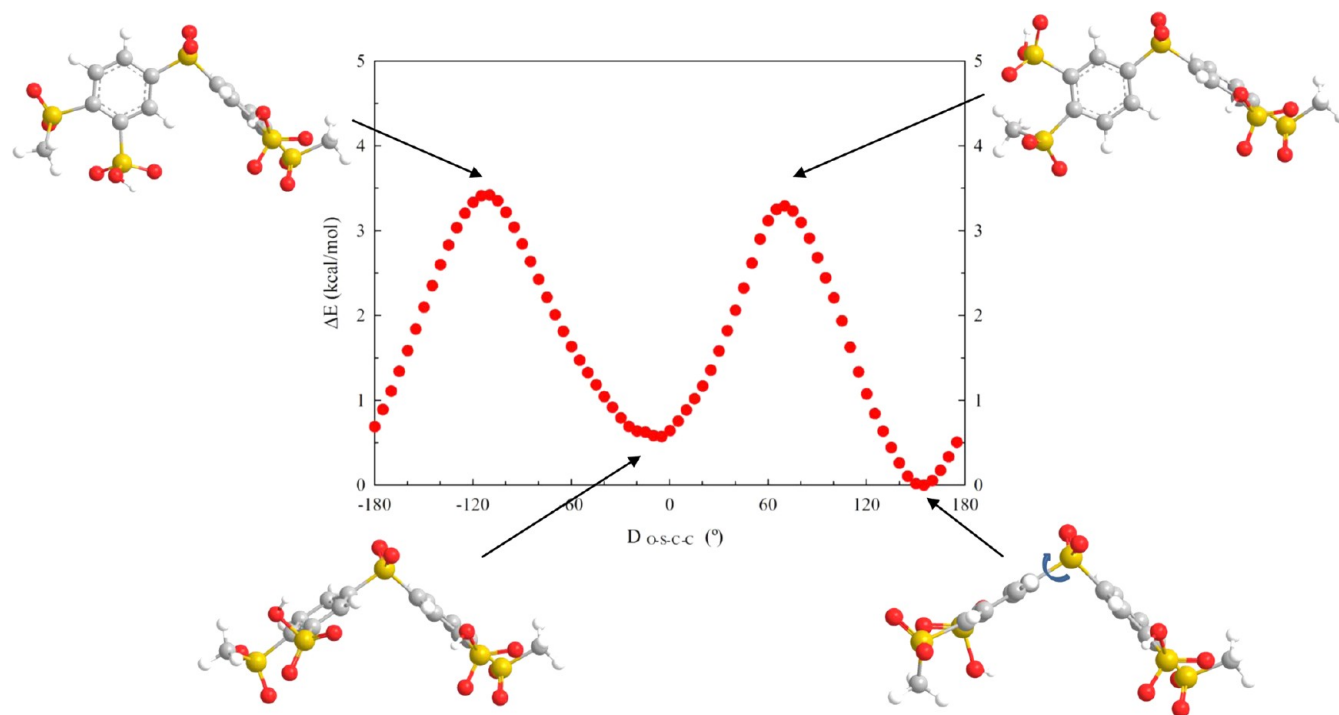


Figure 2. Relative rotational energies along central C–S bonds of *meta*–*meta*-sPSO₂ dimer obtained at B3LYP/6-31G**. The starting structure possesses a *trans* conformation where –SO₃H groups reside on opposite sides of the –SO₂– group. The total electronic energies of this structure are 3.41 kcal/mol more than the corresponding global minimum structures. Two peaks of relative rotational energies are 3.29 and 3.43 kcal/mol, respectively.

of the *ortho*–*ortho* dimer (see Figure 1d) due to the hydrogen bonding between the –SO₃H group and –SO₂– unit. Again, rotational energy peaks are found when the two planes made by the rings are perpendicular to each other (see Figure 3). The

largest energy barrier (i.e., 15.5 kcal/mol) is nearly 9 kcal/mol greater than that observed in PFSA fragments,⁶⁸ indicating that the phenylene backbone is substantially stiffer than a PTFE backbone.

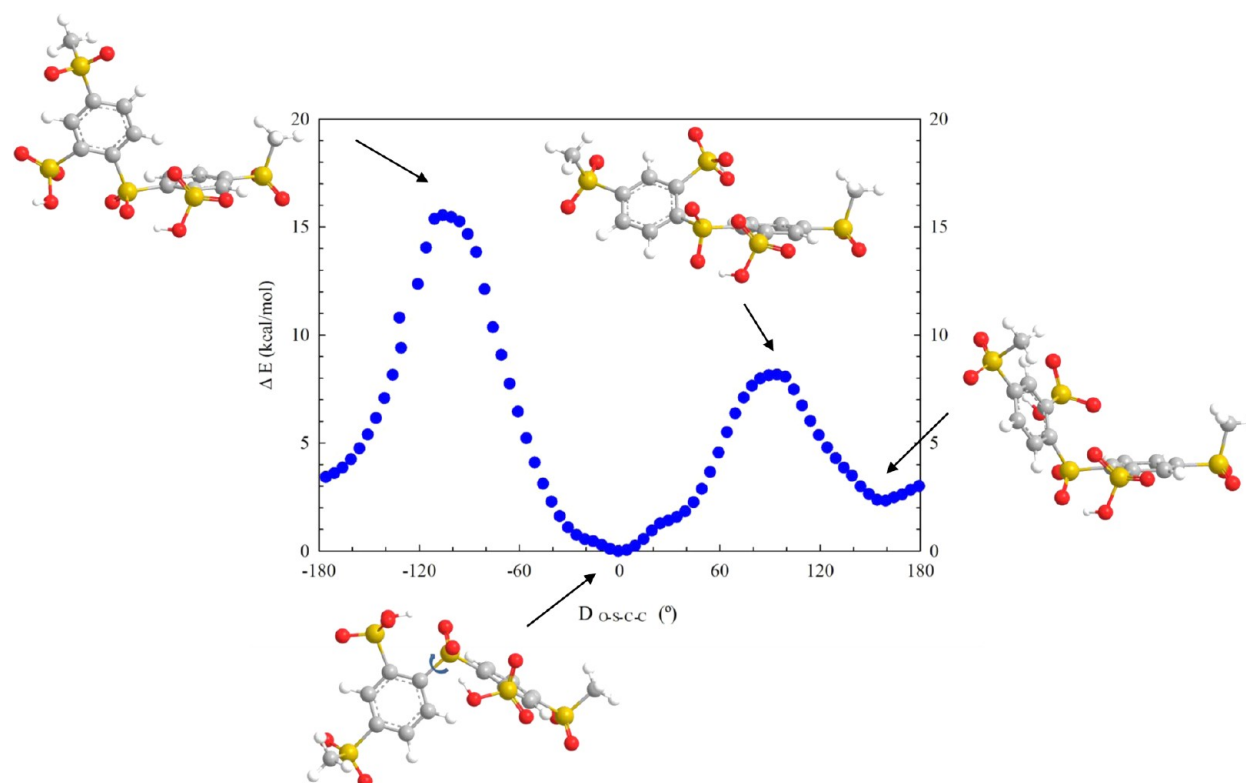


Figure 3. Relative rotational energies along central C–S bonds of *ortho-ortho*-sPSO₂ dimer obtained at B3LYP/6-31G**. The starting structure possesses a *trans* conformation where –SO₃H groups reside on opposite sides of the –SO₂– group. The total electronic energies of this structure are 2.91 kcal/mol more than the corresponding global minimum structures. Two peaks of relative rotational energies are 15.54 and 8.17 kcal/mol, respectively.

Microsolvation. It has been shown that the conformations of the equilibrium structures of the sPSO₂ dimers are significantly influenced by the configuration of the hydrogen bonding between the sulfonic acid groups and relative positions of the neighboring aromatic rings. In order to investigate proton transfer in close proximity to the sulfonic acid groups at low degrees of hydration, a small number of water molecules were incrementally added to each of the sPSO₂ fragments. The fully-optimized structures (at B3LYP/6-31G** level) of multihydrated sPSO₂ dimers were obtained from a variety of starting structures as a function of the initial position of the water molecules. The resultant conformations of the *meta-meta* and *ortho-ortho* fragments are displayed in Figures 4 and 5, respectively. The binding energies of these fragments and water molecules were calculated at the B3LYP/6-31G** level and are reported in Tables 2 and 3. A selection of structural parameters (i.e., dihedral angles of rotating aromatic fragments, separation of sulfonic acid groups, and separation of the acidic proton from the conjugate base) of each of the molecules are listed in Table 1.

Previous work^{13,67} involving the microsolvation of PFSA ionomers revealed that the onset of proton dissociation is mostly dependent upon the water content of the system (i.e., H₂O/SO₃H), the backbone conformation, and the separation of the sulfonic acid groups. For simple monosulfonated systems such as triflic acid, the proton dissociation will not occur until three water molecules are added. In PFSA fragments with more than one sulfonic acid group, a continuous hydrogen bond network is usually formed between the terminal –SO₃H groups. It was determined that the number of water molecules required to form such hydrogen bonding is a function of the separation of the

sulfonic acid groups. Specifically, one, two, and three water molecules are required to bridge two sulfonic acid groups separated by five, seven, and nine (CF₂) on backbones.⁶⁷

Because of the aromatic backbone, the local hydration of sPSO₂ fragments is quite different from what is found in PFSA fragments. In *meta-meta*-sPSO₂ dimers, for instance, only three water molecules are necessary to witness both protons dissociated from the acidic groups (as shown in Figure 4b). In contrast, it was found that, for the fragments of the short-side-chain PFSA ionomers, at least five water molecules are needed to observe the dissociation of both protons.⁶⁷ The protons dissociated from sulfonic acid groups are stabilized by forming two hydronium ions highlighted in Figure 4b. The first hydronium ion is hydrogen bonded with two sulfonic acid groups and a water molecule. The second one, however, closely interacts with two sulfonic acid groups and a sulfone unit. When the fourth water molecule is added, two water molecules form a hydrogen-bonded wire connecting the two sulfonic acid groups (see Figure 4c). The protons, as expected, remain within the first hydration shell. Subsequently, an Eigen ion (H₃O₄⁺) is observed when six water molecules are added to the system as displayed in Figure 4d. In the process of hydration, the hydronium ion, which is stabilized by two sulfonic acid groups and a sulfone unit, is nearly unaffected by the additional water molecules. The other hydronium ion, however, is now fully hydrated by three water molecules and forms an Eigen ion indicating that the proton has shifted to the second hydration shell.

The hydration of the *ortho-ortho* fragment displayed in Figure 5 is apparently different from the *meta-meta* fragment. In addition to the hydrogen bonding between the two sulfonic acid groups, hydrogen bonding was also observed between a

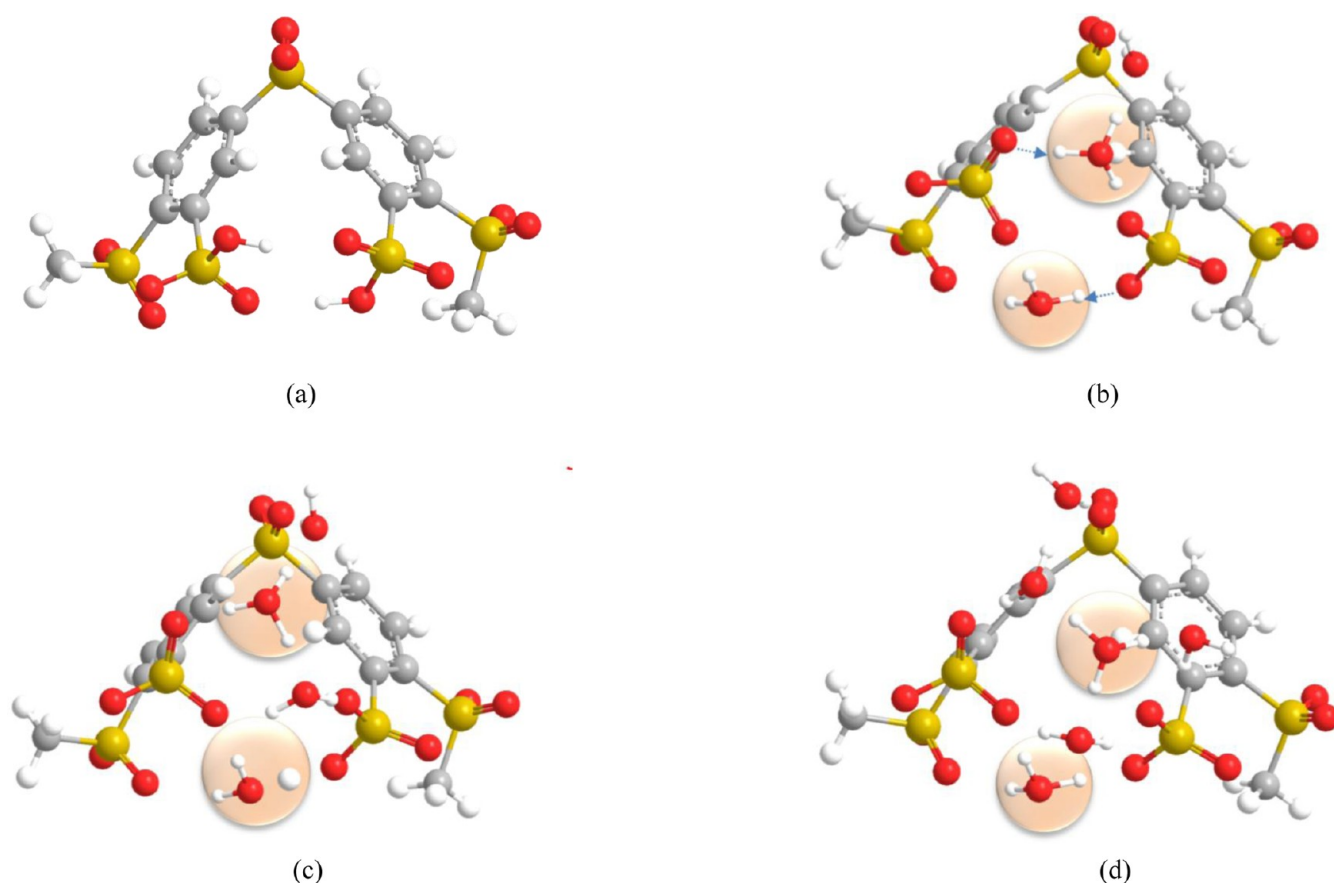


Figure 4. Fully-optimized (B3LYP/6-31G**) global minimum energy structures of *meta*–*meta*-sPSO₂ dimer with n water molecules: (a) $n = 0$; (b) $n = 3$; (c) $n = 4$; (d) $n = 6$. The proton dissociation occurs when three water molecules were added.

sulfonic acid group and a sulfone unit as shown in Figure 5a. This hydrogen bond is stable and is barely interrupted even after further water molecules are added. Thus, the hydration of the ortho–ortho fragment only occurs in the close proximity of one of the sulfonic acid groups, where at least four water molecules are required to observe the transfer of a proton (see Figure 5b). These results suggest that the position of the sulfonic acid substituents will greatly change the local hydration and proton transfer of a sPSO₂ polymeric fragment.

Binding energies (per water molecule) were computed at the B3LYP/6-31G** level to obtain a measure of the interaction of the first hydration shell water molecules to the sulfonic acid groups. The computed BSSE corrected binding energies listed in the last columns of Tables 2 and 3 reveal that the water is consistently more strongly bound in the *meta*–*meta* fragments (approximately 3 kcal/mol higher binding energy per water molecule) than in the ortho–ortho fragments. This result is probably due to the fact that both sulfonic acid groups in the *meta*–*meta*-sPSO₂ fragments are involved in forming hydrogen bonds to the dissociated protons. Furthermore, the relative trends in the (BSSE corrected) binding energies for *meta* and ortho fragments are virtually the same prior to proton dissociation: the magnitude of the binding energy increases with increasing hydration.

The dihedral angles are listed in the first two columns of Table 1 and indicate that the rotation of the phenylene rings occurs in accordance with the hydration of the fragments. The degree of rotation is primarily determined by the separation of the sulfonic acid groups and degree of hydration. As discussed previously, the energy penalty for rotation of the rings in the *meta* conformations

are much lower than in the ortho conformations. Therefore, a small variance in the dihedral angles associated with rotating the aromatic rings is expected for the ortho fragments when the water molecules are added. For *meta*–*meta*-sPSO₂, in contrast, rotation of the phenylene rings is more sensitive to the degree of hydration.

Proton Transfer. As mentioned earlier, the substituent position of the sulfonic acid groups on the aromatic rings have a significant influence on the formation of the hydrogen bond network and transfer of protons under limited hydration conditions. With an intermediate separation of the protogenic groups, the *meta*–*meta* fragment has a double hydrogen bond between a sulfonic acid pair when no water molecules are present. Once water molecules are incrementally added, both sulfonic acid groups participate in forming continuous hydrogen bonds and hence facilitate proton transfer from acidic sites to the adjacent water molecules. However, hydration of the ortho–ortho fragments (as seen in Figure 5b–d) only occurs in close proximity to a sulfonic acid group, whereas the other one is strongly hydrogen bonded to a nearby sulfone unit. Hence, the hydration of the ortho–ortho acid dimer seems to resemble that of fragments with single sulfonic acid groups. As seen in Figure 5b, four water molecules are needed to dissociate one proton. The acidic proton will not be transferred to the second hydration shell until the fifth water molecule is added (see Figure 5c).

It is known that the formation of a Zundel ion (H_3O_2^+) is important not only for the diffusion of protons in bulk water but also the proton transfer in PEM ionomers at low degrees of hydration.^{67,87} As a result of the continuous hydrogen bond network formed between interacting terminal groups, shuttling

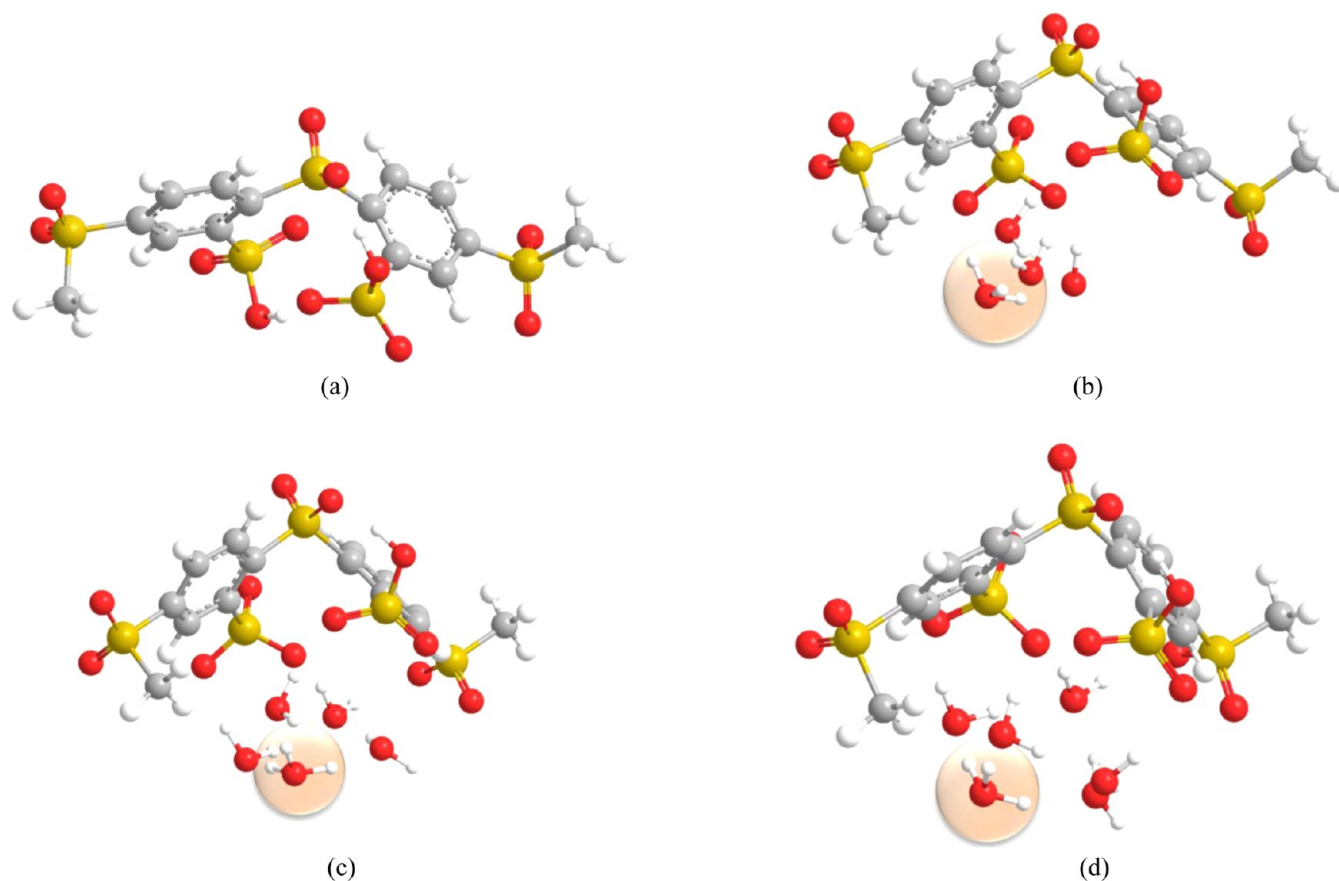


Figure 5. Fully-optimized (B3LYP/6-31G**) global minimum energy structures of *ortho-ortho*-sPSO₂ dimer with n water molecules: (a) $n = 0$; (b) $n = 3$; (c) $n = 4$; (d) $n = 6$. The proton dissociation occurs when four water molecules were added.

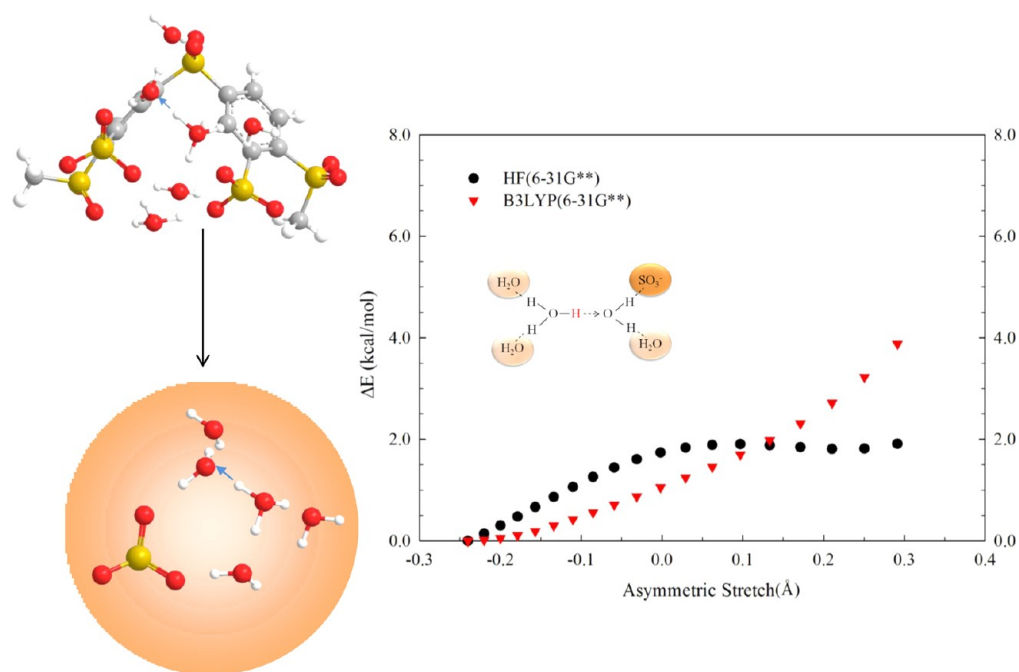


Figure 6. Relative energy profiles of proton transfer in the *meta-meta*-sPSO₂ dimer + 6H₂O at HF/6-31G** and B3LYP/6-31G** levels as a function of the asymmetric stretch coordinate. Only one $-\text{SO}_3$ group is involved in the transfer model. The energy barrier is 1.91 kcal/mol.

of the dissociated proton between sulfonic acid groups and/or water molecules is now possible. Thus, three distinct proton transfers were considered differentiated on the basis of the

environment in the proximity of one or two sulfonic acid groups. In each case, the hydrated proton is hydrogen bonded to either water molecules or sulfonic acid groups.

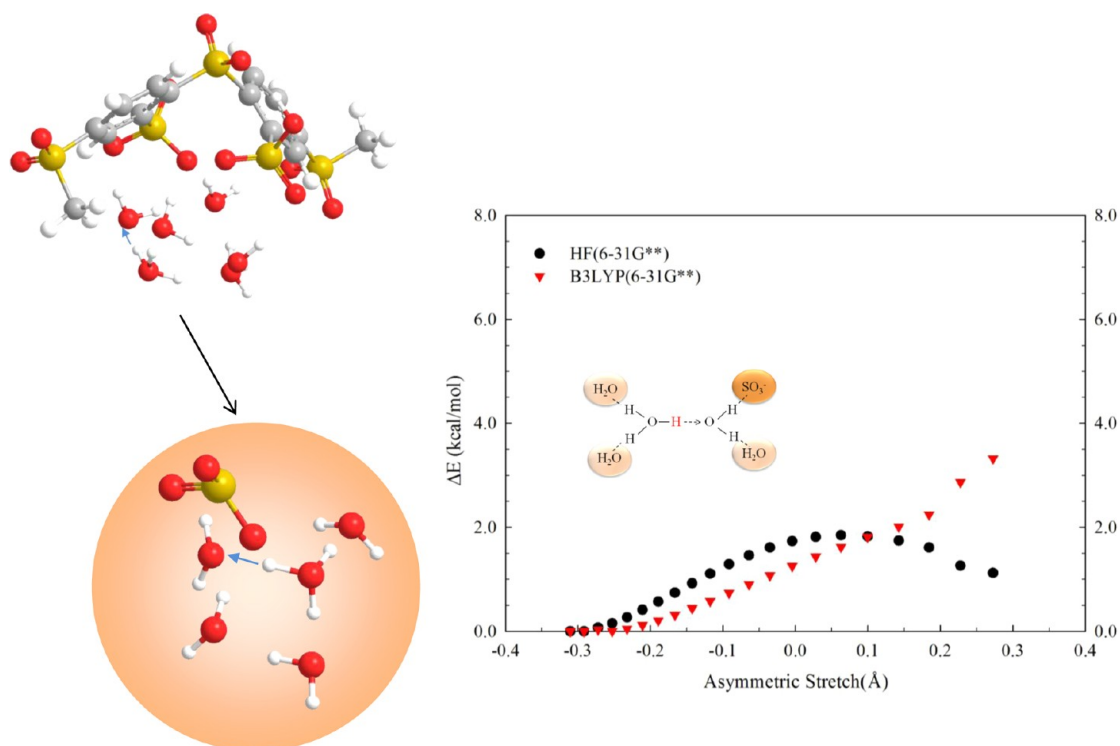


Figure 7. Relative energy profiles of proton transfer in the *ortho-ortho*-sPSO₂ dimer + 6H₂O at HF/6-31G** and B3LYP/6-31G** levels as a function of the asymmetric stretch coordinate. Only one SO_3 group is involved in the transfer model. The energy barrier is 1.85 kcal/mol.

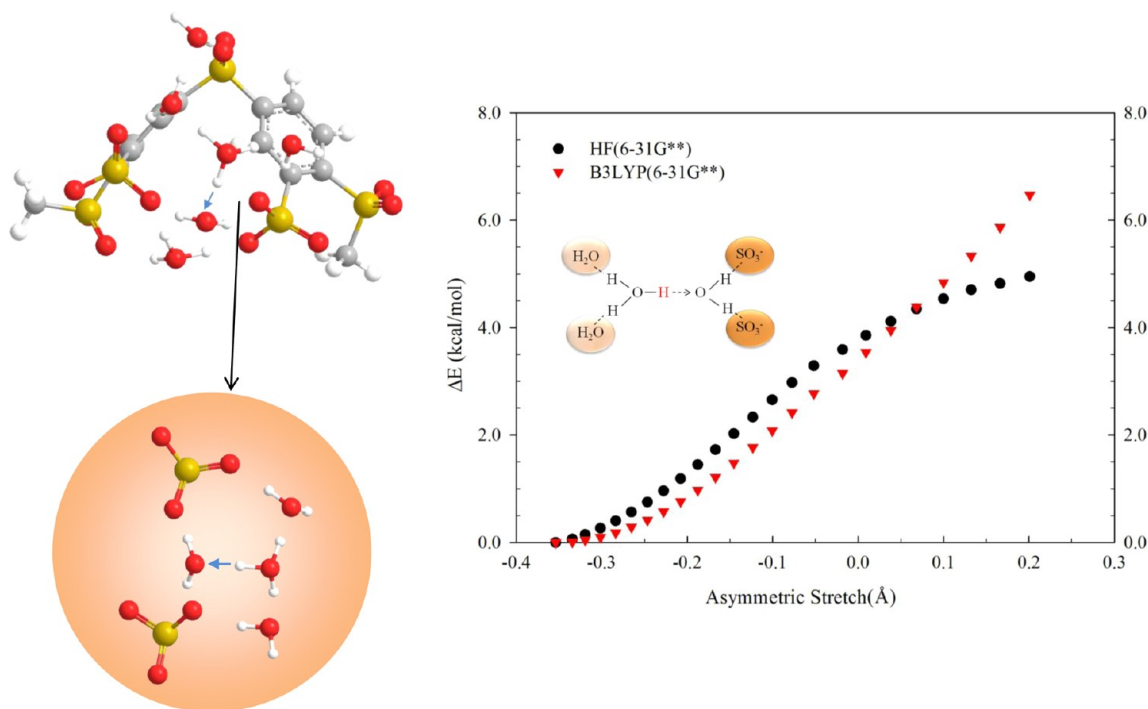


Figure 8. Relative energy profiles of proton transfer in the *meta-meta*-sPSO₂ dimer + 6H₂O at HF/6-31G** and B3LYP/6-31G** levels as a function of the asymmetric stretch coordinate. Two SO_3 groups at the same side of the Zundel ion are involved in the transfer model. No apparent barrier was found.

The energetics associated with proton transfer in each system is then investigated by forcing a specific proton to move to the first hydration shell of a sulfonic acid. The proton transfer patterns and corresponding energy profiles are illustrated in Figures 6–9. We have plotted the energy profiles as a function

of the asymmetric stretching coordinate, q_{asym} to facilitate comparison to proton transfer energetics obtained for other systems including the Zundel ion in bulk water.^{88–91}

The initial structures of the first model (see Figures 6 and 7) are obtained from equilibrium structures of the *meta-meta*-sPSO₂

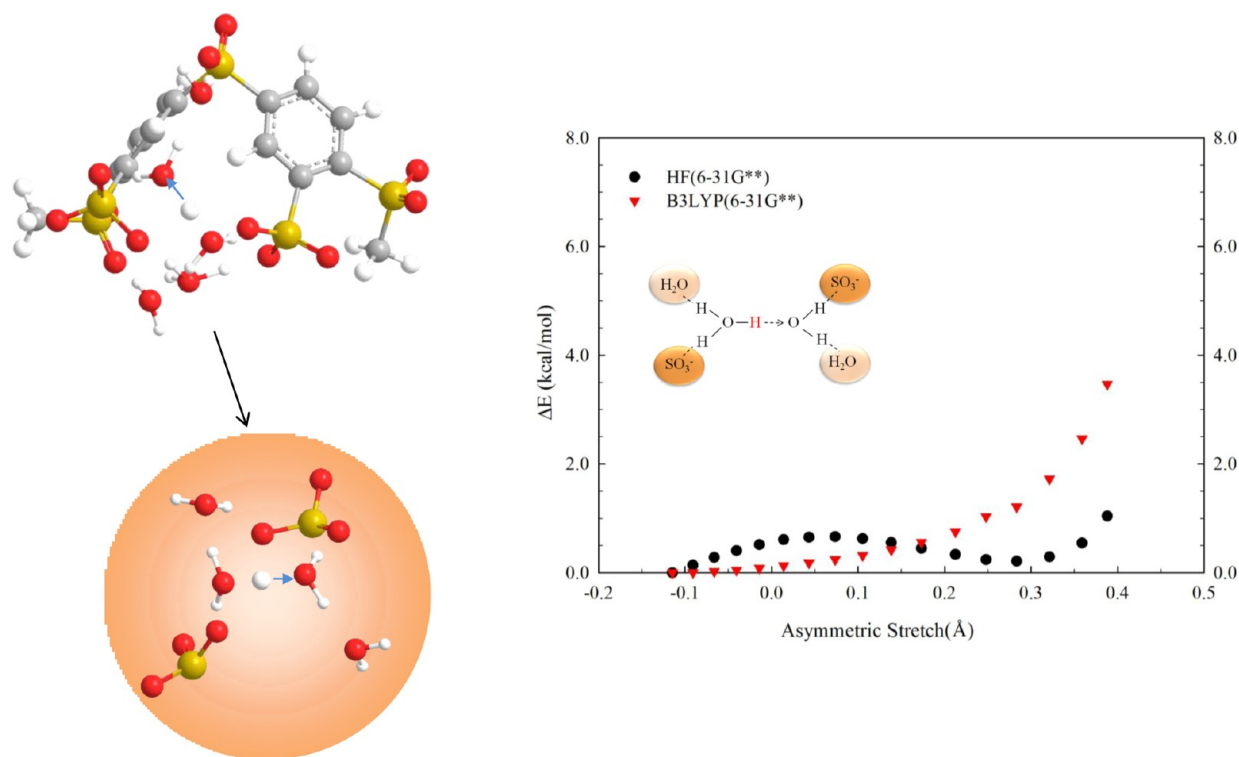


Figure 9. Relative energy profiles of proton transfer in the *meta*–*meta*-sPSO₂ dimer + H₂O at HF/6-31G** and B3LYP/6-31G** levels as a function of the asymmetric stretch coordinate. Two –SO₃ groups at opposite sides of Zundel ion are involved in the transfer model. The energy barrier is 0.66 kcal/mol.

dimer with six water molecules and *ortho*–*ortho*-sPSO₂ dimer with five water molecules. In each of the cases, the selected proton (present as an hydronium ion hydrogen bonded to three water molecules) is transferred back to the oxygen atom of a water molecule bridging a sulfonic acid group and a water molecule. As a consequence of forming a contact ion pair in the final structures, the relative energy was observed to increase in both two systems. However, distinctly different energy profiles were obtained dependent on the choice of the calculation method. The energy profiles computed with the HF method show that the energy barriers are about 1.91 and 1.85 kcal/mol for the *meta*–*meta* and *ortho*–*ortho* systems, respectively. Hybrid DFT (B3LYP) calculations, however, failed to predict a distinct energy barrier with the formation of a Zundel ion in either system. Calculations based on B3LYP are usually more sensitive to the presence of intermolecular interactions than HF and generally lead to a reorganization of the corresponding structures. This was confirmed by examining the structural changes throughout the potential energy surface scan conducted with the two methods: the hydrogen bonds (estimated by the O–H···O distances) obtained at the B3LYP/6-31G** level are always contracted by nearly 0.1 Å when compared to those obtained with HF.

The proton transfer path and corresponding energetic profiles for a second system are shown in Figure 8. Here, the acidic proton is forced to transfer back to the water molecule that connects two terminal sulfonic acid groups. Transferring a proton in this manner leads to a particularly unfavorable structure and a constantly increasing energy. This indicates that the role of neighboring sulfonic acid group is crucial to facilitate proton transfer. Both calculation methods give nearly the same trend of energy profile prior to the formation of Zundel ion.

Once a pair of sulfonic acid groups is bridged by two water molecules, the excess proton tends to shuttle symmetrically

between the two water molecules. This transfer pathway and the associated energetics are shown in Figure 9. Again, the two calculation methods exhibit different energy profiles: the presence of an energy barrier is only found in the HF calculations. It is also worth noting that the proton transfer in this manner corresponds to a very low energy barrier (only 0.66 kcal/mol) indicating that the proton transfer is almost barrierless resembling the rattling that frequently occurs in bulk water. As this transfer only occurs within the primary hydration shell of the sulfonic acid groups, it probably does not contribute to the overall proton conductivity.

CONCLUSIONS

Extensive searches for global minimum energy structures of two different sPSO₂ dimer fragments without water molecules revealed a preference for the *cis* conformation, where the two sulfonic acid groups are located on the same side of the backbone. The source of the stabilization is mainly due to the strong interaction of the sulfonic acid groups that is absent in a *trans* conformation and decreases as the separation of the groups is increased. Furthermore, rotational energy profiles determined from potential energy scans reveal that the aromatic backbones are much stiffer than the PTFE backbone found in PFSA ionomers. Specifically, the largest energy penalty of rotating phenylene units (i.e., 15.5 kcal/mol for *ortho*–*ortho*-sPSO₂) is found to be nearly twice that obtained by rotating CF₂ units in a PTFE backbone.

Prior investigation of the microsolvation of PFSA ionomers suggests that the minimum amount of water needed to witness dissociation of the protons is a function of the separation of the sulfonic acid groups. For sPSO₂ ionomers, however, the number of water molecules required to transfer a proton to the first hydration shell is closely related to the nature of

hydrogen bonding in proximity of the sulfonic acid groups: three water molecules for the meta conformation and four water molecules for the ortho conformation. It is also worth noting that only three water molecules are needed to observe dissociation of both protons in the *meta*–*meta*-sPSO₂ dimer, where both sulfonic acid groups facilitate the proton transfer. This suggests that the sPSO₂ ionomers may more effectively contribute mobile protons at low water contents.

Several distinct proton transfers in proximity to one or two sulfonic acid groups were examined by performing potential energy surface scans along individual hydrogen bonds. The energetics obtained at the HF/6-31G** level indicate that the energy barriers for transferring a proton when only one sulfonic acid group is present is approximately 1.9 kcal/mol, which is 2.1 kcal/mol lower than similar calculations for hydrated triflic acid molecules. However, the increasing energy associated with a second proton transfer indicates that the hydrated proton is highly unstable when it is hydrogen bonded to both sulfonic acid groups. When two sulfonic acid groups are connected by two water molecules, the excess proton (existing as a Zundel ion) tends to shuttle through this continuous water wire back and forth with a relatively small energy barrier with 0.66 kcal/mol. This symmetric bidirectional transfer, however, in and of itself, is not likely to contribute to long-range proton transport.

In systems with hydrogen bonded water molecules, it is important to take into account the quantum nuclear effects due to the small mass of the protons. It has been shown that these effects play an important role in the proton transfer in water and hydrated systems.⁹¹ However, the inclusion of them requires sophisticated ab initio path integral techniques, which are not presently available with electronic structure calculations. Thus, the calculated proton transfer properties (e.g., energetic barriers) may be influenced by these effects. In addition, the hydrogen bonding reorganization may account for the different energetic barriers calculated by HF and B3LYP. The results of this study should not be taken as absolute values, but rather as a relative comparison as to how neighboring sulfate groups and hydrogen bonding affect the energetics of proton transfer.

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Notes

The authors declare no competing financial interest.

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