Supplementary Information

Calculations Using B-97D Functional

Additional test calculations were performed using the B-97D functional, which includes empirical corrections for dispersion interactions, with the 6-31G** basis set to compare the results to those obtained with B3LYP. The PES scan presented in Figure 3 of the manuscript was repeated using this functional and is shown in Figure S1. The hydrogen bond changes throughout the scan are extremely similar to those obtained using B3LYP. The relative energy profile contained similar features with the transition state and local minimum located at approximately the same points of the scan. A lower transition state energy (2.7 vs. 4.2 kcal/mol) and a lower relative local minimum energy (0.23 vs 1.1 kcal/mol) were found using the B-97D functional but the qualitative insight into the results are consistent.

Extended information from the manuscript

$\lambda = 2.5 H_3O^+$ to SO_3^-

Figure S2 shows the optimized EW 590 at $\lambda = 2.5$ with both protons dissociated as hydronium ions, one of which connects the sulfonate groups through hydrogen bonding and the other hydronium ion hydrogen bonds to an oxygen atom from one sulfonate group and two water molecules which also hydrogen bond to sulfonate oxygen atoms forming a connectivity bridge. The proton from the hydronium ion with only one hydrogen bond to a sulfonate group was forced to transfer to the neighboring sulfonate oxygen atom, as indicated by the arrow. The resulting relative energy profile monotonically increases with the transfer of the proton. Transferring the proton to the sulfonate oxygen atom again repels away the other water molecule and hydronium ion donating hydrogen bonds to other oxygen atoms on the same sulfonate group as a result of charge transfer. At $q_{asym} = 0$ (Figure S2b), the O···O distance between the

hydronium ion and the sulfonate oxygen atom receiving the proton contracts from initially 2.62 to 2.45 Å attributed mostly to the migration of the hydronium ion towards the sulfonate group. The strong hydrogen bond between the hydronium ion and the top left water molecule drags the water molecule in the direction of the hydronium ion motion pulling it away from the left sulfonate group which, in turn, promotes stronger hydrogen bonding between the other hydronium ion and the left sulfonate group (the hydrogen bond distance between the transferring hydronium ion and the top left water molecule increases due to the contracted hydrogen bond length between the hydronium and sulfonate oxygen atoms). In this way, a concerted shift in the hydrogen bond distances occurs as a result of the transfer of a single proton. However, as seen in the results at $\lambda = 2$, shifts in hydrogen bond lengths to compensate for the transfer of charge do not result in a transition state to a local minimum without a reorientation of the hydrogen bond network. The all-encompassing hydrogen bond network precludes structural reorganization in this proton transfer event as there are no nearby available sites to form new hydrogen bonds. This results in a hydrogen bond pattern that maintains the same bond pairs as the original geometry but with an energetic penalty of 11.4 kcal/mol upon reprotonation. However, when a proton was transferred across the hydrogen bond between the bottom hydronium ion and right sulfonate group oxygen atom (Figure S3) a reorganization of the hydrogen bond network did, indeed, occur. Namely, the hydrogen bond between the top hydronium ion and the right sulfonate group oxygen atom was broken as the sulfonate group gained positive charge from the proton transfer. The loss of the proton in the hydronium ion significantly weakened the hydrogen bond it made with the oxygen atom on the left sulfonate group (from an O···O distance of 2.61 to 2.90 Å) increasing its excess negative charge. This resulted in the formation of a hydrogen bond from the top hydronium ion with this oxygen atom via an abrupt jump across sulfonate groups.

The resultant relative energy profile of the PES scan, again, was found to monotonically increase due to the resistance of reprotonation at this level of hydration but to a lesser extent than the other case. The shift in the hydrogen bond network evidently provides some degree of stabilization resulting in a singly dissociated state only 6.0 kcal/mol higher in energy than the initial structure.

A monotonically increasing relative energy profile was also found in PES scan of the transfer of a proton from a hydronium ion to a sulfonate oxygen atom for EW 690 at a hydration of $\lambda = 2.5$. The optimized geometry for this PES scan, shown in Figure S4, contains two dissociated protons with one hydronium ion connecting the sulfonate groups through individual hydrogen bonds. Initially, the top water molecule donates individual hydrogen bonds to two oxygen atoms on the left sulfonate group, one being the oxygen atom receiving the proton (Figure S4a). As the proton is transferred, the additional positive charge received by the sulfonate oxygen atom forces this hydrogen bond to break, and the water molecule rotates away from the oxygen atom while maintaining the other hydrogen bond (Figure S4b). The other water molecule also donating a hydrogen bond to the sulfonate group is also repelled away to compensate for the transfer of charge. No hydrogen bond network reorganization was observed throughout the PES scan other than the breaking of the one hydrogen bond due to the lack of available hydrogen bonding sites. Thus, only expansions and contractions in the hydrogen bonds lengths were observed resulting in a configuration 8.5 kcal/mol higher in energy upon reprotonation (Figure S4c). A nearly identical relative energy profile (not shown) was also obtained for the transfer of the proton from the top hydronium ion (which actually resembles more of a Zundel cation) to the sulfonate oxygen atom it is hydrogen bonded to. The Zundel-like character observed was immediately lost as proton transfer brings the initially shared proton towards the hydronium ion to compensate for the

transfer of charge. This, in turn, resulted in less positive charge the water molecule in the original Zundel-like complex can delocalize through hydrogen bonds which led to the breaking of one of the hydrogen bonds it originally made with the two oxygen atoms of the left sulfonate group. Again, other than the breaking of one hydrogen bond, no hydrogen bond network reorganization was observed resulting in a singly dissociated state 8.4 kcal/mol higher in energy than the original geometry.

H_2O to SO_3^-

The results of the PES scan shown in Figure S5 start with the same optimized EW 590 geometry as Figure 5 at $\lambda = 2$, but now a proton is transferred from a water molecule to the right sulfonate group. The early steps in the scan (up to point b) lead to a relatively steep increase in the relative energy profile with the most noticeable changes in the hydrogen bond distances occurring between the water molecule transferring the proton and its neighboring hydronium ion (Figure S5b). This is a result of the concerted transfer of charge where, as the sulfonate group accepts more positive charge, the hydronium ion is repelled away from the right sulfonate oxygen atom it hydrogen bonds with while also being drawn towards the water molecule to compensate for a loss of positive charge (likely the primary contributor to the steep energy profile since there is no 'excess' proton in a water molecule like a hydronium ion). Once the water molecule has accepted an 'excess' proton from the hydronium ion, the relative energy profile broadens. This, however, also leads to the loss of a hydrogen bond with the final state of the initial hydronium ion being a water molecule with 'quasi-hydrogen bonds' shared between two oxygen atoms of the sulfonate/sulfonic acid groups and a much weaker hydrogen bond (as indicated by the hydrogen bond length) to the left sulfonate group than in the initial configuration (Figure S5c). The disruption in the hydrogen bond network from the initial configuration and the reprotonation of

the sulfonate group result in a state that is 7.4 kcal/mol higher in energy. A similar monotonically increasing energy profile was found for the analogous proton transfer PES scan for EW 690 at $\lambda = 2$ shown in Figure S5. This result starts from the same optimized geometry as Figures 2 and 6 but a proton is transferred from a water molecule to the right sulfonate group. The relatively selective solvation of the right sulfonate group clusters the water molecules/hydronium ion together leading to changes in hydrogen bond distances throughout most of the hydrogen bond network as the proton is transferred (Figure S6b). The transfer of positive charge repels away other hydrogen bond donors which have no reasonable open sites to form new hydrogen bonds. This forces the side chains to separate from a S···S distance of 6.35 to 6.56 Å and breaks multiple hydrogen bonds leading to a final state (Figure S6c) with both protons associated and an accompanying energetic penalty of 10.1 kcal/mol. It is important to note that, although this energetic penalty for reprotonation is higher than that of EW 590, this does not suggest that EW 690 has a greater propensity for proton dissociation at this level of hydration as each system started and ended with a different number of dissociated protons and hydrogen bonds.

The transfer of a proton from a water molecule to a sulfonate group at $\lambda = 2.5$ (not shown) led to similar changes in the hydrogen bond network as those observed in Figures S2 and S4 for proton transfer from a hydronium ion to a sulfonate group at this hydration level for EW 590 and EW 690, respectively. Using the same optimized EW 590 geometry as Figure S2, a proton was transferred from the top left water molecule to the sulfonate oxygen atom it hydrogen bonds to resulting in no changes in the hydrogen bond pairs throughout the scan. As with the other results containing no reorientation events, the relative energy profile was found to monotonically increase, and only fluctuations in the hydrogen bond distances to adjust for charge transfer were observed. The reprotonation of the sulfonate group resulted in a configuration 11.7 kcal/mol

higher in energy than the initial configuration. Using the optimized EW 690 geometry in Figure S4 to transfer a proton from the bottom left water molecule to the neighboring oxygen atom of the left sulfonate group led to a monotonically increasing relative energy PES scan. The water molecule that initially formed two hydrogen bonds with two sulfonate oxygen atoms again was repelled away from the sulfonate group resulting in a loss of one of its hydrogen bonds. Contractions and expansions of hydrogen bond lengths attributed to the transfer of charge were observed resulting in a configuration with only one dissociated proton 8.6 kcal/mol higher in energy than the initial doubly dissociated geometry.

Figure S1. The PES scan of Figure 3 in the manuscript repeated using the B-97D functional.

Figure S2. Top left panel: Optimized (B3LYP/6-31G**) structure of the EW 590 3M™ PFSA ionomer at a hydration of $\lambda = 2.5$ used in the PES scan of the proton transfer indicated by the arrow. Top right panel: Relative energy profile with respect to the original configuration as a function of the asymmetric stretch coordinate. Bottom panel: rotated bottom view of the sulfonic acid/sulfonate and water molecules with hydrogen bonds denoted by dashed lines and the hydrogen bond distances (Å): (a) initial configuration; (b) an intermediate point in the scan at $q_{asym} = 0$; and (c) the point in the scan when the proton is fully transferred to the sulfonic acid group.

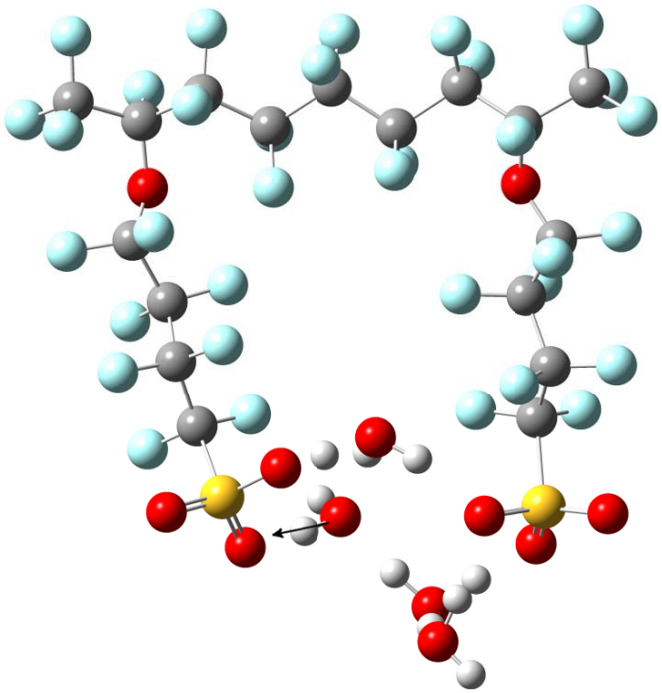
Figure S3. Top left panel: Optimized (B3LYP/6-31G**) structure of the EW 590 3M™ PFSA ionomer at a hydration of $\lambda = 2.5$ used in the PES scan of the proton transfer indicated by the arrow. Top right panel: Relative energy profile with respect to the original configuration as a function of the asymmetric stretch coordinate. Bottom panel: rotated bottom view of the sulfonic acid/sulfonate and water molecules with hydrogen bonds denoted by dashed lines and the hydrogen bond distances (Å): (a) initial configuration; (b) an intermediate point in the scan at $q_{asym} = 0$; and (c) the point in the scan when the proton is fully transferred to the sulfonic acid group.

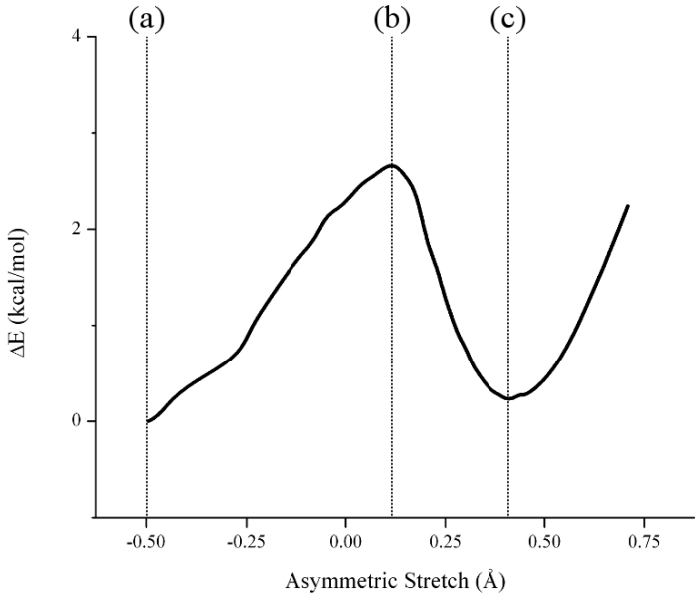
Figure S4. Top left panel: Optimized (B3LYP/6-31G**) structure of the EW 690 3M™ PFSA ionomer at a hydration of $\lambda = 2.5$ used in the PES scan of the proton transfer indicated by the arrow. Top right panel: Relative energy profile with respect to the original configuration as a function of the asymmetric stretch coordinate. Bottom panel: rotated bottom view of the sulfonic acid/sulfonate and water molecules with hydrogen bonds denoted by dashed lines and the hydrogen bond distances (Å): (a) initial configuration; (b) an intermediate point in the scan at $q_{asym} = 0$; and (c) the point in the scan when the proton is fully transferred to the sulfonic acid group.

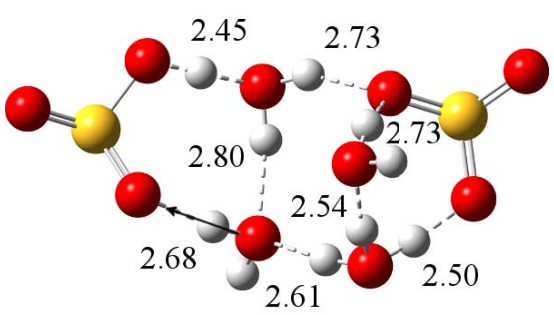
Figure S5. Top left panel: Optimized (B3LYP/6-31G**) structure of the EW 590 3M™ PFSA ionomer at a hydration of $\lambda = 2$ used in the PES scan of the proton transfer indicated by the arrow. Top right panel: Relative energy profile with respect to the original configuration as a function of the asymmetric stretch coordinate. Bottom panel: rotated bottom view of the sulfonic acid/sulfonate and water molecules with hydrogen bonds denoted by dashed lines and the hydrogen bond distances (Å): (a) initial configuration; (b) a pseudo-transition state; and (c) the point in the scan when the proton is fully transferred to the sulfonic acid group.

Figure S6. Top left panel: Optimized (B3LYP/6-31G**) structure of the EW 690 3M™ PFSA ionomer at a hydration of $\lambda = 2$ used in the PES scan of the proton transfer indicated by the arrow. Top right panel: Relative energy profile with respect to the original configuration as a function of the asymmetric stretch coordinate. Bottom panel: rotated bottom view of the sulfonic acid/sulfonate and water molecules with hydrogen bonds denoted by dashed lines and the

hydrogen bond distances (Å): (a) initial configuration; (b) a pseudo-transition state; and (c) the point in the scan when the proton is fully transferred to the sulfonic acid group.







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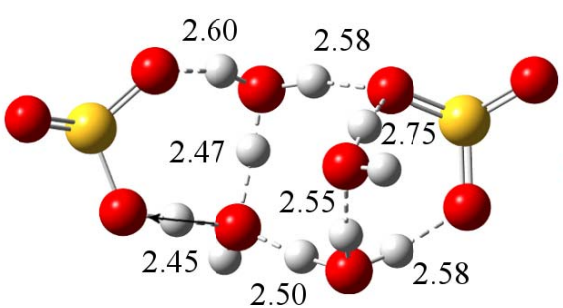

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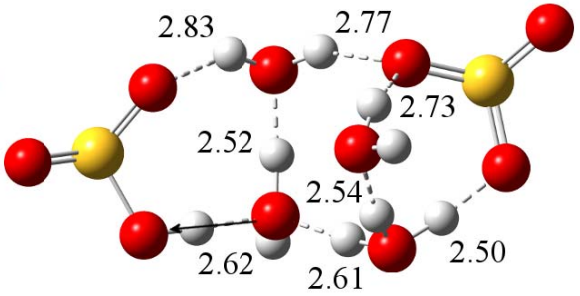

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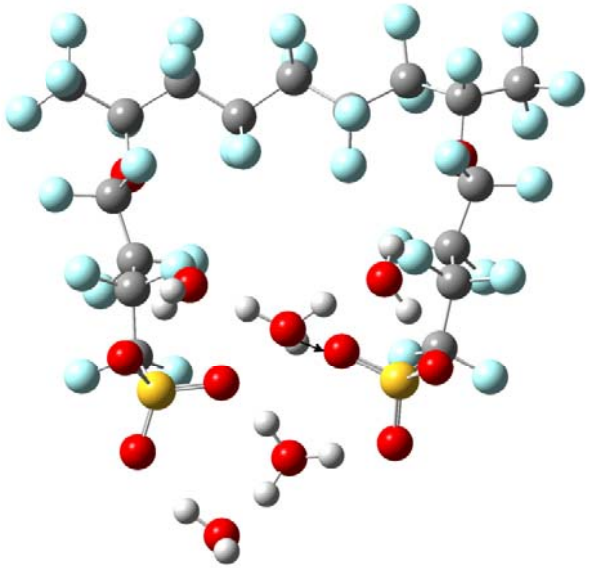
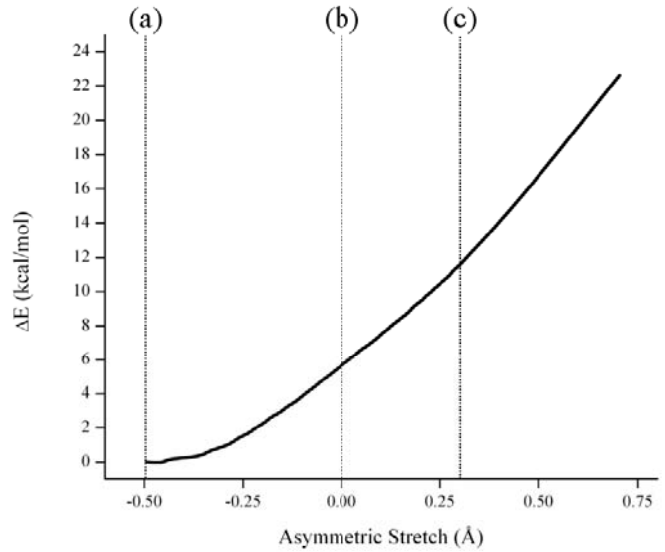
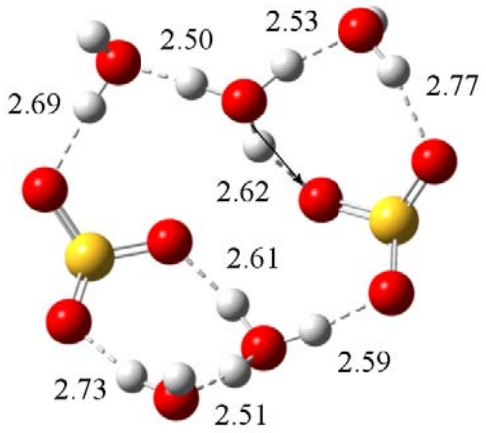
Fig. S1







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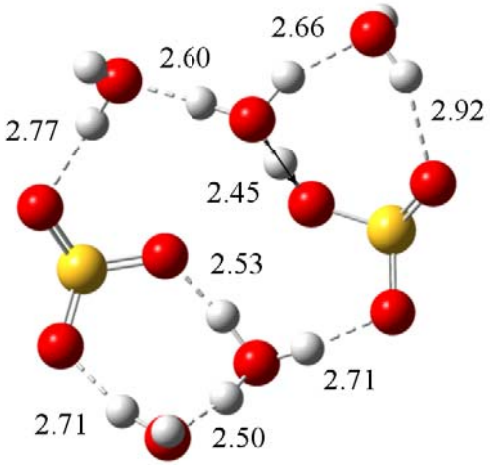

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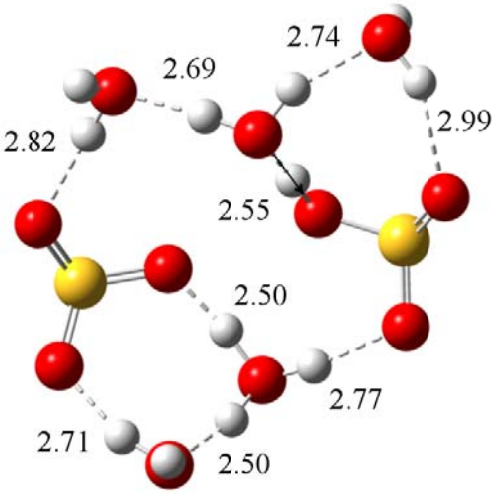

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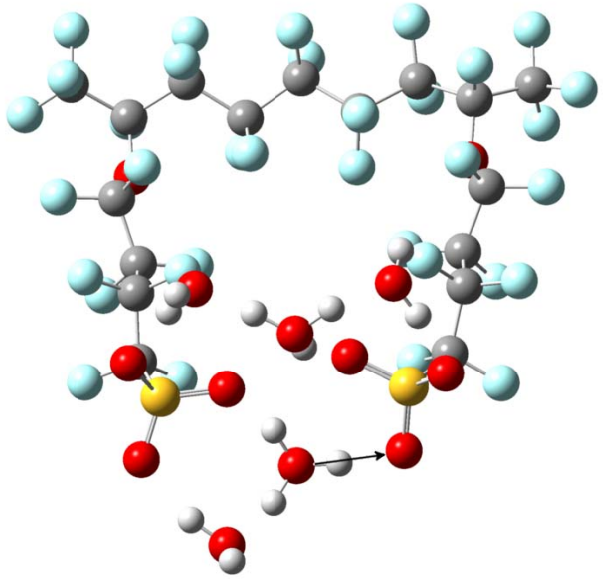
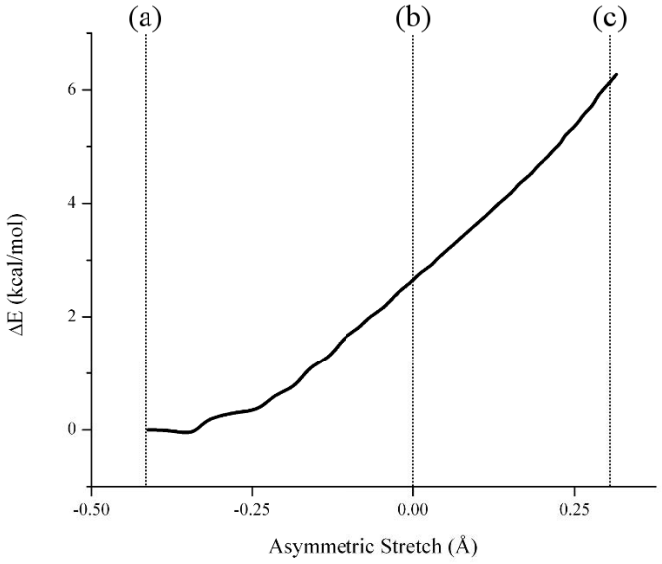
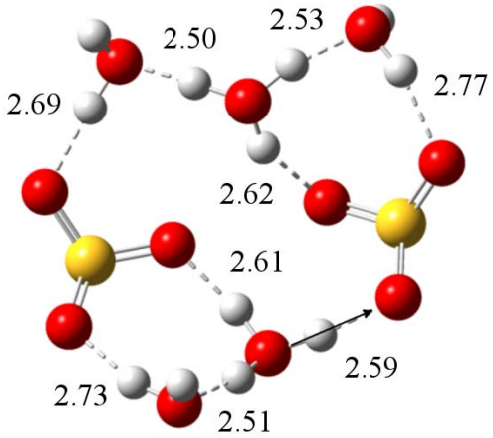
Fig. S2







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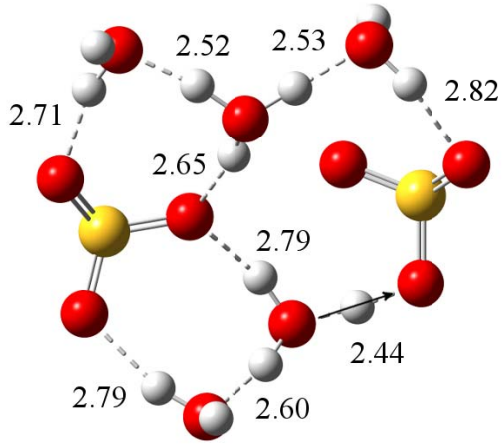

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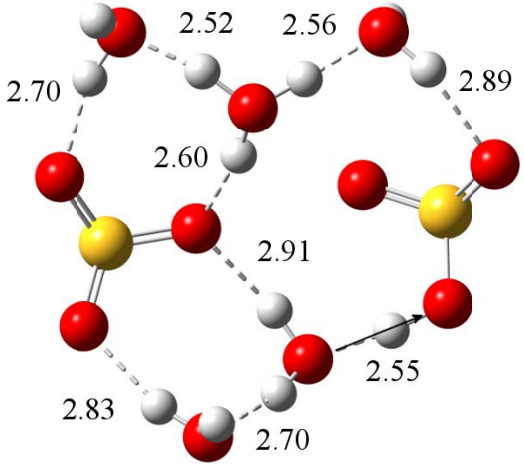

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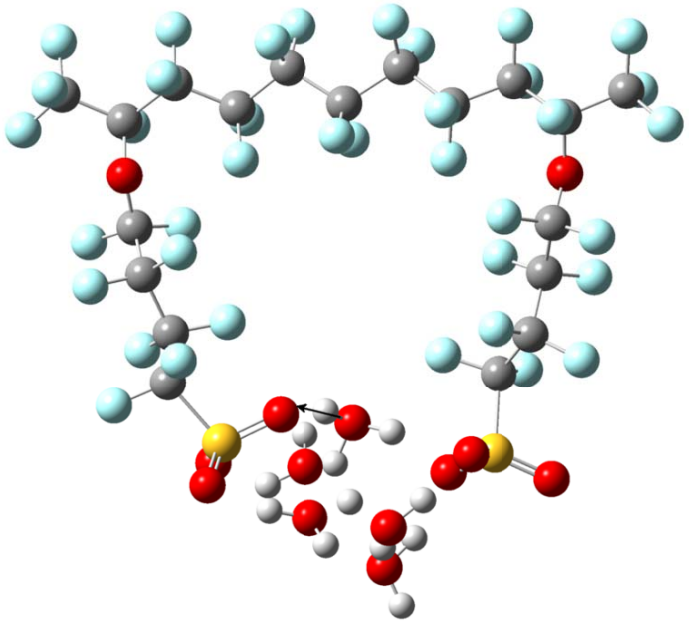
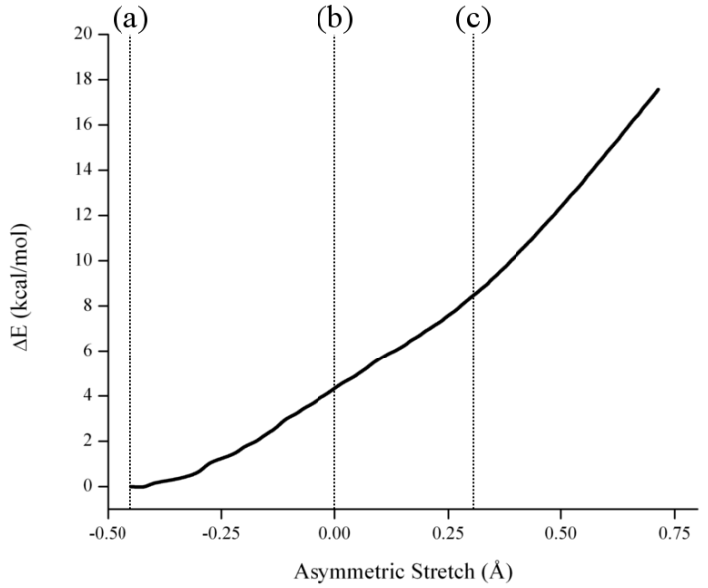
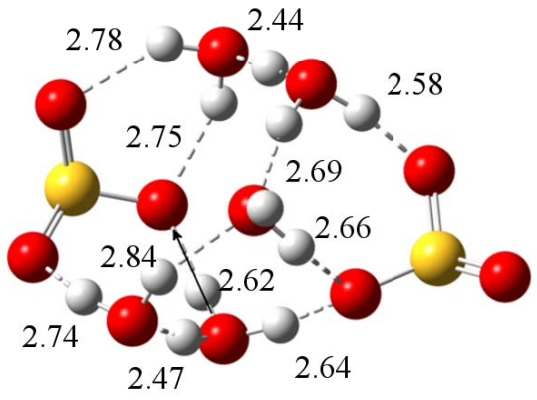
Fig S3







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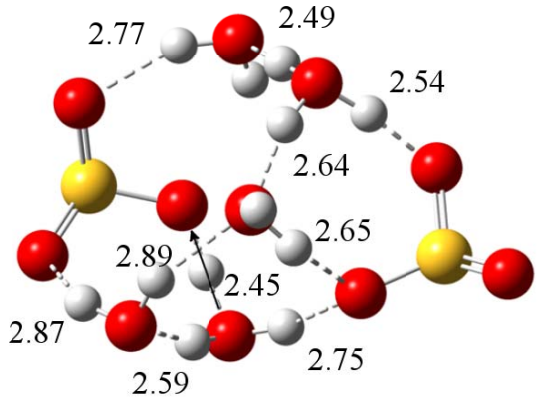

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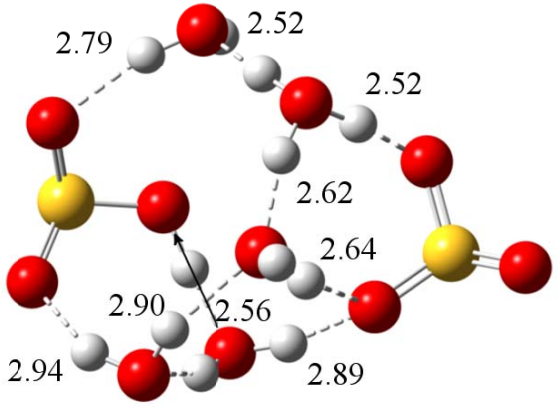

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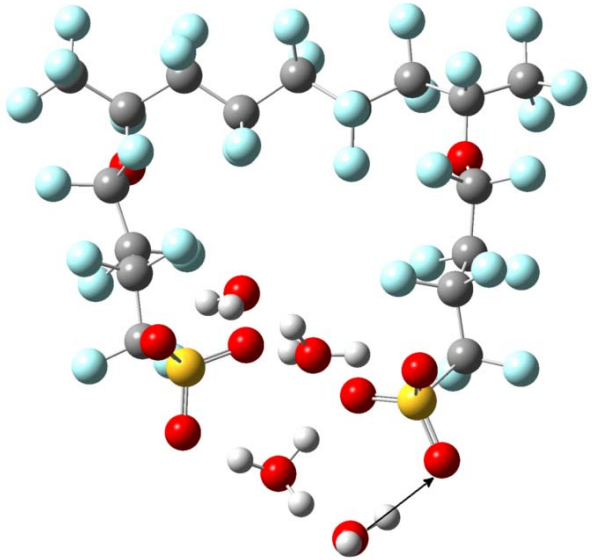
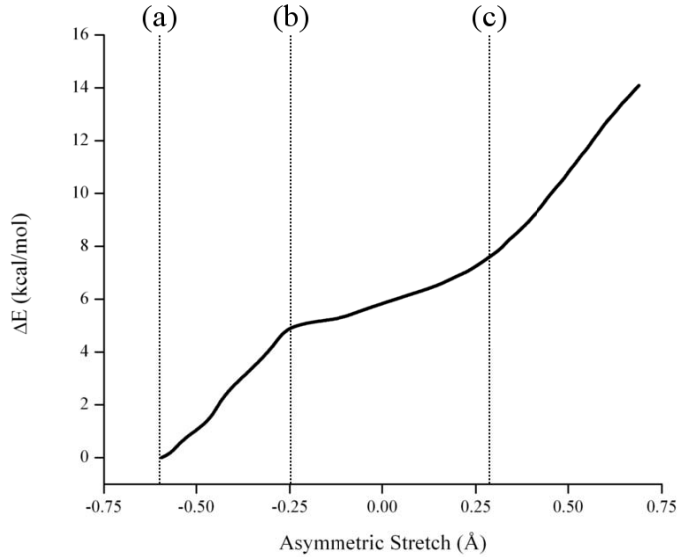
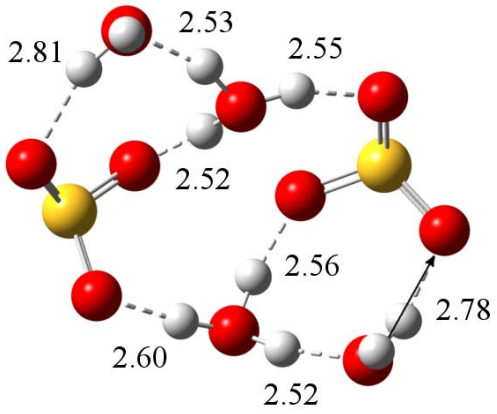
Fig. S4







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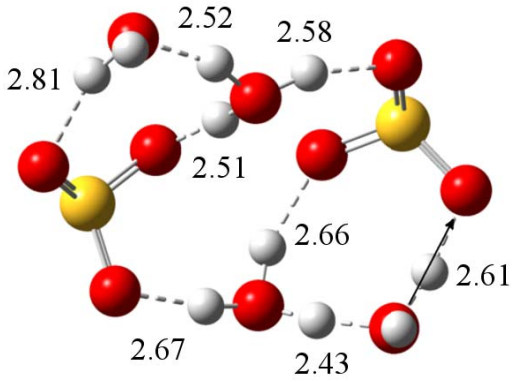

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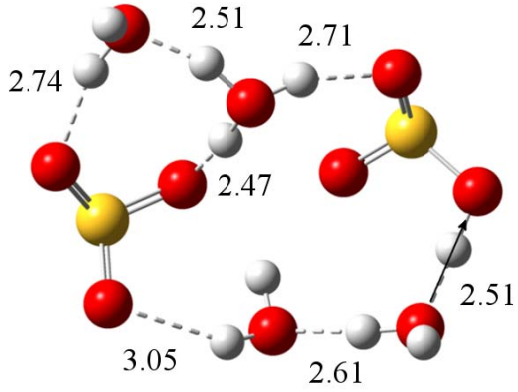

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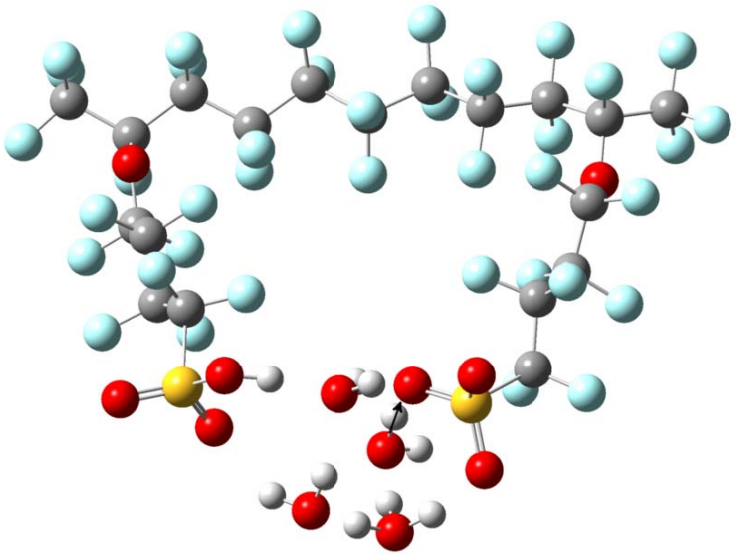
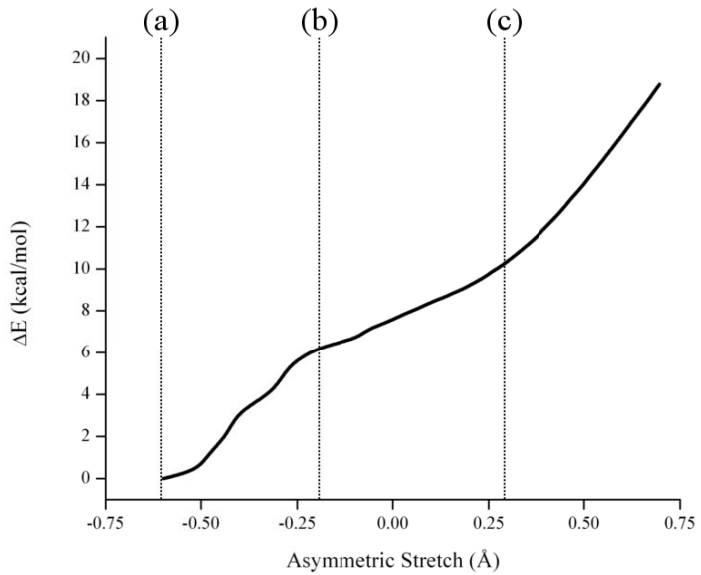
Fig. S5





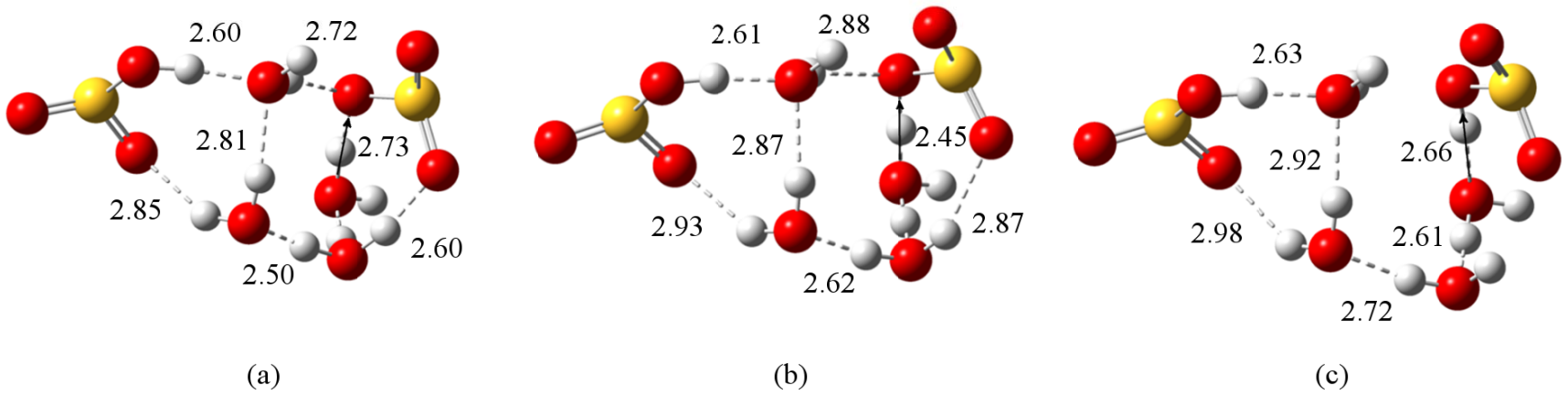


Fig. S6