Molecular Modeling of Trifluoromethanesulfonic Acid for Solvation Theory

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Abstract

Reported here are theoretical calculations on the trifluoromethanesulfonic (triflic) acid and water molecules, establishing molecular scale information necessary to molecular modeling of the structure, thermodynamics, and ionic transport of Nafion® membranes. The optimized geometry determined for the isolated triflic acid molecule, obtained from *ab initio* molecular orbital calculations, agrees with previous studies. In order to characterize side chain flexibility and accessibility of the acid proton, potential energy and free energy surfaces for rotation about both carbon-sulfur and sulfur-oxygen(hydroxyl) bonds are presented. A continuum dielectric solvation model is used to obtain free energies of electrostatic interaction with the solvent. Electrostatic solvation is predicted to reduce the free energy barrier to rotation about the F_3C-SO_3 bond to about 2.7 kcal/mol. This electrostatic effect is associated with slight additional polarization of the CF bond in the eclipsed conformation. The energetic barrier to rotation of the acid hydroxyl group away from the sulfonic acid oxygen plane, out into the solvent is substantially flattened by electrostatic solvation effects. The maximum free energy for those solvent accessible proton conformations is about 1.0 kcal/mol. We carried out additional *ab initio* electronic structure calculations with a probe water molecule interacting with the triflic acid. The minimum energy structures found here for the triflic acid molecule with the probe water these results revise structures reported previously. To investigate the reaction path for abstraction of a proton from triflic acid, we found minimum energy structures, energies, and free energies for: (a) a docked configuration of triflate anion and hydronium cation and

(b) a transition state for proton interchange between triflic acid and a water molecule. Those configurations are structurally similar but energetically substantially different. The activation free energy for that proton interchange is predicted to be 4.7 kcal/mol above the reaction end-points.

Keywords: chemical equilibrium, electric conductivity, hydration, Nafion®, solvation theory, trifluoromethanesulfonic acid.

Introduction

Nafion®, a perfluorinated ionomer widely used in polymer electrolyte fuel cells [1], consists of a hydrophobic Teflon backbone with randomly attached side chains terminating with trifluoromethanesulfonic (triflic) acid groups. These sulfonic acid functional groups are hydrophilic and preferentially hydrated. The Nafion® membrane functions as both a separator and an electrolyte in the fuel cell and the overall performance of the fuel cell is strongly influenced by the membrane conductivity, itself a function of the hydration [2–5]. The water content of the membrane is determined both by equilibrium absorption and by nonequilibrium currents of ions and water. Extensive experimental measurement of electroosmotic drag coupling proton and water fluxes for various sulfonated membranes over a wide range of water content [6–8] has suggested that sulfonic acid interactions dominate proton transport. A molecular level understanding of these processes in Nafion® is not available. Here we work towards a molecular description of these systems by securing information on molecular structures, energies, and charge distribution upon which molecular scale solution theory might be based.

Electrostatic interactions of triflic acid with the environment are expected to be of first importance in this solution chemistry. Continuum dielectric solvation modeling is an appropriate approach to studying these solution processes; it is physical, computationally feasible, and can provide a basis for more molecular theory [9-19].

Computational Methods

Electronic Structure Calculations

Standard *ab initio* molecular orbital calculations were performed using the GAUSSIAN 92/DFT [20] and 94 [21] systems of programs. Both the 6-31G** split valence basis set [22] and the D95** Dunning double zeta basis set [23] were employed at the Hartree-Fock plus second-order Møller-Plesset (MP2) level of theory. Full geometry optimizations were computed for isolated triflic acid (CF_3SO_3H), the triflate anion ($CF_3SO_3^-$), and triflic acid with a probe water molecule ($CF_3SO_3H+H_2O$) using gradient methods [24]. Atom centered partial charges were obtained by the CHelpG scheme [25]. Potential energy surfaces for triflic acid were constructed from calculations at the MP2/6-31G** level by rotation about the carbon-sulfur and sulfur-oxygen(hydroxyl) bonds with optimization of all other degrees of freedom. Finally, the optimized structures and energies were determined for the triflate-hydronium ion pair in two ways: (a) by docking triflate and hydronium ions, each rigidly constrained at their separate equilibrium geometries; and (b) by finding a transition state for interchange of a proton in the triflic-acid-water complex as $CF_3SO_3H^* + HOH = CF_3SO_3H + HOH^*$ using Synchronous Transit-guided Quasi-Newton (STQN) methods [26].

Continuum Dielectric Model

A continuum dielectric model of aqueous solution chemistry has become a standard theoretical tool in recent years and discussions of basic issues can be found elsewhere [17]. The model identifies a solute molecule in a solution environment, defines a realistic solute molecular volume based on the geometry of the molecule, positions partial charges describing the solute electric charge distribution in that molecular volume, and assumes that the solvent exterior to the molecular volume may be idealized as a dielectric continuum. The

numerical task is then the solution of the Poisson equation for which a defined local dielectric constant jumps from one (1.0) in the inside the molecular volume to the experimental value for the solution in the region exterior to the solute molecular volume. The numerical methods used here were boundary integral techniques outlined in References 16 and 17. The molecular volume is modeled as the union of spherical volumes centered on solute atoms. The radii adopted for those spheres depend on atomic type and are essentially empirical. Here we used the values determined by Stefanovich and Truong [27]. The value 77.4 was used for the solvent dielectric constant.

Results and Discussion

The optimized geometries of both triflic acid and the triflate anion are essentially identical to the structures reported by Lindgren *et al* [28,29] at the same levels of theory. Both structures are in good agreement with experimentally determined structures [30,31], the only difference being that the sulfur-oxygen and carbon-fluorine bond lengths are 0.03-0.08Å longer in the theoretical structures.

To characterize the flexibility of the side chains of the perfluorinated membrane and the accessibility of the acidic protons, potential energy surfaces for triflic acid were determined for rotation about the carbon-sulfur bond and the sulfur-oxygen(hydroxyl) bond. The relative energies for rotation about both of these bonds are reported in Tables 1 and 2. The conformational potential energy surface for rotation about the carbon-sulfur bond is given in Figure 1. The highest energy structure occurs when the oxygen and fluorine atoms are eclipsed and the minimum energy structure when those atoms are staggered. The activation energy is 3.5 kcal/mol but the solvation free energy lowers that barrier to about 2.7 kcal/mol. This is mostly due to a slight additional polarization of the C-F bonds in the eclipsed conformation. Figure 2 shows as function of rotation about the carbon-sulfur bond the atom centered partial charges obtained for the triflic acid molecule.

The sulfur-oxygen(hydroxyl) rotational potential energy surface possesses two physically equivalent minima (Figure 3). The lowest barrier between these minima corresponds to the proton directed axially, out into the solvent and has an energy of 2.0 kcal/mol. Electrostatic solvation substantially flattens that barrier so that the maximum free energy between the two minima is about 1.0 kcal/mol. This stabilization of the barrier configuration is due to the better access of the proton to the solvent.

The position of a probe water molecule interacting with triflic acid was determined by fully optimizing the pair of molecules at the MP2 level using both the 6-31G** and D95** basis sets. Recently, Ricchiardi and Ugliengo [32] reported a geometry optimization of triflic acid plus a water molecule at the SCF/DZP level. There result is qualitatively similar but quantitatively substantially different from that presented below. Because our results differed from those previous ones, several different basis sets and starting conditions were considered. The differences we observed among those difference optimizations were slight and do not account for the differences with the previous work. Those differences may be traceable to different level of effort in achieving the optimum structure. Our results are shown in Figure 4. That structure is of lower energy than the structure reported by Ricchiardi and Ugliengo. However, our experience with this optimization is that the triflic-acid-water configurations are floppy as might be expected from noncovalent hydrogen-bonding interactions. For example, we several times found a local minimum of the energy surface with the exterior proton of Figure 4 directed into the plane of that drawing. Potential energy minima of that sort are only slightly higher in energy, of the order of one kcal/mol, than the structure shown. Note that the dihedral angle positioning the triflic acid proton is nearly the same in the minimum energy complex and the minimum energy triflic acid molecule (Figure 3). The floppiness of these structures is consistent with the prediction of the dielectric solvation model that free energy varies only gently with disposition of the acid proton in the region between the two minima (Figure 3).

Attempts were made to determine a minimum energy conformation for triflate-hydronium ion pair but those configurations always relaxed to the optimum geometry of the triflic-acid-water molecule pair. Separately optimized structures for the triflate anion and the hydronium cation were then docked in an optimization that adjusted only the relative positions of the two ions constrained separately to be rigid. That optimum ion pair geometry is presented in Figure 4 also. The energy of the docked ion pair is 27.0 kcal/mol higher than the fully optimized molecule pair. The electrostatic solvation free energy of the docked ion pair relative to that of the optimized molecular complex is computed to be -16.0 kcal/mol so that net free energy of the docked ion pair, as a complex, is approximately 11.0 kcal/mol above that of the minimum energy molecule complex.

Further efforts to determine a reaction path for abstraction of the proton from the triflic acid molecule were based upon the observation (Figure 4) that another minimum energy structure for the triflic-acid-water complex is obtained by cycling a triflic acid proton with a distinct water proton to achieve a physically equivalent but different triflic-acid-water molecule pair. This can be alternatively described by considering that one of the two close protons of the docked hydronium ion will be donated to the triflate anion when it is neutralized. We defined those two possibilities as end-points for a reaction path and found a transition state (Figure 4) using STQN methods [26]. Structurally, the docked ion pair and the transition state are quite similar. The energy of this transition state is 9.3 kcal/mol higher than the end-points of the reaction path or about 18 kcal/mol lower in than the energy of the docked structure. The electrostatic solvation free energy relative to the reaction end-point is predicted to be -4.6 kcal/mol so the activation free energy is about 4.7 kcal/mol.

Conclusions

The results reported here establish molecular scale information necessary to molecular modeling of the structure, thermodynamics, and ionic transport of Nafion®

membranes. Because of a slight additional polarization of the CF bond in the eclipsed conformation, electrostatic solvation reduces the free energy barrier to rotation about the F_3C-SO_3 bond to about 2.7 kcal/mol. Solvation enhances the accessibility of the acid proton by substantially flattening the energetic barrier to rotation of the acid hydroxyl group away from the sulfonic acid oxygen plane, out into the solvent. The maximum free energy for those solvent accessible proton conformations is about 1.0 kcal/mol relative to the minimum energy conformations. The minimum energy structures found for the triflic acid molecule with the probe water these results revise structures reported previously. A doubly hydrogen-bonded configuration is found in which the triflic acid proton forms a short hydrogen-bond. The second hydrogen-bond is of a more traditional type. Minimum energy structures, energies, and free energies were found for: (a) a docked configuration of triflate anion and hydronium cation and (b) a transition state for proton interchange between triflic acid and a water molecule. Those configurations are structurally similar but energetically substantially different. The activation free energy for that proton interchange is predicted to be 4.7 kcal/mol above the reaction end-points. Experimentally determined values of activation energies for protonic conductivity in Nafion and similar perfluorosulfonic acid membranes are roughly 3 kcal/mole for a fully hydrated membrane and increases with decreasing water content [5].

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Table 1: Triflic acid relative potential energy for rotation about the $F_3C\text{-}SO_3$ bond

angle (deg)	MP2 Relative Energy (kcal/mol)
60	0.07
50	0.03
40	0.38
30	1.07
20	1.96
10	2.84
0	3.44
-10	3.50
-20	2.99
-30	2.12
-40	1.19
-50	0.45
-60	0.05
-65.42	0.00

Table 2: Triflic acid relative potential energy for rotation about the sulfur-oxygen (hydroxyl) bond

angle,deg	MP2 Relative Energy (kcal/mol)
180	0.74
170	0.31
160	0.07
150	0.00
140	0.09
130	0.31
120	0.62
110	0.98
100	1.34
90	1.66
80	1.89
70	1.98
60	1.92
50	1.73
40	1.43
30	1.07
20	0.71
10	0.38
0	0.14
-10	0.01
-20	0.03
-30	0.23
-40	0.61
-50	1.18
-60	1.94
-70	2.87
-80	3.90
-90	4.93
-100	5.79
-110	6.28
-120	6.02
-130	5.23
-140	4.23
-150	3.17
-160	2.19
-170	1.37
-13.52	0.00

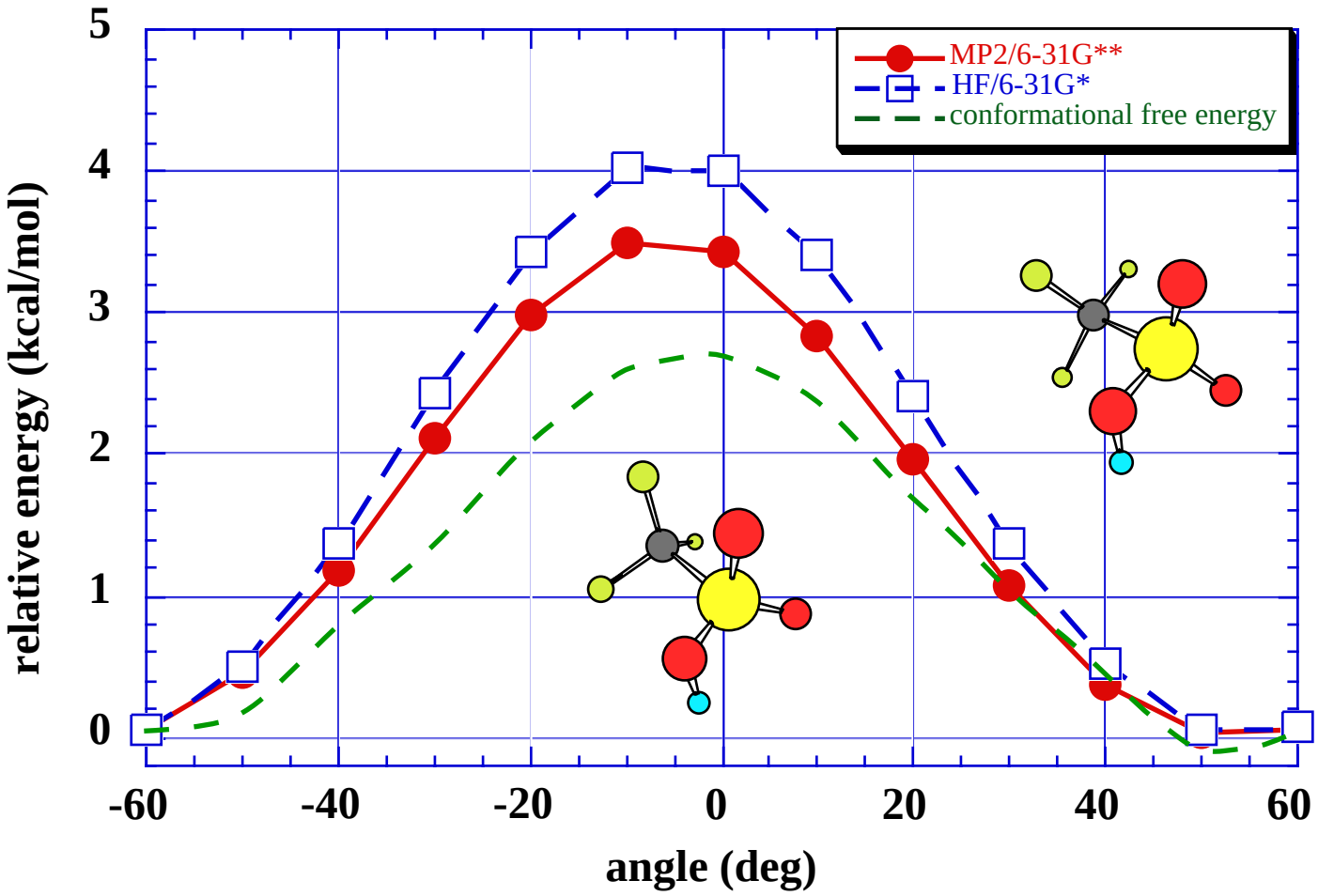
Figure Captions

Figure 1 Relative potential energy as function of rotation about the carbon-sulfur bond in triflic acid. The inset structures show the molecular geometries for the eclipsed (left, barrier maximum) and staggered (right, minimum) conformations.

Figure 2 Atom centered partial charges for the triflic acid molecule as a function of the rotation about the $F_3C\text{-}SO_3$ bond.

Figure 3 Relative potential energy as function of rotation about the sulfur-oxygen (hydroxyl) bond in triflic acid. The inset structures show the molecular geometries for the successive extrema starting at the left from the maximum energy.

Figure 4 (upper) MP2/6-31G** optimized geometry of the triflic-acid-water molecule pair. (middle) Docked structure geometry of the triflate anion and hydronium cation pair. The free energy of this structure is about 11 kcal/mol higher than that of optimum molecular complex above. (lower) STQN Transition structure $CF_3SO_3^- + H_3O^+$. The free energy of this structure is about 4.7 kcal/mol higher than that of upper configuration.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HF/6-31G*
conformational free energy
relative energy (kcal/mol)
angle (deg)
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-60
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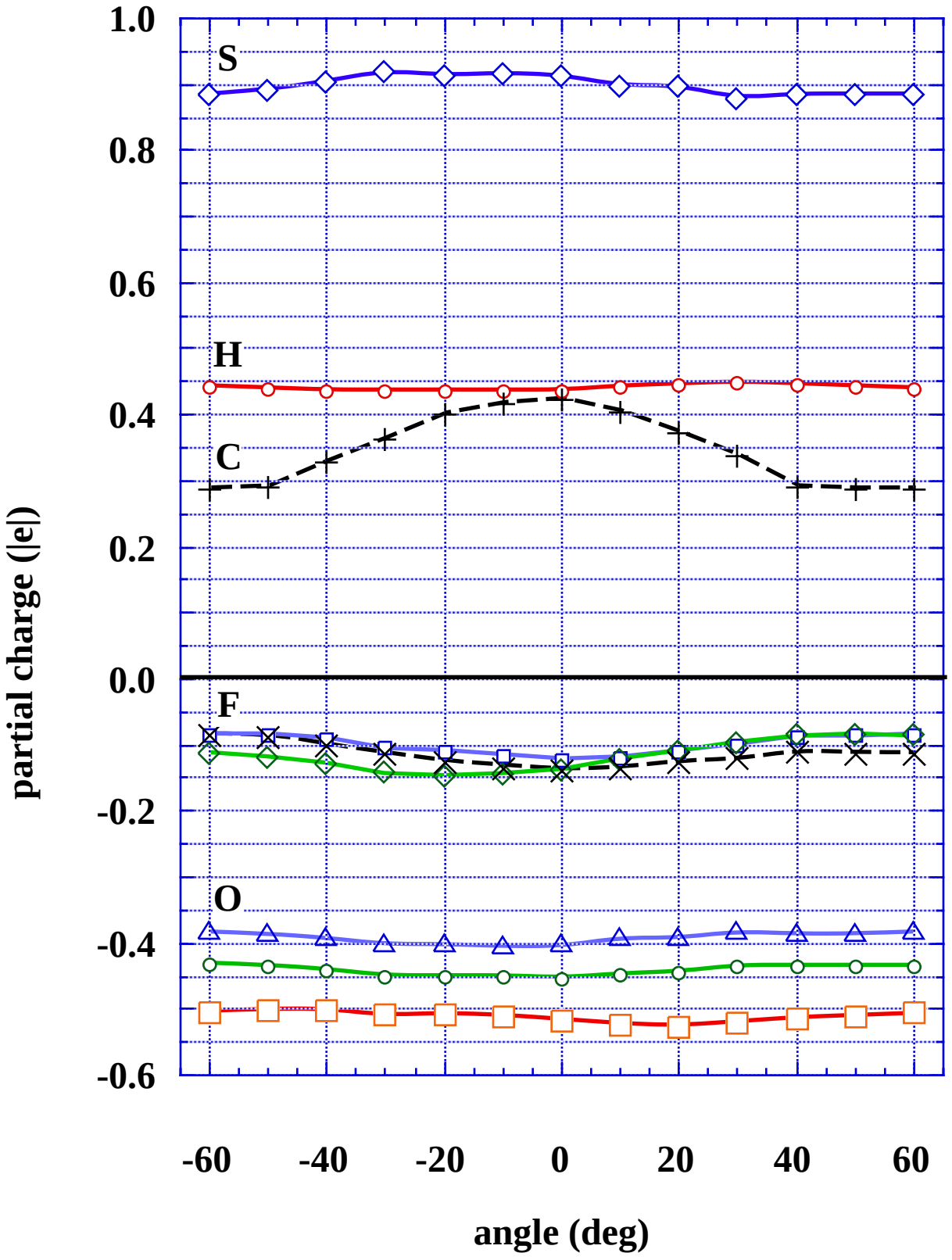
figure 1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60
angle (deg)

figure 2

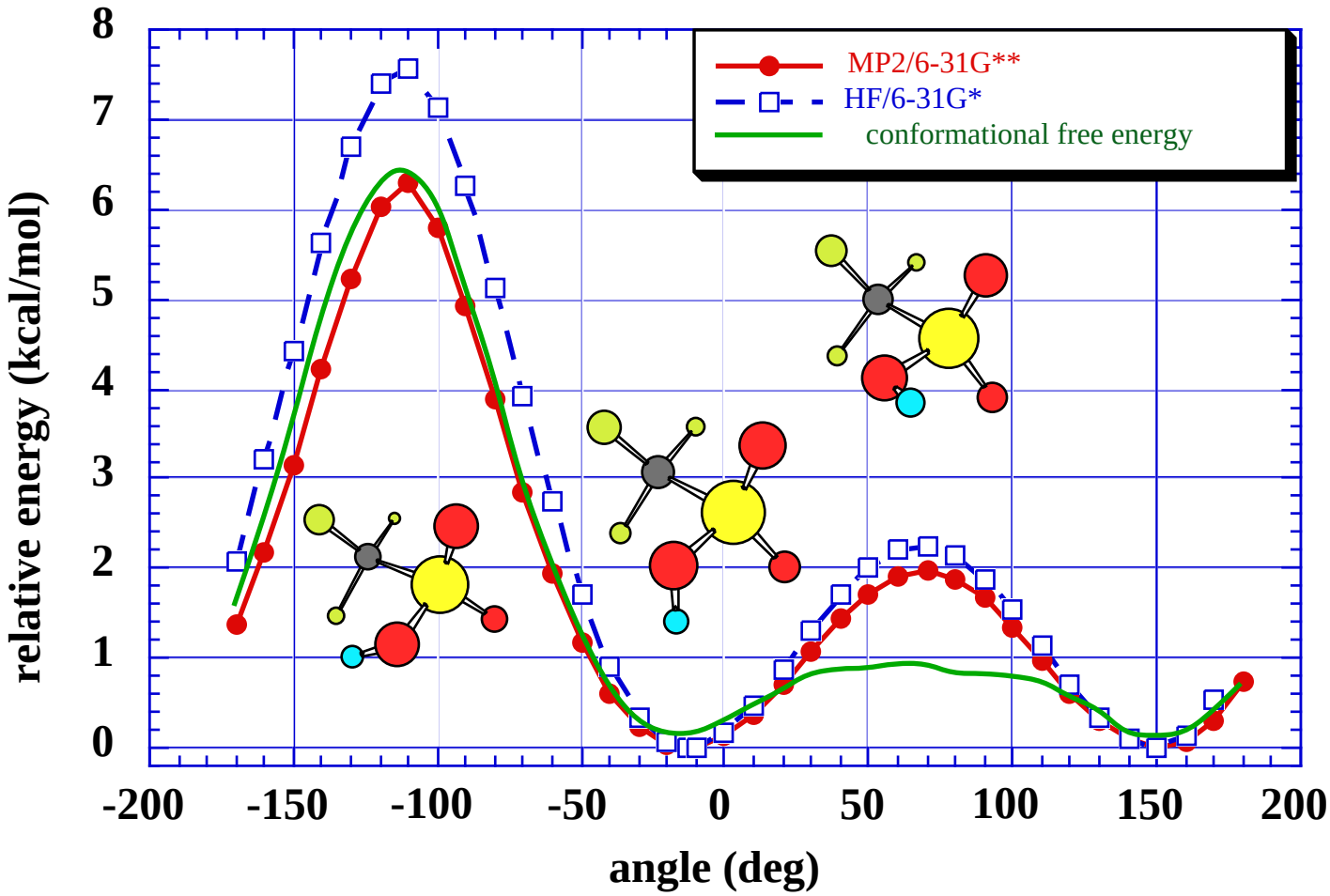
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figure 3

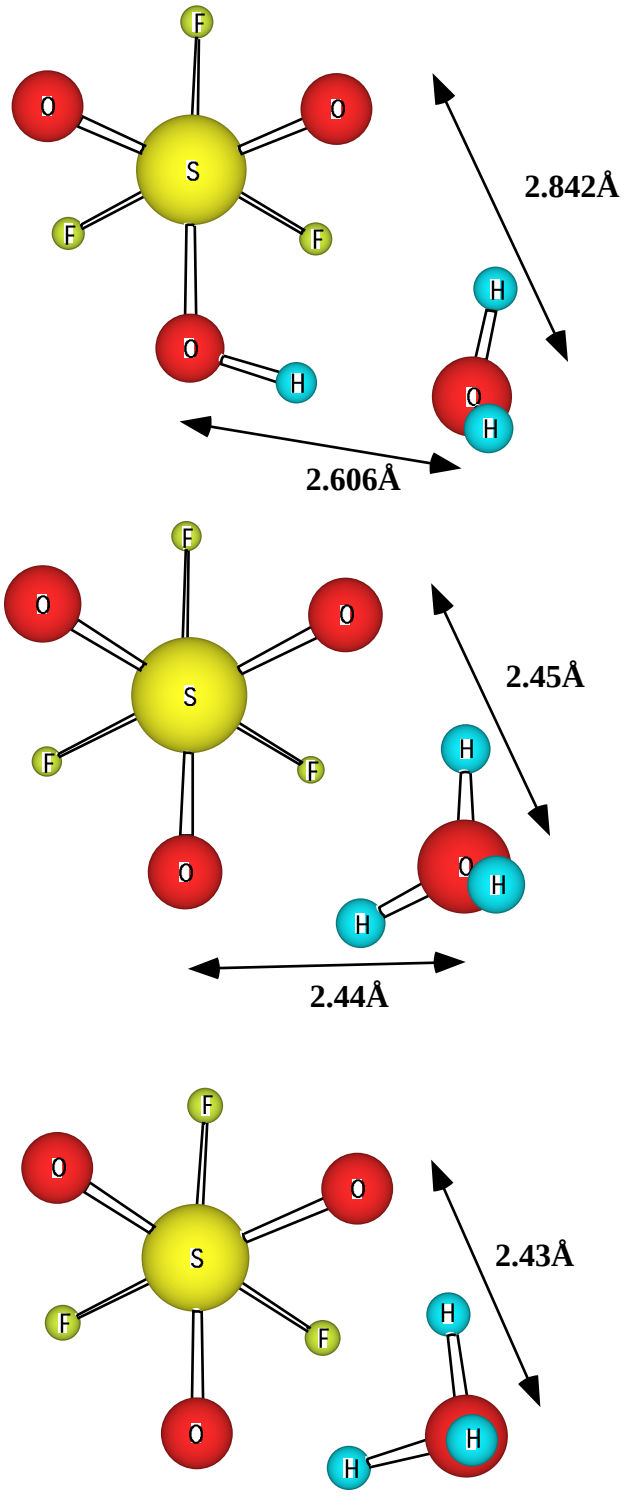
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figure 4