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Two Sulfuric Acids in Small Water Clusters

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We have studied clusters containing two sulfuric acid (SA) molecules and 0−8 water molecules using density functional methods. Our main interest was to study the energies and structures of the formed clusters. We are interested in the SA-assisted nucleation of water, and the formation free energies of the clusters will help to understand the first steps of this process. Also, the deprotonation of SA is interesting. For single SA, the first deprotonations happen when three waters are present. Here, the second SA will replace the water, and the deprotonation will happen when two waters are present. The second SA will deprotonate in clusters containing four waters. At the larger cluster ($n = 5-8$) both of the acids are singly deprotonated. We did not observe any doubly deprotonated sulfuric acids, SO_4^{2-}. We also obtained several stable structures of these clusters. The most stable structures contain solvent separated acid-hydronium ion pairs whenever it is was possible.

1. Introduction

Sulfuric acid (SA) plays an important role in atmospheric chemistry and physics.[1−3] Acid rain, formation of atmospheric particulate matter, aerosol forcing of climate, as well as stratospheric ozone depletion are all processes influenced by sulfuric acid. It is also known to be an effective nucleation agent,[4,5] and extremely low concentrations of sulfuric acid will enhance the homogeneous nucleation rate of water significantly.[6] The microscopic mechanism of this process is not known, but it's first step is the hydration of single SA.[7] The next step is very likely the formation of clusters having two or more SAs.[8]

Sulfuric acid has a tendency to form hydrates, the acids will produce small clusters containing a few water molecules. At 298 K and 50% relative humidity (RH), a cluster with one sulfuric acid will contain about 1.5 waters (this estimate is based on equilibrium constants measured by Hanson and Eisele[7]). Ball et al. have measured that the critical cluster will contain from 7 to 13 sulfuric acids at RH 2.3−15.3%.[6] At 236 K and ca. 50% RH, the critical cluster should have 4 or 5 SAs.[8] Thus, it is important to understand the acid−water and acid−acid interactions in clusters having several SAs to gain some insight of this nucleation process.

SA with water has been studied computationally, both using ab initio methods[9−15] and empirical models.[16−18] The ab initio studies were mostly limited to one sulfuric acid, except for the excellent work by Ianni and Bandy[15], in which they studied two SAs and water clusters. In general, the ab initio calculations can provide information that are experimentally very difficult to obtain. One such process is the proton transfer from SA to a water: $H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$. From previous ab initio calculations, three water molecules were enough to facilitate the dissociation of one sulfuric acid.[11,13] In these clusters, one water molecule acts as a proton acceptor, while the other water molecules stabilize the newly formed hydronium ion. The water has a similar stabilizing effect in the hydration reaction of SO_3 to H_2SO_4.[10]

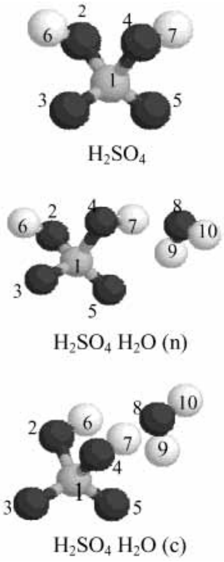

Figure 1. Structures of the H_2SO_4 and H_2SO_4 H_2O.

To further explore the dissociation mechanisms, we expand the studies to the hydrates of two sulfuric acids. Here, the clusters are more complex than the hydrates of one sulfuric acid. There are three kinds of hydrogen bonds, the acid−water, the acid−acid, and water−water bonds. Also there are three kinds of isomeric forms, the neutral isomers $(H_2SO_4)_2(H_2O)_n$, one ionic pair isomers H_2SO_4 HSO_4^- H_3O^+ $(H_2O)_{n-1}$, and two ionic pairs isomers $(HSO_4^-)_2$ $(H_3O^+)_2$ $(H_2O)_{n-2}$, which are assigned as 2AnW(I), 2AnW(II), and 2AnW(III) types, respectively. Ianni and Bandy have calculated the clusters of $(H_2SO_4)_2$ $(H_2O)_n$ ($n = 1-6$) using the Gaussian-98 program, B3LYP theory, and a large basis set, 6-311++G(2d,2p).[15] Unfortunately, they gave only one structure for each size, and many stable isomers were missing. Another shortcoming is that they did not include any ionic isomers to their studies. In other words, they limit their calculations[15] to only the most stable 2AnW(I) type clusters.

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TABLE 1: Total Energies and Selected Bond Lengths Obtained in This Work with Comparisons to Some Other ab Initio Calculations[12−14] and Experiments[23,24]

total energies (Hartree)

structure	this work	Re et al.[a]	Bandy and Ianni[b]
H_2SO_4	−700.34479	−700.30383	−700.3878
H_2SO_4 H_2O (n)	−776.80728	−776.77688	−776.8679
H_2SO_4 H_2O (c)	−776.80221	−776.77334	

bond length (Å)

structure	bond	this work (exptl)	Re et al.[a]	Bandy and Ianni[b]	Beichert and Schrems[c]
H_2SO_4	1−2	1.640 (1.574)[d]	1.634	1.609	1.60
	1−3	1.451 (1.422)	1.456	1.429	1.43
	2−6	0.979 (0.97)	0.975	0.968	0.97
H_2SO_4 H_2O (n)	1−2	1.634 (1.578)[e]	1.636	1.611	1.61
	1−4	1.604 (1.567)	1.603		1.67
	1−3	1.453 (1.410)	1.458	1.430	1.43
	1−5	1.463 (1.464)	1.466	1.439	1.44
	2−6	0.978 (0.95)	0.975		
	4−7	1.023 (1.04)	1.009	0.999	0.99
	7−8	1.621 (1.645)	1.651 (1.623)	1.682	1.69
	5−9	2.141 (2.05)	2.230 (2.100)	2.207	2.17
H_2SO_4 H_2O (c)	1−2	1.631	1.627		
	1−3	1.443	1.448		
	1−5	1.468	1.471		
	2−6	0.988	0.982		
	7−8	2.067	2.076 (2.032)		
	5−9	2.156	2.319 (2.155)		

[a] From ref 13, the values in parentheses are calculated with D95(d,p) basis. [b] From ref 12. [c] From ref 14. [d] From ref 23. [e] From ref 24.

TABLE 2: The a Water Addition Energies and Free Energies (in kcal/mol) of the Most Stable H_2O, H_2SO_4, and 1AnW ($n = 1-6$) Cluster, and Comparisons to the Calculations of Re et al. (Ref 13) and Bandy and Ianni (Ref 12)[a]

structure	ΔE_{add} (kcal/mol)	Re et al.[b]	ΔG_{add}	Re et al.[b]	Bandy and Ianni[c]	exp
1A1W (neutral)	−13.4	−12.8	−2.5	−2.4	−0.6	−3.6 ± 1
1A2W (neutral)	−12.6	−12.8	−1.8	−2.0	−0.1	−2.3 ± 0.3
1A3W (neutral)	−13.4	−12.9	−2.2	−1.5	−0.5	
1A3W (ionic)	−15.8		−1.6			
1A4W (ionic)	−14.2	−14.6	−3.7	−1.8		
1A5W (ionic)	−13.3	−12.1	−2.4	−1.6		
1A6W (ionic)	−14.0		−1.5		0.7	

[a] The addition energies has been calculated as $\Delta E_{add} = E_0(1AnW) - E_0(1An\text{-}1W) - E_0(H_2O)$, and the free energies have been calculated at 1 atm pressure and 298 K. [b] Ref 13. [c] Ref 12. [d] Ref 7.

The other ionic types will have lower energy.[13] We are also interested in how many water molecules are necessary to dissociate one or two of the sulfuric acids.

The role of the fully deprotonated SO_4^{2-} in these clusters is not very important, or at least we did not see any of them in our calculations. First, the OH bond is stronger in HSO_4^- than in SA, and when the cluster is very small, the dissociated proton increase the acidity of the cluster considerably. Both these facts suppress the probability of the second proton dissociations. However, probably the most important reason we did not see any fully deprotonated sulfuric acids is that, in our structures, both OH groups were very seldom well hydrated.

In this paper, we have mainly investigated the $(H_2SO_4)_2(H_2O)_n$ ($n = 1-6$) clusters. On the larger clusters $n = 7$ and 8 we focused to the lowest energy type-III structures. We explored the structural and electronic properties of different isomers, especially the proton transferred ones. We also studied the formation energies of these hydrates from different constituents. The computational details are described in section 2 and the results and discussion are in section 3. Finally the conclusion is given in section 4.

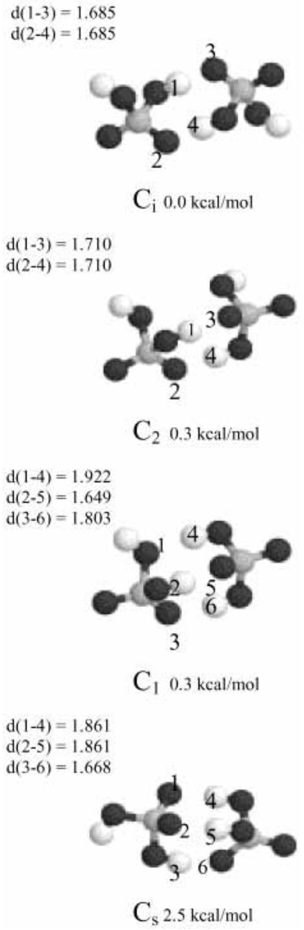
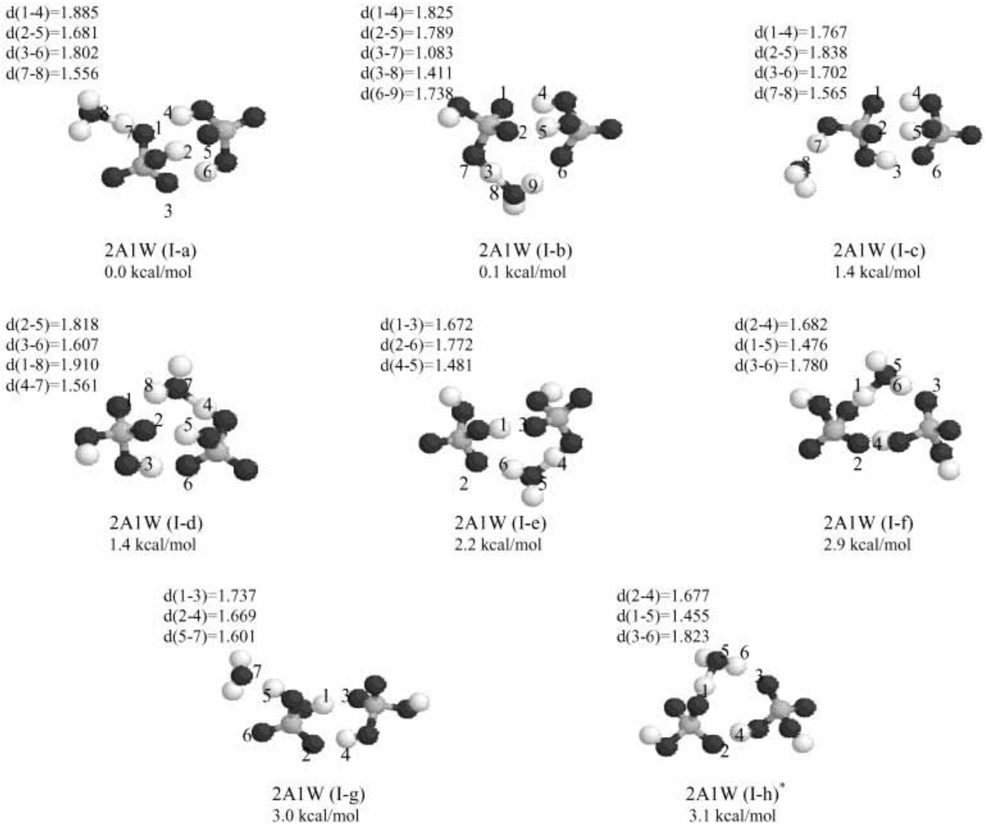


Figure 2. Structures of $(H_2SO_4)_2$ isomers.

2. Computational Detail

Our calculations were carried out by using the generalized gradient approximation (GGA) based on the density functional theory (DFT). The computations were done with the DMol3 package.[19] In the GGA, we used the Perdew-Wang exchange and correlation correction functions[20] together with the DNP basis functions.[19] The DNP is similar to 6-31G** basis in Gaussian, but the basis functions are numerical atomic orbitals augmented by polarization functions. This basis does not include diffuse functions, but the basis functions have longer exp(-kr)-type tails than do the Gaussian functions. When we did comparisons to Gaussian calculations using the PW91 functional the 6-31+(d,p) and 6-31++(d,p) basis produces similar results.[21] The medium grid mesh points were employed for the matrix integrations. Self-consistent field procedures were done with a convergence criterion of 10^{-6} a.u. on the energy and electron density. Geometry optimizations were performed using the Broyden−Fletcher−Goldfarb−Shanno (BFGS) algorithm,[22] with a convergence criterion of 10^{-3} a.u. on the gradient, 10^{-3} a.u. on the displacement, and 10^{-5} a.u. on the energy.

To check the reliability of our computational method, we first studied the H_2SO_4 and $H_2SO_4 \cdot H_2O$ structures. Our results are represented in Figure 1 and Table 1. From this, one can see that the total energies correspond well with the calculations of Re et al.[13] and Bandy and Ianni.[12] The water addition energies to SA are 13.4 and 10.2 kcal/mol, with final structures of $H_2SO_4 \cdot H_2O$ (*n*) and (*c*), respectively. The water addition energy was defined as $\Delta E_{add} = E_0(1AnW) - E_0(1An\text{-}1W) - E_0(H_2O)$. These are in good agreement with the values of 12.8 and 10.5 kcal/mol by Re et al.[13] and 12.5 kcal/mol by Beichert and Schrems.[14]



2A1W (I-a)
0.0 kcal/mol

2A1W (I-b)
0.1 kcal/mol

2A1W (I-c)
1.4 kcal/mol

2A1W (I-d)
1.4 kcal/mol

2A1W (I-e)
2.2 kcal/mol

2A1W (I-f)
2.9 kcal/mol

2A1W (I-g)
3.0 kcal/mol

2A1W (I-h)*
3.1 kcal/mol

Figure 3. Structures of $(H_2SO_4)_2$ H_2O isomers.

The bond lengths of the H_2SO_4 and $H_2SO_4 \cdot H_2O$ obtained compare very well with other theoretical calculations,[12−14] especially with the calculations by Re at al.[13] using D95(d,p) basis and experiments by Kuczkowski et al.[23] and Fiacco et al.[24] The oxygen−hydrogen distance 5−9 (and 7−8) seem to be the most sensitive to the basis and GGA functional. When using Gaussian-98 and PW91 functionals, this distance was 1.96 Å with 6−31(d,p) basis, 2.11 Å with 6-31+(d,p) basis, and 2.15 Å with 6-31++(d,p) basis. With the same basis but BLYP functional, this distance was 2.08 Å, 2.22, and 2.21 Å. The other distances changed very little. From this comparison, our calculation agree well with the 6-31++(d,p) basis. The calculations by Re et al. were done with B3LYP theory using D95-(d,p) and D95++(d,p) basis sets.[13] Bandy and Ianni used B3LYP and 6-311++G(2d,2p) basis;[12] Beichert and Schrems used MP2 with 6-311++G(2d,2p) basis.[14]

We also compared the binding energy differences of the singe SA neutral and ionic isomers to the Re et al. calculations. Our model will favor the ionic clusters by ca. 2 kcal/mol compared to Re et al.[13] At $n = 3$, the ionic cluster was 2.3 kcal/mol lower in energy than the neutral one. In the Re et al. calculations, the neutral one was 0.9 kcal/mol lower. At $n = 4$, the ionic structure was lower by 2.4 kcal/mol and in the Re et al. calculations, the ionic one was 0.6 kcal/mol lower. We also calculated the energy difference between the 2A6W(IIIa) and (Ib) structures using BLYP functional both with DMol3 and Gaussian-98[21] using 6-31+G(d,p) basis. The energy difference was 17.0 kcal/mol (dmol), 17.9 kcal/mol (Gaussian), whereas our original PW91 value was 20.2 kcal/mol. Also, single point calculations with the BLYP/6-31+G(d,p) geometries using B3LYP and 6-311++G-(2d,2p) basis was done. The energy difference between 2A6W-(IIIa) and (Ib) was 14.7 kcal/mol. Even our model favors the ionic structures by a few kcal/mol compared to Re et al. or Bandy and Ianni. This change does not depend of the size of the cluster and thus does not change the conclusions.

TABLE 3: Binding Energies ΔE_0 and Average Binding Energies (ΔE_0 / $n + 2$) of the 2AnW(I-a), 2AnW(II-a), and 2AnW(III-a) ($n = 0-8$) in kcal/mol

n	ΔE_0, $\Delta E_0 / (n + 2)$ (I-a)	ΔE_0, $\Delta E_0 / (n + 2)$ (II-a)	ΔE_0, $\Delta E_0 / (n + 2)$ (III-a)
0	−14.4, −7.2		
1	−29.4, −9.3		
2	−43.0, −10.8	−45.5, −11.4	
3	−58.1, −11.6	−61.4, −12.3	−61.1, −12.3
4	−70.3, −11.7	−76.7, −12.8	−79.4, −13.2
5	−82.6, −11.8	−89.7, −12.8	−93.7, −13.4
6	−96.4, −12.1	−100.6, −12.6	−109.1, −13.6
7			−121.8, −13.5
8			−134.5, −13.4

Table 2 gives the water addition energies and free energies to different size of clusters. These energies are compared with the calculations of Re et al.,[13] Bandy and Ianni[12] and the experimental estimations of Hanson and Eisele.[7] As one can see, the agreement with the addition energies are good, but the free energies are not very consistent. The values of Bandy and Ianni,[12] in particular, are much higher than the other values.

The free energies are calculated at 298 K and 1 atm pressure as

$$G = H - TS$$

$$H = E_0 + ZPE + \delta E_{\mathrm{vib}} + \delta E_{\mathrm{rot}} + \delta E_{\mathrm{tra}} + pV. \qquad (1)$$

where the H is the enthalpy of the system and S is the entropy. The E_0 is the electronic energy at 0 K, ZPE is the Zero Point Energy correction, the δE_{vib}, δE_{rot}, and δE_{tra} denote the finite temperature corrections from the vibration, rotation, and translation degrees of freedom, respectively. To the pV term, the ideal gas law was used and $pV = nRT$. T is the temperature (=298 K), R is the gas constant. All these terms are based on the

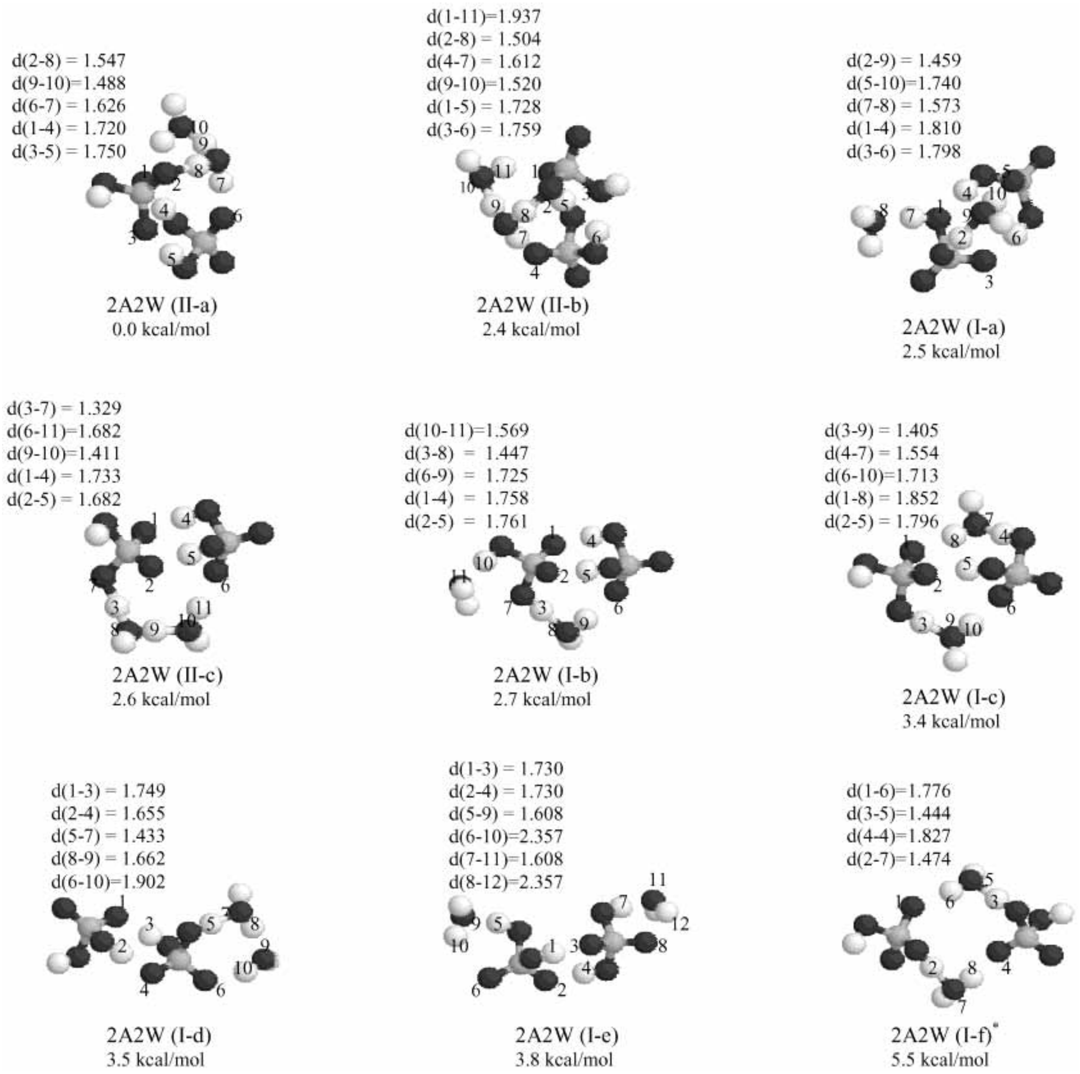


Figure 4. Structures of $(H_2SO_4)_2$ $(H_2O)_2$ isomers.

structure and harmonic frequencies of the clusters. The standard equations are used and the details can be found from Physical Chemistry textbooks.[25] We have used the values provided by the DMol3 program. The isotope masses used were: S, 32.0600 amu; O, 15.9994 amu; and H, 1.0079 amu. No scaling to the frequencies are used.

These preliminary calculations and their good agreement with previous works and experiments demonstrate that our computational scheme is suitable to study the hydrated sulfuric acid clusters.

3. Results and Discussion

3.1. $(H_2SO_4)_2$. Figure 2 shows the four structures (C_i, C_s, C_2 and C_1) of $(H_2SO_4)_2$, their energies, and some distances. The lowest energy C_i cluster has two strong hydrogen bonds (H···O distance: 1.685 Å), and the binding energy is 14.4 kcal/mol. This can be compared with the Ianni and Bandy's work,[15] in which they report for C_i structure a distance of 1.685 Å and binding energy of 12.6 kcal/mol. The next lowest energy structure that has C_2 symmetry is only 0.3 kcal/mol higher in energy, and the H···O distance is 1.710 Å. The nonsymmetrical structure, C_1, has one very short hydrogen bond (1.649 Å) and two long ones (1.803 and 1.922 Å). Its energy is the same as the C_2 structure. The C_s structure is 2.5 kcal/mol less stable than the C_i. The C_s has one strong hydrogen bond (1.668 Å) and two weak bonds (1.861 Å).

3.2. $(H_2SO_4)_2$ H_2O. There are two ways to form $(H_2SO_4)_2 \cdot H_2O$ clusters from two sulfuric acids and one water molecules. In one, the water molecule is between the two sulfuric acids. In the other, the water is outside of the $(H_2SO_4)_2$ unit, and it interacts with only one sulfuric acid. The optimized structures are shown in Figure 3. The most stable structure 2A1W(I−a) belongs to the class where the water is outside of the sulfuric acid dimer. The SOH···OH_2 hydrogen bond has shortened somewhat (0.06 Å) compared to the $H_2SO_4 \cdot H_2O$. This cluster can also be seen as the $(H_2SO_4)_2$ C_1 structure interacting with one water molecule. By inserting one water molecule between H(6) and O(12) in the C_s structure of $(H_2SO_4)_2$, we get the 2A1W(I−b) structure, which has almost the same energy as 2A1W(I−a). The bond length between O(2) and H(6) turns out to be 0.07 Å longer, and the hydrogen bond between H(6) and water molecule becomes very short, 1.411 Å, or 0.2 Å shorter compared to $H_2SO_4 \cdot H_2O$. This indicates that the proton transfer might be easier in the case of the hydrates of two sulfuric acids. We have examined many different structures of $(H_2SO_4)_2 \cdot H_2O$ and found that they are less stable than 2A1W(I−a) and (I−b). All the lowest energy structures I-a−I-d have four hydrogen bonds, whereas the other structures have three H-bonds. The energies of the 2A1W clusters do not correlate with the 2A0W clusters. The I-g structure contains $(H_2SO_4)_2$ with C_i symmetry, which was lowest in energy above, and the I-c contains SA dimer with C_s symmetry, which when unhydrated was 3 kcal/

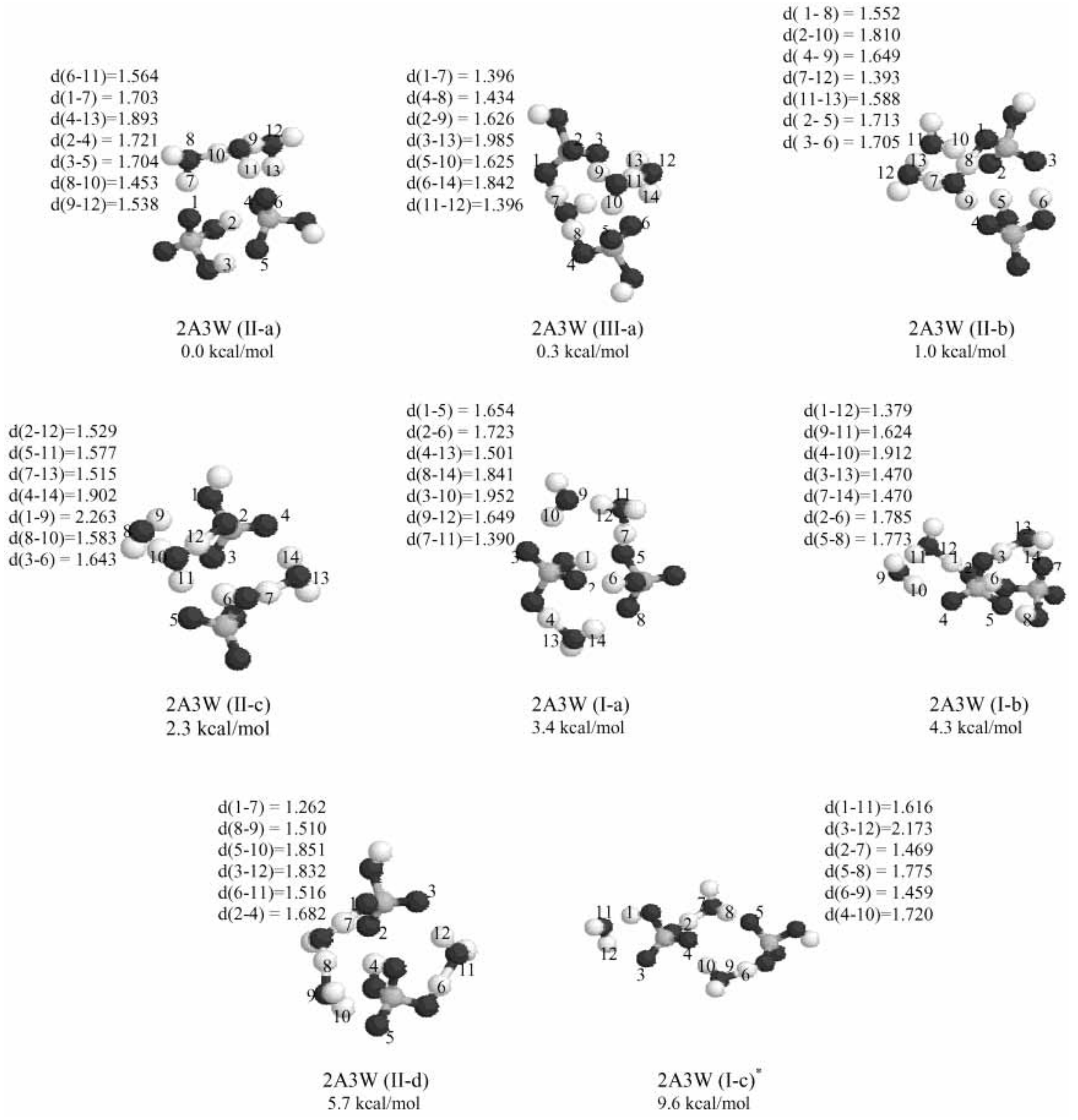


Figure 5. Structures of $(H_2SO_4)_2$ $(H_2O)_3$ isomers.

mol higher in energy, but the I-c is 1.6 kcal/mol lower in energy. When compared to the Ianni and Bandy work,[15] their structure 2A1W(I−h) is 3.1 kcal/mol less stable than the 2A1W(I−a).

Table 3 shows the binding energies ΔE_0(2AnW) ($n = 0-8$) of the most stable structures for all three types of isomers. The binding energy ΔE_0 of 2AnW is defined as

$$\Delta E_0 = E_0(2\text{AnW}) - 2 \cdot E_0(H_2SO_4) - n \cdot E_0(H_2O)$$

where E_0(2AnW), $E_0(H_2SO_4)$ and $E_0(H_2O)$ are the electronic energies at 0 K of the 2AnW, H_2SO_4, and H_2O, respectively.

3.3. $(H_2SO_4)_2$ $(H_2O)_2$. We obtained the most stable nonionic isomer 2A2W(I-a) by adding a water molecule between H(2) and O(5) of the 2A1W(I-a) structure (Figure 4). This second water molecule has a very strong hydrogen bond (1.459 Å) with H(2) and weak bond (1.740 Å) with O(5). Adding a water to 2A1W(I-c) and 2A1W(I-d), we have 2A2W(I-b) and 2A2W-(I-c) isomers that are only slightly less stable than 2A2W(I-a), with 0.2 and 0.9 kcal/mol, respectively. We found that structures consisting of a water dimer bonding to one sulfuric acid is less stable than the 2A2W(I-a) isomer (see 2A2W(I−d) of Figure 4). Two water molecules of 2A2W(I-e) are bonded individually to the two sulfuric acids and its energy is 1.3 kcal/mol higher than 2A2W(I-a). Ianni and Bandy's structure,[15] 2A2W(I-f), where the SA's are bridged with the waters, is 3.0 kcal/mol less stable than the 2A2W(I-a).

When a water dimer interacts with both the SAs, there will be proton dissociation from one of the SAs (II-a, II-b, or II-c). Figure 4 shows 2A2W(II-a), which is the most stable deprotonated isomer. It is interesting to compare the structure of 2A2W-(II-a) with one of the H_2SO_4 $(H_2O)_3$ (ionic-a). The three hydrogen atoms of H_3O^+ have three strong hydrogen bonds (1.488, 1.547, and 1.626 Å), which are very similar to those of 1A3W (ionic-a).[13] Here, the second sulfuric acid takes the place of the third water molecule of 1A3W (ionic-a), except that there are two hydrogen bonds between the acids. The 2A2W(II-c) was obtained by optimizing a structure 2A1W(I−b) with an additional water between O(6) and H(9). We found that the second water molecule not only lead to the formation of a strong hydrogen bond (1.411 Å) with the first water but also pulls the H(3) from the acid and formed a hydronium ion. This is a different ionic structure than the previous ones, because all the protons of the hydronium are not H-bonded.

We think that we have mapped all the basic hydrogen bonding configurations here. The I-a and I-b structures have one water

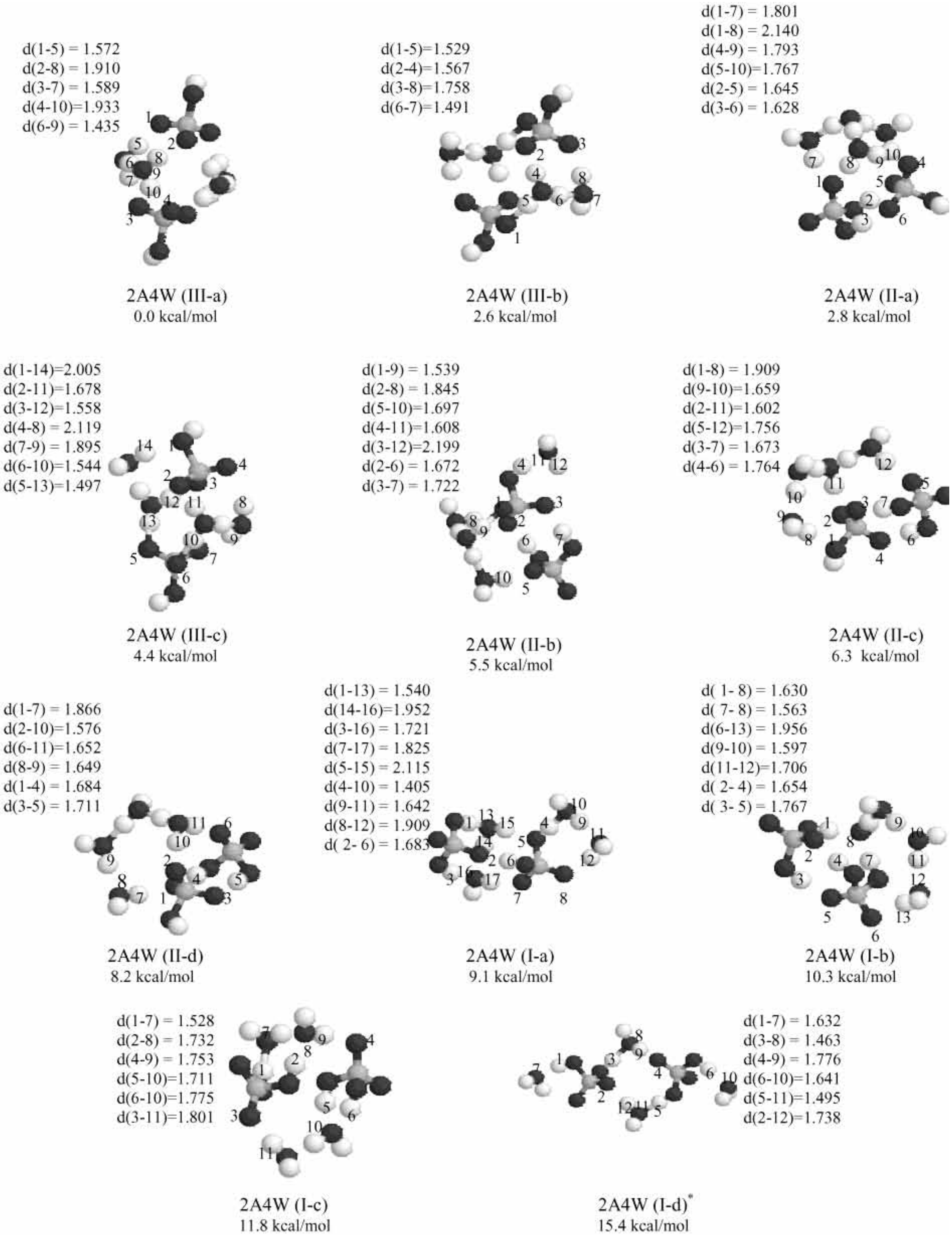


Figure 6. Structures of $(H_2SO_4)_2$ $(H_2O)_4$ isomers.

between the acids and one water "outside". In I-c, there are two acid bridging waters and one H-bond between the acids. The I-d and I-e have no bridging waters, and last, the I-f have only bridging waters and no direct H-bonds between the acids. The water-acid structure of the ionic II-a and II-b are similar to I-a and I-b. The II-c is similar to I-d. Only missing ionic structure would be similar to I-c. Ianni and Bandy reported[15] only the (I-f) structure, which is 3.0 kcal/mol higher than 2A2W-(I-a) and 5.5 kcal/mol higher than (II-a). As in the case of one water, the direct acid−acid H-bonds are stronger, and they are favored over the water bridging bonds.

3.4. $(H_2SO_4)_2$ $(H_2O)_3$. For trihydrates of $(H_2SO_4)_2$, we found that the proton transferred clusters are becoming clearly lower in energy than the neutral ones. The energy difference of the II-a and I-a structures is 3.4 kcal/mol (see Figure 5). The ionic structures of 2A3W can be classified into two groups. In the first group, the $H_7O_3^+$ forms three hydrogen bonds with H_2SO_4 HSO_4^-, in the other group, the proton is in a $H_5O_2^+$ complex,

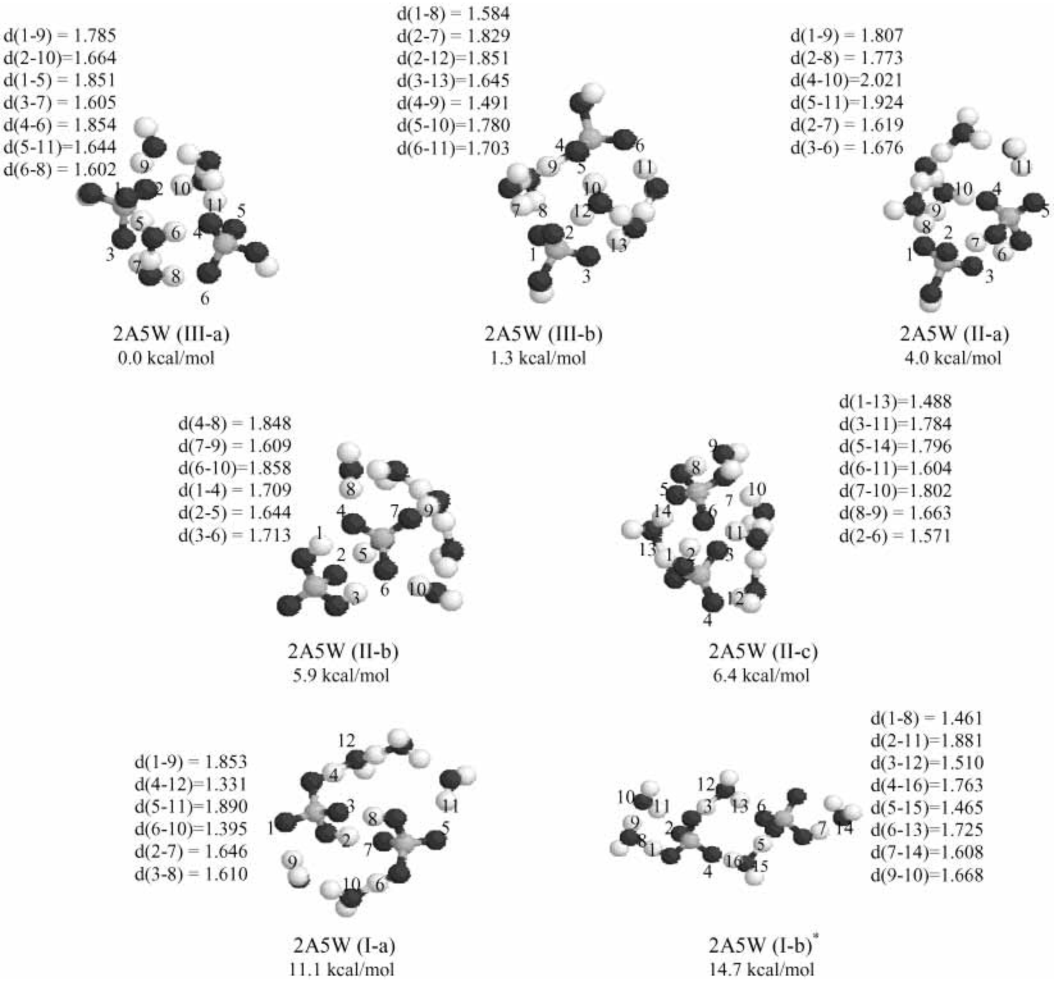


Figure 7. Structures of $(H_2SO_4)_2$ $(H_2O)_5$ isomers.

and the third water is separate. Both these groups are bonded to H_2SO_4 HSO_4^-. The calculations show that the first group has lower energy (II-a and II-b). The $H_7O_3^+$ in 2A3W(II-a) have three hydrogen bonds with H_2SO_4 HSO_4^- (1.564, 1.703, and 1.893 Å). The 2A3W(II-c) belongs to the second group and is 2.3 kcal/mol less stable than 2A3W(II-a).

We also explored the possibility of having two ion pairs in the cluster $(HSO_4^-)_2$ $(H_3O^+)_2$ H_2O. One such structure was found, 2A3W(III-a). Here, all six O═S of $(HSO_4^-)_2$ are connected with the $H_5O_2^+$ and H_3O^+ complexes. This structure is only 0.3 kcal/mol less stable than the most favorable one ionic pair cluster 2A3W(II-a).

The neutral water bridging structure 2A3W(I-c), also obtained by Ianni and Bandy,[15] is 6.2 less stable than the most stable neutral isomer 2A3W(I-a) and 9.3 kcal/mol less stable than ionic isomers 2A3W(II-a). In the type-I and type-II structures, there are always several direct acid−acid H-bonds, indicating that this type of bond is stronger than the different water bridging bonds. The situation in the type-III is very different; there, all the waters are between the acids.

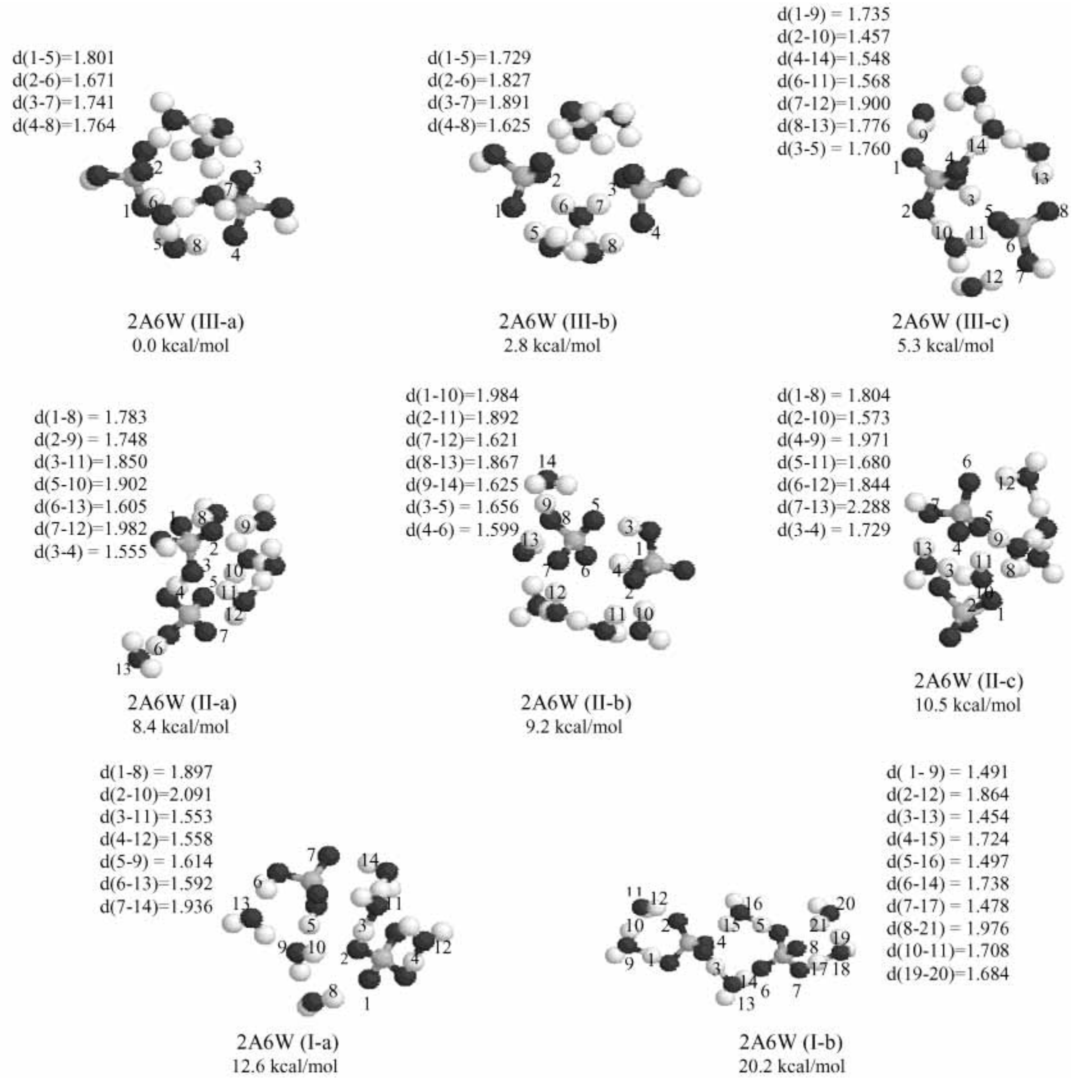
3.5. $(H_2SO_4)_2$ $(H_2O)_4$. Our optimized results for $(H_2SO_4)_2$ $(H_2O)_4$ structures are listed in Figure 6. The most stable isomer is the 2A4W(III-a), which is more stable than the neutral isomer 2A4W(I-a) and the singly deprotonated 2A4W(II-a) by 9.1 and 2.8 kcal/mol, respectively. III-a has a very compact structure with symmetry of C_2. The six O═S of the two HSO_4^- have four strong hydrogen bonds (ca. 1.58 Å) within the two $H_5O_2^+$ ions and several weak hydrogen bonds (ca. 1.92 Å) between the $H_5O_2^+$'s and the acids. The 2A4W(III-b) is a structure with C_i symmetry, in which three O═S of each HSO_4^- have three hydrogen bonds (1.529, 1.567, and 1.758 Å) with the hydrogen atoms of H_3O^+ and H_2O. It is 2.6 kcal/mol less stable than the 2A4W(III-a).

In the 2A4W(II-a) cluster, the H_3O^+ ion is not in direct contact with the acids. There are always waters between them. Like the 1A4W ionic case,[13] this water bridging ion pair structure is more stable than the direct ones, 2A4W(II-b) and 2A4W(II-c). The lowest energy neutral cluster, 2A4W(I−a) is formed from 1A2W (neutral-a) and 1A2W (cis neutral).[13] It is more stable than the water bridging structure (I−d) by 6.2 kcal/mol. Like above, the direct acid−acid H-bonds are favored in the type-I and II structures, but the type-III structures have waters and hydronium ions between the acids.

3.6. $(H_2SO_4)_2$ $(H_2O)_5$. In general, the five water clusters do not add much new to the previous clusters (see Figure 7). The two ion clusters (type-III) are the most stable ones, the type-II are next, and the neutral clusters are relatively high in energy.

From Figures 3−7, we found that in the neutral and one ionic pair isomers the acid molecules will favor direct acid−acid bonds, while the isomers with two ion pairs favor the indirect H-bonds via the water/hydronium molecules. The latter is due to the Coulomb repulsion of the negative HSO_4^- ions. When enough water is available ($n > 3$) the hydronium in type-I clusters are separated with waters from the acids. As the number of water molecules is increased, the structures with two ion pairs become more stable than the other types, but we have not seen any fully deprotonated acids, SO_4^{2-}.

3.7. $(H_2SO_4)_2$ $(H_2O)_6$. The 2A6W isomers are shown in



2A6W (III-a)
0.0 kcal/mol

2A6W (III-b)
2.8 kcal/mol

2A6W (III-c)
5.3 kcal/mol

2A6W (II-a)
8.4 kcal/mol

2A6W (II-b)
9.2 kcal/mol

2A6W (II-c)
10.5 kcal/mol

2A6W (I-a)
12.6 kcal/mol

2A6W (I-b)
20.2 kcal/mol

Figure 8. Structures of $(H_2SO_4)_2$ $(H_2O)_6$ isomers.

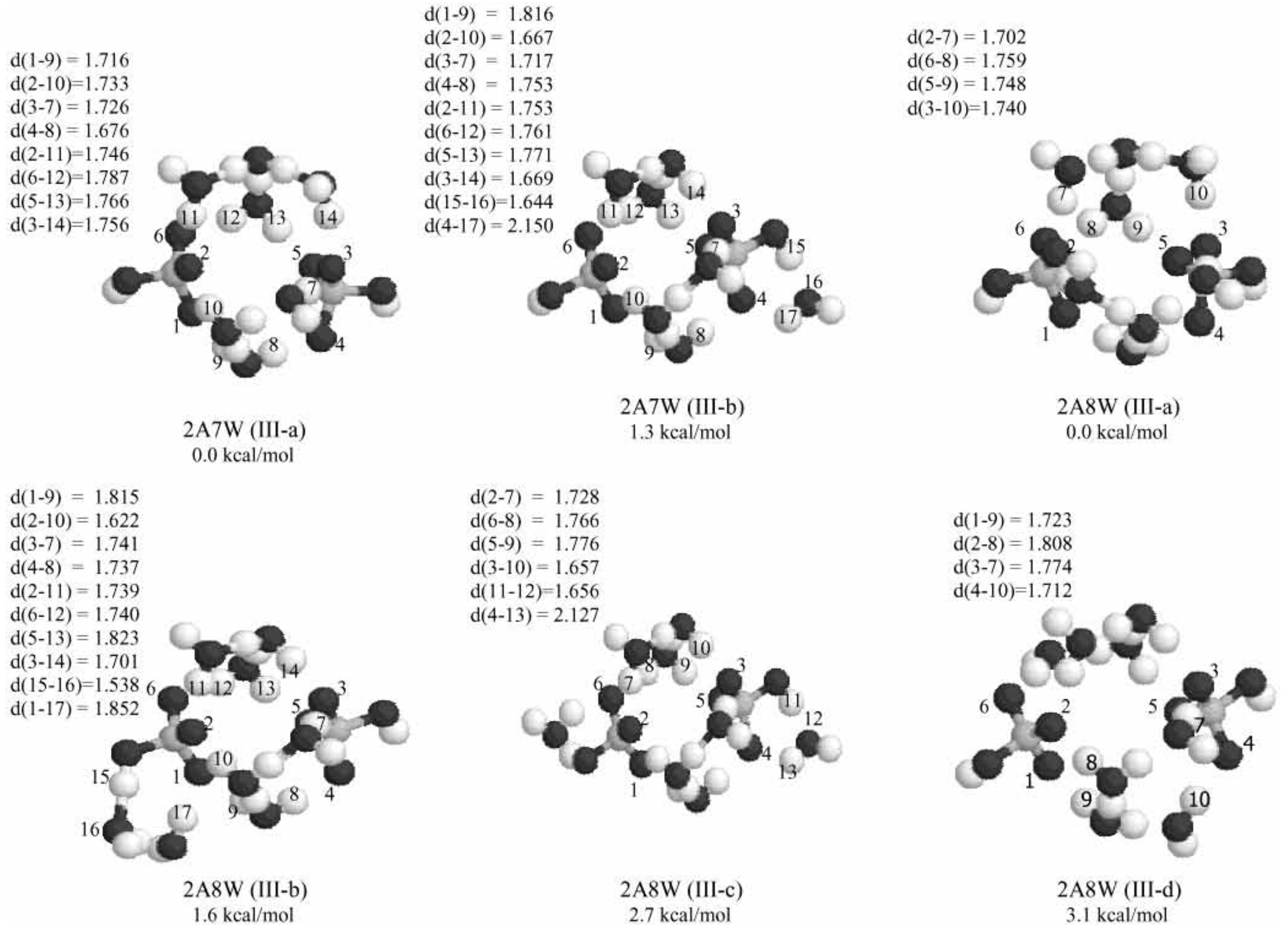
Figure 8. The 2A6W(III-a) has the C_2 symmetry, and the bond lengths between the S═O of HSO_4^- and $H_7O_3^+$ are 1.671, 1.741, 1.764, and 1.801 Å. The structure of 2A6W(III-b) is similar to 2A6W(III-a), and the hydrogen bonds of 2A6W(III-b) are slightly weaker than 2A6W(III-a) (1.625, 1.729, 1.827, and 1.891 Å). Both have the common property that the two bisulfate ions interact indirectly via the $H_7O_3^+$, just as stated above. However, in the structure of 2A6W(III-c), there is one direct bond between two bisulfate ions, and it is 5.3 and 2.5 kcal/mol less stable than III-a and III-b, respectively.

We found that two ionic pairs clusters here are clearly more favorable than the neutral and one ionic pair isomers. The energy differences from 2A6W (III-a) to 2A6W(II-a) and 2A6W(I−a) are 8.4 and 12.6 kcal/mol, which are significantly larger than in the 2A5W structures (4.0 and 11.1 kcal/mol). Figure 8 also shows the structure 2A6W(I−b) studied by Ianni and Bandy.[15] As we stated before,[18] our neutral structures are more compact, and the number of hydrogen bonds is larger (12) than in the Bandy and Ianni structure (10 bonds).[12] The compact neutral isomer is 7.6 kcal/mol more stable than the neutral isomer studied by them.

Here, we also reoptimized and calculated the energy differences of some of the structures using BLYP functional. The III-a structure was the lowest. The II-a was 6.1 kcal/mol, the I-a 10.5 kcal/mol, and the I−b 17.1 kcal/mol higher. The energy changes were not very large, and more importantly, the order of the structures did not change.

3.8. $(H_2SO_4)_2$ $(H_2O)_7$ and $(H_2SO_4)_2$ $(H_2O)_8$. Because the studies above clearly indicate that the 2AnW(III) structures are much more stable than the 2AnW(I) and 2AnW(II) when the cluster size increases, we concentrate only on the 2A7W(III) and 2A8W(III) structures. The structures are shown in Figure 9. We got the most stable isomer 2A7W(III-a) by adding a water molecule between the two bisulfate ions of 2A6W(III-a). Note that adding this water molecule leads to a solvent-separated ion pair and thus stabilizes the structure. We also obtained the structure 2A7W(III-b), in which a water molecule interacts with one of the acids from “outside” and forms a strong bond (1.644 Å). This structure is only 1.3 kcal/mol less stable than the 2A7W(III-a).

For the 2A8W clusters, the most stable III-a has symmetry of C_2, in which both of the H_3O^+s are interacting indirectly with HSO_4^-s. The hydroniums ions are surrounded by three water molecules. It is interesting to compare the III-a with III-d. In the 2A8W(III-d) structure, H_3O^+ is directly interacting with HSO_4^-, and it is 3.1 kcal/mol less stable than III-a (i.e., the structure with solvent-separated ion pairs are more favorable than the one with the contact ion-pairs). We obtained the III-b isomer by adding a water dimer to 2A6W(III-a), forming a hydrogen-bonding cyclic structure with a HSO_4^-. The 2A8W-



2A7W (III-a)
0.0 kcal/mol

2A7W (III-b)
1.3 kcal/mol

2A8W (III-a)
0.0 kcal/mol

2A8W (III-b)
1.6 kcal/mol

2A8W (III-c)
2.7 kcal/mol

2A8W (III-d)
3.1 kcal/mol

Figure 9. Structures of $(H_2SO_4)_2\ (H_2O)_7$ and $(H_2SO_4)_2\ (H_2O)_8$ isomers.

(III-c) is a symmetric structure and can be produced by adding single water molecules on each side of 2A6W(III-a). The 2A8W-(III-b) and (III-c) are 1.6 and 2.7 kcal/mol less stable than 2A8W(III-a), respectively.

3.9. Hydration Energies. From Tables 2 and 3, we can calculate the reaction energies to form 2AnW's from 1AnW + H_2SO_4, 2A(n − 1)W + H_2O and $1An_1W + 1An_2W$ ($n_1 + n_2 = n$), as shown in Table 4. We have also calculated the corresponding free energies at 298 K and 1 atm pressure. The free energy calculations has been explained in section 2. The (free) energy differencies in Table 4 were obtained by subtracting the (free)energies of the reactants and products.

Clearly, the reactive energies of 1AnW + H_2SO_4 → 2AnW are more than those of 2A(n − 1)W + H_2O → 2AnW, because the addition of an acid can create more hydrogen bonds than the addition of a water. We found that the reactive channels from $1An_1W + 1An_2W$ ($n_1 = n/2$ or $n_1 = (n - 1)/2$, $n_1 + n_2 = n$) are more favorable than those from 1AnW + H_2SO_4 when $n = 4$, 5, and 6. Also, all the free energies are negative, so at 1 atm, all these reactions would happen. Note that Ianni and Bandy[15] have also computed the same quantities as we have, but with different structures. We did some comparison to their structures, and the agreement in binding energies are good.

On the other hand, to use 1 atm partial pressure for sulfuric acid is not realistic if we are interested in atmospheric conditions. In the atmosphere, the density of sulfuric acid is only of the order of 10^7 particles/cm^3.[26] This corresponds to partial pressures of 10^{-12} atm. To estimate the partial pressures p of the products in Table 5 we used the definition of the equilibrium constant K°

$$K^\circ = \frac{p/p^\circ}{p1/p^\circ \times p2/p^\circ}\, K^\circ = \exp(-\Delta G^\circ/RT) \qquad (2)$$

Here p° is 1 atm, $p1$ and $p2$ are the partial pressures of the reactants, and ΔG° is the free energy difference of the reaction.

The partial pressures of the reactants are difficult to obtain in general. Using the equilibrium constants from ref 7 at 298 K and 50% RH, there are 8% of unhydrated sulfuric acids, 51% of monohydrates, and 41% of dihydrates. The equilibrium constants for larger hydrates were not measured, so the concentrations of them are not known, but as a crude estimate we use the same partial pressure for all species containing one SA, 10^{-12} atm. In our case, the most important are the mono-, di-, and trihydrates. For water, we used partial pressure of 0.016 atm, which corresponds to 50% RH at 298 K, and partial pressure of the reacting 2AnW was taken from Table 4. The highest partial pressure for each reacting dimer was chosen. As one can see, the model is crude, but we feel it will give reasonable values for the partial pressures of 2AnW species. A more realistic model will require several different reaction channels, and we are working with such a model.

In this model, partial pressures of all 2AnW are lower than 10^{-12} atm, but in channel 1A3W + 1A3W → 2A6W the partial pressure is ca. 10^{-15} atm (or 10^4 cm^{-3}), thus the 2A6W dimers are rather common. This is in good agreement with recent experiments by Hanson and Eisele[28], in which they detect partial pressure of SA dimers of 3×10^6 cm^{-3} at 265 K. In this

TABLE 4: Reactive Energies without the Zero-Point Energy Corrections (ΔE_0), Enthalpies (ΔH), Free Energies ($\Delta G°$) and Partial Pressures of the Products of 2AnW from $1An_1W + 1An_2W$ ($n_1 + n_2 = n$) and $2A(n - 1)$ W + H_2O Channels[a]

	ΔE_0	ΔH	$\Delta G°$	$\log(p/p°)$
$2H_2SO_4$ → 2A0W(C_i)	−14.4	−13.4	−3.1	−21.7
1A1W+H_2SO_4 → 2A1W(I−a)	−16.0	−14.9	−3.3	−21.6
2A0W+H_2O → 2A1W(I−a)	−15.0	−13.5	−2.6	−21.6
1A2W+H_2SO_4 → 2A2W(II−a)	−19.5	−18.3	−4.0	−21.0
1A1W+1A1W → 2A2W(II−a)	−18.7	−17.8	−3.4	−21.5
2A1W(I−a)+H_2O → 2A2W(II−a)	−16.1	−14.9	−2.6	−21.5
1A3W+H_2SO_4 → 2A3W(II−a)	−19.6	−18.8	−6.6	−19.2
1A1W+1A2W → 2A3W(II−a)	−21.9	−21.1	−5.7	−19.8
2A2W(II−a)+H_2O → 2A3W(II−a)	−15.9	−14.8	−4.2	−20.3
1A2W+1A2W → 2A4W(III−a)	−27.3	−25.6	−9.0	−17.4
1A2W+1A2W → 2A4W(I−d)	−11.9 (−11.7)[b]			
1A1W+1A3W → 2A4W(III−a)	−24.1	−22.8	−9.2	−17.3
1A4W+H_2SO_4 → 2A4W(III−a)	−23.4	−22.1	−8.0	−18.1
2A3W(II−a)+H_2O → 2A4W(III−a)	−18.0	−16.0	−5.1	−17.9
1A2W+1A3W → 2A5W(III−a)	−25.8	−24.8	−11.7	−15.4
1A2W+1A3Wna → 2A5W(I−b)	−13.4 (−11.7)[b]			
1A5W+H_2SO_4 → 2A5W(III−a)	−24.3	−23.9	−9.9	−16.8
1A1W+1A4W → 2A5W(III−a)	−24.2	−23.5	−9.8	−16.8
2A4W(III−a)+H_2O → 2A5W(III−a)	−14.2	−13.4	−4.3	−16.8
1A3W+1A3W → 2A6W(III−a)	−25.4	−23.9	−12.0	−15.2
1A3Wna+1A3Wna → 2A6W(I−b)	−9.9 (−12.1)[b]			
1A2W+1A4W → 2A6W(III−a)	−27.0	−25.5	−10.0	−16.7
1A1W+1A5W → 2A6W(III−a)	−26.3	−25.3	−9.3	−17.2
1A6W+H_2SO_4 → 2A6W(III−a)	−25.7	−24.7	−10.2	−16.5
2A5W(III−a)+H_2O → 2A6W(III−a)	−15.4	−13.5	−1.9	−17.2
1A3W+1A4W → 2A7W(III−a)	−23.9	−23.1	−9.8	−16.8
1A2W+1A5W → 2A7W(III−a)	−26.3	−25.8	−9.0	−17.4
1A1W+1A6W → 2A7W(III−a)	−25.0	−24.6	−9.2	−17.2
2A6W(III−a)+H_2O → 2A7W(III−a)	−12.7	−12.0	−1.5	−17.2
1A4W+1A4W → 2A8W(III−a)	−22.3	−20.5	−8.2	−18.0
1A3W+1A5W → 2A8W(III−a)	−23.2	−21.6	−9.4	−17.1
1A2W+1A6W → 2A8W(III−a)	−25.0	−23.2	−9.5	−17.0
2A7W(III−a)+H_2O → 2A8W(III−a)	−12.7	−10.1	−2.1	−17.5

[a] All energies are in kcal/mol and at 298 K. The $p° = 1$ atm. The free energies have been calculated at 1 atm pressure. See details of the calculations of partial pressures in the text [b] Refs 12 and 15.

experiment, the SA total concentration was 4×10^9 cm^{-3}. Also a very interesting result here is that the free energies ($\Delta G°$) decrease first rapidly until $n = 6$, but then start to increase. At $n = 8$, the free energy is only −10.8 kcal/mol. This means that the 2A6W is the most stable dimer, not only up to $n = 8$, but very likely in all sizes. The main reason for this minimum is the large drop of the energies and (free) energies of the hydrated monomers at $n = 4$ (see Table 2). The energies of the dimers decreases rather monotonically when the n increaces (Table 3). For the monomers, the $n = 4$ is a special point, because there the ionic structures become more stable.

In this case, the reactions happen between two H-bonded clusters, which can adapt rather well when they approach each other. Thus, we believe that the reaction barriers are rather small and do not slow the reactions. We feel that it is sensible to assume that the system is in equilibrium and the free energy differences reflect the actual partial pressures of the products.

4. Conclusion

In conclusion, we have reported a comprehensive study of the structural properties of $(H_2SO_4)_2$ $(H_2O)_n$ ($n = 1-6$) and the few most stable structures of the $n = 7,8$ clusters. The deprotonation of a single sulfuric acid in water clusters is rather easy. Only three waters were needed for the deprotonation to occur. We found that adding another sulfuric acid did not hinder the deprotonation. In fact, two water molecules are enough to carry out the dissociation, where one water molecule acts as a proton acceptor, while another water and second sulfuric acid molecules stabilize the newly formed hydronium ion. Furthermore, the deprotonation of the second sulfuric acid will also take place at the larger clusters. In the case of $n = 4$ to 8, the two ionic pairs isomers $(HSO_4^-)_2$ $(H_3O^+)_2$ $(H_2O)_{n-2}$ are more stable than the neutral isomers $(H_2SO_4)_2(H_2O)_n$ or one ion pair isomers H_2SO_4 HSO_4^- H_3O^+ $(H_2O)_{n-1}$.

When the number of water molecules increase, the two sulfate ions have a tendency to form indirect hydrogen bonds via the water molecules. This is due to the Coulomb repulsion of the two negative HSO_4^- ions. Due to the very limited amount of water in the clusters, all the waters and hydronium ions will prefer to be between the acids, and the hydronium ions will repel each other. This explains the bipyramidal structure of 2A4W(III-a) and similar structures of 2A5W(III-a) to 2A8W-(III-a). In general, the sulfate and hydronium ions prefer to be solvent separated when possible. This has been seen in the case of single acid[13] and in this work in several clusters where only one acid is deprotonated. When both the acids are deprotonated, the fully solvent-separated structure is possible only at 2A8W and larger clusters. The structure of 2A8W(III-a) clearly confirms the hypothesis above.

It is interesting that we did not see any doubly deprotonated sulfuric acids, SO_4^{2-}. The reason for this is that the solvation of the singly deprotonated acid is not very good in small clusters. In the stable clusters, the waters are between the acids, and the other hydroxyl groups of the acids are seldom solvated. We think that the doubly deprotonated sulfuric acid could be found only when the clusters are large enough (at least 10 waters) to solvate well the whole acid molecule.

How would additional sulfuric acids effect to the proton transfer and the structures of the clusters? The trend probably would be similar to here. The sulfuric acids would take part in the solvation, and only a few water molecules are needed to deprotonate a sulfuric acid. An educated guess would be that two waters per acid would be enough. The tendency to favor the solvent separated ions should preserve, and all ions with the same charge will repel each other. If the acids become doubly deprotonated, the situation becomes more complex, but it is very difficult to predict when this happens.

Last, the energies and free energies of the acid dimer formation are very interesting (Table 4). They show that the formation energy will first decrease very rapidly when the number of waters around the acids increses to six but then start to increase again. Our results suggest that the 2A6W would be the most stable dimer, and at low sulfuric acid pressure its partial pressure is not much lower than that of SA. This is in good agreement with the recent experiments by Hanson and Eisele,[28] in which they detect partial pressure of SA dimers of 10^6 cm^{-3} at 265 K.

Experimentally, it has been verified that the sulfuric acids are hydrated,[7,27] and at 298 K there are few waters around them.[7] Thus, it is reasonable to assume that the nucleation will occur via the hydrated acids, and the dimerizations should occur with the trihydrates. The critical cluster is measured to contain 7−13 sulfuric acids at 15.3%-2.3% RH,[6] (SA partial pressure was of the order of 10^9 molec/cm^3 and temperature 298 K). Eisele and Hanson[8] speculate that at 236 K, $[H_2SO_4] \approx 10^9$ molec/cm^3, and ca. 50% RH, the critical cluster should have 4 or 5 sulfuric acids. From our data, we cannot say what happens with the larger sulfuric acid clusters, but very likely, the growth will happen by adding hydrated acids to dimers, trimers, etc. Do the trimers and tetramers have similar minimum with respect to the water content as observed here? There probably is a minimum, but it is less clear because the energies of the dimers are smoother.

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