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Coexistence of Neutral and Ion-Pair Clusters of Hydrated Sulfuric Acid $H_2SO_4(H_2O)_n$ ($n = 1-5$)—A Molecular Orbital Study

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Various isomeric structures of the hydrated clusters of sulfuric acid, $H_2SO_4(H_2O)_n$ ($n = 1-5$), are examined using a density functional molecular orbital method. Due to the small energy difference between trans and cis conformations about two OH groups of sulfuric acid, there are three types of isomeric forms of the hydrated clusters of sulfuric acid which involve the proton nontransferred trans conformer, the proton transferred trans conformer, and the proton nontransferred cis conformer of sulfuric acid. In the case of transoid H_2SO_4, the proton transferred ion-pair structures become more stable than the proton nontransferred structures as the number of water molecules increases. The hydrated clusters of the cis conformation remain neutral hydrogen-bonded structures even if the number of water molecules increases. All stable clusters tend to form multicyclic structures. While both protons of sulfuric acid participate in cyclic hydrogen bonding in the neutral structures, the OH group of HSO_4^- in the ion-pair structures remains dangling because the counterion H_3O^+ prefers to make strong hydrogen bonds with water molecules and/or the HSO_4^- moiety. The energy difference between the most stable structures of proton transferred and proton nontransferred isomers is found to be less than 1 kcal/mol in the case of $n = 3$ and 4 clusters. The ion-pair structure of $HSO_4^-H_3O^+(H_2O)_4$ becomes 2 kcal/mol more stable than the hydrogen-bonded neutral cluster $H_2SO_4(H_2O)_5$ in the case of $n = 5$. Analyzing the interaction energies, many-body interaction is shown to be essential to describe the stability between neutral and ionic clusters owing to the difference of charge flow on the neutral and ion-pair structures in multi-cyclic hydrogen bonding. The calculated IR spectra of stable isomers of $H_2SO_4(H_2O)_n$ clusters clearly demonstrate the significant red-shift of OH stretching of sulfuric acid and hydrogen-bonded OH stretching of water molecules as the number of cluster size increases. The IR spectra of the OH stretching of hydrated sulfuric acid are predicted to appear in three regions, hydrogen-bonded OH stretching of H_3O^+ (2500∼2800 cm^{-1}), hydrogen-bonded OH stretching of water molecules (3100∼3500 cm^{-1}), and nonhydrogen-bonded OH stretching of water molecules (3800∼3900 cm^{-1}).

I. Introduction

The detail mechanism of the hydration of sulfuric acid is of great current interest in conjunction with environmental chemistry. Sulfuric acid/water aerosols are known to play an important role in the formation of the polar stratospheric clouds which catalyze the ozone depletion process.[1] In addition, the warming of the Earth's climate may be partially offset by sulfate particles in atmosphere[2] which is thought to be formed by the nucleation of sulfuric acid and water vapors.[3] The microphysics of sulfuric acid/water clusters, thus, has received considerable attention in recent years.[4−8] Considering the fact that the infrared spectra of the microclusters of a sulfuric acid/water system must strongly depend on the structure of the clusters, the geometrical change of sulfuric acid interacting with water molecules should be explored not only to analyze the spectra but also to understand the nature of the strong acid in aqueous solution. The spectroscopic studies on the sulfuric acid solution on electrode/electrolyte interfaces have also been interested in the electrochemical reactions of the coadsorpted water and sulfur trioxide.[9,10] The formation process of acid rain containing sulfuric acid is also an important problem of how a sulfuric acid droplet is formed from gaseous SO_3 by reacting with water molecules.[11−16]

Since sulfuric acid is a dehydrating substance, the interaction between sulfuric acid and water molecules must be very strong and gives large stabilization in the desoluting process. Another characteristics of sulfuric acid is that H_2SO_4 has two protons and undergoes two-step dissociation. It is evident that strong acid generally completes ion-dissolution in aqueous solution. This fact is also supported by the X-ray crystal structure of sulfuric acid dihydrate which consists of H_3O^+ and SO_4^{2-}.[17] The dissociation process of the strong acid as well as the microscopic solvation of ion pairs, however, would be difficult to observe experimentally, and the critical number of water molecules needed for the proton transfer is still unclear.

There have been few ab initio molecular orbital studies on the sulfuric acid−water cluster system. Kurdi and Kochanski suggested that the ionic complex $[H_3O^+\cdot HSO_4^-]$ is less stable than the neutral complex $[H_2SO_4\cdot H_2O]$ in the sulfuric acid−single water cluster.[18] Arstila et al. show that the proton transfer is unlikely to occur for the mono- and dihydrate of sulfuric acid, while the proton transfer has almost occurred in the trihydrate.[19]

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TABLE 1: Total Energies (E(hartree)), Relative Energies (ΔE(kcal/mol)), and Relative Energies Corrected with Zero-Point Vibrations (ΔE_{ZPC}(kcal/mol)) for the [$H_2SO_4(H_2O)_n$] Clusters Calculated Using the B3LYP Method with the D95(d,p) and D95++(d,p) Basis Sets

	D95(d,p)			D95++(d,p)		
	E (Hartree)	ΔE (kcal/mol)	ΔE_{ZPC} (kcal/mol)	E (Hartree)	ΔE (kcal/mol)	ΔE_{ZPC} (kcal/mol)
H_2O	−76.44505			−76.45272		
$(H_2O)_2$	−152.90063			−152.91493		
$(H_2O)_3$	−229.36932			−229.38658		
$(H_2O)_4$	−305.84007			−305.86227		
H_3O^+	−76.72627			−76.72701		
H_2SO_4 (trans)	−700.29076	0.0	0.0	−700.30383	0.0	0.0
H_2SO_4 (ts1)	−700.28843	1.5	1.1	−700.30145	1.5	1.0
H_2SO_4 (ts2)	−700.28499	3.6	3.0	−700.29785	3.8	3.1
H_2SO_4 (cis)	−700.28857	1.4	1.1	−700.30164	1.4	1.1
HSO_4^-	−699.77301			−699.79999		
$H_2SO_4 \cdot H_2O$						
(I-n)	−776.75983	0.0	0.0	−776.77688	0.0	0.0
(I-c)	−776.75563	2.6	2.9	−776.77334	2.2	2.5
$H_2SO_4(H_2O)_2$						
(II-n-a)	−853.22818	0.0	0.0	−853.25003	0.0	0.0
(II-n-b)	−853.22834	−0.1	0.3	−853.24910	0.6	0.7
(II-n-c)	−853.22499	2.0	2.2			
(II-n-d)	−853.22079	4.6	4.2			
(II-c)	−853.22746	0.5	1.4	−853.24858	0.9	1.6
$H_2SO_4(H_2O)_3$						
(III-n-a)	−929.69799	0.0	0.0	−929.72332	0.0	0.0
(III-n-b)	−929.69444	2.2	1.5	−929.72103	1.4	1.1
(III-n-e)	−929.69450	2.2	2.2			
(III-n-d)	NA			−929.71631	4.4	3.0
(III-n-e)	NA			−929.71517	5.1	4.3
(III-c)	−929.69859	−0.4	0.3	−929.72382	−0.3	0.4
(III-i-a)	−929.69899	−0.6	−0.4	−929.72229	0.6	0.9
(III-i-b)	−929.69667	0.8	1.1	−929.72080	1.6	1.9
(III-i-c)	−929.69565	1.5	1.7			
$H_2SO_4(H_2O)_4$						
(IV-i-a)	−1006.17067	0.0	0.0	−1006.19929	0.0	0.0
(IV-i-b)	−1006.16744	2.0	1.8	−1006.19655	1.7	1.4
(IV-i-c)	−1006.16635	2.7	3.0			
(IV-i-d)	−1006.16470	3.7	3.8			
(IV-i-e)	−1006.16380	4.3	4.6			
(IV-i-f)	−1006.15976	6.8	6.6			
(IV-i-g)	−1006.15591	9.3	8.6			
(IV-n-a)	−1006.16816	1.6	1.6	−1006.19790	0.9	0.6
(IV-n-b)	−1006.16196	5.5	5.0			
(IV-n-c)	−1006.15898	7.3	5.7			
(IV-c-a)	−1006.16692	2.4	3.5	−1006.19619	1.9	2.8
(IV-c-b)	−1006.16542	3.3	3.8			
(IV-c-c)	−1006.16382	4.3	4.7			
(IV-c-d)	−1006.16425	4.0	4.9			
(IV-c-e)	−1006.16378	4.3	5.0			
$H_2SO_4(H_2O)_5$						
(V-i-a)	−1082.63696	0.0	0.0	−1082.67130	0.0	0.0
(V-i-b)	−1082.63535	1.0	0.8	−1082.66957	1.1	0.9
(V-i-c)	−1082.63882	−1.2	−0.7	−1082.67021	0.7	0.9
(V-i-d)	−1082.63674	0.1	0.5	−1082.66909	1.4	1.7
(V-i-e)	−1082.62923	4.9	5.2			
(V-i-f)	−1082.62850	5.3	5.2			
(V-i-g)	−1082.62379	8.3	7.9			
(V-i-h)	−1082.62177	9.5	9.2			
(V-n-a)	−1082.63164	3.3	3.0	−1082.66696	2.7	2.4
(V-n-b)	−1082.62929	4.2	3.9	−1082.66432	4.1	3.9
(V-n-c)	−1082.63029	4.8	4.3	−1082.66479	4.4	4.0
(V-n-d)	−1082.62424	8.0	7.1			
(V-c)	−1082.63472	1.4	2.8	−1082.66830	1.9	3.2

While we were preparing this manuscript, Bandy and Ianni have very recently published the structures of $H_2SO_4(H_2O)_n$ ($n = 1-7$) clusters and their hydration energies using high level of density functional method.[20] Although their study seems to be systematic for the hydration processes of sulfuric acid, many stable structures of $H_2SO_4(H_2O)_n$ are missing especially in the case of large n.

Our previous study on the hydrated clusters of the hydrochloric acid, $HCl(H_2O)_n$ ($n = 1-5$), shows that the proton transfer strongly depends on the size of clusters, and the proton transfer completely occurs at the $n = 5$ cluster size.[21] Since the sulfuric acid molecule also has strong acidity, we would expect that the proton transfer occurs at a similar cluster size. In this study, we have explored various stable structures of the H_2-

$SO_4(H_2O)_n$ cluster systems in the range of $n = 1-5$ by employing the density functional (DFT) methods. The present study would tell the stability of the hydrated clusters of H_2SO_4 depending on the number of water molecules as well as the critical number of water molecules to dissociate the proton of the H_2SO_4 molecule.

There are many studies of the vibrational spectra of sulfuric acid, but its spectrum is very different between gas phase and liquid phase.[22-27] The IR spectrum of $H_2SO_4{\cdot}H_2O$ complex trapped in argon matrix has been reported very recently.[28] Since its IR spectrum involves some other isomers, it is hard to distinguish each size of clusters. Our calculated IR spectra of the hydrated H_2SO_4 clusters can be used for the identification of the structures as well as the nature of hydrogen bonding of sulfuric acid. The theoretically predicted vibrational spectra would also give useful information for analyzing the vapor or aerosols of sulfuric acid which is an important species in the chemistry of the atmosphere.

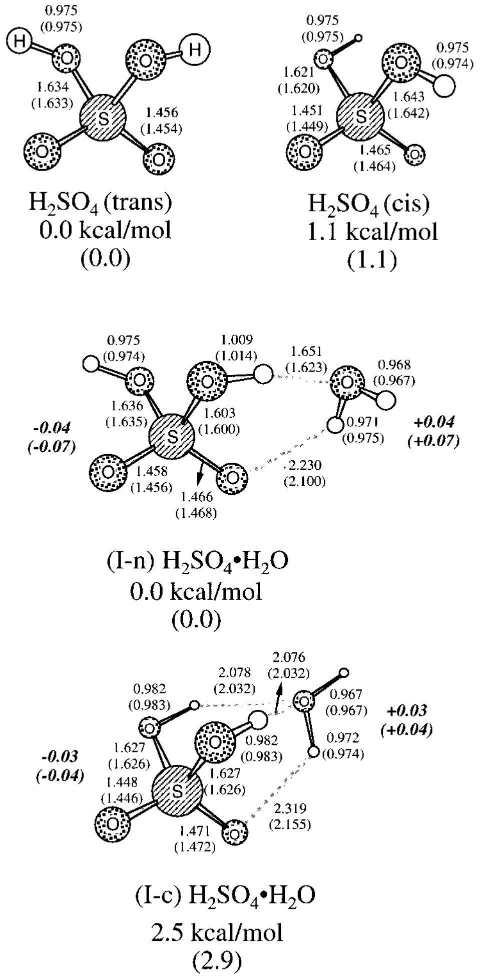
II. Theoretical Calculations

In the present DFT calculations, we have employed the B3LYP method which is the Becke's three-parameter hybrid method using the LYP local and nonlocal-exchange functional of Lee, Yang, and Parr.[29-31] Recent studies for hydrogen-bonded systems show that the DFT methods give accurate thermodynamic characteristics for hydrogen bonding.[32-37] We have also shown that the hybrid Hartree−Fock/density functional method for the hydrated clusters of the phenol cation radical gives good agreement with the experimental result for not only the structures but also the IR spectra.[38] The Huzinaga−Dunning double-ζ plus polarization (D95(d,p)) basis set[39,40] has been used in the geometry optimization for the various isomers of the $[H_2SO_4(H_2O)_n]$ ($n = 1-5$) clusters. We have also optimized the structures by using the D95++(d,p) basis set for the several most stable isomers $n = 1-5$ in order to confirm the energy difference among isomers. The vibrational analyses have been carried out using the analytical second derivative method for the structures of all clusters to confirm the energy minima and to calculate the zero-point energy correction (ZPC). All calculations have been carried out with the GAUSSIAN 94 program package.[41]

In this paper, the relative energies are discussed in terms of the corrected values of zero-point vibrational energies obtained with D95++(d,p) basis set. We have confirmed that the augmentation of the diffuse functions does not cause significant structural changes, especially on the position of the proton, although the relative energies among various isomers may change within 1 kcal/mol. Table 1 summarizes the energies calculated for all species studied in this paper. We classify the isomeric forms of hydrated clusters of sulfuric acid into three structure types and designate n, i, and c for trans neutral, trans ion-pair, and cis neutral structures, respectively. For example, (IV-i-b) means the second ionic form of the $H_2SO_4(H_2O)_4$ cluster.

III. Results and Discussion

A. Sulfuric Acid and Its Monohydrate. Figure 1 shows the structures of sulfuric acid and its monohydrate $[H_2SO_4{\cdot}H_2O]$ optimized using the B3LYP method with D95(d,p) and D95++(d,p) basis sets. The optimized geometry of the sulfuric acid with density functional theory indicates that the bond lengths of S−O tend to be overestimated, especially for the S−OH bond length (1.634 Å) which is ca. 0.07 Å longer than that of the experimental value,[42] while the Hartree−Fock method gives good agreement with the experimental structure. The stable structure of sulfuric acid has C_2 symmetry in the trans form of two OH groups. The optimized structure of the cis form is in C_1 symmetry and is 1.1 kcal/mol less stable than the trans structure. There are two pathways of the isomerization between trans and cis conformers of H_2SO_4, where one OH group rotates inward or outward relative to the other OH group. The energy barrier of inward rotation is calculated to be 3 kcal/mol relative to the trans structure, but the energy of the transition state of outward rotation is almost same as the energy of the cis conformer when we correct the zero-point vibrational energies. Thus, although the trans conformer is the global minimum, sulfuric acid can easily sample two conformations with small energy of ca. 1 kcal/mol.



H_2SO_4 (trans) 0.0 kcal/mol (0.0)

H_2SO_4 (cis) 1.1 kcal/mol (1.1)

(I-n) $H_2SO_4{\cdot}H_2O$ 0.0 kcal/mol (0.0)

(I-c) $H_2SO_4{\cdot}H_2O$ 2.5 kcal/mol (2.9)

Figure 1. Optimized structures of H_2SO_4 and $H_2SO_4{\cdot}H_2O$ complex determined with the B3LYP/D95++(d,p) method. The bond lengths are shown in Å. The values indicated in parentheses were obtained with the B3LYP/D95(d,p) method. Electronic charge of each monomeric moiety is indicated as the value of bold italic.

We have examined various types of hydrogen-bonded complex between H_2SO_4 and H_2O and have obtained the two structures illustrated in Figure 1. The most stable structure (I-n) is a cyclic form with the strong hydrogen bond (1.651 Å) between the oxygen atom of water and a proton of sulfuric acid. This strong hydrogen bond causes the elongation of the O−H bond of sulfuric acid by 0.034 Å and the shortening of the S−OH bond by 0.031 Å from the isolated species, and leads to the stabilization of the system by 10 kcal/mol with a zero-point vibration correction as shown in Table 2. There is also weak interaction between the hydrogen atom of water and the oxygen

TABLE 2: Interaction Energies (kcal/mol) without (ΔE) and with (ΔE_{ZPC}) the Zero-Point Vibrational Correction, and the Changes of the Enthalpies, Entropies, and the Free Energies Obtained with the B3LYP/D95(d,p) and B3LYP/D95++(d,p) Methods[a]

	B3LYP/D95(d,p) method					B3LYP/D95++(d,p) method				
	$-\Delta E$	$-\Delta E_{ZPC}$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta E$	$-\Delta E_{ZPC}$	$-\Delta H$	ΔS	$-\Delta G$
$H_2SO_4(H_2O)_{n-1} + H_2O \rightarrow H_2SO_4(H_2O)_n$										
$n = 1$										
I-n	−15.1	−12.6	−13.4	30.4	−4.3	−12.8	−10.4	−11.1	29.3	−2.4
I-c	−12.4	−9.7	−10.5	30.8	−1.3	−10.5	−7.9	−8.6	28.6	−0.1
$n = 2$										
II-n-a	−14.6	−12.5	−13.3	31.0	−4.0	−12.8	−10.5	−11.3	31.3	−2.0
II-n-b	−14.7	−12.2	−13.0	31.6	−3.6	−12.2	−9.8	−10.5	30.6	−1.4
$n = 3$										
III-n-a	−15.5	−12.7	−13.6	33.0	−3.8	−12.9	−10.2	−11.0	32.1	−1.5
III-n-b	−13.3	−11.2	−11.9	31.7	−2.5	−11.5	−9.1	−9.9	31.4	−0.6
III-c	−15.9	−12.2	−13.5	38.9	−1.9	−13.2	−9.9	−11.0	36.6	−0.1
III-i-a	−16.2	−13.1	−14.6	39.1	−2.9	−12.3	−9.3	−10.7	39.3	+1.0
III-i-b	−14.7	−11.7	−13.1	39.4	−1.3	−11.3	−8.3	−9.8	39.8	+2.1
$n = 4$										
IV-n-a	−15.8	−13.2	−14.2	33.5	−4.2	−13.7	−11.1	−12.0	34.0	−1.9
IV-c-a	−15.0	−11.3	−12.7	40.1	−0.7	−12.6	−8.9	−10.3	39.9	+1.6
IV-i-a	−17.3	−14.8	−16.0	35.0	−5.6	−14.6	−11.7	−13.2	38.0	−1.8
IV-i-b	−15.3	−13.0	−14.1	34.4	−3.8	−12.9	−10.3	−11.5	36.3	−0.7
$n = 5$										
V-n-a	−10.0	−8.0	−8.3	26.9	−0.2	−9.4	−7.5	−7.6	24.4	−0.3
V-n-b	−9.1	−7.1	−7.4	30.4	+1.6	−8.0	−6.0	−6.1	26.8	+1.9
V-n-c	−8.5	−6.7	−7.1	30.0	+1.8	−7.7	−5.9	−6.0	26.1	+1.7
V-c	−11.9	−8.2	−9.3	39.9	+2.6	−10.2	−6.7	−7.4	34.6	+2.9
V-i-a	−13.3	−11.0	−11.6	31.8	−2.1	−12.1	−9.9	−10.4	29.7	−1.6
V-i-b	−12.3	−10.2	−10.8	31.0	−1.5	−11.0	−9.0	−9.5	28.1	−1.1
V-i-c	−14.5	−11.7	−12.6	37.6	−1.4	−11.4	−9.0	−9.6	34.1	+0.5
V-i-d	−13.2	−10.5	−11.4	34.0	−1.3	−10.7	−8.2	−9.0	33.2	+0.9

[a] The values of the $n = 2$, 3, 4, and 5 clusters were obtained using the numbers of the (I-n), (II-n-a), (III-n-a), and (IV-i-a) clusters, respectively. Gibb's free energies are calculated at $P = 1$ atm, $T = 298.15$ K.

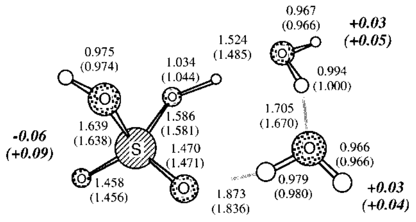
atom of the $S{=}O$ group, whose distance is calculated to be 2.230 Å. When we optimized the geometry from the ionic form $[HSO_4^- \cdots H^+OH_2]$, this structure converges to the neutral form (I-n). This means that the single water molecule is unable to induce the proton transfer reaction, in agreement with the previous studies.[18−20]

In another type of complex (I-c), two hydrogen atoms of sulfuric acid contribute to the hydrogen bonding with a single water molecule. This structure is calculated to be only 2.5 kcal/mol less stable than the structure (I-n), although both lone-pair electrons of a water molecule participate in the hydrogen bonding with two OH groups in H_2SO_4 being cis conformation. This result indicates that energy gain due to the hydrogen bonding of two protons of sulfuric acid is quite large, even if the system has strained structure to form doubly coordinated hydrogen bonds.

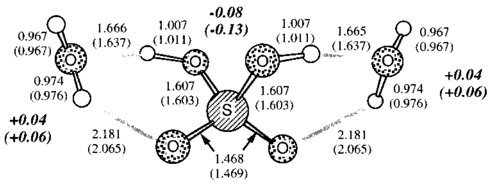
The lone-pair electrons of oxygen atoms of sulfuric acid have the possibility to form a hydrogen bond with a water molecule. When we optimize the structure starting from the hydrogen-bonded geometry toward the lone-pair electrons of the OH group of sulfuric acid, we could not obtain the corresponding structure but reach to the most stable 1:1 complex (I-n). Furthermore, we have not found the hydrogen-bonded structures between water molecule and $S{=}O$ groups of sulfuric acid. Since the ability of H_2SO_4 as a proton acceptor is very small, the interaction between water molecule and the $S{=}O$ group is shown to be extremely weak.[17]

B. $[H_2SO_4(H_2O)_2]$ Cluster. Figure 2 shows the optimized structures of the dihydrated complex $[H_2SO_4(H_2O)_2]$. The structure (II-n-a) has a water dimer forming a hydrogen-bonding cyclic structure with sulfuric acid, while the symmetric structure (II-n-b) has single water molecule interacting with H_2SO_4 on each side. The structure (II-n-a) indicates a significant shortening of the $SOH \cdots OH_2$ hydrogen bond (0.127 Å) and elongation of the $SO{-}H$ bond (0.025 Å) compared to the monohydrated complex (I-n). It is noticeable in Table 1 that the energy difference among three structures (II-n-a), (II-n-b), and (II-c) is calculated to be less than 2 kcal/mol. Such near degeneracy is caused by the cancellation of the interaction energies among one strong $SOH \cdots OH$ hydrogen bond in structure (II-n-a), two relatively weak $SOH \cdots OH$ hydrogen bonds in structure (II-n-b), and the strained multiple hydrogen bonds involving two protons of sulfuric acid (II-c). The linear hydrogen-bonded structure (II-n-d) is calculated to be 4 kcal/mol less stable than the structure (II-n-a). To find the difference of the proton acceptability of oxygen lone-pair electrons between the $S{=}O$ group and the $S{-}OH$ group, we have calculated the structure (II-n-c) shown in Figure 2. The energy of (II-n-c) obtained is 2.2 kcal/mol less stable than that of (II-n-a). This energy difference would correspond to the preference of proton acceptability between two types of oxygen atoms of sulfuric acid. The calculated charge densities of each moiety in dihydrates, shown with bold italic numbers in Figure 2, indicate that all these clusters are hydrogen-bonded systems among electronically neutral species.

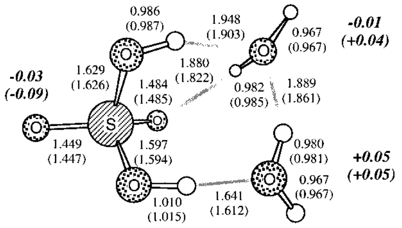
C. $[H_2SO_4(H_2O)_3]$ Cluster. As was demonstrated in the case of $HCl(H_2O)_3$ clusters,[21] one might expect that three water molecules initiate proton dissociation from sulfuric acid. Figure 3 depicts optimized structures of various isomers of the trihydrate $[H_2SO_4(H_2O)_3]$. There are three most stable isomers, i.e., one proton transferred structure (III-i-a) and two proton nontransferred forms (III-n-a) and (III-c). The energy difference between the proton transferred structure (III-i-a) and proton nontransferred structures (III-n-a) and (III-c) is calculated to be less than 1 kcal/mol with both D95(d,p) and D95++(d,p) basis sets. This evidence has very recently been shown by Bandy



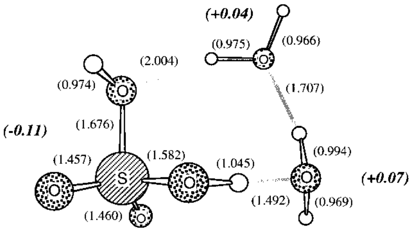
(II-n-a) $H_2SO_4•(H_2O)_2$
0.0 kcal/mol
(0.0)



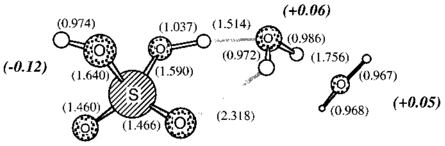
(II-n-b) $H_2SO_4•(H_2O)_2$
0.7 kcal/mol
(0.3)



(II-c) $H_2SO_4•(H_2O)_2$
1.6 kcal/mol
(1.4)



(II-n-c) $H_2SO_4•(H_2O)_2$
(2.2)



(II-n-d) $H_2SO_4•(H_2O)_2$
(4.2)

Figure 2. Optimized structures of stable isomers of $H_2SO_4(H_2O)_2$ calculated with the B3LYP/D95++(d,p) method. The bond lengths are shown in Å. The values indicated in parentheses were obtained with the B3LYP/D95(d,p) method. Electronic charge of each monomeric moiety is indicated as the value of bold italic.

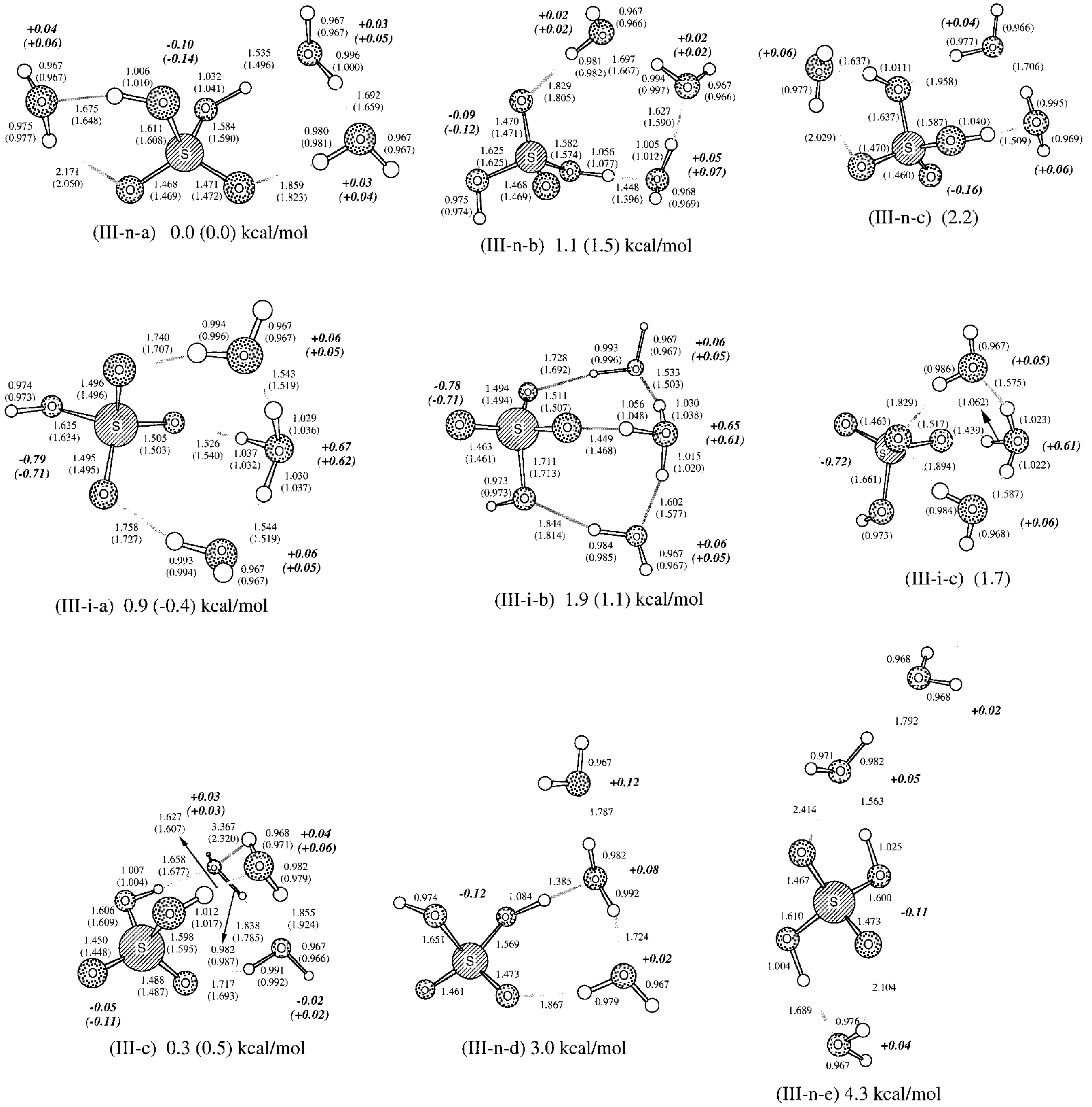
and Ianni.[20] Although the calculation without diffuse function results that the most stable structure is an ion-pair structure (III-i-a), we can conclude that the proton nontransferred neutral clusters and the proton transferred ionic structure coexist in the trihydrate $[H_2SO_4(H_2O)_3]$ owing to the very small energy difference among the isomers. It is clearly shown that the proton transferred complex (III-i-a) has an ion-pair structure in which negative charge (−0.79) is located on the HSO_4^- ion and positive charge (+0.67) is located on the H_3O^+ moiety. Three hydrogen atoms of the H_3O^+ ion form very strong hydrogen bonds (1.52−1.54 Å) which lead to the stabilization of this system. Note that the neutral isomer (III-c) involving sulfuric acid in cis conformation is greatly stabilized by the interaction with water trimer because multi-cyclic hydrogen bonding becomes a less strained structure in (III-c).

Figure 3 also illustrates the optimized structures of other less stable isomers for trihydrate calculated with the B3LYP/D95-(d,p) method. The mono cyclic structure (III-n-b) has a very short distance (1.45 Å) for hydrogen bonding bound to the proton of sulfuric acid. Since this isomer is only 1 kcal/mol less stable than the most stable neutral structure (III-n-a), the stabilization owing to the single strongest interaction between sulfuric acid and water trimer cannot compete with the multi cyclic interactions. When the hydrated cluster loses multi cyclic interaction, destabilization becomes significant as is seen in the neutral isomers (III-n-d and III-n-e). These isomers are calculated to be more than 3 kcal/mol unstable compared to the stable multi-cyclic structure, even though the system releases the strain energy. In addition to the fact that the structures (III-n-d) and (III-n-e) reported by Arstila et al.[19] are found to be energetically high species, these structures are not energy minima at the B3LYP/D95(d,p) level of calculation and are only obtained as local minima with the B3LYP/D95++(d,p) method. Since water molecules of these isomers do not fully take part in the hydrogen bonding, the proton transfer cannot take place in these species.

It is interesting to see that all of the ionic structures, (III-i-a), (III-i-b), and (III-i-c), have tri-cyclic hydrogen bonding between HSO_4^- and H_3O^+ using two water molecules. Even if we start to optimize the neutral structures of these isomers, the result turns out to be ionic structures. The stability of these ionic structures consists of three strong hydrogen bonds toward three hydrogen atoms of H_3O^+ moiety. The most preferable tri-cyclic hydrogen bond is shown to be between three S═O groups of HSO_4^- and three hydrogens of $H_7O_3^+$.

D. $[H_2SO_4(H_2O)_4]$ Cluster. Figure 4 depicts the optimized structures of the stable species of the $[H_2SO_4(H_2O)_4]$ clusters which include two ionic structures, (IV-i-a) and (IV-i-b), and the neutral structure (IV-n-a). Brandy and Ianni have only shown the structures (IV-n-a) and (IV-i-a).[20] In both ionic structures, (IV-i-a) and (IV-i-b), the positive charge on the H_3O^+ moiety (ca. +0.7) represents some delocalization of charge through three hydrogen bonds toward the water molecules and/or HSO_4^-. In the case of $n = 4$ cluster size, the proton transferred structure (IV-i-a) becomes slightly favorable in energy relative to the neutral structure (IV-n-a). Since the energy difference between most stable ionic and neutral structures is less than 1 kcal/mol, it is hard to conclude which isomer is the most stable in the present calculation. We have also optimized the several possible isomers besides the clusters shown in Figure 4 using the B3LYP/D95(d,p) method. All of these isomers not illustrated in Figure 4 turn out to be highly unstable species.

In the neutral clusters, the most stable isomer forms cyclic hydrogen bonding with two water dimers in symmetric structure (IV-n-a). When the hydrogen-bonding network breaks the symmetry, both asymmetric multi-cyclic hydrogen-bonding structure (IV-n-b) and single hydrogen-bonding structure (IV-n-c) are calculated to be energetically unstable. The most stable neutral cluster involving the cis conformer of sulfuric acid (IV-c-a) is calculated to be 2.8 kcal/mol less stable than the most stable ionic structure (IV-i-a). This hydrated cis conformer



(III-n-a) 0.0 (0.0) kcal/mol

(III-n-b) 1.1 (1.5) kcal/mol

(III-n-c) (2.2)

(III-i-a) 0.9 (-0.4) kcal/mol

(III-i-b) 1.9 (1.1) kcal/mol

(III-i-c) (1.7)

(III-c) 0.3 (0.5) kcal/mol

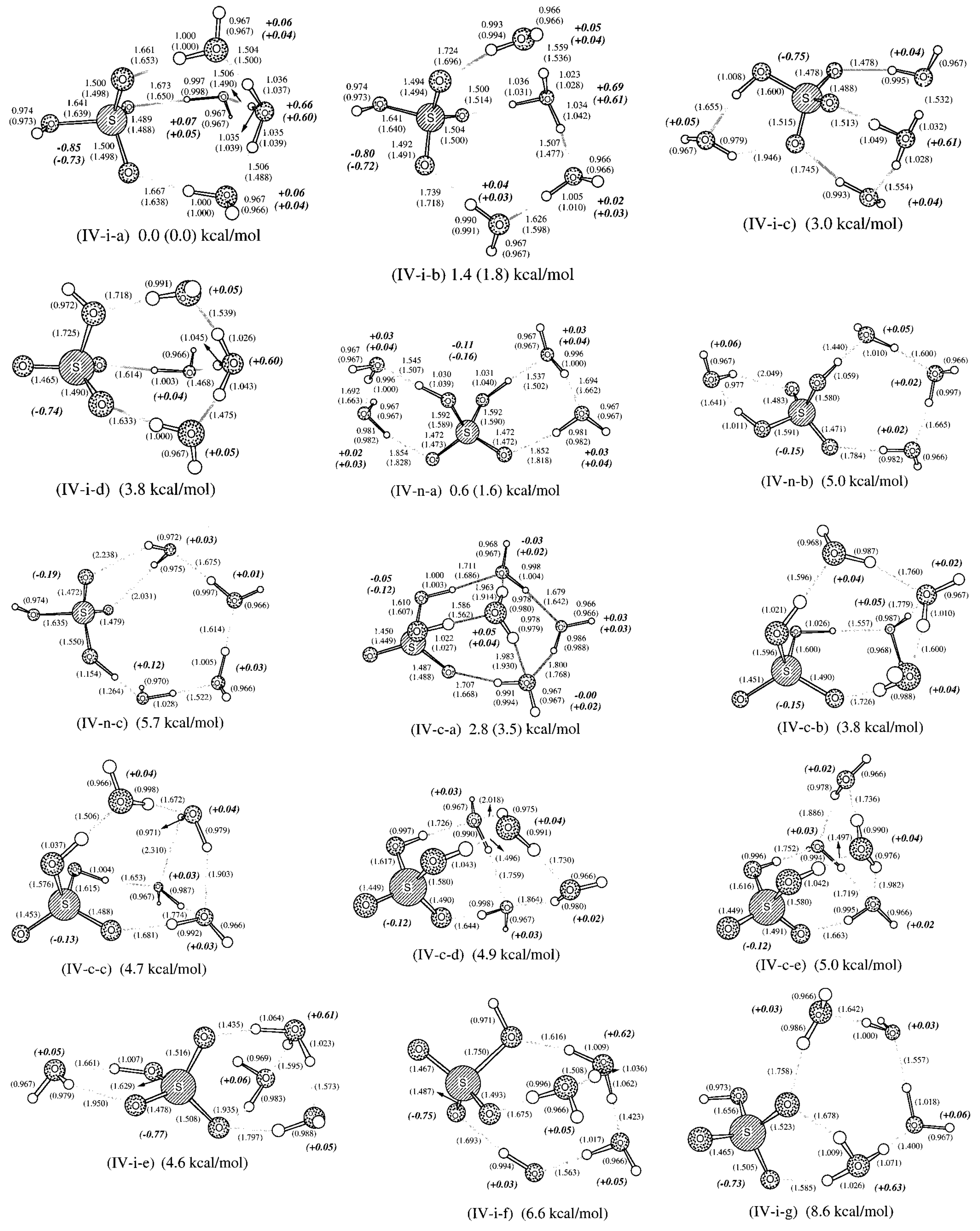
(III-n-d) 3.0 kcal/mol

(III-n-e) 4.3 kcal/mol

Figure 3. Structures of several isomers of $H_2SO_4(H_2O)_3$ determined with the B3LYP/D95++(d,p) method. The bond lengths are shown in Å. The values indicated in parentheses were obtained with the B3LYP/D95(d,p) method. Electronic charge of each monomeric moiety is indicated as the value of bold italic.

interacts two protons of sulfuric acid with water tetramer, and there are various isomeric forms. We have calculated five isomers, (IV-c-a)−(IV-c-e), by inserting one water molecule into the various hydrogen-bonded sites of the structure (III-c). The structures (IV-c-a), (IV-c-d), and (IV-c-e) contain a cyclic water tetramer, while the structures (IV-c-b) and (IV-c-c) have a branched water tetramer. The energies of all these five isomers are not significantly different and lie within 2 kcal/mol. Regarding the evidence that two neutral structures (I-n) and (I-c) of the monohydrate differ 2.5 kcal/mol in energy, multi-cyclic hydrogen bondings of cis conformer with water clusters lead to the comparable stabilization despite the strained hydrogen-bonding network in addition to the less stable cis conformation of sulfuric acid.

The ionic structures of $H_2SO_4(H_2O)_4$ can be classified into two groups. One is the group in which H_3O^+ is directly interacting with HSO_4^-, and the other is the group in which H_3O^+ is indirectly interacting with HSO_4^- via water molecules. The most stable structure of the $H_2SO_4(H_2O)_4$ cluster (IV-i-a) has pseudo C_{3v} symmetry where three hydrogen atoms of H_3O^+ are equally connected to the water molecules through strong hydrogen bonds. The second stable ionic isomer (IV-i-b) has direct hydrogen-bonding between H_3O^+ and HSO_4^-. The energy difference between two stable isomers in ionic form may be explained by the fact that the structure (IV-i-b) has more strain in one of the hydrogen-bonded cycles than the structure (IV-i-a). We cannot, however, observe significant difference in the stabilization between direct and indirect ion pair structures. We


(IV-i-a) 0.0 (0.0) kcal/mol

(IV-i-b) 1.4 (1.8) kcal/mol

(IV-i-c) (3.0 kcal/mol)

(IV-i-d) (3.8 kcal/mol)

(IV-n-a) 0.6 (1.6) kcal/mol

(IV-n-b) (5.0 kcal/mol)

(IV-n-c) (5.7 kcal/mol)

(IV-c-a) 2.8 (3.5) kcal/mol

(IV-c-b) (3.8 kcal/mol)

(IV-c-c) (4.7 kcal/mol)

(IV-c-d) (4.9 kcal/mol)

(IV-c-e) (5.0 kcal/mol)

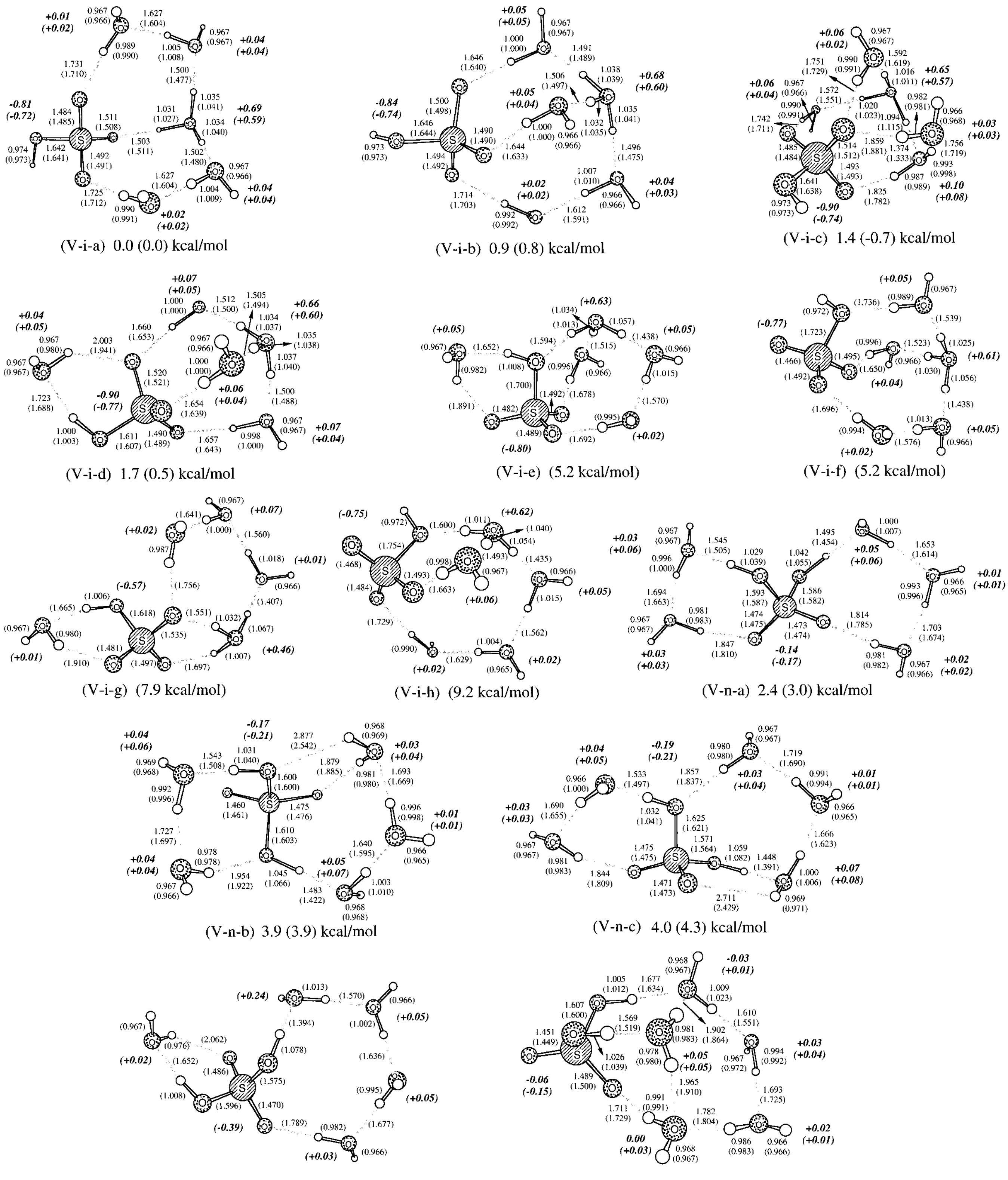
(IV-i-e) (4.6 kcal/mol)

(IV-i-f) (6.6 kcal/mol)

(IV-i-g) (8.6 kcal/mol)

Figure 4. Structures of several isomers of $H_2SO_4(H_2O)_4$ determined with the B3LYP/D95++(d,p) method. The bond lengths are shown in Å. The values indicated in parentheses were obtained with the B3LYP/D95(d,p) method.

have examined other less stable direct and indirect ion-pair structures (IV-i-c)−(IV-i-g) as shown in Figure 4. These results indicate that four water molecules prefer to fully participate to the multi-cyclic hydrogen bonding between HSO_4^- and $H_9O_4^+$ complex and all of three S═O groups prefer to interact with water sites.



(V-i-a) 0.0 (0.0) kcal/mol

(V-i-b) 0.9 (0.8) kcal/mol

(V-i-c) 1.4 (-0.7) kcal/mol

(V-i-d) 1.7 (0.5) kcal/mol

(V-i-e) (5.2 kcal/mol)

(V-i-f) (5.2 kcal/mol)

(V-i-g) (7.9 kcal/mol)

(V-i-h) (9.2 kcal/mol)

(V-n-a) 2.4 (3.0) kcal/mol

(V-n-b) 3.9 (3.9) kcal/mol

(V-n-c) 4.0 (4.3) kcal/mol

(V-n-d) (7.1 kcal/mol)

(V-c) 3.2 (2.8) kcal/mol

Figure 5. Structures of stable isomers of $H_2SO_4(H_2O)_5$ determined with the B3LYP/D95(d,p) method. The bond lengths are shown in Å. The values indicated in parentheses were obtained with the B3LYP/D95(d,p) method.

Although there must be many more isomeric structures of the $[H_2SO_4(H_2O)_4]$ clusters due to the various combination of hydrogen bonding sites, we can conclude that the feature of the strong binding site in the hydration of sulfuric acid is due to either the deprotonation from one of the S−OH groups leading to the ionic structures or the cyclic hydrogen bonding between two S−OH groups and the S=O group connected by water molecules leading to the neutral structures.

E. $[H_2SO_4(H_2O)_5]$ Cluster. When we add one more water molecule to the structures (IV-i-a), (IV-i-b), and (IV-n-a), we obtain the stable structures (V-i-b), (V-i-a), and (V-n-a) for the $[H_2SO_4(H_2O)_5]$ clusters, respectively, as shown in Figure 5. The most stable structure (V-i-a) is the proton transferred form, and the neutral stable isomer (V-n-a) has the form in which water molecules bind on both sides of the sulfuric acid molecule. The energy difference between ionic structure (V-i-a) and neutral isomer (V-n-a) is predicted to be 2.4 kcal/mol which becomes large in comparison with the case of $n = 4$ clusters (0.6 kcal/mol). This clearly indicates that the proton transferred structures tend to be superior to the nontransferred structures when the cluster size increases. The relative energies of four proton transferred structures (V-i-a), (V-i-b), (V-i-c), and (V-i-d) lie within 2 kcal/mol.

The recent study by Bandy and Ianni only shows the structure (V-i-d) as an ionic cluster of $n = 5$, but this structure (V-i-d) is not the most stable isomer. Moreover, they have shown that the structure (V-n-b) is most stable among the neutral clusters, but this isomer is 1.5 kcal/mol less stable than the most stable neutral structure (V-n-a) in our calculation. One SOH group of this isomer (V-n-b) is acting as both proton donor and proton acceptor. In the structure (V-n-a), all SOH and SO groups of H_2SO_4 are participating to the hydrogen bonding. This situation makes the structure (V-n-a) more stable than the isomers (V-n-b) and (V-n-c).

We have also optimized other types of isomers using the B3LYP/D95(d,p) method, but all other isomers are calculated to be more than 5 kcal/mol unstable than the most stable ionic structure (V-i-a). Since the energy difference between direct and indirect ion-pairs is not significant enough to conclude the preferable conformation of the hydrated clusters $[H_2SO_4(H_2O)_n]$, both indirect ion-pair $HSO_4^-(H_2O)_{n-1}H_3O^+$ and direct ion-pair $HSO_4^-H_3O^+(H_2O)_{n-1}$ structures coexist in the proton transferred structures.

By looking at the optimized geometries of the proton transferred structures obtained in this study, major stabilization of the ion-pair structures is caused by the strong hydrogen bonding with three hydrogen atoms of the H_3O^+ moiety. This means that one of the S−OH groups does not contribute to the stabilization of the system by forming hydrogen bonds. In other word, the second proton hardly dissociates. As Bandy and Ianni stated, the structures of hydrated H_2SO_4 clusters are far from complete ionization to SO_4^{2-} in bulk-phase solutions of H_2SO_4.[20] Such difficulty of the second ionization must be overcome by the cooperative hydrogen bonding between water molecules and multiple H_2SO_4 molecules in bulk solution.

For the hydrated clusters of cisoid H_2SO_4, the structure (V-c) seems to resemble the chemisorbed form of sulfuric acid on the water clusters. The coordination of the sulfuric acid onto the freezing stratospheric aerosols is an important process and the structures (III-c), (IV-c-a), and (V-c) obtained in the present calculations seem to correspond to the evidence that the IR peaks observed for the water molecules of sulfuric acid/water aerosols show the characteristic of ice.[7]

F. Hydration Energies. Table 1 lists the calculated total energies and the relative energies for the $[H_2SO_4(H_2O)_n]$ ($n = 1-5$) clusters. The zero-point vibrational correction does not change the relative stability when we use the D95++(d,p) basis set. The effect of the diffuse functions in the basis set is somewhat significant to determine the relative energies among stable isomers, especially in the case of $n = 3$ clusters. We observe that the energy relation between (III-n-a) and (III-i-a) is reversed by the inclusion of diffuse functions, although the change of the relative energies is within 1 kcal/mol. We have not refined the relative energies with further accurate methods due to the computational limitations, but we would require future study in order to determine the most stable structures based on much reliable prediction.

TABLE 3: Energy Decomposition of the Stabilization Energies (E_{Bind}) of Hydrated Clusters of Sulfuric Acid into Deformation Energies (DEF), Two-Body Interaction Energies (2INT), Many-Body Interaction Energies (MINT), and Relative Energies without Many-Body Interactions (ΔE_{2INT})[a]

clusters	E_{bind}[b]	DEF	2INT	MINT[c]	ΔE_{2INT}[d]
neutral cluster					
$n = 3$ (III-n-a)	−38.5	4.8	−37.8	−5.5	−33.0
(III-c)	−38.8	6.4	−40.2	−4.9	−33.9
$n = 4$ (IV-n-a)	−52.2	7.6	−48.7	−11.1	−41.1
$n = 5$ (V-n-a)	−62.5	8.9	−55.8	−15.7	−46.8
ionic cluster					
$n = 3$ (III-i-a)	−181.7	8.4	−208.5	18.3	−56.1
$n = 4$ (IV-i-a)	−197.0	7.6	−217.4	12.8	−65.9
$n = 5$ (V-i-a)	−209.1	7.7	−233.8	17.0	−82.2

[a] Energy values are shown in kcal/mol. [b] $E_{bind}(\text{neutral}) = H_2SO_4(H_2O)_n - \{H_2SO_4 + nH_2O\}$, $E_{bind}(\text{ionic}) = H_2SO_4(H_2O)_n - \{(n-1)H_2O + H_3O^+ + HSO_4^-\}$. [c] Many-body interaction: MINT = E_{bind} − DEF − 2INT. [d] $\Delta E_{2INT} = H_2SO_4(H_2O)_n - \{H_2SO_4 + nH_2O\} - \text{MINT}$.

Table 2 summarizes the stabilization energies for the $[H_2SO_4(H_2O)_n]$ ($n = 1-5$) clusters relative to the most stable form of the $[H_2SO_4(H_2O)_{n-1}]$ ($n = 1-5$) clusters. While each successive hydration process gives ca. 10 kcal/mol stabilization in enthalpy, the free energy differences ΔG at 298 K are within a few kcal/mol. Some of the ionic cluster formation increases the free energy due to the increasing entropy factors. Consequently, the results of ΔG values indicate that the hydration processes $H_2SO_4(H_2O)_{n-1} + H_2O \rightarrow H_2SO_4(H_2O)_n$ do not gain large free energy at the room temperature. Since there is not significant energy difference between proton transferred and nontransferred isomers among the $n \leq 5$ clusters, we would expect that both neutral and ionic structures coexist in the bulk aqueous solution of H_2SO_4.

G. Analysis of Interaction Energies. Since sulfuric acid has many sites of hydrogen bonding, stabilization caused by hydration involves multiple interactions between H_2SO_4 and water molecules. To analyze the interaction energies of the hydrated clusters of sulfuric acid, we have calculated two-body and many-body interaction energies of the most stable neutral and ionic structures for $n = 3-5$ clusters. Table 3 shows the energy decomposition of the binding energies into the deformation, two-body interaction, and residual energies. In the case of ionic clusters, we have calculated the interaction energies relative to the species, HSO_4^-, H_3O^+, and H_2O molecules. As Table 3 shows, the deformation energies are relatively small, and most of the binding energies are described with two-body interactions. The many-body interaction energies indicate the negative values (attractive) for neutral clusters and the positive values (repulsive) for ionic isomers. The attractive many-body interaction of the neutral clusters can be rationalized by the fact that the interaction between neutral species has cyclic charge flow from proton donor H_2SO_4 to proton acceptor H_2O and back to H_2SO_4 through water molecules. Such cooperative interaction makes the systems more stable via many-body interactions. In the case of ionic clusters, charge flow is one way from H_3O^+ to HSO_4^- moieties and this flow reduces the fragment charges and thus reduces the Coulombic attractive force between ionic moieties.

The many-body interaction plays the key role in the relative stabilities of the neutral vs ionic clusters. If one neglects the many-body terms, the ionic clusters would be more than 20 kcal/mol more stable than the neutral complex even for $n = 3$. As seen in Table 3, the binding energies of neutral clusters (III-

TABLE 4: Calculated Vibrational Frequencies of $H_2SO_4 \cdot H_2O$ (I-n) and (I-c) Isomers, H_2SO_4 Monomers, and HSO_4^- Ion Obtained with the B3LYP/D95++(d,p) Method[a]

	I-n		I-c	trans H_2SO_4	cis H_2SO_4	HSO_4^-
1	3903 (s)	H_2O asym	3910 (s)			
2	3758 (m)	H_2O sym	3776 (w)			
3	3770 (s)	non H-bond SO−H	3651 (vs)	3764	3711	
4	3110 (vs)	H-bond SO−H	3626 (vw)	3760	3763	3652
5	1618 (m)	H_2O bend	1599 (s)			
6	1445 (s)	H-bond SO−H bend	1400 (s)	1393	1374	
7	1322 (s)	SO−H bend	1237 (w)	1155	1181	1160
8	1152 (m)	S═O	1198 (s)	1148	1148	1102
9	1134 (s)	S═O	1139 (s)	1140	1118	1041
10	866 (s)	S−O	826 (s)	819	822	909
11	840 (s)	S−O	775 (s)	764	761	
12	774 (m)		617 (s)			
13	531 (s)		579 (s)			
14	516 (w)		507 (w)	507	504	595
15	502 (w)		503 (vw)	499	492	484
16	476 (w)		477 (w)	457	468	473
17	403 (m)		399 (w)	411	398	443
18	375 (s)		352 (w)	348	376	350
19	342 (w)		349 (s)	317	346	324
20	258 (w)		334 (na)	248	109	42
21	230 (s)		331 (m)			
22	214 (vw)		186 (vw)			
23	125 (w)		115 (w)			
24	49 (vw)		26 (vw)			

[a] IR intensity: vs, s, m, w, vw, and na denote very strong (>500), strong (>100), medium (>50), weak (>10), very weak (<10), and not active (0), respectively.

n-a) and (III-c) without many-body interaction energies (MINT) would be −33.0 and −33.9 kcal/mol, whereas the corresponding energy for the ionic cluster (III-i-a) is −56.1 kcal/mol. Thus, any simulation without strong three-body terms would result in erroneous dominance of ionic clusters.

H. Vibrational Analyses. Tables 4 and 5 and Figure 6 summarize the predicted IR spectra for the $[H_2SO_4(H_2O)_n]$ ($n = 1-5$) clusters calculated with the B3LYP/D95++(d,p) method. The IR spectra for HSO_4^- and H_2SO_4 molecules are also illustrated and listed in Table 4 in order to consider the frequency shifts due to the hydrogen bonding. In the IR spectra for the bisulfate anion HSO_4^-, theoretical stretching frequency for ν_{S-OH} (909 cm^{-1}) and symmetric ν_{SO_3} (1041 cm^{-1}) are in good agreement with the experimental values 895 and 1057 cm^{-1}, respectively.[9] The calculated value for the asymmetric ν_{SO_3} (1102 cm^{-1}) and bending ν_{SOH} (1160 cm^{-1}) are, however, underestimated compared to the previous theoretical value obtained with the MP2 level of calculation.[43] The theoretical values of $\nu_{S=O}$ of the sulfuric acid molecule, 1393 cm^{-1} for the asymmetric and 1155 cm^{-1} for the symmetric modes, agree well with the experimentally observed values (1364 cm^{-1} for the former and 1181 cm^{-1} for the latter), while the calculated values ν_{S-OH}, 819 cm^{-1} for the asymmetric and 764 cm^{-1} for the symmetric, lie below the experimental values (1055 and 992 cm^{-1}, respectively).[9] This discrepancy is due to the defect of describing S−O bond with B3LYP method as seen in the long bond distances stated in section IIIA.

The OH stretching frequencies of H_2SO_4 are calculated to be 3764 and 3760 cm^{-1}. While the experimental OH streching frequencies of H_2SO_4 vapor are reported to be 3625 and 2610 cm^{-1},[22] these frequencies become 2970 and 2450 cm^{-1} in liquid.[24] This means that the hydrogen bond formation of SOH group leads to the red-shift of 700 or more than 1000 cm^{-1}. This evidence can be proofed by looking at the vibrational frequencies of the complex between H_2SO_4 and water molecules.

The hydrogen bonding with a water molecule causes a remarkable red-shift for one of SO−H stretching frequencies as shown in Figure 6 and Table 4. The hydrogen-bonded OH stretching frequency of the sulfuric acid for $n = 1$ cluster (I-n) appears at 3110 cm^{-1}, resulting in the red-shift of 650 cm^{-1} from that of the bare sulfuric acid molecule, while the OH stretching without hydrogen bonding remains at 3770 cm^{-1}. The gentle red-shift of the OH stretching of the water molecule is caused by the weak interaction between water molecule and S═O group. Recently, Givan et al. reported the IR spectra of the $H_2SO_4 \cdot H_2O$ complex trapped in argon matrixes.[28] They have assigned various peaks to the possible complexes among H_2SO_4 and water molecules, and have stated that the more stable forms of sulfuric acid with water molecules are in the open chain form. Their assignment is based on the temperature dependence (5−18 K) and on the small frequency shifts from monomers. While their results agree with theoretically predicted facts that the complexes between sulfuric acid and water monomer or water dimer have proton nontransferred structure, assignment of the IR absorption bands might be reconsidered from the fact that the hydrogen bonding is very strong between H_2SO_4 and water molecule even if the complex is in open chain form. They have not reported the strong peak around the 3100 cm^{-1} region which is calculated to be hydrogen-bonded OH streching of H_2SO_4 in $H_2SO_4 \cdot H_2O$ cluster (I-n). Givan et al. have assigned the hydrogen-bonded OH frequency to be 3573 cm^{-1}, but this peak is very close to the non hydrogen-bonded OH streching frequency.

In the case of $n = 2$ cluster (II-n-a), the hydrogen-bonded OH stretching of H_2SO_4 is red-shifted by ca. 450 cm^{-1} compared to that of the $n = 1$ cluster, while the other OH stretching of sulfuric acid is appeared at 3768 cm^{-1}. In addition to the remarkable red-shift of the SO−H stretching, the hydrogen-bonded OH stretching band between two water molecules is also red-shifted to 3355 cm^{-1} and the other hydrogen-bonded OH stretching of water moiety toward S═O group appears at 3653 cm^{-1}. The spectrum of cluster (II-n-b) is essentially the same as the spectrum of cluster (I-n), where both OH stretchings

TABLE 5: Vibrational Frequencies of $H_2SO_4(H_2O)_n$ ($n = 2-4$) Clusters Calculated with the B3LYP/D95++(d,p) Method[a]

	II-n-a	II-n-b	II-c	III-n-a	III-c	III-i-a	IV-n-a	IV-c-a	IV-i-a	IV-i-b
1	3902 (s) W	3901 (s) W	3893 (m) W	3900 (s) W	3892 (m) W	3890 (s) W	3896 (m) W	3899 (m) W	3891 (m) W	3897 (s) W
2	3890 (m) W	3900 (m) W	3891 (s) W	3897 (s) W	3889 (s) W	3887 (s) W	3894 (s) W	3884 (s) W	3889 (s) W	3895 (w) W
3	2768 (s) SOH	3745 (m) W	3542 (s) W	3885 (m) W	3885 (s) W	3778 (s) SOH	3884 (s) W	3879 (m) W	3887 (s) W	3887 (m) W
4	3653 (vs) W	3744 (m) W	3589 (s) W	3740 (m) W	3610 (vs) W	3405 (vs) W	3883 (m) W	3721 (vs) W	3784 (m) SOH	3782 (m) SOH
5	3355 (vs)W	3159 (s) SOH	3527 (s) SOH	3637 (vs) W	3565 (s) W	3367 (vs) W	3626 (s) W	3654 (s) W	3331 (vs) W	3446 (vs) W
6	2663 (vs) SOH	3136 (vs) SOH	3075 (vs) SOH	3328 (vs) W	3416 (vs) W	2896 (vs) W+	3613 (vs) W	3521 (vs) W	3283 (vs) W	3396 (vs) W
7	1678 (m) W	1622 (s) W	1638 (w) W	3167 (vs) SOH	3136 (vs) SOH	2688 (vs) W+	3331 (vs) W	3419 (vs) W	3260 (vs) W	3148 (vs) W
8	1634 (m) W	1621 (vw) W	1590 (s) W	2704 (vs) SOH	3040 (vs) SOH	2576 (vs) W+	3319 (vs) W	3308 (vs) SOH	2815 (vs) W+	2926 (vs) W+
9	1478 (s) SOH	1438 (s) SOH	1436 (s)SOH	1667 (w) W	1655 (w) W	1784 (m) W+	2740 (vs) SOH	3209 (vs) W	2562 (vs) W+	2685 (vs) W+
10	1330 (s)	1377 (m) SOH	1330 (s)SOH	1631 (m) W	1638 (m) W	1740 (m) W+	2696 (vs) SOH	2862 (vs) SOH	2548 (vs) W+	2556 (vs) W
11	1156 (s)	1264 (s) SO	1250 (s)SO	1622 (m) W	1620 (m) W	1653 (w) W	1667 (w) W	1706 (w) W	1773 (w) W+	1793 (m) W
12	1130 (s)	1127 (s) SO	1110 (s)SO	1430 (s) SOH	1430 (s) SOH	1641 (m) W	1666 (w) W	1677 (s) W	1771 (w) W+	1758 (w) W+
13	984 (s)	893 (s)	888 (s)	1385 (m) SOH	1354 (s) SOH	1485 (vs) W+	1635 (m) W	1657 (m) W	1669 (vw) W	1685 (w) W
14	896 (s)	859 (s)	876 (s)	1262 (s) SO	1290 (s) SO	1202 (s) SOH	1630 (m) W	1635 (m) W	1656 (m) W	1650 (m) W
15	852 (m)	855 (vw)	799 (m)	1134 (s) SO	1106 (s) SO	1166 (s) SO	1475 (s) SOH	1436 (s) SOH	1652 (m) W	1644 (w) W
16	776 (s)	804 (m)	779 (w)	1091 (w)	958 (s)	1101 (s) SOH	1419 (s) SOH	1338 (s) SOH	1463 (s) W+	1381 (s) W+
17	607 (w)	546 (vw)	693 (s)	956 (s)	898 (s)	999 (s)	1265 (s) SO	1287 (s) SO	1224 (s) SOH	1209 (s) SOH
18	588 (s)	533 (s)	555 (w)	905 (s)	880 (m)	985 (s)	1135 (s) SO	1123 (s) SO	1148 (s) SO	1172 (s) SO
19	518 (w)	518 (s)	522 (w)	862 (w)	817 (m)	910 (m)	1095 (w)	1092 (w)	1128 (s) SO	1107 (s) SO
20	513 (m)	513 (w)	508 (w)	814 (m)	807 (vw)	835 (w)	1009 (s)	926 (s)	1071 (s)	1052 (s)
21	496 (w)	501 (s)	495 (w)	647 (s)	783 (s)	807 (s)	960 (s)	882 (s)	1067 (s)	1003 (s)
22	405 (s)	413 (vw)	440 (s)	540 (s)	673 (s)	761 (s)	937 (s)	862 (s)	1007 (s)	939 (w)
23	395 (m)	350 (vw)	393 (w)	529 (s)	528 (w)	746 (s)	913 (s)	814 (m)	881 (vw)	905 (w)
24	370 (vw)	342 (m)	369 (vw)	521 (w)	523 (m)	557 (m)	838 (w)	794 (m)	872 (vw)	849 (m)
25	301 (w)	331 (w)	355 (m)	518 (m)	516 (m)	544 (w)	681 (s)	751 (m)	825 (s)	799 (s)
26	273 (m)	241 (s)	342 (vw)	501 (w)	498 (w)	525 (m)	661 (s)	719 (s)	809 (s)	775 (s)
27	245 (m)	235 (m)	268 (s)	412 (w)	452 (w)	512 (w)	567 (m)	620 (w)	779 (s)	737 (m)
28	240 (m)	231 (w)	230 (w)	386 (w)	439 (s)	499 (s)	535 (m)	590 (s)	553 (vw)	577 (m)
29	228 (m)	226 (vw)	204 (vw)	368 (vw)	390 (vw)	419 (vw)	523 (w)	529 (w)	545 (m)	558 (w)
30	165 (w)	132 (m)	191 (w)	346 (s)	362 (w)	410 (vw)	516	528 (w)	542 (m)	541 (w)
31	108 (vw)	130 (vw)	131 (vw)	335 (w)	356 (m)	352 (m)	497 (m)	519 (w)	532 (w)	523 (m)
32	50 (vw)	41 (vw)	97 (vw)	296 (w)	298 (s)	327 (s)	424 (m)	507 (w)	523 (m)	498 (s)
33	25 (vw)	31 (vw)	56 (vw)	258 (s)	285 (m)	326 (s)	397 (vw)	492 (s)	517 (m)	466 (m)
34				241 (m)	255 (w)	292 (w)	391 (vw)	425 (m)	413 (vw)	430 (w)
35				230 (w)	231 (w)	249 (m)	367 (w)	399 (w)	403 (w)	384 (vw)
36				224 (m)	217 (w)	182 (w)	354 (s)	381 (m)	371 (vw)	379 (m)
37				170 (w)	204 (vw)	166 (vw)	337 (s)	365 (w)	353 (s)	333 (m)
38				129 (w)	178 (vw)	124 (vw)	299 (w)	317 (w)	352 (s)	319 (w)
39				113 (vw)	120 (vw)	117 (m)	292 (m)	291 (w)	327 (w)	290 (s)
40				53 (vw)	96 (vw)	90 (vw)	265 (m)	263 (m)	306 (m)	272 (w)
41				32 (vw)	41 (vw)	77 (vw)	258 (s)	253 (m)	297 (m)	258 (m)
42				26 (vw)	35 (vw)	50 (vw)	242 (w)	232 (w)	350 (m)	238 (m)
43							238 (m)	202 (vw)	195 (w)	197 (w)
44							199 (w)	197 (w)	183 (vw)	178 (w)
45							143 (vw)	162 (vw)	131 (m)	140 (m)
46							118 (vw)	141 (vw)	120 (vw)	118 (vw)
47							112 (vw)	121 (vw)	83 (vw)	88 (vw)
48							66 (vw)	94 (vw)	82 (vw)	82 (vw)
49							39 (vw)	70 (vw)	62 (vw)	70 (vw)
50							30 (vw)	57 (vw)	57 (vw)	31 (vw)
51							27 (vw)	44 (vw)	20 (vw)	26 (vw)

[a] Assignments: W, SOH, SO, and W+ denote the vibration related to H_2O, SOH, S═O, and H_3O^+ moieties, respectively. IR intensity vs, s, m, w, and vw denote very strong (>500), strong (>100), medium (>50), weak (>10), and very weak (<10), respectively.

of the sulfuric acid molecule exhibit the red-shift due to the hydrogen bonding to both sides of the H_2SO_4 molecule.

The IR spectrum of the most stable $n = 3$ cluster (III-n-a) is the simple overlap of the spectra of (I-n) and (II-n-a). In the case of proton transferred isomer (III-i-a), the OH stretchings of the hydronium ion appear in the region 2500∼2900 cm^{-1}. The similar situation can be seen in the IR spectra of $n = 4$ clusters.

In the case of $n = 5$ clusters, both ionic structures (V-i-a,b) and neutral isomer (V-n-a) give very similar spectral patterns. The SO−H stretching frequencies of the neutral cluster (V-n-a) are red-shifted more than 1000 cm^{-1} relative to those of bare H_2SO_4. These frequencies are in the same region with the OH stretchings of hydrogen-bonded H_3O^+ species. The hydrogen-bonded OH stretchings of water molecules in (V-n-a) also have frequencies similar to those of ionic clusters. The red-shift of the SO−H stretching of the hydrated clusters of cisoid H_2SO_4 is only 200 cm^{-1} as the cluster size increases. Overviewing the IR spectra of $n = 1-5$ clusters, there is no IR peak in the 1700−2500 cm^{-1} region except in the case of strained ionic clusters (III-i-e) and (V-i-c).

IV. Concluding Remarks

The hydration process of sulfuric acid involves many interesting aspects in the molecular level. Since the sulfuric acid has many binding sites for hydrogen bonding not only as the proton donor but also as the proton acceptor, the structures of the hydrated clusters of $[H_2SO_4(H_2O)_n]$ take various isomeric forms. Although main characteristics of the proton transferred and proton nontransferred clusters $[H_2SO_4(H_2O)_n]$ ($n = 1-5$) have been shown by Bandy and Ianni,[20] we have demonstrated that both neutral and ionic structures coexist in the range of $n = 1-5$ clusters according to the free energy calculation. There are two types of neutral clusters. The trans conformation of H_2SO_4 forms the structure in which two SOH groups independently participate in the hydrogen-bonding network. The cis conformation of H_2SO_4 takes the absorbed structure onto water clusters. The relative energies between two types of neutral hydrogen-

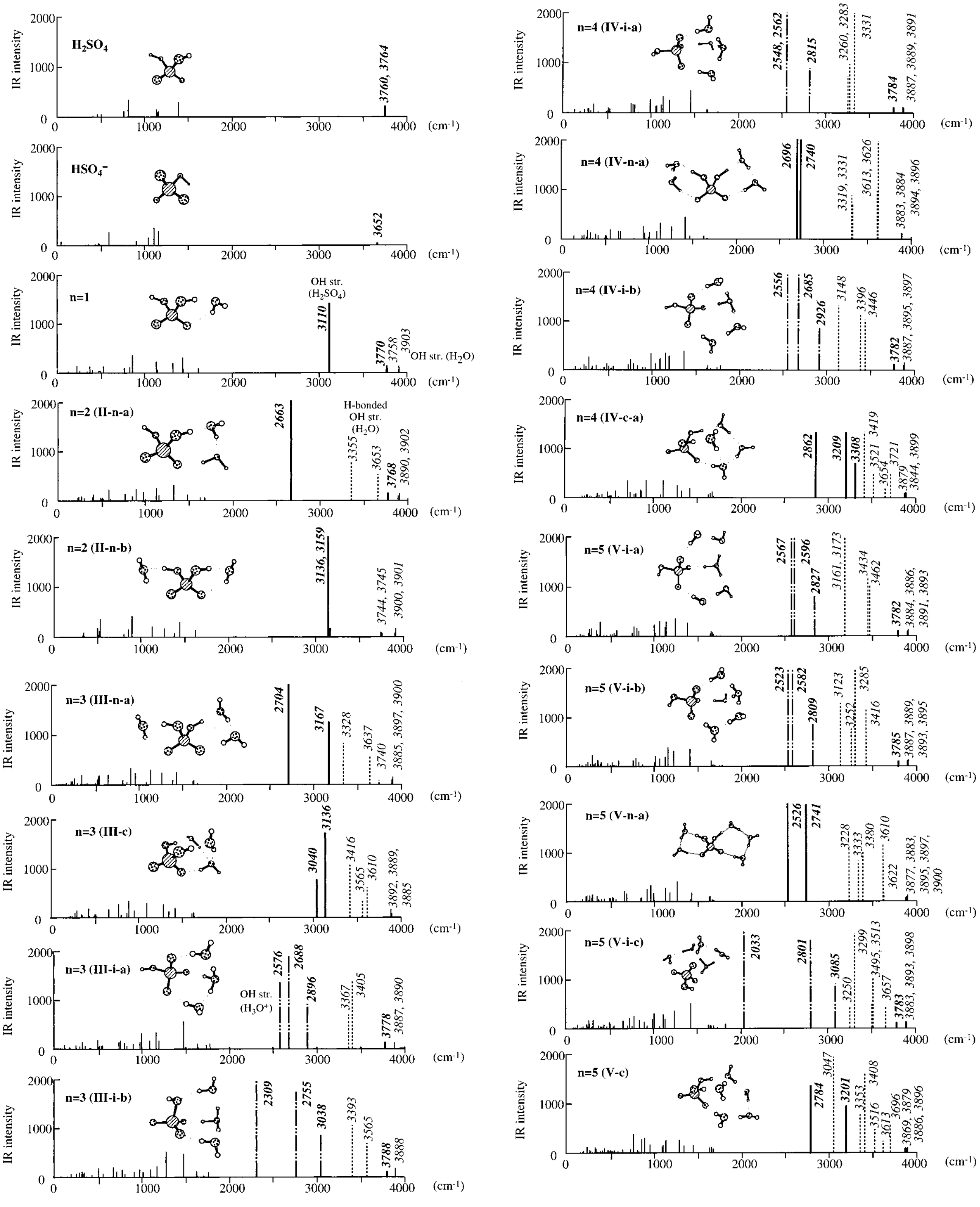


Figure 6. Predicted IR spectra of H_2SO_4, HSO_4^-, and several stable $H_2SO_4(H_2O)_n$ clusters (for $n = 1-5$) determined with the B3LYP/D95++(d,p) method.

bonded structures are not significantly different and lie within 3 kcal/mol. Furthermore, the relative energies in the case of the proton transferred ionic structures are not significantly different among the direct ion-pair $HSO_4^-H_3O^+(H_2O)_{n-1}$ and the indirect ion-pair $HSO_4^-(H_2O)_{n-1}H_3O^+$ structures. Consequently, various types of hydrated structures are expected to coexist in the aqueous H_2SO_4 solution. All of the stable structures of the $[H_2SO_4(H_2O)_n]$ clusters in both neutral and ionic forms tend to be stabilized by forming the hydrogen-bond network as many as possible. The theoretical IR spectra suggest that the O−H stretching frequencies of the sulfuric acid and water molecules exhibit significant red-shift due to the hydrogen bonding, while the O−H stretching frequencies of H_2SO_4 and H_2O moieties without hydrogen bonding remain in the 3800∼3900 cm^{-1} region. We can observe from the calculated IR spectra of $[H_2SO_4(H_2O)_n]$ clusters ($n = 1-5$) that there are three spectral regions, non hydrogen-bonded OH stretching (3800−3900 cm^{-1}), hydrogen-bonded OH stretching of water molecules (3100−3600 cm^{-1}), and the hydrogen-bonded OH stretching of H_3O^+ moiety (2500−2900 cm^{-1}). The predicted IR spectra of each hydrated H_2SO_4 cluster will be helpful to identify the species of aerosol formation and nucleation of atmospheric sulfate particles as well as to understand the nature of hydrogen bonding of aqueous solutions of sulfuric acid.

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