Sulfuric Acid and Sulfuric Acid Hydrates in the Gas Phase: A DFT Investigation[†]

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The gaseous sulfuric acid and its hydrates play an essential role in the formation and evolution of atmospheric aerosols via nucleation of binary sulfuric acid−water vapors. Recently, it has been pointed out that the dipole moment of vapor molecules and small preexisting clusters is a new parameter controlling the nucleation rates. In this paper, the dipole moments of the mono-, di-, and trihydrates of the sulfuric acid are calculated for the first time. We also report on the molecular structures, energies, vibrational frequencies, absorption intensities and dipole moments of the hydrates and compare our model predictions with the results of other studies. The density functional theory (DFT) calculations have been carried out using the PW91 method and TZP basis set. We have determined the optimized conformations of gas-phase sulfuric acid and mono-, di-, and trihydrates of sulfuric acid using different starting scenarios and computed their dipole moments. The obtained results can be utilized directly in the modeling of the atmospheric aerosol formation and they are applied for the analysis of the hydration thermodynamics.

Introduction

Sulfuric acid is one of the key substances controlling the aerosol and cloud formation in the Earth's atmosphere.[1] In humid air gas-phase sulfuric acid tends to form hydrates, small clusters consisting of a few water molecules associated with the sulfuric acid molecule. Most of the sulfuric acid molecules in the atmosphere are likely hydrated, and consequently, the hydration significantly influences the nucleation rates.[1] Although the nucleation has been studied in detail in the past, there are still major uncertainties concerning the nucleation mechanisms in the atmospheric conditions and laboratory experiments because the measured nucleation rates often deviate from the theoretical estimations by several orders of magnitude. Different reasons for the observed deviations, including a limited validity of the capillarity approximation, inaccurately measured surface tension and kinetic limitations, have been discussed in the literature, yet the major sources of the uncertainties are not clearly identified. Recently, it has been pointed out that the incomplete description of the interactions between vapor molecules and molecular clusters in the nucleating vapors are a new essential source of the discrepancies.[2,3] It is well-known that both the classical homogeneous and ion-induced nucleation theories largely ignore the microphysical properties of the vapor molecules and molecular clusters and that the uptake mechanism in these theories is reduced to simple mechanical collisions. Recently, we have pointed out that such properties as size and dipole moment of the vapor molecules and preexisting clusters significantly affect both the thermodynamics of the cluster formation and kinetics in the ion-induced nucleation (IIN) and kinetic interactions in the ion-mediated nucleation (IMN).[2−5] Homogeneous nucleation in the polar vapors is somewhat similar to the ion-induced nucleation in the sense that polar vapor molecules may also be involved in the molecular dipole-polar cluster or/and molecular dipole−induced dipole interactions.

To quantify the effect of the dipole-cluster interactions on the nucleation rates, one has to determine the electric dipole moments of the vapor molecules and small molecular clusters, which are the key parameters controlling both the free energy of the cluster formation and kinetic interactions associated with the uptake efficiency. Because most of the sulfuric acid in the Earth's atmosphere is hydrated and the hydration is accompanied by changes in the dipole moment, the determination of the dipole moments mono-, di- and trihydrates of the sulfuric acid, which are the most common forms of the sulfuric acid in the atmosphere, is necessary.

The purpose of this paper is to investigate the electric properties of different equilibrium structures of gas-phase sulfuric acid and mono-, di-, and trihydrates of the sulfuric acid. Although the paper is focused mainly on the values of the dipole moments, we have, to justify the obtained results, reported the equilibrium structures and their properties and compare our model predictions with the results of other studies. The computations are carried out using the PW91 method[7] for exchange correction and correlation parts, in conjunction with the VWN formal version 5 of local density approximation (LDA),[8] and the TZP[9] basis set. To ensure the validity and estimate the accuracy of the results obtained, we applied six different high-level density functional methods specifically PW91, Becke−Perdew,[10,11] BLYP,[10,12−14] PBE,[15] RPBE,[15,16] and revised PBE[15,17] for the exchange correction and correlation

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parts, and the VWN formal version 5 of LDA and performed the computations employing the following basis sets DZ, DZP, TZP, TZ2P, ET-pVQZ, and ET-QZ3P-1DIFFUSION.[9,18,19] The total bonding energy will be used to verify the degree of stability of the minima structures.

Approach and Methods

The density functional theory (DFT) technique seems to be a relevant and precise tool for studies of cluster formation at the molecular scale because it is able to reproduce the experimental structure of a variety of molecules and complexes with quite high precision. Recent studies for hydrogen bonded systems show that DFT methods give accurate thermodynamic characteristics of hydrogen bonding.[20−30]

In the past, the calculations of the hydrogen bonded structures have been performed using the B3LYP[12,31] functional;[27,32−34] however, a number of recent and careful investigations of nonbonded interactions have shown that the B3LYP functional does not provide a complete picture of the nonbonded interactions. This has been illustrated through calculations of the structural data and energies of nonbonded interactions.[34−37] Furthermore, these investigations have shown clearly that the functional B3LYP does not give a reliable representation of the nonbonded interactions, whereas the functional PW91 seems to be a better candidate.[34−37] In ref 34 Tsuzuki et al. have shown that the intermolecular interaction potentials for hydrogen bonded and van der Waals systems were repulsive when calculated with the B3LYP functional. Moreover, the B3LYP potential has the same problems in describing the dispersion interactions as the Hartree−Fock (HF) method. On the other hand, Tsuzuki et al.[34] showed that the interaction potentials calculated using the PW91 exchange and correlation functional are attractive and that the results agree with the studies[38,39] based on the second-order Møller−Plesset perturbation (MP2) model. It has been pointed out[34] that the PW91 exchange and correlation functional are able to reproduce the structures and intermolecular interactions energies, which are similar to those obtained using MP2 method.

To study the structure and subsequent properties of sulfuric acid associated with 1−3 water molecules, the PW91 method, which was originally proposed by Perdew and Wang,[7] have been employed. The PW91 method includes both the exchange correction and correlation parts as the generalized gradient approximation (GGA) part of the density function and the VWN formal version 5 as the local density approximation (LDA) part. Five other DFT methods (Becke−Perdew, BLYP, PBE, RPBE, and revised PBE) have been used as the GGA part of the density function and the VWN formal version 5 in the LDA part to determine the sensitivity of the calculated structural data and molecular properties to the method used.

The Becke−Perdew method has the exchange part by Becke[10] and the correlation part from Perdew.[11] The BLYP method combines the exchange part produced by Becke[10] and the correlation part by Lee et al.,[12−14] assuming pureexchange form of LDA. The PBE method consists of both the exchange correction and correlation sections produced by Perdew et al.[15] The RPBE method includes the exchange correction part produced by Hammer−Hansen−Norskov[16] and the correlation part formalized by Perdew et al.[15] The revised PBE includes the exchange correction suggested by Zhang et al.[17] and the correlation part produced by Perdew et al.[15]

For the calculations of the structures and properties of the sulfuric acid and its hydrates the TZP[9] basis set, which has been proven to be a high quality basis set with low average and absolute errors according to tests conducted in refs 9 and 18, has been employed. We have investigated the sensitivity of the results to the quality of the basis set, by performing calculations using the basis sets DZ, DZP, TZP, TZ2P, ET-pVQZ and ET-QZ3P-1DIFFUSION.[9,18] The structures of the sulfuric acid and its hydrates were optimized and equilibrium structures with real and positive frequencies were obtained. The energy is converged to 1×10^{-7} hartrees, root mean square (RMS) and maximum force of at least 6.6×10^{-4} and 1×10^{-3} hartrees/Å, respectively, and RMS and maximum displacement steps at 6.6×10^{-2} and 1×10^{-1} Å as threshold criteria. The harmonic frequencies were computed by numerical differentiation of energy gradients in slightly displaced geometries.[40,41] The computations are performed using the Amsterdam density functional (ADF) software package version 2002.03.[42−44]

TABLE 1: Comparison of Different DFT Methods Applied with the TZP Basis Set for the Computations of the Electrical Dipole Moments and Total Bonding Energy of the S−t Structure of the Gas-Phase Sulfuric Acid

method	dipole moment (Debye)	total bonding energy (kcal/mol)
BLYP	2.7615	−808.31
RPBE	2.7545	−824.38
rev.PBE	2.7637	−828.17
Becke−Perdew	2.7943	−847.88
PBE	2.7938	−857.98
PW91	2.8165	−860.78

TABLE 2: Comparison of Different Basis Sets Applied for the Computations of the Electrical Dipole Moments and Total Bonding Energy of the S−t Structure of the Gas-Phase Sulfuric Acid by the PW91 Method

basis set	dipole moment (Debye)	total bonding energy (kcal/mol)
DZ	2.4509	−637.70
DZP	2.8316	−851.75
TZP	2.8165	−860.78
TZ2P	2.9220	−876.63
ET-pVQZ	2.9356	−881.73
ET-QZ3P+1D.	2.8897	−884.35

Results and Discussion

Structure and Properties of Gas-Phase Sulfuric Acid [H_2SO_4]. We have computed several possible structures of gas-phase sulfuric acid and calculated their dipole moments, vibrational transitions, and values of the total bonding energy (E_{TB}).[6] The total bonding energy has been defined as the difference in energy between the molecule as whole and the constituent atoms $E_{TB} = \Delta E_{elstat} + \Delta E_{kin} + \Delta E_{coul} + \Delta E_{xc}$, where E_{elstat} is the electrostatic energy, E_{kin} is the kinetic energy, E_{coul} is the coulomb energy including the steric and orbital interaction energies and E_{xc} is the exchange-correlation energy.

Method and Basis Investigations. To estimate the accuracy of the results, we have investigated the sensitivity of the results with respect to the 1-electron basis set and density functional method. We have performed calculations of the dipole moment and total bonding energies of the structure S−t of sulfuric acid employing the following six GGA methods PW91, Becke-Perdew, PBE, RPBE, revised PBE and BLYP and the VWN v.5 as the LDA part and furthermore and we also calculated the same quantities using the PW91 method with six different 1-electron basis sets. The obtained results are summarized in Tables 1 and 2.

Comparison of the results presented in the Table 1 shows that all the above methods give close values of the dipole moment whereas the total bonding energy deviates significantly

TABLE 3: S−t Structure Details Computed by Different Methods and the TZP Basis Set, Where *R* Is the Bond Length in Å, ∠ Is the Angle in Degrees, and τ Is the Dihedral Angle in Degrees

method	BLYP	BP	PBE	RPBE	rev PBE	PW91	exptl
R(O1−H)	0.983	0.982	0.982	0.982	0.981	0.980	0.97 ± 0.01
R(S−O1)	1.648	1.630	1.629	1.641	1.638	1.626	1.574 ± 0.01
R(SO2)	1.450	1.443	1.443	1.448	1.447	1.441	1.422 ± 0.01
∠(H−O1−S)	106.8	106.5	106.4	106.1	106.2	106.5	108.5 ± 1.5
∠O1−S−O1)	102	102.2	102.2	102.2	102.2	102.3	101.3 ± 1
∠(O2−S−O2)	125.1	125.1	125.1	125.1	125.1	125.0	123.3 ± 1
τ(H−O1−S−O2)	26.5	26.0	26.0	26.5	26.5	25.4	20.8 ± 1
τ(H−O1−S−O1)	−84.1	−84.7	−84.7	−84.1	−84.2	−85.1	−90.9 ± 1

TABLE 4: Dipole Moments and Total Bonding Energies of the Gas-Phase Sulfuric Acid Calculated by the PW91 Method with the TZP Basis Set

structure type	dipole moment (Debye)	total bonding energy (kcal/mol)
S-t	2.817	−860.78
S-c	3.643	−859.70

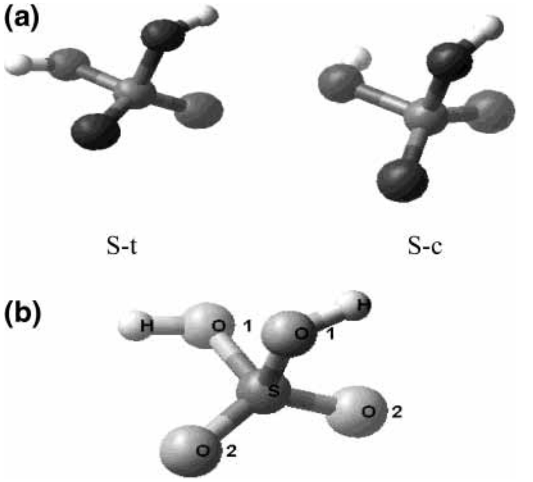


Figure 1. (a) Molecular geometries of sulfuric acid. (b) Indexes for the sulfuric acid geometry.

varying from −808.31 to −860.78 kcal/mol. As may be seen from Table 1, the PW91 method gives consistent results compared with the other methods, which indicates that this method is rather optimal for the present study of hydrogen bonding complexes.

Table 2 presents the comparison of the results obtained using the PW91 model with different basis sets. As seen from Table 2, the influence of the size of the basis set on the values of the dipole moment and total bonding energy is quite strong. Although the variations of dipole moments and especially bonding energies are significant, the values obtained using five out of six basis sets are quite close. Considering the precision, cost of calculations, convenience, and applicability of the basis set for the future investigations of the H_2SO_4 hydrates, we have chosen the TZP basis set. Among the basis sets the TZP basis set leads to a dipole moment that is close to the experimental value (2.725 D).[45] On the basis of the sensitivity study, we have selected the PW91 as the method and TZP as the basis set for the investigation of the hydrated H_2SO_4 complexes.

We have also conducted a sensitivity study of S−t sulfuric acid conformation. Table 3 presents the structural details of the S−t molecular geometry computed by six DFT methods. As seen from Table 3, values obtained using different methods are in good agreement with each other and at the same time the PW91 method has the best agreement with the experimental data.

Dipole Moments of Sulfuric Acid. The calculations indicated the presence of two equilibrium structures of gas-phase sulfuric acid. The dipole moments and the total bonding energies of the obtained equilibriums are presented in Table 4, and the corresponding structures are given in Figure 1a. As seen from Table 4, the S−t conformation is the trans configuration of sulfuric acid and the value of the dipole moment for this conformation is in good agreement with the experimental study by Kuczkowski et al.[45]

The second equilibrium structure is the cis configuration, which has a higher dipole moment than the trans conformation due to the orientation of the O−H groups. The dipole moment of the O−H group (1.608 D) calculated with the PW91 method and ET-pVQZ basis set in the present study is a slightly larger (by ∼0.1 D) than that estimated from the experimental data (∼1−1.5 D [45]).

Sulfuric Acid Structural Data. We have investigated the sulfuric acid molecular structure and the geometries of the two minima have been identified. The trans structure has the lower total bonding energy and the cis structure has a slightly higher energy with less than 1 kcal/ mol.

Figure 1a presents the different molecular structures of sulfuric acid, Figure 1b shows the indexes for the sulfuric acid geometry, and Table 5 provides a detailed geometrical analysis of the sulfuric acid structures in addition to the two earlier

TABLE 5: Comparison of the Sulfuric Acid Geometry Computed in This Paper with Other Theroretical Studies and the Experimental Data

	S-a	Re et al.	Bandy et al.	S-c	Re et al.	exptl
basis set	TZP	D95++(d, p)	6-311++G(2d,2p)	TZP	D95++(d, p)	
shape	(trans)			(cis)		(trans)
method	PW91	B3LYP		PW91	B3LYP	
R(O1−H), Å	0.980 0.981	0.975	0.968	0.98	0.975	0.97 ± 0.01
R(S−O1),Å	1.626	1.634	1.609	1.626	1.643 1.621	1.574 ± 0.01
R(SO2), Å	1.441	1.456	1.429	1.443	1.464	1.422 ± 0.01
∠(H−O1−S), deg	106.5		108.3	106.4		108.5 ± 1.5
∠O1−S−O1), deg	102.3			101.9		101.3 ± 1
∠(O2−S−O2), deg	125			124.9		123.3 ± 1
τ(H−O1−S−O2), deg	25.4			18.6		20.8 ± 1
τ(H−O1−S−O1), deg	−85.1			−94.9		−90.9 ± 1

TABLE 6: the Vibrational Frequencies of Different Sulfuric Acid Molecular Structures[a]

	assignment	S-t		S-c	
1	SO—H sym (str)	3632	(m)	3643	(s)
2	SO—H asym (str)	3627	(s)	3636	(m)
3	S═O asym (str)	1426	(s)	1426	(s)
4	S═O sym (str)	1160	(s)	1172	(s)
5	SO—H asym (bend)	1153	(m)	1133	(w)
6	SO—H sym (bend)	1138	(m)	1124	(m)
7	S—O asym (str)	801	(s)	804	(s)
8	S—O sym (str)	745	(s)	744	(m)
9		513	(w)	514	(w)
10		499	(w)	499	(w)
11		463	(w)	466	(vw)
12		413	(w)	398	(w)
13		341	(vw)	349	(m)
14		321	(w)	323	(w)
15		221	(m)	105	(w)

[a] Abbreviations: sym, symmetric; asym, antisymmetric; str, stretching; bend, bending.

theoretical studies conducted by Re et al.,[27] Bandy et al.,[33] and the experimental study by Kuczkowski et al.[45]

As seen from Table 5, the bond lengths obtained in this study are in better agreement with the measurements of Kuczkowski et al.[45,46] than the earlier study by Re et al.[27] in which the B3LYP method and the D95++(d,p) basis set have been used. The study accomplished by Bandy et al.[33] is in best agreement with the experimental data.

The change in the O—H group orientation leads to an adaptation in the symmetry of the molecular structure of the sulfuric acid from a trans C_2 symmetry to a cis C_1 symmetry, which is less stable and higher in energy.

The inward and the outward movement of the O—H groups govern the structure of the sulfuric acid molecular. The energy barrier of the inward rotation has been calculated to be 3 kcal/mol for the trans structure by Re et al.[27] and also they predict a similar value of the outward rotation for the cis structure.

Vibrational Frequencies of Sulfuric Acid. Tables 6 and 7 show a comparison of the vibrational frequencies of the sulfuric acid molecular structures obtained in this study with the earlier experimental and theoretical values.

It may be seen from Table 7 that the vibrational frequencies calculated in this study are in good agreement with the experimental values. The symmetric and antisymmetric stretching of $\nu_{\mathrm{SO-H}}$ are in better agreement with the recent experimental values determined by Hintz et al.[30] than the other studies.[27,30] We obtained the same value of the $\nu_{\mathrm{SO-H}}$ symmetric bending vibrational frequency 1138 cm^{-1} as the measurement done by Chackalackal et al.[48] and a value of the $\nu_{\mathrm{SO-H}}$ antisymmetric bending vibrational frequency, with about 4 cm^{-1} difference, very close to the measurements done by Hintz et al.[30] It is

TABLE 7: Vibrational Frequencies for the Sulfuric Acid

					calcd				
	exptl							this work	
	Hintz[a]	Shingaya[b]	Chackalackal[c]	Stopperka[d]	Hintz[a]	Re[e] (trans)	Re[e] (cis)	S-t (trans)	S-c (cis)
mehod					B3LYP	B3LYP	B3LYP	PW91	PW91
basis set					6-311++G(2d,2p)	D95++(d,p)	D95++(d,p)	TZP	TZP
SO—H sym (str)	3609				3769	3764	3711	3632	3643
SO—H asym (str)	3609				3773	3760	3763	3627	3636
S═O asym (str)	1464	1364	1450	1456	1437	1148	1148	1426	1426
S═O sym (str)	1220	1181	1223	1224	1185	1140	1118	1160	1172
SO—H asym (bend)	1157	1055	1159	1160	1184	1393	1374	1153	1133
SO—H sym (bend)		992	1138	1141	1174	1155	1181	1138	1124
S—O asym (str)	891		883	882	831	819	822	801	804
S—O sym (str)	834		834	831	775	764	761	745	744

[a] Reference 30. [b] Reference 47. [c] Reference 48. [d] Reference 49. [e] Reference 27.

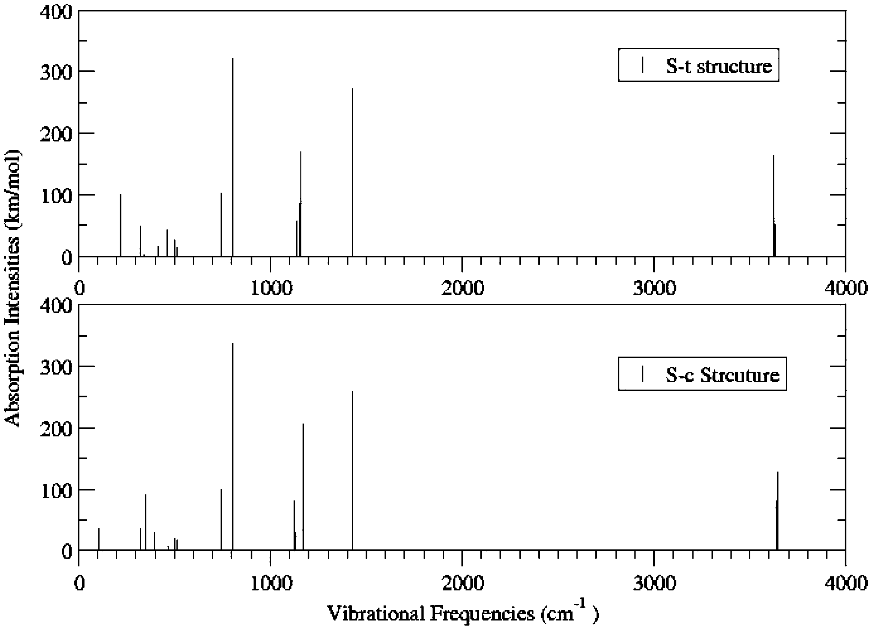


Figure 2. Vibrational frequencies and abosption intensities of the diferent conformations of the sulfuric acid.

TABLE 8: Dipole Moments and Total Bonding Energies of Sulfuric Acid Monohydrate, Calculated Using the PW91 Method and TZP Basis Set

structure type	dipole moment (Debye)	total bonding energy (kcal/mol)
SW-a	2.147	−1202.49
SW-b	2.393	−1202.46
SW-c	3.411	−1200.59

important to note that most of the vibrational frequencies produced by the PW91 method are in better agreement with experimental data than the B3LYP except for the ν_{S-O} stretching, for which the B3LYP method provides a slightly better agreement.

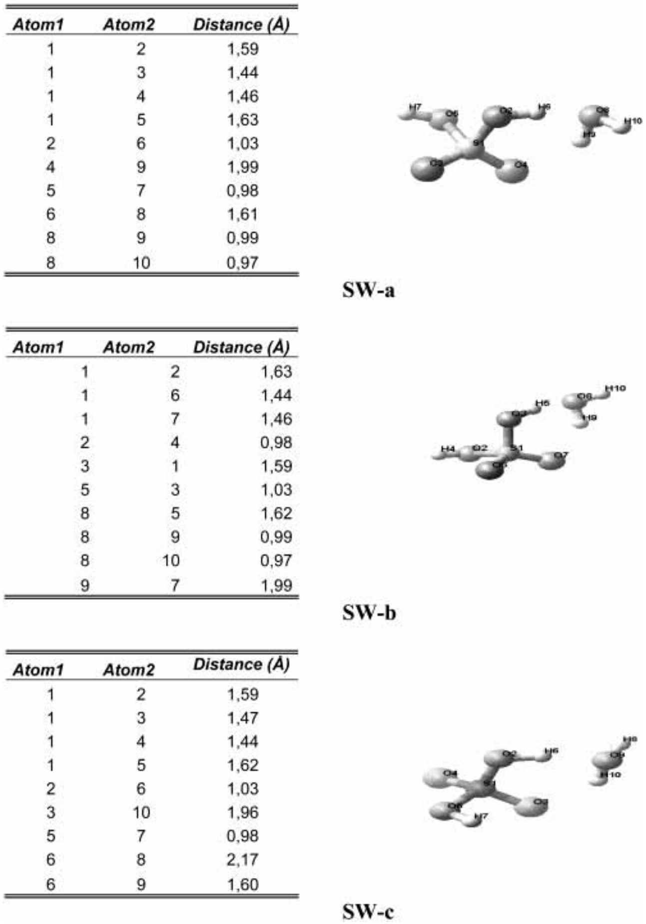
We have calculated the absorption intensities of different sulfuric acid molecular conformations. As seen from Figure 2 the highest absorption intensities belong to the ν_{S-O} antisymmetric vibrational frequency and then to the $\nu_{S=O}$ antisymmetric vibrational stretching.

Furthermore, the absorption intensity of the SO−H stretching bands of the S−t molecular geometry is 164 km/mol, which is consistent with the experimental value 180 km/mol determined by Hintz et al.,[30] which corresponds to the transition at 3627 cm^{-1}. The absorption intensity calculated in this study agrees better with the expermental data than the predictions of the other theoretical studies.[27,30] Hintz et al.[30] calculated the absorption intensities for sulfuric acid using B3LYP/ 6-311++G(2d,2p), QCISD/ 6-311++G(2d,2p) and HF and obtained 205, 210, and 353 km/ mol, respectively. The comparison of the obtained results shows that the PW91 method is an appropriate method for studying the structures and properties of H_2SO_4.

Structures and Properties of Gas-Phase Sulfuric Acid Monohydrate Cluster [$H_2SO_4(H_2O)$]. *Dipole Moments of Sulfuric Acid Monohydrates.* Figure 3 shows the monohydrate of the sulfuric acid has three different structures, whereas earlier studies[27,33] could identify only two conformations. We have optimized the molecular structures and obtained positive values of the vibrational frequencies, thereby, verifying the location of the equilibrium structures. In Table 8 we present the dipole moments and total bonding energies values for monohydrates.

As seen from Table 8, the dipole moments of the monohydrates vary significantly with the structure. Comparison of the dipole moments of S−t and S−c with SW-a, SW-b, and SW-c shows that the difference in the electric properties of monohydrates is related to the variations in the structure of the gas-phase sulfuric acid whereas the influence of the water molecules seems to be minor. We have calculated the water dipole moment value as 1.813 D using the PW91 method and ET-pVQZ basis set, and the obtained value is quite close to the experimental value, which is 1.85 D.[50] It is important to note that the electric properties of the monohydrates formed from the S−t and S−c structures are different. Therefore, we conclude that the geometry of the gas-phase sulfuric acid is a dominating factor.

Structural Data of Sulfuric Acid Monohydrates. Figure 3 presents the detailed molecular structure of different conformations of the sulfuric acid monohydrate. SW-a and SW-b structures are quite similar with a slight difference in the bond length between H6−O8 in the SW-a structure and H5−O8 in the SW-b structure, in addition to the difference in orientation of the hydrogen bond of the water molecule. This minor difference leads to a slight variation of the energy for these structures. On the other hand, we find that the corresponding bond in the SW-c structure is shorter than that in the other two structures.



Atom1	Atom2	Distance (Å)
1	2	1,59
1	3	1,44
1	4	1,46
1	5	1,63
2	6	1,03
4	9	1,99
5	7	0,98
6	8	1,61
8	9	0,99
8	10	0,97

SW-a

Atom1	Atom2	Distance (Å)
1	2	1,63
1	6	1,44
1	7	1,46
2	4	0,98
3	1	1,59
5	3	1,03
8	5	1,62
8	9	0,99
8	10	0,97
9	7	1,99

SW-b

Atom1	Atom2	Distance (Å)
1	2	1,59
1	3	1,47
1	4	1,44
1	5	1,62
2	6	1,03
3	10	1,96
5	7	0,98
6	8	2,17
6	9	1,60

SW-c

Figure 3. Detailed molecular structure of monohydrates.

TABLE 9: Comparison of the Experimental Data by Fiacco et al.[51] and Theoretical Values of Monohydrate Structures Preducted by Re et al.[27] and This Study

parameter, Å	exptl[51]	theo[27]	this work (SW-a)
R(O1−H1)	1.04(1)	1.009	1.03
R(O2−H2)	0.95	0.975	0.98
R(S−O1)	1.567(1)	1.603	1.59
R(S−O2)	1.578(3)	1.636	1.63
R(S−O3)	1.464(1)	1.466	1.46
R(S−O4)	1.410(4)	1.458	1.44
R(H6−O8)	1.645(5)		1.61

As seen from Table 9, which presents the detailed picture of the molecular structure of the monohydrates, the bond lengths calculated in this study are in very good agreement with the experimental data by Fiacco et al.[51] and they are in better agreement with those of Fiacco et al.[51] than with the earlier study by Re et al.[27] where the B3LYP method has been applied.

Vibrational Frequencies of Sulfuric Acid Monohydrates. Figure 4 and Table 10 present the calculated vibrational frequencies and the corresponding absorption intensities of the monohydrates of sulfuric acid.

As may be seen from Figure 4 and Table 10 that the hydrogen bonded S−OH stretching frequency of the sulfuric acid monohydrates appears at 2771 cm^{-1}, which leads to a red-shift of 860 cm^{-1} from the sulfuric acid molecule; however, the frequency of the other non hydrogen bonded S−OH stretching remains almost unchanged (3638 cm^{-1}). Results of this study are in good agreement with the study by Re et al.[27] and experimental work of Givan et al.[52] Givan et al.[52] performed the experimental study of [$H_2SO_4 \cdot H_2O$] trapped in an argon matrix at 5 K, and they did not report any strong peak for SO−H stretching of hydrogen bonds near 2771 cm^{-1}. The assigned peak (3638 cm^{-1}) is located near the (non hydrogen bonded)

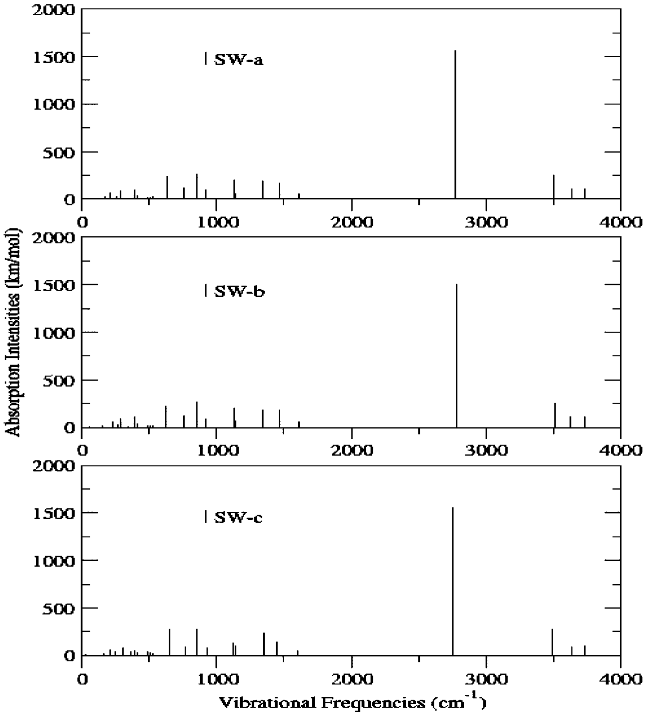


Figure 4. Vibrational frequencies and the corresponding absorption intensities of different conformations of the sulfuric acid monohydrate.

TABLE 10: Vibrational Frequencies of Different Conformation of Sulfuric Acid Monohydrate

	assignment	SW-a	SW-b	assignment	SW-c
1		48 (vw)	55 (vw)		30 (vw)
2		167 (w)	155 (w)		160 (w)
3		212 (m)	228 (m)		204 (m)
4		258 (w)	263 (w)		249 (w)
5		284 (m)	286 (m)		304 (m)
6		339 (vw)	345 (vw)		359 (w)
7		389 (m)	391 (s)		387 (m)
8		411 (w)	412 (w)		407 (w)
9		491 (w)	488 (w)		489 (w)
10		509 (w)	509 (w)		510 (w)
11		527 (w)	525 (w)		530 (w)
12	W	635 (s)	624 (s)	W	646 (s)
13	S−OH	761 (s)	759 (s)	S−OH	768 (m)
14	S−OH	856 (s)	853 (s)	S−OH	848 (s)
15	SO−H	917 (m)	920 (m)	SO−H	930 (m)
16	S−OH	1131 (s)	1131 (s)	S−OH	1121 (s)
17	SO−H	1140 (m)	1144 (m)	SO−H	1144 (s)
18	SO−H	1343 (s)	1343 (s)	S−OH	1351 (s)
19	SO−H	1467 (s)	1469 (s)	SO−H	1452 (s)
20	W	1607 (m)	1606 (m)	W	1601 (m)
21	SO−H	2771 (vs)	2778 (vs)	SO−H	2757 (vs)
22	W	3508 (s)	3509 (s)	W	3495 (s)
23	SO−H	3638 (s)	3631 (s)	SO−H	3638 (m)
24	W	3730 (s)	3734 (s)	W	3731 (s)

SO−H stretching frequency 3572.6 cm^{-1}. On the other hand, the calculated IR spectra of SO−H hydrogen bonded in this study is 2771 cm^{-1}, which is very close to the O−D IR-spectral peak assigned by Givan et al.[52] (2634.6 cm^{-1}). This possible mixing of IR-spectral peaks can be traced back to the complicated condition of the experiment due to both multicomponent composition of the vapor phase and the formation in the argon matrix, as has been reported by Givan et al.[52]

Structures and Properties of Gas-Phase Sulfuric Acid Dihydrate Cluster [$H_2SO_4(H_2O)_2$]. *Dipole Moments of the Sulfuric Acid Dihydrates.* We have optimized the structures of the sulfuric acid dihydrates and obtained 13 different equilibrium structures whereas the earlier studies[33,27] report only on 2 and 5 structures, respectively. All the equilibrium structures have been obtained with real values of the vibrational frequencies. Figure 5 illustrates the structures of the dihydrates and Table 11 presents the corresponding values of the dipole moments and total bonding energies.

TABLE 11: Dipole Moments and Total Bonding Energies of Di-hydrates of the Sulfuric Acid, Calculated Using the PW91 Method and the TZP Basis Set

structure type	dipole moment (Debye)	total bonding energy (kcal/mol)
S2W-a	2.423	−1543.90
S2W-b	3.257	−1543.25
S2W-c	3.302	−1543.11
S2W-d	3.346	−1543.02
S2W-e	3.688	−1542.98
S2W-f	2.988	−1542.17
S2W-g	6.303	−1541.57
S2W-h	3.770	−1541.03
S2W-i	3.148	−1540.73
S2W-j	3.684	−1540.23
S2W-k	3.396	−1534.09
S2W-l	4.745	−1533.39
S2W-m	2.514	−1532.7Y

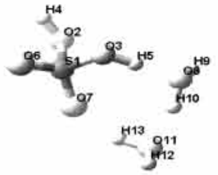
As seen from Table 11, the dipole moments of the dihydrates vary within a quite wide range from 2.423 D for the S2W-a structure to 6.303 D for the S2W-g structure. For the S2W-a conformation, where the hydrogen bonds form a ring with the trans sulfuric acid, reduction of the dipole moment due to the opposite directions of the dipole moment of water molecules is observed. The configuration of the two water molecules in this conformation is the most stable configuration, and that is supported by Gregory et al.[53] S2W-g is close to forming a ring with the O−H groups in the cis sulfuric acid, which is oriented almost in the same direction as the oxygen atoms in the water molecules attracted by the sulfuric acid. This leads to a very large dipole moment of this configuration. The third distinguishable feature is that the two water molecules are not bonded together and both of them are only bonded to the sulfuric acid molecule such as in the S2W-f, S2W-i, S2W-j, and S2W-l structures. The dipole moments in these conformations vary depending on the location and orientation of the water molecules, but generally the oxygen atom in the water molecule is bonded with one of the hydrogen atoms in the sulfuric acid, and thus, the orientation of the water molecule is the dominating factor.

In the rest of the group, including the conformations with the highest (S2W-m) and the lowest (S2W-a) total bonding energies, the dipole moments vary strongly from 2.514 to 4.745 D. It is important to note that despite the wide variations of the dipole moments the total bonding energies are very close. Comparison of the dipole moments given in Table 11 does not indicate clear correlation between properties of the gas-phase sulfuric acid or water molecules and dihydrates formed. This means that both the sulfuric acid and the water molecules are responsible for the properties of the dihydrates.

Sulfuric Acid Dihydrates Structural Data. Figure 5 presents the optimized structural data of the 13 sulfuric acid dihydrates complexes. The structures are ranked according to their stability, which is based on their total bonding energy. The structures can be divided into three groups. Structures from first group, where the water dimer and one of the O−H groups of the sulfuric acid form a hydrogen bonded cyclic ring structure, feature a similar orientation of the O−H groups in the water dimer. The S2W-a structure is the most stable and it has the shortest and strongest hydrogen bonds between the SO−H···OH_2 and the hydrogen bond between the water

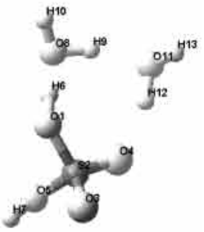
Atom1	*Atom2*	*Distance (Å)*
1	2	1,64
1	3	1,57
1	6	1,45
1	7	1,46
2	4	0,98
3	5	1,07
5	8	1,46
7	13	1,79
8	9	0,97
8	10	1,02
10	11	1,63
11	12	0,97
13	11	0,99

S2W-a



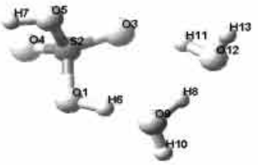
Atom1	*Atom2*	*Distance (Å)*
1	6	1,06
2	1	1,57
2	3	1,45
2	4	1,46
2	5	1,63
5	7	0,98
8	6	1,47
8	9	1,01
8	10	0,97
9	11	1,65
11	12	0,99
11	13	0,97
12	4	1,79

S2W-b



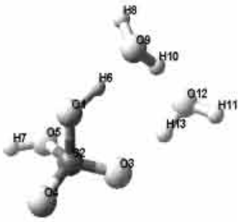
Atom1	*Atom2*	*Distance (Å)*
1	6	1,07
2	1	1,57
2	3	1,46
2	4	1,44
2	5	1,63
5	7	0,98
6	9	1,46
8	12	1,63
9	8	1,02
9	10	0,97
11	3	1,79
12	11	0,99
12	13	0,97

S2W-c



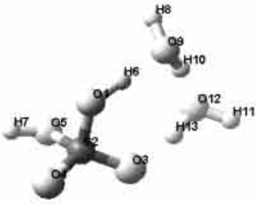
Atom1	*Atom2*	*Distance (Å)*
1	6	1,06
2	1	1,57
2	3	1,46
2	4	1,44
2	5	1,64
5	7	0,98
6	8	2,03
6	9	1,47
6	10	2,02
9	8	0,97
9	10	1,01
12	10	1,64
12	11	0,97
12	13	0,99
13	3	1,79

S2W-d



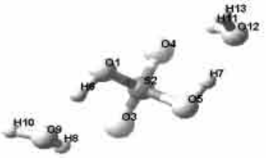
Atom1	*Atom2*	*Distance (Å)*
1	6	1,07
2	1	1,57
2	3	1,46
2	4	1,44
2	5	1,64
3	13	1,79
5	7	0,98
6	8	2,03
6	9	1,47
6	10	2,00
9	8	0,97
9	10	1,01
12	11	0,97
13	12	0,99

S2W-e



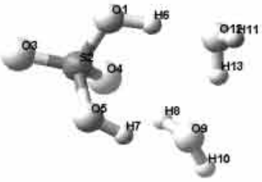
Atom1	*Atom2*	*Distance (Å)*
1	6	1,03
2	1	1,60
2	3	1,46
2	4	1,46
2	5	1,59
3	8	1,99
5	7	1,03
6	9	1,62
8	6	1,88
11	4	2,00
12	7	1,64
12	13	0,97

S2W-f



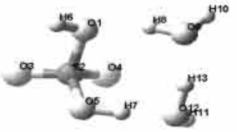
Atom1	*Atom2*	*Distance (Å)*
1	6	1,03
2	1	1,58
2	3	1,43
2	4	1,47
2	5	1,62
5	7	0,99
6	11	2,15
6	12	1,60
7	8	1,99
7	9	1,92
8	4	1,74
9	8	1,00
9	10	0,97
13	9	1,82

S2W-g



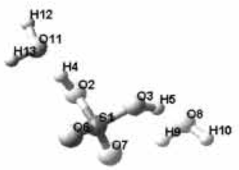
Atom1	*Atom2*	*Distance (Å)*
2	1	1,68
2	3	1,44
2	4	1,45
2	5	1,57
5	7	1,07
8	1	1,89
8	4	3,17
9	8	0,99
12	7	1,47
13	9	1,69

S2W-h



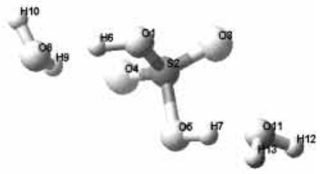
Atom1	Atom2	Distance (Å)
1	2	1,60
1	3	1,60
1	6	1,45
1	7	1,46
2	4	1,01
3	5	1,02
4	11	1,65
5	8	1,65
5	9	1,88
7	9	1,92
8	10	0,97
11	12	0,97
11	13	0,98

S2W-i



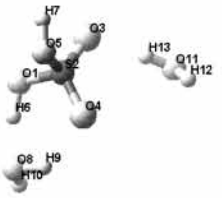
Atom1	Atom2	Distance (Å)
1	6	1,02
2	1	1,60
2	3	1,45
2	4	1,46
2	5	1,60
5	7	1,01
6	8	1,65
7	11	1,66
8	9	0,99
8	10	0,97
9	4	1,91
11	12	0,97
11	13	0,97

S2W-j



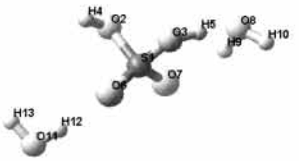
Atom1	Atom2	Distance (Å)
1	6	1,04
2	1	1,58
2	3	1,45
2	4	1,46
2	5	1,62
3	13	2,06
5	7	0,98
6	8	1,57
8	9	0,99
8	10	0,97
9	4	2,03
11	12	0,97
11	13	0,98

S2W-k



Atom1	Atom2	Distance (Å)
1	2	1,63
1	3	1,58
1	6	1,45
1	7	1,45
2	4	0,98
3	5	1,03
6	12	2,02
8	5	1,59
8	10	0,97
9	8	0,98
11	12	0,98
11	13	0,97

S2W-l



Atom1	Atom2	Distance (Å)
1	2	1,64
1	3	1,59
1	6	1,44
1	7	1,45
2	4	0,98
2	13	2,20
3	5	1,04
5	8	1,57
8	9	0,98
8	10	0,97
9	7	2,07
11	12	0,97
11	13	0,98

S2W-m

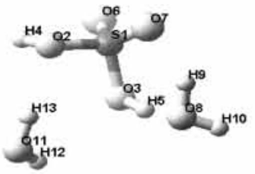


Figure 5. Structural data for the sulfuric acid dihydrates.

molecules, but at the same time it elongates the SO−H bond in the sulfuric acid.

The second group can be distinguished by the distribution of the water molecules on both sides of the sulfuric acid structure and the resulting linear chain structure such as the S2W-f structure. The conformations from this group are less stable than those from the first group due to the long and weak hydrogen bonds. The hydrogen bonds of the structures of the second group are about 0.2 Å longer than those of the first group.

The third group contains only the S2W-g molecular structure, where the sulfuric acid has the cis molecular structure. In this case the sulfuric acid O−H groups form a cyclic ring with the water dimer. This structure has the longest and weakest hydrogen bonds, but also the shortest and strongest SO−H bond.

Comparison of the structural data of the S2W-a conformation with the earlier studies by Bandy et al.[33] and Re et al.,[27] where the B3LYP method has been used with three different basis sets (311++G(2d,2p), D95(d,p), and D95++(d,p)), shows that hydrogen bond lengths of SO−H···OH_2 in their studies have been overestimated by 0.1, 0.02, and 0.06 Å, respectively. Similar overestimation in the other hydrogen bond lengths has been observed within all the structural groups. The elongation of the hydrogen bonds calculated by the B3LYP method is most likely related to the problems of the B3LYP method in calculating intermolecular interaction potentials for weak bonds, as stated by Tsuzuki et al. [34]

Sulfuric Acid Dihydrates Vibrational Frequencies. In this study the vibrational frequencies of all molecular confirmations

TABLE 12: Vibrational Frequencies of the Sulfuric Acid Dihydrates

	S2W-a	S2W-b	S2W-c	S2W-d	S2W-e	S2W-f	S2W-g	S2W-h	S2W-I	S2W-j	S2W-k	S2W-l	S2W-m
1	48 (vw)	28 (vw)	11 (vw)	25 (vw)	41 (vw)	45 (vw)	52 (vw)	41 (vw)	31 (w)	20 (w)	1 (vw)	15 (vw)	14 (vw)
2	51 (vw)	52 (vw)	42 (vw)	37 (vw)	46 (vw)	55 (vw)	98 (vw)	73 (vw)	44 (vw)	35 (vw)	26 (vw)	25 (vw)	41 (vw)
3	119 (vw)	108 (vw)	118 (vw)	119 (vw)	121 (vw)	150 (vw)	118 (vw)	106 (vw)	63 (w)	49 (vw)	50 (w)	54 (vw)	59 (vw)
4	176 (vw)	171 (vw)	176 (vw)	178 (vw)	182 (vw)	159 (m)	204 (vw)	154 (vw)	130 (w)	103 (w)	109 (w)	91 (m)	99 (vw)
5	236 (m)	228 (m)	218 (m)	224 (m)	212 (m)	236 (w)	222 (w)	246 (m)	187 (w)	186 (w)	113 (w)	117 (w)	142 (w)
6	270 (m)	262 (m)	262 (m)	254 (w)	257 (w)	251 (m)	244 (w)	258 (w)	225 (w)	224 (w)	156 (w)	150 (w)	148 (w)
7	296 (s)	311 (w)	311 (s)	280 (s)	313 (m)	283 (m)	314 (w)	300 (w)	237 (m)	239 (w)	204 (m)	230 (m)	205 (m)
8	322 (w)	323 (w)	329 (w)	321 (w)	323 (w)	307 (m)	319 (s)	308 (w)	314 (s)	296 (s)	255 (w)	272 (m)	221 (s)
9	349 (w)	342 (w)	353 (vw)	350 (m)	359 (w)	347 (m)	357 (w)	351 (vw)	324 (m)	317 (m)	269 (w)	278 (w)	256 (w)
10	370 (s)	360 (w)	380 (m)	365 (m)	386 (m)	364 (w)	397 (w)	395 (w)	351 (m)	328 (m)	274 (m)	299 (w)	269 (m)
11	426 (w)	412 (w)	416 (m)	393 (w)	402 (m)	403 (s)	421 (s)	413 (s)	366 (m)	361 (m)	343 (vw)	352 (vw)	342 (vw)
12	440 (m)	426 (s)	427 (w)	419 (m)	428 (w)	421 (vw)	475 (w)	445 (m)	391 (m)	382 (m)	397 (s)	398 (s)	392 (s)
13	504 (w)	505 (m)	503 (w)	497 (w)	497 (w)	506 (m)	513 (w)	493 (w)	424 (vw)	416 (vw)	411 (w)	411 (m)	404 (m)
14	512 (vw)	516 (w)	513 (w)	515 (w)	515 (m)	521 (w)	514 (w)	506 (vw)	514 (w)	511 (w)	445 (s)	456 (m)	453 (w)
15	524 (m)	523 (m)	519 (m)	518 (m)	521 (w)	538 (w)	533 (w)	515 (w)	516 (w)	513 (w)	496 (w)	496 (w)	497 (w)
16	577 (w)	612 (s)	585 (m)	552 (m)	563 (m)	631 (s)	583 (m)	563 (w)	533 (w)	532 (w)	519 (w)	509 (w)	508 (w)
17	688 (s)	731 (m)	712 (s)	695 (s)	716 (m)	654 (m)	758 (s)	669 (vw)	677 (s)	686 (s)	528 (w)	532 (w)	525 (w)
18	758 (s)	761 (s)	755 (s)	754 (s)	755 (s)	799 (m)	776 (s)	700 (s)	793 (m)	789 (m)	619 (s)	609 (s)	595 (s)
19	905 (s)	880 9s)	905 (s)	899 (s)	900 (s)	872 (s)	825 (w)	882 (s)	855 (s)	854 (s)	769 (s)	764 (s)	743 (s)
20	1006 (s)	900 (s)	1009 (m)	1029 (m)	1036 (m)	907 (m)	873 (s)	943 (s)	879 (s)	892 (s)	873 (s)	868 (s)	855 (s)
21	SO—H1 31 (s)	SO—H 1091 (w)	SO—H 1094 (w)	SO—H 1102 (w)	SO—H 1086 (m)	SO—H 949 (m)	SO—H 930 (s)	SO—H 1141 (m)	SO—H 896 (s)	SO—H 910 (s)	SO—H 945 (m)	SO—H 936 (m)	SO—H9 50 (m)
22	SO—H 1144 (m)	SO—H 1136 (m)	SO—H 1139 (s)	SO—H 1135 (s)	SO—H 1130 (s)	S═O 1122 (s)	S═O 1106 (s)	S═O 1154 (s)	S═O 1126 (s)	S═O 1125 (s)	S═O 1131 (s)	S═O 1130 (s)	SO—H1 133 (m)
23	SO—H 1125 (m)	SO—H 1144 (m)	SO—H 1147 (s)	SO—H 1145 (m)	SO—H 1143 (s)	S═O 1277 (s)	SO—H 1266 (s)	SO—H 1246 (m)	SO—H 1291 (s)	SO—H1 283 (s)	SO—H1 136 (s)	SO—H1 143 (s)	S═O 1141 (s)
24	SO—H 1334 (s)	SO—H 1348 (s)	SO—H 1351 (s)	SO—H 1347 (s)	S═O 1349 (s)	SO—H 1412 (m)	SO—H 1355 (s)	SO—H 1360 (s)	SO—H 1363 (m)	SO—H1 345 (s)	SO—H1 330 (s)	SO—H1 334 (s)	SO—H1 355 (s)
25	SO—H 1412 (s)	SO—H 1480 (m)	SO—H 1481 (m)	SO—H 1451 (s)	SO—H 1472 (m)	SO—H 1475 (s)	SO—H 1454 (s)	SO—H 1455 (s)	SO—H 1458 (s)	SO—H1 456 (s)	SO—H1 471 (s)	SO—H1 473 (s)	SO—H1 483 (s)
26	W 1604 (w)	W 1615 (w)	W 1608 (m)	W 1607 (m)	W 1613 (m)	W 1604 (m)	W 1580 (m)	W 1614 (m)	W 1589 (m)	W 1592 (m)	W 1603 (w)	W 1604 (m)	W 1597 (w)
27	W 1643 (w)	W 1657 (w)	W 1648 (w)	W 1648 (vw)	W 1653 (vw)	W 1613 (w)	W 1631 (w)	W 1649 (w)	W 1614 (m)	W 1614 (m)	W 1627 (m)	W 1624 (m)	W 1621 (s)
28	SO—H 2199 (vs)	SO—H 2264 (vs)	So—H 2216 (vs)	SO—H 2258 (vs)	SO—H 2236 (vs)	SO—H 2805 (vs)	SO—H 2749 (vs)	SO—H 2234 (vs)	SO—H 2871 (vs)	SO—H2 869 (vs)	SO—H2 662 (vs)	SO—H2 711 (vs)	SO—H2 663 (vs)
29	W 2971 (vs)	W 3006 (vs)	W 2968 (vs)	W 3007 (vs)	W 2988 (vs)	SO—H 2838 (s)	W 3230 (s)	W 3112 (vs)	SO—H 3024 (vs)	SO—H 3050 (vs)	W 3530 (s)	W 3533 (s)	W 3546 (s)
30	W 3401 9vs)	W 3407 (vs)	W 3406 (vs)	W 3415 (vs)	W 3398 (vs)	W 3499 (s)	W/SO—H 3351 (vs)	W 3472 (vs)	W 3454 (s)	W 3444 (s)	W 3631 (s)	W 3616 (s)	W 3626 (s)
31	SO—H 3632 (s)	SO—H 3639 (s)	SO—H 3639 (m)	SO—H 3635 (s)	SO—H 3641 (m)	W 3505 (s)	SO—HW 3408 (vs)	SO—H 3633 (m)	W 3665 (w)	W 3673 (w)	SO—H 3635 (m)	SO—H 3632 (s)	SO—H 3655 (m)
32	W 3720 (m)	W 3732 (m)	W 3730 (m)	W 3751 (s)	W 3732 (m)	W 3720 (s)	W 3737 (m)	W 3709 (m)	W 3732 (m)	W 3730 (m)	W 3727 (s)	W 3731 (s)	W 3734 (s)
33	W 3736 (m)	W 3738 (m)	W 3739 (m)	W 3753 (m)	W 3735 (m)	W 3740 (m)	W 3748 (m)	W 3743 (s)	W 3761 (s)	W 3768 (s)	W 3757 (m)	W 3748 (s)	W 3750 (m)

have been calculated. Table 12 and Figure 6 present the vibrational frequencies for all 13 sulfuric acid dihydrates and the corresponding absorption intensities.

The highest absorption intensity is associated with $\nu_{\text{SO-H}}$, which is red-shifted about 570 cm^{-1} from the sulfuric acid monohydrate in the case of the S2W-a conformation. In contrast, the other SO—H stretching, which appears at 3638 cm^{-1} is hardly changed due to its location far away from any effect of the water molecules. The other hydrogen bonded stretching of the water moiety toward the S═O group is also red-shifted to 3401 cm^{-1}. The spectra of the other dihydrates are essentially the same as the spectrum of S2W-a, with the difference in S2W-f,i,j,l where both O—H groups' stretching are red-shifted due to the positions of the water molecules. In the study of Re et al.[27] the assignments of the vibrational frequencies were similar but with different values of the vibrational frequencies. The red-shifting of the SO—H stretching obtained in this study is higher by about 120 cm^{-1} than that reported by Re et al.[27]

Structures and Properties of Gas-Phase Sulfuric Acid Trihydrate Cluster [$H_2SO_4(H_2O)_3$]. In the case of the trihydrates we have optimized the molecular structures of the 10 conformations and obtained real values of the vibrational frequencies for all of them. Structural data of the trihydrates, values of the dipole moments and total bonding energies are presented in Figure 7 and Table 12.

Dipole Moments of Sulfuric Acid Trihydrates. As seen from Table 12, the dipole moments of trihydrates are consistently large, varying from 3.024 D for SW3-i to 6.469 D for SW3-j. The structure S3W-i has a smaller dipole moment because the O—H groups in the cis sulfuric acid form some sort of a ring with the three water molecules, where two of them are oriented oppositely to each other, which leads to a reduction of the dipole moment. The structure of the water trimer configuration in this molecular structure is very similar to the structure of the lowest energy reported by Gregory et al.[53] On the other hand, the S3W-j structure has a very large dipole moment due to the presence of an almost linear chain of the three water molecules centered over one of the O—H groups in the sulfuric acid. This means that the location and orientation of the water molecules are likely to play the dominating role in the properties of the trihydrates.

Sulfuric Acid Trihydrates Structural Data. Figure 7 depicts the optimized molecular structures of the sulfuric acid trihydrates based on their stability. The trihydrates structures can be divided into two groups. The first group represents the nontransferred

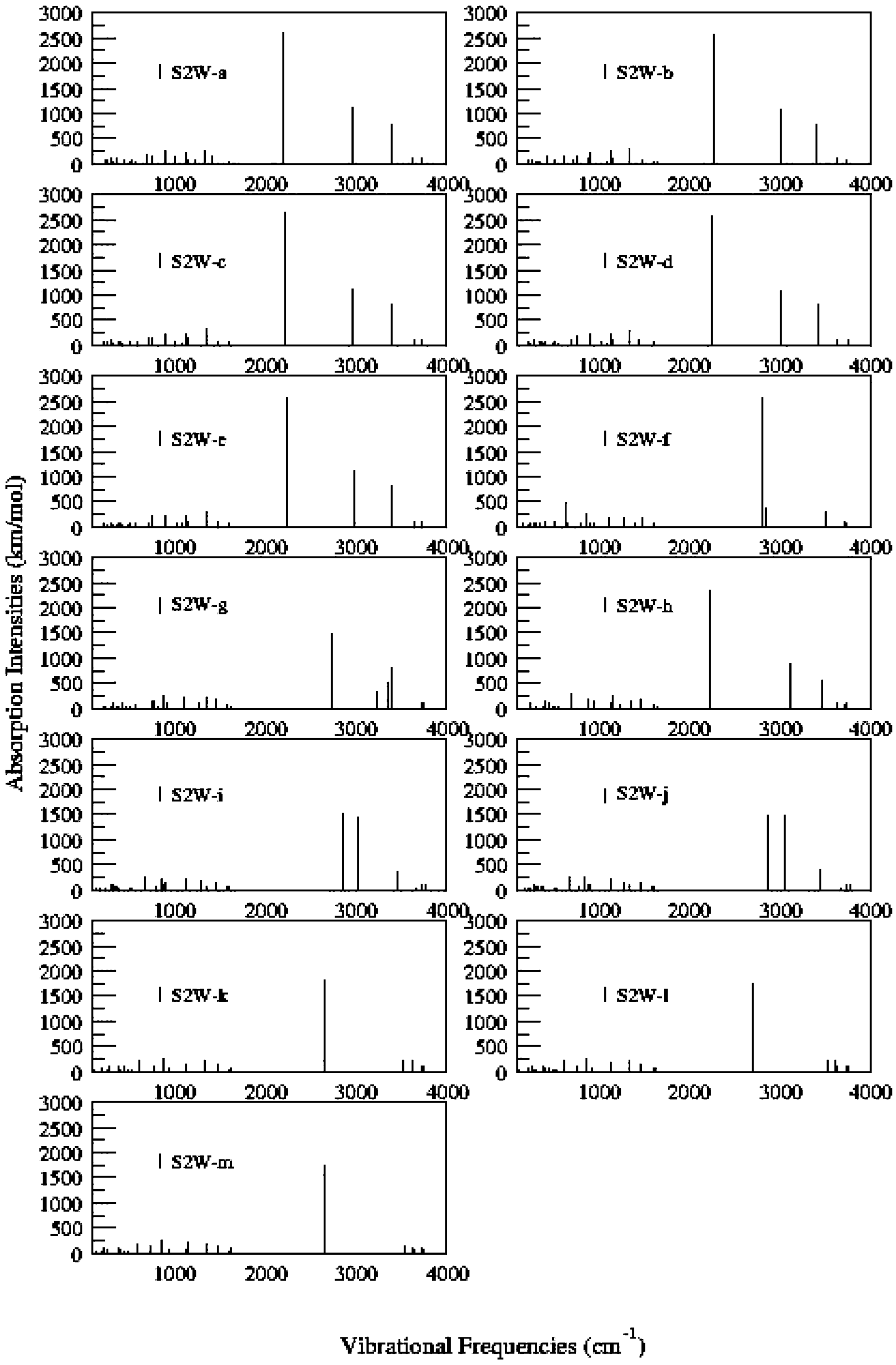


Figure 6. Vibrational frequencies and the corresponding absorption intensities of different dihydrates of the sulfuric acid.

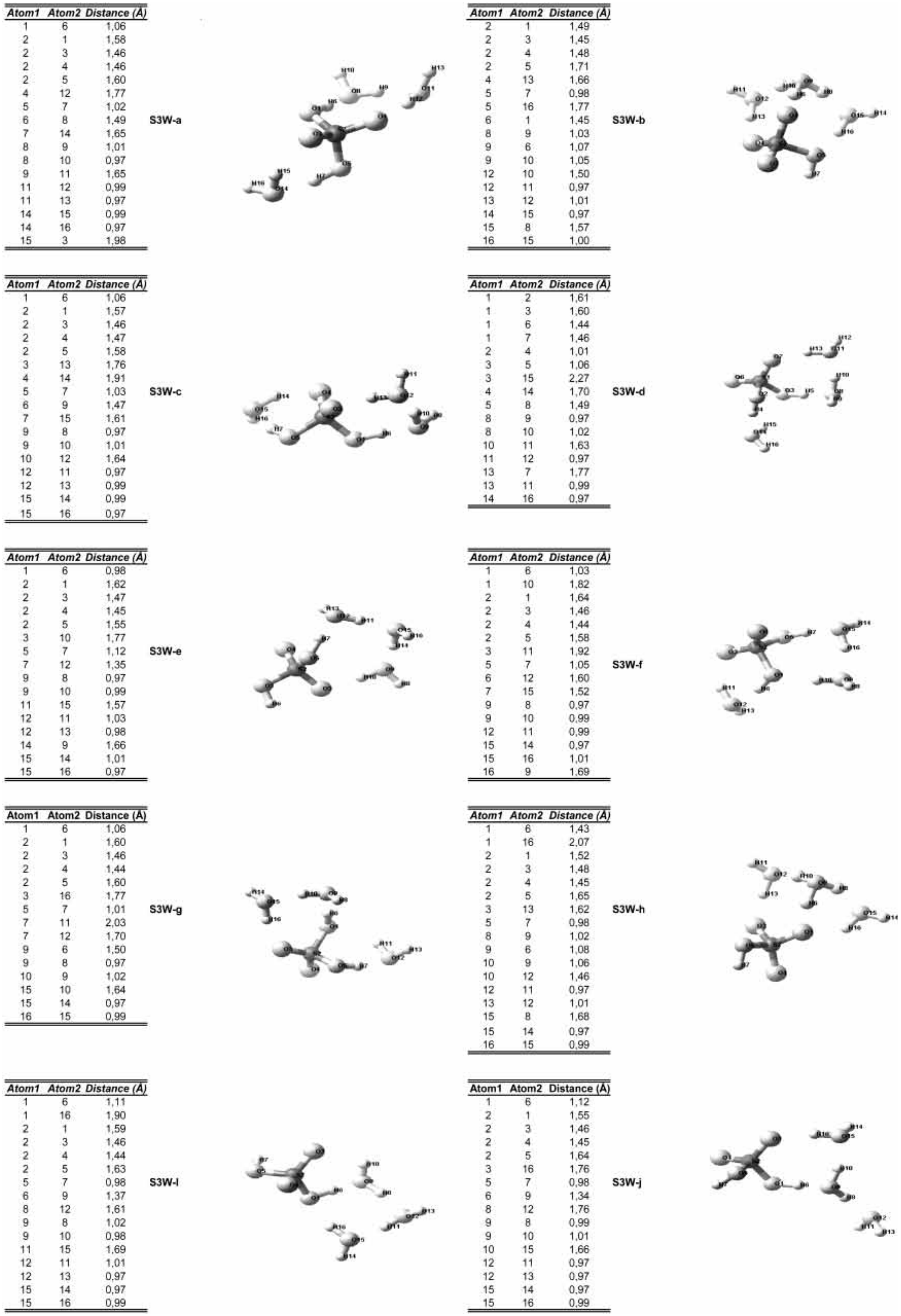
TABLE 13: Dipole Moments and Total Bonding Energies of Trihydrates of the Sulfuric Acid, Calculated Using the PW91 Method and the TZP Basis Set

structure type	dipole moment (Debye)	total bonding energy (kcal/mol)
S3W-a	3.8379	−1884.10
S3W-b	4.3997	−1883.43
S3W-c	3.7036	−1882.37
S3W-d	4.8627	−1881.50
S3W-e	3.4839	−1881.29
S3W-f	5.0326	−1880.42
S3W-g	4.7860	−1880.37
S3W-h	3.6682	−1879.24
S3W-i	3.0242	−1878.95
S3W-j	6.4686	−1878.47

proton structures and can be divided into subgroups based on the locationof the water trimer.

In the first subgroup of the first category two water molecules are hydrogen bonded to each other and to one O−H group in sulfuric acid and the third water molecule is hydrogen bonded to the second O−H group of sulfuric acid. The S3W-a,c,d,f,g structures belong to this group. The S3W-a structure is the most stable structure among the trihydrates and differs only by 0.67 kcal/mol from the second stable proton transferred structure. The comparison of the S3W-a molecular structure with similar minima structures reported by Bandy et al.[33] and Re et al.[27] shows that B3LYP calculations overestimate the hydrogen bonds due to the problems the method used in their studies in describing the intermolecular interaction potentials.[34]

The S3W-e,l,j represent second subgroup. In the second subgroup the constituents of the water trimer are hydrogen bonded to each other on one side of the sulfuric acid. The two main shapes that distinguish this subgroup are the cyclic ring



S3W-a

Atom1	Atom2	Distance (Å)
1	6	1,06
2	1	1,58
2	3	1,46
2	4	1,46
2	5	1,60
4	12	1,77
5	7	1,02
6	8	1,49
7	14	1,65
8	9	1,01
8	10	0,97
9	11	1,65
11	12	0,99
11	13	0,97
14	15	0,99
14	16	0,97
15	3	1,98

S3W-b

Atom1	Atom2	Distance (Å)
2	1	1,49
2	3	1,45
2	4	1,48
2	5	1,71
4	13	1,66
5	7	0,98
5	16	1,77
6	1	1,45
8	9	1,03
9	6	1,07
9	10	1,05
12	10	1,50
12	11	0,97
13	12	1,01
14	15	0,97
15	8	1,57
16	15	1,00

S3W-c

Atom1	Atom2	Distance (Å)
1	6	1,06
2	1	1,57
2	3	1,46
2	4	1,47
2	5	1,58
3	13	1,76
4	14	1,91
5	7	1,03
6	9	1,47
7	15	1,61
9	8	0,97
9	10	1,01
10	12	1,64
12	11	0,97
12	13	0,99
15	14	0,99
15	16	0,97

S3W-d

Atom1	Atom2	Distance (Å)
1	2	1,61
1	3	1,60
1	6	1,44
1	7	1,46
2	4	1,01
3	5	1,06
3	15	2,27
4	14	1,70
5	8	1,49
8	9	0,97
8	10	1,02
10	11	1,63
11	12	0,97
13	7	1,77
13	11	0,99
14	16	0,97

S3W-e

Atom1	Atom2	Distance (Å)
1	6	0,98
2	1	1,62
2	3	1,47
2	4	1,45
2	5	1,55
3	10	1,77
5	7	1,12
7	12	1,35
9	8	0,97
9	10	0,99
11	15	1,57
12	11	1,03
12	13	0,98
14	9	1,66
15	14	1,01
15	16	0,97

S3W-f

Atom1	Atom2	Distance (Å)
1	6	1,03
1	10	1,82
2	1	1,64
2	3	1,46
2	4	1,44
2	5	1,58
3	11	1,92
5	7	1,05
6	12	1,60
7	15	1,52
9	8	0,97
9	10	0,99
12	11	0,99
15	14	0,97
15	16	1,01
16	9	1,69

S3W-g

Atom1	Atom2	Distance (Å)
1	6	1,06
2	1	1,60
2	3	1,46
2	4	1,44
2	5	1,60
3	16	1,77
5	7	1,01
7	11	2,03
7	12	1,70
9	6	1,50
9	8	0,97
10	9	1,02
15	10	1,64
15	14	0,97
16	15	0,99

S3W-h

Atom1	Atom2	Distance (Å)
1	6	1,43
1	16	2,07
2	1	1,52
2	3	1,48
2	4	1,45
2	5	1,65
3	13	1,62
5	7	0,98
8	9	1,02
9	6	1,08
10	9	1,06
10	12	1,46
12	11	0,97
13	12	1,01
15	8	1,68
15	14	0,97
16	15	0,99

S3W-i

Atom1	Atom2	Distance (Å)
1	6	1,11
1	16	1,90
2	1	1,59
2	3	1,46
2	4	1,44
2	5	1,63
5	7	0,98
6	9	1,37
8	12	1,61
9	8	1,02
9	10	0,98
11	15	1,69
12	11	1,01
12	13	0,97
15	14	0,97
15	16	0,99

S3W-j

Atom1	Atom2	Distance (Å)
1	6	1,12
2	1	1,55
2	3	1,46
2	4	1,45
2	5	1,64
3	16	1,76
5	7	0,98
6	9	1,34
8	12	1,76
9	8	0,99
9	10	1,01
10	15	1,66
12	11	0,97
12	13	0,97
15	14	0,97
15	16	0,99

Figure 7. Structural data of the sulfuric acid trihydrates.

shape and the linear shape centered on the O−H group of the sulfuric acid.

The second group is the transferred proton or ion-pair structures due to the proton dissociation and formation of the [$H_2SO_4^-$.H_3O^+] complex. In both the S3W-b and S3W-h structures of this category the hydronium [H_3O^+] ions form triple hydrogen bonds with the water molecules and the sulfuric acid. In the S3W-b conformation the [H_3O^+] ions form a cyclic shape by the hydrogen bonds with water molecules and the sulfuric acid and form some sort of linear chain centered over one oxygen atom in the sulfuric acid in the S3W-h molecular structure.

Vibrational Frequencies of Sulfuric Acid Trihydrates. Table 14 and Figure 8 present the vibrational frequencies and the

TABLE 14: Vibrational Frequencies of the Sulfuric Acid Trihydrates

	S3W-a	S3W-b	S3W-c	S3W-d	S3W-e	S3W-f	S3W-g	S3W-h	S3W-i	S3W-j
1	19 (vw)	41 (vw)	19 (vw)	27 (vw)	30 (vw)	31 (vw)	23 (vw)	11 (vw)	19 (vw)	23 (vw)
2	29 (vw)	81 (vw)	30 (vw)	38 (vw)	38 (vw)	36 (vw)	32 (vw)	37 (w)	43 (vw)	33 (vw)
3	54 (vw)	92 (vw)	44 (vw)	53 (vw)	57 (vw)	76 (vw)	52 (vw)	55 (m)	55 (vw)	44 (vw)
4	116 (vw)	127 (vw)	120 (vw)	100 (w)	80 (vw)	107 (vw)	89 (w)	71 (vw)	94 (vw)	75 (vw)
5	150 (w)	171 (vw)	170 (vw)	110 (vw)	98 (w)	147 (w)	110 (vw)	91 (w)	105 (vw)	86 (w)
6	190 (w)	193 (vw)	181 (m)	180 (w)	154 (m)	182 (vw)	175 (w)	114 (vw)	143 (vw)	110 (vw)
7	239 (w)	222 (w)	249 (m)	216 (m)	167 (w)	246 (m)	193 (w)	190 (w)	213 (m)	160 (w)
8	256 (m)	281 (m)	255 (w)	218 (vw)	226 (m)	269 (w)	220 (w)	230 (w)	243 (m)	202 (w)
9	290 (m)	330 (m)	310 (w)	264 (m)	252 (s)	285 (w)	264 (m)	260 (s)	257 (m)	210 (m)
10	306 (w)	344 (w)	324 (s)	303 (s)	308 (m)	309 (w)	304 (w)	312 (m)	297 (s)	283 (m)
11	312 (w)	367 (w)	327 (w)	312 (w)	335 (w)	320 (s)	308 (s)	359 (m)	328 (vw)	285 (s)
12	343 (w)	387 (w)	361 (w)	347 (m)	343 (s)	356 (w)	342 (m)	376 (w)	354 (m)	307 (w)
13	354 (w)	393 (m)	368 (w)	372 (m)	382 (w)	374 (w)	372 (w)	388 (w)	371 (w)	330 (m)
14	383 (w)	426 (w)	388 (s)	384 (m)	438 (s)	387 (s)	384 (m)	399 (s)	393 (w)	351 (w)
15	414 (m)	367 (w)	412 (w)	418 (m)	448 (s)	412 (w)	413 (s)	420 (w)	426 (m)	375 (w)
16	434 (m)	503 (vw)	450 (s)	438 (w)	483 (w)	435 (vw)	440 (w)	507 (s)	484 (W)	416 (S)
17	519 (s)	522 (s)	520 (w)	496 (m)	503 (s)	498 (m)	487 (m)	524 (w)	498 (s)	431 (w)
18	528 (w)	533 (w)	524 (m)	511 (w)	520 (m)	510 (m)	514 (w)	536 (m)	507 (w)	507 (s)
19	532 (w)	562 (m)	545 (w)	525 (w)	522 (m)	532 (w)	521 (w)	578 (w)	522 (w)	514 (s)
20	617 (s)	653 (s)	599 (m)	537 (m)	559 (w)	567 (m)	534 (m)	608 (s)	575 (s)	529 (vw)
21	657 (s)	779 (w)	681 (s)	582 (w)	663 (vw)	680 (s)	583 (w)	745 (s)	626 (m)	709 (s)
22	705 (m)	843 (s)	707 (m)	715 (s)	693 (m)	737 (s)	709 (s)	785 (w)	662 (m)	748 (s)
23	810 (m)	891 (w)	830 (m)	786 (w)	772 (s)	766 (s)	787 (m)	819 (m)	762 (s)	793 (vw)
24	897 (s)	969 (s)	905 (m)	811 (m)	901 (w)	864 (s)	820 (m)	902 (m)	861 (s)	883 (s)
25	921 (m)	990 (m)	928 (s)	857 (s)	923 (s)	889 (s)	861 (s)	951 (s)	894 (m)	929 (s)
26	937 (s)	1055 (s)	981 (s)	1016 (s)	1053 (s)	96 (m)	1003 (s)	1052 (s)	1020 (s)	942 (w)
27	1081 (M)	1110 (M)	1101 (m)	1133 (s)	1084 (s)	1122 (s)	1133 (s)	1115 (m)	1117 (s)	1105 (s)
28	S=O 1124 (s)	S=O 1185 (s)	SO−H 1114 (s)	SO−H 1221 (m)	SO−H 1144 (m)	SO−H 1131 (s)	SO−H 1222 (m)	SO−H 1132 (m)	SO−H 1143 (m)	SO−H 1140 (s)
29	S=O 1272 (s)	S=O 1307 (s)	S=O 1243 (s)	S=O 1315 (s)	S=O 1310 (s)	S=O 1324 (s)	S=O 1314 (s)	S=O 1311 (s)	SO−H 1252 (s)	SO−H 1210 (s)
30	SO−H 1420 (s)	H 1501 (s)	SO−H 1429 (m)	SO−H 1398 (w)	SO−H 1321 (m)	SO−H 1438 (m)	SO−H 1401 (w)	H 1479 (s)	S=O 1366 (s)	S=O 1339 (s)
31	SO−H 1483 (m)	W 1614 (m)	SO−H 1453 (s)	SO−H 1437 (s)	SO−H 1504 (m)	SO−H 1478 (s)	SO−H 1436 (s)	W 1605 (m)	SO−H 1589 (s)	SO−H 1500 (vs)
32	W 1610 (w)	W 1625 (w)	W 1606 (w)	W 1610 (m)	W 1611 (vs)	W 1607 (w)	W 1607 (m)	W 1612 (w)	W 1611 (m)	W 1601 (m)
33	W 1624 (w)	H 1699 (w)	W 1613 (w)	W 1618 (w)	W 1622 (m)	W 1610 (m)	W 1619 (w)	H 1665 (w)	W 1628 (s)	W 1613 (s)
34	W 1660 (w)	H 1721 (m)	W 1656 (w)	W 1654 (w)	W 1654 (w)	W 1640 (vw)	W 1653 (w)	H 1748 (s)	W 1648 (w)	W 1640 (s)
35	SO−H 2329 (vs)	H 2122 (vs)	SO−H 2261 (vs)	SO−H 2321 (vs)	SO−H 1713 (vs)	SO−H 2434 (vs)	SO−H 2348 (vs)	H 1988 (vs)	SO−H 1761 (vs)	SO−H 1711 (vs)
36	SO−H 2854 (vs)	H 2419 (vs)	SO−H 2774 (vs)	W 2952 (vs)	W 2761 (vs)	SO−H 2765 (vs)	W 2979 (vs)	H 2350 (vs)	W 2868 (vs)	W 3023 (vs)
37	W 3001 (vs)	H 2778 (vs)	W 2994 (vs)	SO−H 3028 (vs)	W 3078 (vs)	W 3102 (vs)	SO−H 3019 (vs)	HW 3028 (vs)	W 3140 (vs)	W 3347 (vs)
38	W 3375 (vs)	W 3089 (vs)	W 3369 (vs)	W 3363 (vs)	W 3354 (vs)	W 3399 (vs)	W 3375 (vs)	HW 3052 (vs)	W 3464 (vs)	W 3363 (vs)
39	W 3487 (s)	W 3277 (vs)	W 3446 (s)	W 3595 (m)	SO−H 3656 (s)	W 3453 (s)	W 3612 (m)	W 3502 (s)	SO−H 3642 (m)	SO−H 3644 (m)
40	W 3733 (m)	SO−H 3644 (m)	W 3720 (m)	W 3721 (m)	W 3700 (m)	W 3729 (m)	W 3722 (m)	SO−H 3658 (s)	W 3675 (m)	W 3681 (w)
41	W 3734 (s)	W 3728 (s)	W 3723 (m)	W 3735 (m)	W 3738 (m)	W 3733 (m)	W 3738 (m)	W 3731 (m)	W 3741 (m)	W 3742 (m)
42	W 3740 (m)	W 3732 (m)	W 3740 (m)	W 3739 (s)	W 3759 (m)	W 3739 (m)	W 3745 (s)	W 3751 (s)	W 3747 (s)	W 3775 (m)

corresponding absorption intensities of the sulfuric acid trihydrates, which are divided into two subgroups. The difference of the spectra between the two is quite clear with maximum peaks of intensities belonging (1) to the SO−H stretching at 2329 cm^{-1} in the case of the neutral trihydrates and (2) to the O−H stretching of the hydronium in the ion-pair complex in the range of ∼2000−3000 cm^{-1} and maximizes at 2419 cm^{-1} in the case of the S3W-b conformation. Furthermore, different subgroups of the first category of trihydrates demonstrate a similar vibrational frequencies pattern with minor shifting such as the S3W-e conformation where the absorption intensities have a similar pattern like the S3W-a but with 5−100 range of wavenumbers difference.

Furthermore, we present in Figure 9 the variations of the total bonding energies and the dipole moments of the different hydrates. We observe a strong variation of the dipole moments as the structures are changed from 1 to 3 water molecules solvating the H_2SO_4 molecule and also within the hydrates containing 2 or 3 water molecules. The total bonding energies are more or less constant within one class of hydrates.

Thermodynamics Analysis

Relevant thermodynamic properties (entropies, enthalpies, and Gibbs free energies) for the cluster formation have been calculated. In addition, we have investigated the effect of

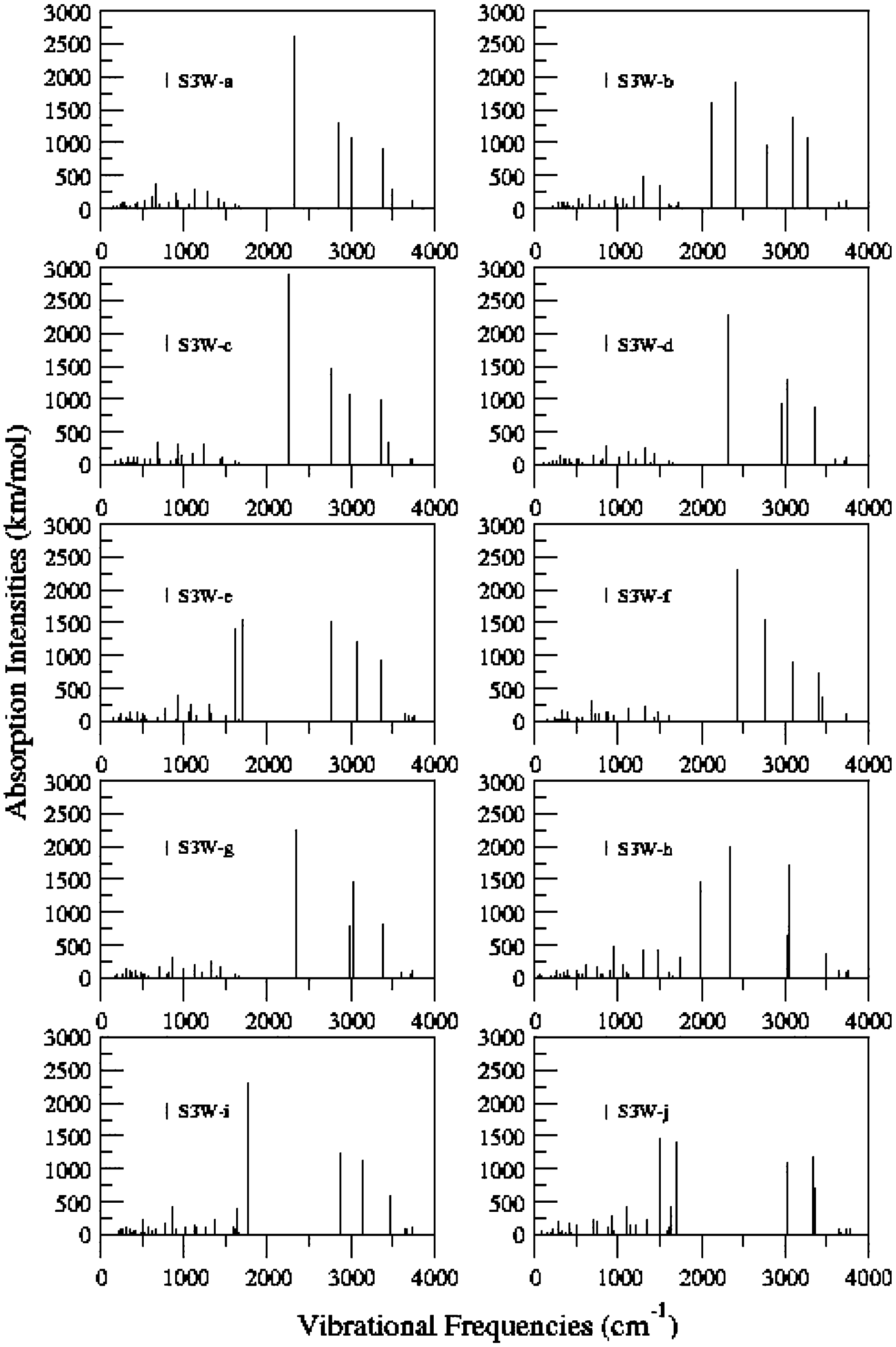


Figure 8. Vibrational frequencies and the corresponding absorption intensities of trihydrates.

temperature and pressure on these properties. We have selected temperatures and pressures that correspond to the different atmospheric zones conditions such as troposphere, stratosphere, and mesosphere.

The thermal analysis has been done using the ADF software package 2002.03.[42−44] and assume ideal gas conditions the energy of the molecule is

$$\frac{E}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3N-6}\left(\frac{h\nu_j}{2kT} + \frac{h\nu_j}{kT(e^{h\nu_j/kT} - 1)}\right) - \frac{D}{kT}$$

where ν_j is the harmonic frequencies, h is Plank's constant, T is the temperature, k is Boltzmann constant, and D is the dissociation energy and equal to $D_0 + \sum_j (h\nu_j/2)$.

Table 15 presents the entropies, enthalpies, and Gibbs free energies of the different structures of sulfuric hydrates at 1 atm pressure and 298.15 K using two possible reactions paths

$$H_2SO_4 + nH_2O \rightarrow H_2SO_4{\cdot}n(H_2O) \qquad n = 1{-}3 \qquad (1)$$

$$H_2SO_4{\cdot}(n-1)(H_2O) + H_2O \rightarrow H_2SO_4{\cdot}n(H_2O) \qquad n = 1{-}3 \qquad (2)$$

The Gibbs free energy has been calculated according to the following formulas

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta(PV) \approx \Delta nRT$$

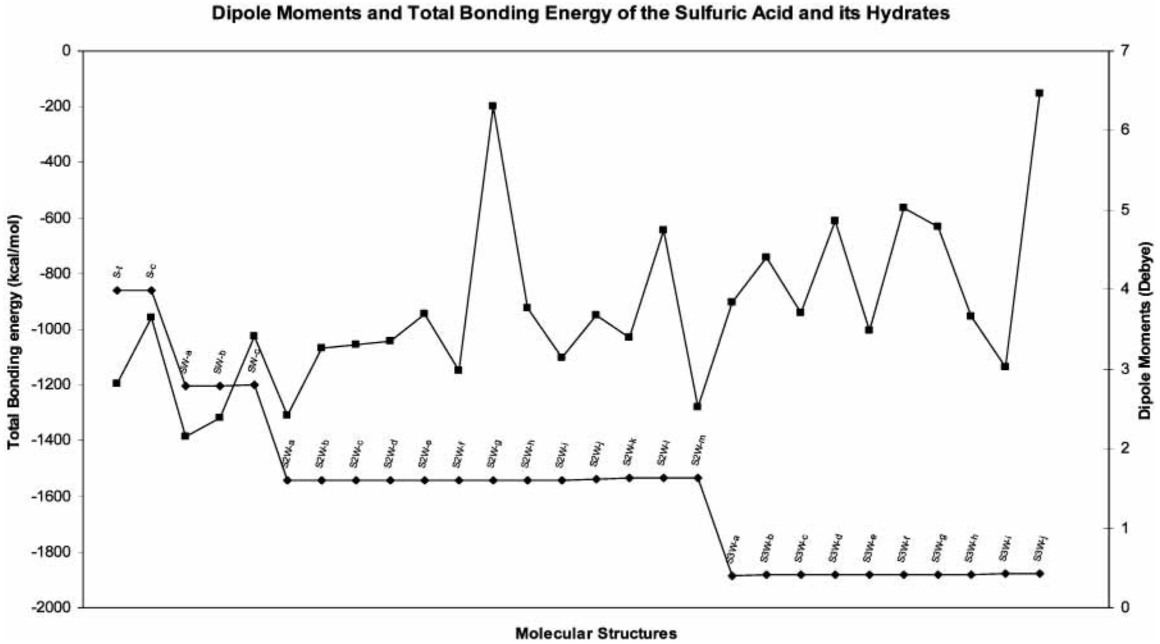


Figure 9. Dipole moment and total bonding energy different conformations of the sulfuric acid and it hydrates.

TABLE 15: Thermodynamic Properties of Sulfuric Hydrates at 298.15K Temperature and 1 Atm Pressure[a]

str name	ΔS_1	ΔS_2	ΔH_1	ΔH_2	ΔG_1	ΔG_2
SW-a	32.1		−2.6		−12.2	
SW-b	32.5		−2.6		−12.3	
SW-c	32.6		−2.6		−12.3	
S2W-a	65.4	33.3	−4.9	−2.3	−24.4	−12.2
S2W-b	64.0	31.9	−4.9	−2.3	−24.0	−11.8
S2W-c	69.8	37.7	−4.4	−1.8	−25.2	−13.0
S2W-d	62.9	30.8	−5.0	−2.4	−23.7	−11.6
S2W-e	64.9	32.7	−5.0	−2.4	−24.3	−12.1
S2W-f	65.4	33.3	−5.4	−2.8	−24.9	−12.7
S2W-g	68.8	36.2	−5.4	−2.8	−26.0	−13.6
S2W-h	65.3	33.1	−5.2	−2.6	−24.7	−12.5
S2W-i	60.2	28.1	−5.3	−2.8	−23.3	−11.1
S2W-j	57.6	25.4	−5.3	−2.7	−22.5	−10.3
S2W-k	59.8	27.7	−4.4	−1.8	−22.3	−10.1
S2W-l	60.3	28.2	−4.5	−1.9	−22.5	−10.3
S2W-m	60.9	28.7	−4.4	−1.8	−22.6	−10.4
S3W-a	102.7	39.3	−7.1	−2.2	−37.7	−13.9
S3W-b	103.3	40.0	−7.5	−2.5	−38.3	−14.5
S3W-c	103.2	39.8	−6.9	−2.0	−37.7	−13.8
S3W-d	95.3	31.9	−7.8	−2.8	−36.2	−12.4
S3W-e	94.9	31.5	−7.0	−2.1	−35.3	−11.5
S3W-f	97.9	34.5	−7.8	−2.9	−37.0	−13.2
S3W-g	93.9	30.6	−7.9	−2.9	−35.9	−12.0
S3W-h	100.7	37.3	−6.5	−1.6	−36.5	−12.7
S3W-i	101.3	37.9	−6.7	−1.8	−36.9	−13.1
S3W-j	89.5	26.2	−7.1	−2.2	−33.8	−10.0

[a] $\Delta S_{1,2}$ [cal/(mol K)] is the cluster entropy change, $\Delta H_{1,2}$ (kcal/mol) is the enthalpies change, and $\Delta G_{1,2}$ (kcal/mol) is the change in the Gibbs free energy.

where ΔG is the Gibbs free energy change, ΔH is the change in the enthalpy, T is the temperature, ΔS is the entropy, ΔE is the internal energy change, P is the pressure of the gas, V is the volume of the gas, Δn is the change of moles, and R is the universal gas constant.

As depicted in Table 15 the Gibbs free energies of the first reaction path are significantly lower than the second reaction path. This indicates that the first reaction path is more favorable. The entropies and the enthalpies of the first reaction path increased with about ~30 cal/(mol K) and ~2.5 kcal/mol, respectively, with each water molecule but with the second reaction path they only increased with about ~10 cal/(mol K) and ~1 kcal/mol, respectively. It is interesting to note that the molecular structure with the highest dipole moment (~6.3 D) in the dihydrates class (S2W-g) has the lowest Gibbs free energy. In addition, the proton transferred trihydrates have a lower ΔG than the neutral trihydrates.

In comparison with the previously reported results by Re et al.[27] and Bandy and Ianni[33] the magnitudes of the Gibbs free energy are larger by factors of 3 and 10, respectively. The values obtained in this study are in better agreement with the strong hygroscopic nature of the sulfuric acid and the exothermic character of the reaction.

Re et al.,[27] reported some positive values of ΔG that means that reaction will be reversed and the sulfuric acid hydrates will be dissociating rather forming On the other hand, values of ΔG reported in ref 33 are quite small and not far from zero for the mono, di- and trihydrates at 298 K temperature.

We have also investigated the effect of the pressure and the temperature on the Gibbs free energy. Figure 10 shows the effect of pressure and temperature on the ΔG of the sulfuric acid mono and di hydrates molecular structures SW-a and S2W-a, respectively.

The effect of the temperature variation on ΔG is significant and as the temperature increases the change in free energy ΔG value decreases which indicates a more favorable reaction path way. On the other hand, the ΔG value increases with the pressure and the reaction path thus become less favorable. Thermodynamically this behavior is due to the fact that the enthalpy is dominating ΔG at low temperatures and as the temperature increases the effect of the entropy starts to increase and the deviation due to the pressure becomes apparent.

Conclusion

In this paper, we have optimized the molecular structures and calculated the vibrational frequencies, dipole moments, and the total bonding energies of gas-phase sulfuric acid and small clusters consisting of 1, 2, and 3 water molecules associated with a sulfuric acid molecule. We have investigated the effect of O−H groups' orientation in the sulfuric acid on the dipole moments of mono-, di-, and trihydrates. We have also performed

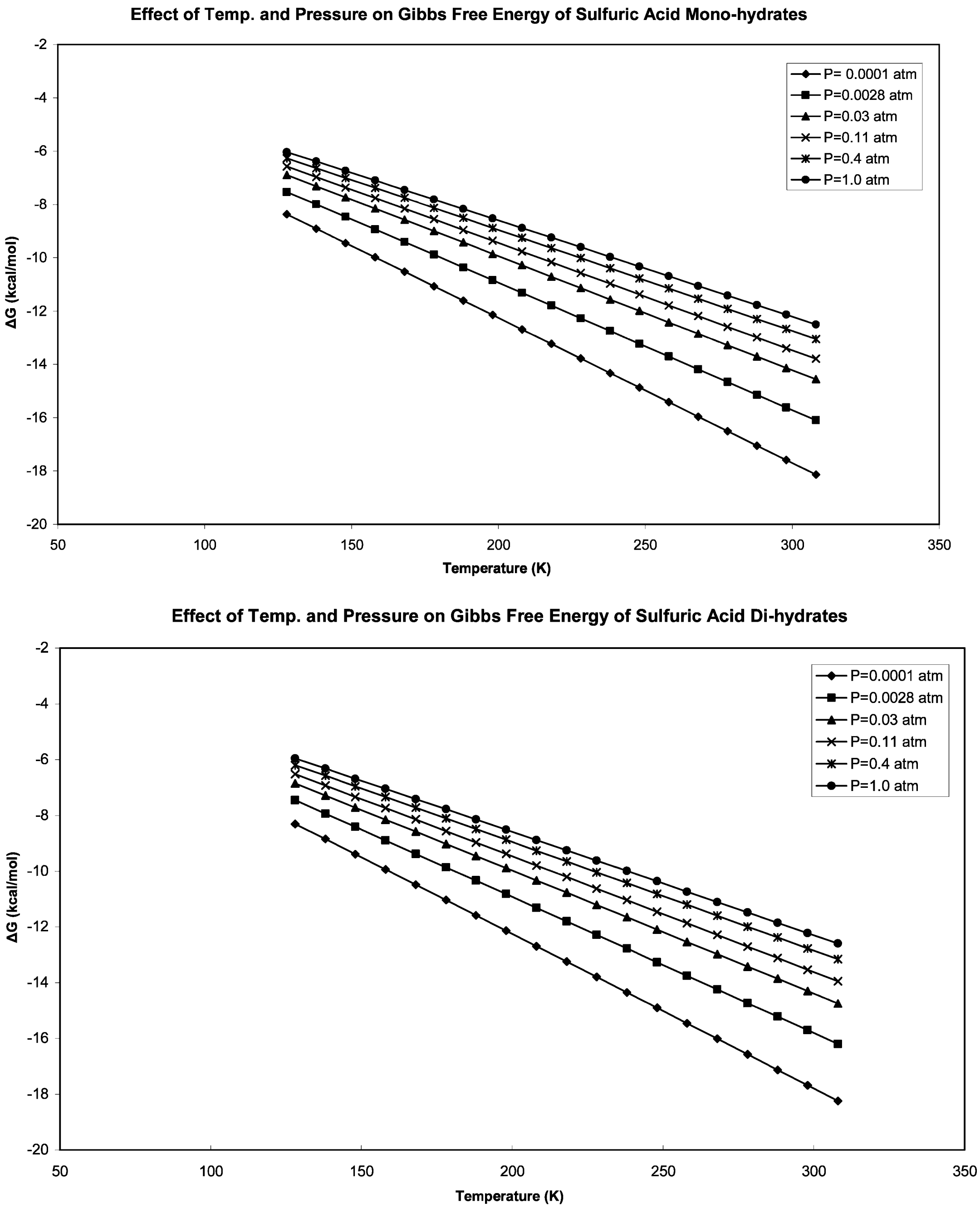


Figure 10. Effect of the pressure and the temperature on the Gibbs free energy of the sulfuric acid mono (SW-a) and di (S2W-a) molecular conformations.

a sensitivity study using six different DFT methods and six different basis sets. We suggest that different properties of the monohydrates depend strongly on the structure of the sulfuric acid whereas the formation of the dihydrates is governed by the properties of both sulfuric acid and water molecules. In the case of trihydrates, the geometry of the water molecules is likely to dominate. The dipole moments of monohydrates, dihydrates, and trihydrates are consistently high, which is important for the nucleation of the ultrafine particles in the atmosphere. The results obtained can be utilized directly as part of the solution routine for simulation of the nucleation in the atmosphere and development of the rigorous microphysical hydration model. The thermodynamics properties of all the sulfuric acid hydrates have also been calculated and discussed.

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