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Study of the Hydrates of H_2SO_4 Using Density Functional Theory

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Density functional molecular orbital theory was used at the B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory to study the hydrates of sulfuric acid ($H_2SO_4 \cdot nH_2O$) for $n = 0-7$ and the dimer of the trihydrate of sulfuric acid, $(H_2SO_4 \cdot 3H_2O)_2$. Six neutrals of the first six $H_2SO_4 \cdot nH_2O$ clusters ($n = 1-6$) were determined to be hydrogen-bonded molecular complexes of H_2SO_4 and H_2O and contain no H_3O^+ ions. An H_3O^+ ion and HSO_4^- formed in clusters of $H_2SO_4 \cdot nH_2O$ for $n = 3-7$. This is in contrast to the bulk phase where H_2SO_4 and two H_2O's have been converted to two H_3O^+ ions and a free SO_4^{2-} ion. The energetics of the hydration reactions also were obtained. The free energy of formation from free H_2SO_4 and H_2O had a minimum at $n = 3-4$ at room temperature. However, the free energy of formation of $H_2SO_4 \cdot nH_2O$ from free H_2SO_4 and H_2O decreased rapidly with temperature with the minimum becoming less pronounced and disappearing completely by 248 K. Below 248 K there is no free energy barrier to the formation of larger hydrates.

Introduction

The hydrates of H_2SO_4 are important intermediates in the formation of new atmospheric particles.[1−12] These new particles are thought to play an important role in determining the concentration of cloud condensation nuclei in the atmosphere in general and the marine atmosphere in particular.[5,13−19] By the influence of the number density and size distribution of cloud droplets, cloud condensation nucleation plays a central role in determining the optical properties of cloud, the radiation budget of the earth, and the temperature of the earth.[2,8] Sulfuric acid hydrates are known to provide surface and/or media for reactions leading to ozone destruction in the arctic and antarctic stratosphere.[5,20−23]

Despite these important roles of H_2SO_4 hydrates in the environment, most previous studies of the $H_2SO_4-H_2O$ system assumed that the properties of particles containing H_2SO_4 and H_2O could be obtained by extrapolation from the properties of the bulk phase.[24−27] Although this extrapolation may be valid for relatively large particles, the properties of small particles approaching the molecular level and the properties of the bulk phase may be considerably different. This is particularly true if the bulk phase contains ionic species that are stabilized by the dielectric properties of the medium. The $H_2SO_4-H_2O$ bulk phase contains H_3O^+ ions and thus is one of those systems for which the properties of the smaller clusters might be considerably different from the properties of the bulk phase.

Computational Details

To gain insight into this problem, we used high-level density functional molecular orbital methods to investigate the energetics and molecular structures of $H_2SO_4 \cdot nH_2O$ clusters from $n = 0$ to $n = 7$ and the structure and energetics of $(H_2SO_4 \cdot 3H_2O)_2$. These results were obtained with density functional methods at the B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory[28] as implemented in the Gaussian 94 program.[29] We chose this level of theory because it is known to give good results for hydrogen-bonded systems.[30−32]

Free energies were calculated as follows:

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

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

$$\Delta E = \Delta E_e^{\ 0} + \Delta E_{\mathrm{Thermal}}$$

$$\Delta E_{\mathrm{Thermal}} = \Delta \mathrm{ZPVE} + \Delta E_{\mathrm{vib}} + \Delta E_{\mathrm{rot}} + \Delta E_{\mathrm{tran}}$$

where ΔG is the free energy change of the reaction, ΔH is the enthalpy change, Δn is the change in moles of the reaction, R is the gas constant, ΔS is the entropy change, ΔE is the energy difference, $\Delta E_e^{\ 0}$ is the difference in electronic energy at 0° K, $\Delta E_{\mathrm{Thermal}}$ contains the difference in the zero-point vibrational energy at 0° K, and ΔE_{vib}, ΔE_{rot}, ΔE_{tran} are the differences in vibrational, rotational, and translational energies, respectively, at temperature T and 1 atm. Table 1 contains all the values required for the above free energy calculation. None of the vibrational frequencies were scaled because the scaling factor for B3LYP is close to unity.[33]

We have tried to find the global minimums to the structures H_2O, H_2SO_4, $H_2SO_4 \cdot nH_2O$ ($n = 1-7$) and $(H_2SO_4 \cdot 3H_2O)_2$ by starting at numerous and various geometries that maximize the hydrogen bond interaction between H_2SO_4 and H_2O. Also, various double ion structures of the type $H_3O^+(H_2O)_nHSO_4^-$ ($n = 1-6$) were also examined by starting the geometry optimizations with H_3O^+ and HSO_4^- and the corresponding amount of waters n. The minima were verified with a frequency analysis. Those structures that had one or more negative frequencies were excluded from this study.

Results and Discussion

Optimized Geometries. For an accurate description of the hydrogen bonds, which are essentially holding these structures together as well as determining their geometry, we will be using hydrogen bond descriptors (HBD). The HBD will be enclosed in parentheses and contain three values: acceptor length, donor

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TABLE 1: DFT Results for Individual Molecules[a]

species	E_{elec}	ZPVE	parameter	173 K	198 K	223 K	248 K	273 K	298 K
H_2O	−76.4620	13.4	E	−47966.2	−47966.1	−47965.9	−47965.8	−47965.6	−47965.5
			S	40.8	41.8	42.8	43.6	44.4	45.1
H_2SO_4	−700.3878	24.3	E	−439474.3	−439474.0	−439473.6	−439473.2	−439472.8	−439472.4
			S	63.3	65.3	67.2	69.1	70.8	72.6
$H_2SO_4 \cdot H_2O$	−776.8679	40.0	E	−487449.9	−487449.4	−487448.9	−487448.3	−487447.6	−487447.0
			S	73.5	76.5	79.3	82.0	84.6	87.1
$H_2SO_4 \cdot 2H_2O$	−853.3474	55.8	E	−535425.1	−535424.4	−535423.6	−535422.8	−535422.0	−535421.1
			S	83.6	87.6	91.3	94.9	98.3	101.5
$H_2SO_4 \cdot 2H_2O$-II	−853.3457	55.7	E						−535420.3
			S						101.5
$H_2SO_4 \cdot 3H_2O$	−929.8276	71.5	E	−583400.7	−583399.9	−583398.9	−583398.0	−583396.9	−583395.8
			S	93.4	98.2	102.8	107.2	111.3	115.3
$H_2SO_4 \cdot 3H_2O$-II	−929.8279	72.0	E						−583395.8
			S						111.6
$H_3O^+ \cdot HSO_4^- \cdot 2H_2O$	−929.8256	71.8	E						−583395.0
			S						106.9
$H_2SO_4 \cdot 4H_2O$	−1006.3071	87.4	E	−631375.8	−631374.8	−631373.7	−631372.6	−631371.4	−631370.1
			S	102.1	107.7	113.1	118.2	123.1	127.8
$H_3O^+ \cdot HSO_4^- \cdot 3H_2O$	−1006.3068	87.8	E						−631370.2
			S						120.9
$H_2SO_4 \cdot 5H_2O$	−1082.7812	102.9	E	−679347.8	−679346.6	−679345.3	−679344.0	−679342.5	−679341.0
			S	113.1	119.7	126.1	132.1	137.8	143.3
$H_2SO_4 \cdot 5H_2O$-II	−1082.7834	103.3	E						−679342.1
			S						139.3
$H_3O^+ \cdot HSO_4^- \cdot 4H_2O$	−1082.7842	103.7	E						−679343.0
			S						133.1
$H_2SO_4 \cdot 6H_2O$	−1159.2584	118.4	E	−727321.6	−727320.3	−727318.8	−727317.2	−679342.5	−727313.8
			S	125.1	132.8	140.0	146.9	153.4	159.7
$H_3O^+ \cdot HSO_4^- \cdot 5H_2O$	−1159.2635	119.6	E						−727317.0
			S						145.9
$H_3O^+ \cdot HSO_4^- \cdot 6H_2O$	−1235.7408	135.2	E	−775298.1	−775296.7	−775295.1	−775293.5	−775291.7	−775289.9
			S	128.5	136.5	144.1	151.4	158.4	165.0
$(H_2SO_4 \cdot 3H_2O)_2$	−1859.6746	143.8	E	−1166812.5	−1166810.7	−1166808.8	−1166806.8	−1166804.7	−1166802.4
			S	152.9	162.6	171.8	180.6	189.0	197.1

[a] *E* and ZPVE are in kcal mol^{-1}, *S* is in cal mol^{-1} K^{-1}, and E_{Elec} is in hartree mol^{-1}.

length, and supplement angle. Acceptor length will show the intermolecular length (in angstroms) of the acceptor oxygen to hydrogen distance ($OH\cdots O$). Donor length will show the intramolecular distance (in angstroms) between the donor's hydrogen and oxygen ($O-H$). The supplement angle value will show the deviation from linearity of the three atoms: $180^\circ - \angle O-H\cdots O$. Neutrals in this paper will be defined as the nondouble ion pair molecules.

Neutrals. Structures for H_2O, H_2SO_4, $H_2SO_4 \cdot nH_2O$ ($n = 1-6$) and $(H_2SO_4 \cdot 3H_2O)_2$ are shown in Figure 1. Morokuma and Muguruma[34] and Hofmann and Schleyer[35] studied sulfuric acid previously at a high level of theory. The only reported high-level study of $H_2SO_4 \cdot H_2O$ (structure 1) was by Morokuma and Muguruma.[34] The molecular structures of these species obtained in this study were virtually identical with those obtained in these previous studies and thus do not warrant further comment. However, in energy computations involving these species the results of this study were used.

There are two conformers of $H_2SO_4 \cdot 2H_2O$ (structures **2-I**, **2-II**) that have almost identical energies (see Table 3) but very different structures. The lowest energy conformer (structure **2-I**) has the two H_2O molecules on opposite sides of the H_2SO_4. The two hydrogen bonds between the oxygen atoms of H_2O and the hydrogen atoms of H_2SO_4 are strong with corresponding HBDs of (1.70, 1.00, 14.7) and (1.70, 1.00, 15.3). There are two much weaker hydrogen bonds between the hydrogen atoms of the H_2O and the $\pi-d$ bonded oxygen atoms of H_2SO_4. These weak bonds have similar HBDs of (2.16, 0.97, 51.2) and (2.17, 0.97, 51.1) and play a more important role in the determination of the geometry of the hydrate than in the determination of its binding energy. The higher energy conformer of the $H_2SO_4 \cdot 2H_2O$ (structure **2-II**) has both H_2O molecules on the same side of H_2SO_4. One of the hydrogen atoms of H_2SO_4 in this conformer is not involved in a hydrogen bond. There is a very strong hydrogen bond between the other hydrogen atom of H_2SO_4 and a H_2O oxygen, which has an HBD of (1.56, 1.02, 21.2). A hydrogen bond of moderate strength having an HBD of (1.76, 0.99, 17.6) exists between the two H_2O molecules. Finally, one of the $\pi-d$ bonded oxygen atoms of H_2SO_4 is weakly hydrogen-bonded to a hydrogen atom of H_2O. Like the weak hydrogen bonds in the lowest energy conformer of $H_2SO_4 \cdot 2H_2O$, this weak bond is important in determining the geometry of the hydrate.

We found two stable conformers of $H_2SO_4 \cdot 3H_2O$ (structures **3-I**, **3-II**) having greatly different structures but almost identical energies. The most stable form (structure **3-I**) has two H_2O's on one side of H_2SO_4 and one H_2O on the other. On the side containing one H_2O there is a strong hydrogen bond between an oxygen atom of H_2O and a hydrogen atom of H_2SO_4. This strong hydrogen bond has a HBD of (1.71, 1.00, 16.2). There is a weak hydrogen bond between a $\pi-d$ bonded oxygen atom of H_2SO_4 and a hydrogen atom of H_2O. On the side containing two H_2O's there is a very strong hydrogen bond with a HBD of (1.58, 1.02, 1.3). This strong hydrogen bond exists between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O. A slightly weaker hydrogen bond with a HBD of (1.75, 0.99, 14.9) exists between the two H_2O's. A much weaker hydrogen bond with a HBD of (1.90, 0.97, 21.9) exists between a $\pi-d$ bonded oxygen and a hydrogen atom of H_2O, which as discussed above is important in determining the geometry of the hydrate.

All three H_2O's of $H_2SO_4 \cdot 3H_2O$ are on the same side of H_2SO_4 in the higher energy conformer of this hydrate (structure

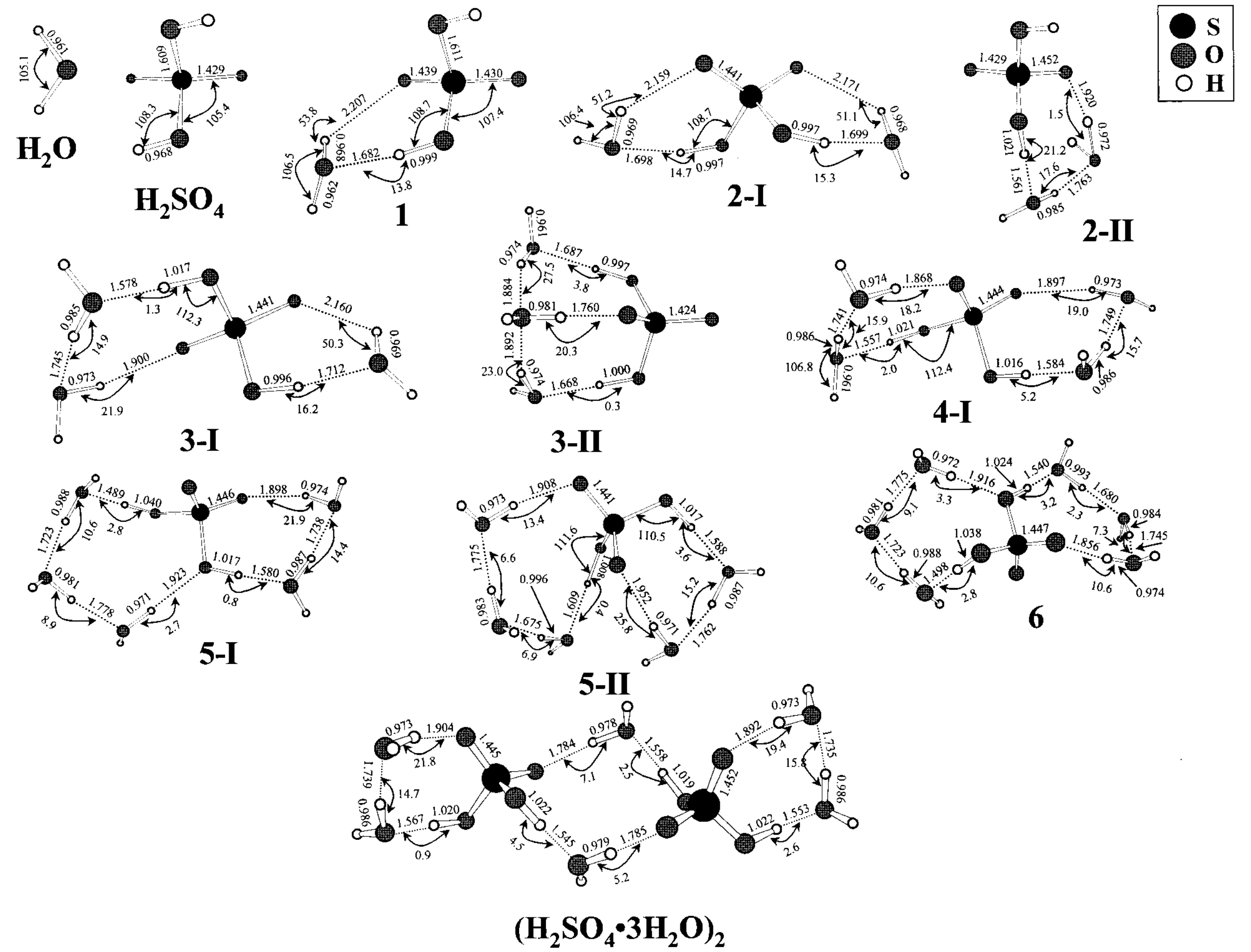

Figure 1. Structures of H_2O, H_2SO_4, $H_2SO_4{\cdot}nH_2O$ ($n = 1-6$) and $(H_2SO_4{\cdot}3H_2O)_2$ calculated at B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p). Angles are in degrees and bond lengths are in angstroms. Angles for hydrogen bonds are supplementary angles: $180° - \angle O{-}H{\cdots}O$.

TABLE 2: Gibbs Free Energy (kcal mol^{-1}) of Hydration for the Hydrates of Sulfuric Acid[a]

reaction	173 K	198 K	223 K	248 K	273 K	298 K
H_2SO_4	0.0	0.0	0.0	0.0	0.0	0.0
$H_2SO_4{\cdot}H_2O$	−4.4	−3.7	−2.9	−2.1	−1.4	−0.6
$H_2SO_4{\cdot}2H_2O$	−4.0	−3.2	−2.4	−1.7	−0.9	−0.1
$H_2SO_4{\cdot}3H_2O$	−4.4	−3.7	−2.9	−2.1	−1.3	−0.5
$H_2SO_4{\cdot}4H_2O$	−3.7	−2.9	−2.1	−1.3	−0.5	0.4
$H_2SO_4{\cdot}5H_2O$	−0.9	−0.2	0.5	1.3	2.0	2.8
$H_2SO_4{\cdot}6H_2O$	−3.0	−2.3	−1.6	−0.8	−0.1	0.6
$H_3O^+{\cdot}HSO_4^-{\cdot}6H_2O$	−4.2	−3.2	−2.3	−1.3	−0.3	0.7
$(H_2SO_4{\cdot}3H_2O)_2$	−10.7	−9.8	−8.9	−8.1	−7.2	−6.3

[a] The values for the last item in this table show the Gibbs free energy of formation from $H_2SO_4{\cdot}6H_2O + H_2SO_4$.

TABLE 3: Enthalpy (kcal mol^{-1}), Entropy (cal mol^{-1} K^{-1}), and Gibbs Free Energy (kcal mol^{-1}) of Isomerization for the Hydrates of Sulfuric Acid

	ΔH	ΔS	ΔG
Neutral to Neutral Isomerizations			
$H_2SO_4{\cdot}2H_2O$-II ⇔ $H_2SO_4{\cdot}2H2O$	−0.85	0.02	−0.9
$H_2SO_4{\cdot}3H_2O$-II ⇔ $H_2SO_4{\cdot}3H_2O$	−0.08	3.74	−1.2
$H_2SO_4{\cdot}5H_2O$-II ⇔ $H_2SO_4{\cdot}5H_2O$	1.14	3.92	0.0
Double Ionic to Neutral Isomerizations			
$H_3O^+{\cdot}HSO_4^-{\cdot}2H_2O$ ⇔ $H_2SO_4{\cdot}3H_2O$	−0.80	8.39	−3.3
$H_3O^+{\cdot}HSO_4^-{\cdot}2H_2O$ ⇔ $H_2SO_4{\cdot}3H_2O$-II	−0.72	4.65	−2.1
$H_3O^+{\cdot}HSO_4^-{\cdot}3H_2O$ ⇔ $H_2SO_4{\cdot}4H_2O$	0.12	6.89	−1.9
$H_3O^+{\cdot}HSO_4^-{\cdot}4H_2O$ ⇔ $H_2SO_4{\cdot}5H_2O$	0.81	6.28	−1.1
$H_3O^+{\cdot}HSO_4^-{\cdot}4H_2O$ ⇔ $H_2SO_4{\cdot}5H_2O$-II	1.95	10.20	−1.1
$H_3O^+{\cdot}HSO_4^-{\cdot}5H_2O$ ⇔ $H_2SO_4{\cdot}6H_2O$	3.21	13.74	−0.9

3-II). Two strong hydrogen bonds with HBD's of (1.67, 1.00, 0.3) and (1.69, 1.00, 3.8) exist between the hydrogen atoms of H_2SO_4 and the oxygen atoms of H_2O. A slightly weaker hydrogen bond with a HBD of (1.76, 0.98, 20.3) exists between a $\pi-$d bonded oxygen atom of H_2SO_4 and a hydrogen atom of H_2O. There are two weak hydrogen bonds with HBD's of (1.89, 0.97, 23.0) and (1.88, 0.97, 27.5) between two hydrogen atoms of two different H_2O molecules and the oxygen atom of the other H_2O molecule.

We found only one stable conformer of $H_2SO_4{\cdot}4H_2O$ (structure **4**). Two H_2O's are on one side of H_2SO_4 and two H_2O's on the other. The bonding on the two sides is almost identical. On both sides there is a strong hydrogen bond between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O with HBD's of (1.58, 1.02, 5.2) and (1.56, 1.02, 2.0). Also, on both sides there is a hydrogen bond of moderate strength with approximately the same HBD of (1.75, 0.99, 15.8) that exists between the two H_2O's. There is a much weaker hydrogen bond with a HBD of (1.90, 0.97, 18.2) between a $\pi-$d bonded oxygen atom of H_2SO_4 and a hydrogen atom of H_2O. An even weaker similar hydrogen bond exists on the other side with a HBD of (1.90, 0.97, 19.0).

We found two conformers of $H_2SO_4{\cdot}5H_2O$ (structures **5-I**, **5-II**). Like the conformers of $H_2SO_4{\cdot}3H_2O$, these conformers of $H_2SO_4{\cdot}5H_2O$ are similar in structure and have almost identical energies. Each conformer has two H_2O's on one side of H_2SO_4 and three H_2O's on the other. On the side containing three

H_2O's, the lowest energy conformer (structure **5-I**) has a very strong hydrogen bond with a HBD of (1.49, 1.04, 2.8) between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O. There are two moderately strong hydrogen bonds with HBD's of (1.72, 0.99, 10.6) and (1.78, 0.98, 8.9) between H_2O molecules and a weak hydrogen bond with a HBD of (1.92, 0.97, 2.7) between a O−H bonded oxygen of H_2SO_4 and a hydrogen atom of H_2O. On the other side of the lowest energy conformer there is a strong hydrogen bond with HBD of (1.58, 1.02, 0.8) between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O. It is noteworthy that this bond is not nearly as strong as a similar bond on the other side of the conformer. There is a bond of moderate strength with a HBD of (1.74, 0.98, 14.4) between the two H_2O molecules and a weak hydrogen bond with a HBD of (1.90, 0.97, 21.9) between a π−d bonded oxygen atom of H_2SO_4 and a hydrogen atom of H_2O. One π−d bonded oxygen atom is not hydrogen-bonded.

A H_2SO_4•$5H_2O$ conformer of slightly higher energy (structure **5-II**) does not have the very strong hydrogen bond that exists in the lowest energy conformer. On the side containing three H_2O molecules, there is only a moderately strong hydrogen bond with a HBD of (1.61, 1.01, 0.4) between the hydrogen of H_2SO_4 and an oxygen atom of H_2O. There is a hydrogen bond of moderate strength having a HBD of (1.68, 1.0, 6.9) between two H_2O molecules and another moderately strong hydrogen bond with a HBD of (1.78, 0.98, 6.6) between two other H_2O molecules. On the other side of the H_2SO_4 there is a strong hydrogen bond of HBD of (1.59, 1.02, 3.6) between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O. There is a moderately strong hydrogen bond of HBD of (1.76, 0.99, 15.2) between two H_2O molecules and a weak hydrogen bond between a π−d bonded oxygen atom of H_2SO_4 and a hydrogen atom of H_2O.

We found only one conformer of H_2SO_4•$6H_2O$ (structure **6**). Three H_2O's are on one side of H_2SO_4 and three H_2O's on the other. The bonding on the two sides is almost identical. There is a strong hydrogen bond between a hydrogen atom of H_2SO_4 and the oxygen atom of H_2O with a HBD of (1.50, 1.04, 2.8) on one side and a strong hydrogen bond between a hydrogen atom of H_2SO_4 and the oxygen of H_2O with a HBD of (1.54, 1.02, 3.2) on the other side. There are hydrogen bonds between the H_2O molecules with HBD's of (1.76, 0.98, 9.1) and (1.72, 0.99, 10.6) on one side and HBD's of (1.68, 1.0, 2.3) and (1.75, 0.98, 7.3) on the other. Bonding on the two sides differs in the way the weak hydrogen bonds form. On one side there is a very weak hydrogen bond with a HBD of (1.92, 0.97, 3.3) between a hydrogen atom of H_2O and an OH-bonded oxygen atom of H_2SO_4. On the other side there a very weak hydrogen bond with a HBD of (1.86, 0.97, 10.6) between a π−d bonded oxygen atom and a hydrogen atom H_2O. The one stable neutral H_2SO_4•$7H_2O$ we found had an imaginary frequency.

We also looked into $(H_2SO_4•3H_2O)_2$ because we believe this molecule is an important step in the formation of new atmospheric particles. After a close examination of the structures above and their relative energies (see Hydrate Energetics below), one can determine a molecular structure that is a good candidate for a global minimum. That structure is one that maximizes the number of hydrogen bonds between H_2O and H_2SO_4. The optimized structure has two waters in the middle bound to H_2SO_4 with two pairs of similar hydrogen bonds. There is a moderately strong hydrogen bond pair with HBD's of (1.78, 0.98, 7.1) and (1.79, 0.98, 5.2) connecting the π−d bonded oxygen atom and a hydrogen atom of H_2O, and there is a strong hydrogen bond pair with very similar HBD's of (1.56, 1.02, 2.5) and (1.55, 1.02, 4.5) between a hydrogen atom of H_2SO_4 and the oxygen of H_2O. On the "outside" of this molecule are also two pairs of similar hydrogen bonds. Two strong hydrogen bonds with similar HBD's of (1.55, 1.02, 2.6) and (1.57, 1.02, 0.9) are located between a hydrogen atom of H_2SO_4 and an oxygen of H_2O, and a pair of weak hydrogen bonds with similar HBD's of (1.90, 0.97, 21.8) and (1.90, 0.97, 19.4) connect the π−d bonded oxygen atom and a hydrogen atom of H_2O.

Double Ions. Structures for $H_3O^+(H_2O)_nHSO_4^-$ where $n = 2-6$ are shown in Figure 2. The double ion structures are less stable than their corresponding neutral structures (see Table 3). For $H_3O^+(H_2O)_nHSO_4^-$, $n = 0$ and $n = 1$, there are no stable double ions found. Double ions do not form until $n = 3$. This is mainly due to the fact that there are not enough water molecules to separate the two ions. Without this separation the electrostatic interaction energy is very large, and consequently, those structures do not exist on the potential energy surface.[36]

We found one structure of $H_3O^+(H_2O)_2HSO_4^-$ (structure **3-D**). This structure has the familiar diamond-shaped "cap" that was found for other hydrated double ions.[36−39] The hydronium ion is indirectly and directly connected to HSO_4^-. It is indirectly connected when H_3O^+ is strongly hydrogen-bonded with similar HBD's of (1.59, 1.02, 16.8) and (1.59, 1.02, 16.1) to two waters. Those two waters are moderately hydrogen-bonded to HSO_4^- with similar HBD's of (1.80, 0.98, 16.7) and (1.79, 0.98, 17.1). The hydronium ion is also directly bonded to the contraion HSO_4^- with an HBD of (1.45, 1.06, 11.1), the shortest and strongest hydrogen bond studied. This is unlike past studies of the hydration of double ions where there are at least three H_2O's needed to separate the ions in the cluster.[36−39] This could be explained by the large contraion (HSO_4^-) compared to results from past studies and could be primarily due to the resonance stabilization present about the three π−d oxygen atoms, which are not present in those past studies. The formation of $H_3O^+(H_2O)_2HSO_4^-$ is most likely a proton-tunneling mechanism between the −OH on H_2SO_4 and an acceptor H_2O.

There is one structure of $H_3O^+(H_2O)_3HSO_4^-$ (structure **4-D**). There is a diamond cap to this structure too. This hydronium ion is indirectly connected to the contraion by three H_2O's. The hydronium ion is strongly hydrogen-bonded to those three H_2O's with three very similar HBD's of (1.51, 1.03, 8.1), (1.50, 1.03, 8.5), and (1.53, 1.02, 9.1). The three H_2O's are moderately hydrogen-bonded to HSO_4^- by three very similar HBD's of (1.67, 1.00, 7.4), (1.68, 1.00, 7.9), and (1.68, 1.00, 9.0). This diamondlike "cap" appears in similar hydrated double ion clusters studied.[36−39]

We found one structure of $H_3O^+(H_2O)_3HSO_4^-$ (structure **5-D**). This structure is very similar to structure **4-D** with the exception of the addition of H_2O to the other "side". The diamondlike "cap" is formed with the usual three sets of strong and moderately strong hydrogen bonds indirectly connecting H_3O^+ to HSO_4^-. The strong hydrogen bonds have HBD's of (1.53, 1.03, 10.1), (1.53, 1.03, 7.1), and (1.67, 1.03, 8.7), and the moderately strong hydrogen bonds have HBD's of (1.68, 1.00, 11.7), (1.70, 1.00, 8.1), and (1.67, 1.00, 8.4). The water on the other side has a moderately strong hydrogen bond with an HBD of (1.79, 0.99, 20.9).

A minimum was located for $H_3O^+(H_2O)_6HSO_4^-$ (structure **6-D**). As before, there is a diamondlike "cap" present on one side. The other side has two waters. The hydrogen bonds holding the diamondlike "cap" are very similar to the previous structure's cap and will not be discussed. On the other side,

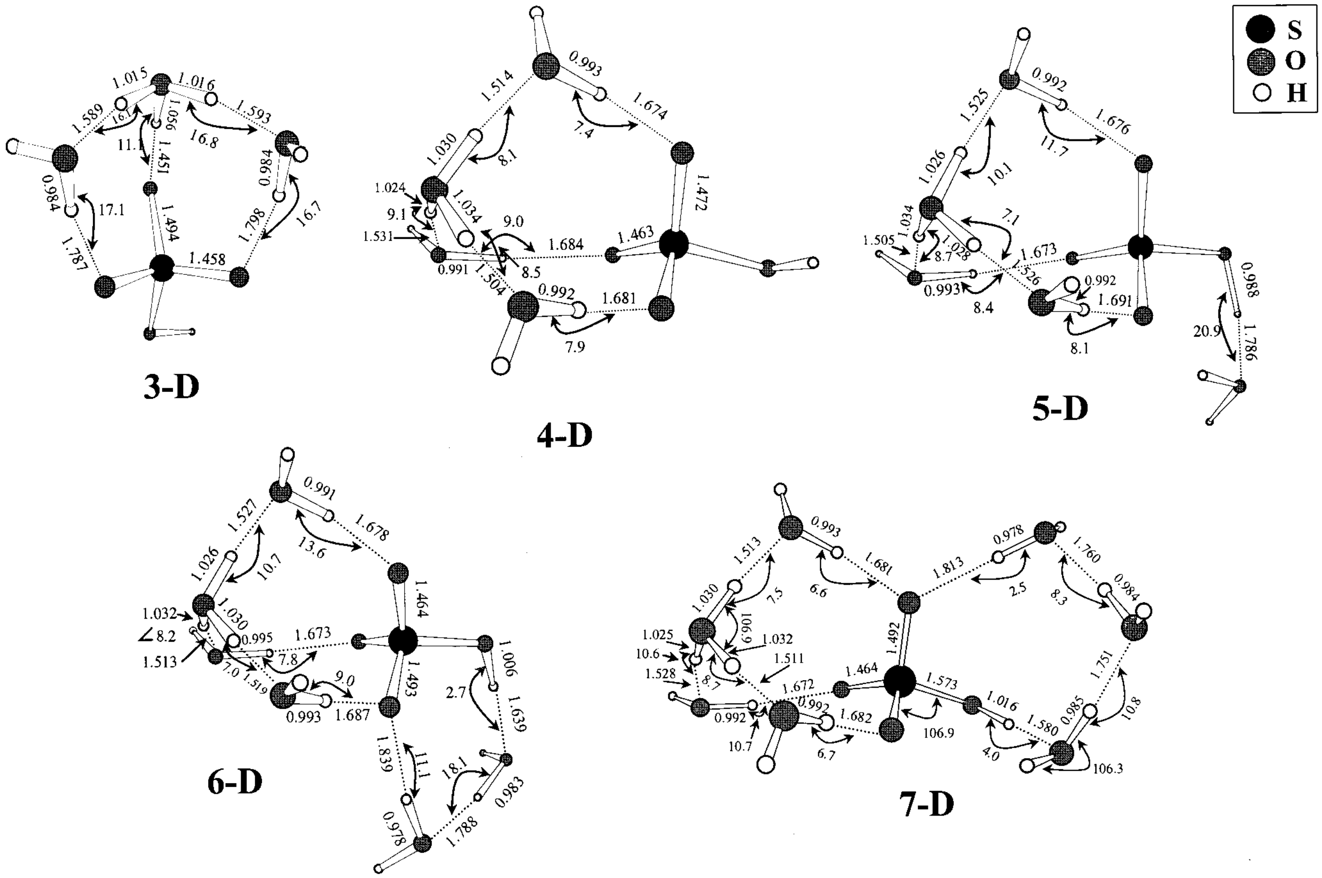

Figure 2. Structures of $H_3O^+(H_2O)_nHSO_4^-$ for $n = 2-6$ calculated at B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p). Angles are in degrees and bond lengths are in angstroms. Angles for hydrogen bonds are supplementary angles: $180° - \angle O-H\cdots O$.

the hydrogen bond between the water and the hydrogen on HSO_4^- strengthened with a HBD of (1.64, 1.01, 2.7). There is a moderate hydrogen bond with a HBD of (1.79, 0.98, 18.1) located between the two waters, and there is a weak hydrogen bond with a HBD of (1.84, 0.98, 11.1) between a water and a $\pi-$d bonded oxygen on HSO_4^-.

We found one structure of $H_3O^+(H_2O)_6HSO_4^-$ (structure **7-D**). Once again, there is a diamondlike "cap" present on one side. The other side has three waters. The hydrogen bonds holding the diamondlike "cap" are very similar to the previous structure's cap and will not be discussed. On the side containing only three H_2O's, there is a strong hydrogen bond with an HBD of (1.58, 1.02, 4.0) between the hydrogen on HSO_4^- and an oxygen atom of water. The two water molecules are bound by two moderately strong hydrogen bonds with HBD's of (1.75, 0.99, 10.8) and (1.76, 0.98, 8.3). There is a weak hydrogen bond between a $\pi-$d bonded oxygen on HSO_4^- and a hydrogen atom on water of HBD of (1.81, 0.98, 2.5).

We believe that the mechanism for the formation of H_3O^+ and HSO_4^- in structures $H_3O^+(H_2O)_nHSO_4^-$, $n = 4-6$, is most likely a synchronous proton transfer as shown for very similar clusters studied in the past.[36,40]

Hydrate Energetics. Shown in Table 3 are the relative enthalpies, entropies, and free energies of hydrates $H_2SO_4{\cdot}nH_2O$ of the same n. All the neutrals are more stable than their corresponding double ions. It is interesting to note that as more waters are added, the difference in free energy between a neutral and double ion decreases. This has been observed experimentally for naphthol in water in which the equilibrium shifts toward the protonated naphthol as the structure size increases (more waters are added).[41]

The electronic energy, zero-point vibrational energy, internal energy, and entropy at 298 K are given in Table 1 for each of the hydrates studied. For the hydrates that are involved in the free energy calculations, the internal energy and entropy are also given at 173, 198, 223, 248, and 273 K in Table 1. The temperature range was selected to correspond to the approximate range of temperatures found in the atmosphere. Free energies of formation of $H_2SO_4{\cdot}nH_2O$ from $H_2SO_4{\cdot}(n-1)H_2O + H_2O$ over this temperature range are given in Table 2. It should be noted that since these clusters are held together by intermolecular hydrogen bonds that are known to be anharmonic,[42] there could be some error in the calculated entropies, but recent calculations by Scott and Radom[43] and Sodupe et al.[44] have shown that B3LYP with very large basis sets can reproduce experimental anharmonic low frequencies of covalent and hydrogen-bonded compounds.

Plots of the free energy for the reactions $H_2SO_4{\cdot}(n-1)H_2O + H_2O \rightarrow H_2SO_4{\cdot}nH_2O$ as a function of n are shown in Figure 3. Its noteworthy that the free energies for these processes are slightly negative for $n = 1-3$ and slightly positive for $n = 4-7$ with a maximum at $n = 5$. An analysis of the entropy and enthalpy terms (see Figure 4) shows that this maximum is entirely caused by the enthalpy term. A possible explanation is that water can no longer directly bind to H_2SO_4 (which is an exothermic process), but it must bind with itself (not nearly as exothermic). This causes the enthalpy term to significantly increase, which then causes the free energy to increase. The decrease in free energy from 25 to −100 °C can be explained in that the absolute values of free energy of hydration are not large at 25 °C, and this reflects the fact that the enthalpy change is almost entirely offset by the entropy term ($\Delta H \cong T\Delta S \cong 10$

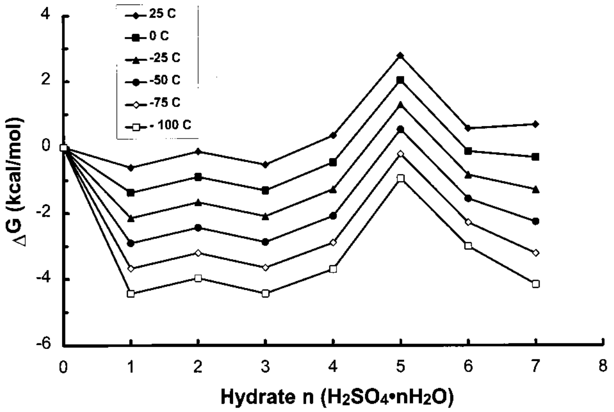

Figure 3. Successive free energy of hydration for $H_2SO_4{\cdot}nH_2O$.

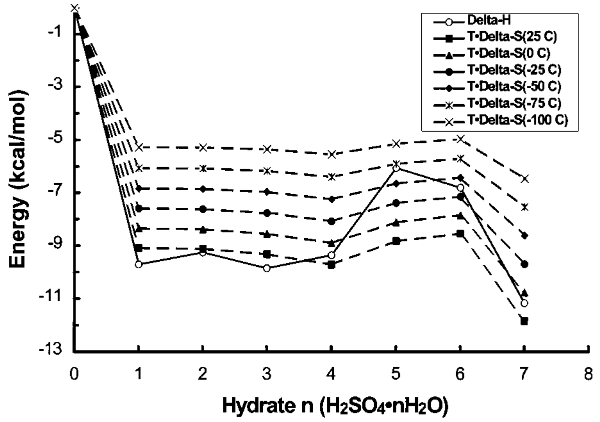

Figure 4. Enthalpy and entropy energy term plot used for the calculation of successive free energy of hydration for $H_2SO_4{\cdot}nH_2O$. There is only one temperature plotted for the enthalpy term, since it changes very slightly over the entire studied temperature range (<0.1 kcal/mol change).

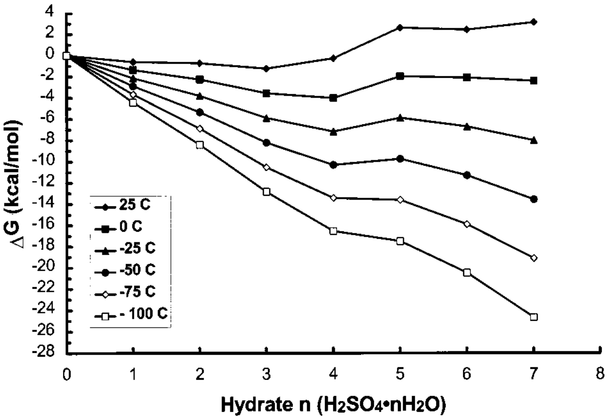

Figure 5. Cumulative free energy of hydration for $H_2SO_4{\cdot}nH_2O$.

kcal mol^{-1}). Lower temperatures favor the enthalpy term because of an increasing entropy term (see Figure 4); thus, the free energy of hydration decreases rapidly as the temperature decreases.

Computed equilibrium constants are shown in Figure 6. For comparison we include equilibrium constants estimated by Jaecker-Voirol et al.[24] using a liquid drop model. A liquid drop model must rely on bulk properties such as surface tension, surface area, spherical drop size, and chemical potentials of bulk-phase solutions of H_2SO_4 and H_2O, which have H_2SO_4 completely ionized (SO_4^{2-}).

Jaecker-Voirol and Mirabel[26] used these equilibrium constants to incorporate the formation of hydrates into homogeneous nucleation theory used to predict new particle formation rates. Our equilibrium constants are orders of magnitude smaller than those reported by Jaecker-Voirol and Mirabel and decrease much more rapidly with the size of the hydrate. We anticipate that the effect of hydrates may play a much smaller role in homogeneous nucleation theory than previously suspected.

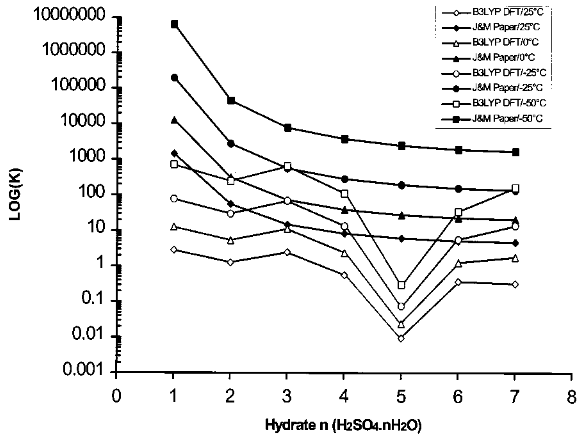

Figure 6. Equilibrium constants for $H_2SO_4{\cdot}(n - 1)H_2O + H_2O = H_2SO_4{\cdot}nH_2O$. J&M Paper refers to the equilibrium constants calculated by Jaecker-Voirol and Mirabel.[26]

The cumulative free energy of formation of $H_2SO_4{\cdot}nH_2O$ from free H_2SO_4 and H_2O is shown in Figure 5 for each of the hydrates studied. Inspection of Figure 5 reveals that at 298 K a minimum in the free energy of formation exists at $n = 3-4$. However, the free energy of formation decreases rapidly with temperature with the minimum becoming less pronounced and then disappearing completely by 248 K. Below 248 K there is no free energy barrier to the formation of larger hydrates.

Table 2 shows one particular important item: the very spontaneous formation of larger hydrates such as $(H_2SO_4{\cdot}3H_2O)_2$. We believe that most of the atmospheric ultrafine particles in the 1−100 nm radius range might be entirely composed of long chains of $H_2SO_4{\cdot}2H_2O$.

Comparison of Small Hydrate and Bulk-Phase Structures. In contrast to the structure of H_2SO_4 and H_2O in bulk phases where H_2SO_4 is almost totally converted to H_3O^+ and SO_4^{-2},[45,46] the $H_2SO_4{\cdot}nH_2O$ studied here are either hydrogen-bonded complexes of H_2SO_4 and H_2O or double ionic clusters containing HSO_4^-, H_3O^+, and H_2O. This was expected because the dielectric property of the bulk phase plays an important role in the stabilization of ions. This dielectric is largely absent in the smaller hydrates of H_2SO_4; thus, ions do not form. More dielectric becomes available as the hydrates grow. Inspection of the structures of H_2SO_4 hydrates indicates that at least one hydrogen bond between a hydrogen atom of H_2SO_4 and an oxygen atom of H_2O decreases in length and thus grows in strength as the number of H_2O's increase. Furthermore, the Mulliken charge on that hydrogen atom increased from 0.3 to 0.5 as the number of H_2O's increased from $n = 1$ to $n = 6$.

This work also suggests an interesting source of surface free energy for the hydrates of H_2SO_4. In the interior of larger hydrates the particle may be totally ionized. Ionization clearly provides a significant source of free energy to stabilize the particle. However, the H_2SO_4 and H_2O molecules near the surface of the particle may not totally be ionized, which robs the system of a significant amount of free energy of stabilization. This loss makes the free energy per mole of the system progressively higher than that of the bulk system as the hydrate size decreases.

In summary our results suggest that the free energy of hydration of the lower hydrates of H_2SO_4 is dominated by the formation of hydrogen bonds and not by the free energy from the conversion of H_2SO_4 to H_3O^+ and SO_4^{-2}. However, as the hydrates grow larger by adding H_2O, the free energy derived from the formation of H_3O^+ and HSO_4^- becomes available at $n = 7$ to offset the so-called surface free energy that destabilizes the particle as calculated for $H_2SO_4 \cdot 7H_2O$. These results also suggest that previous estimates of the properties of the hydrates from bulk properties[24-27] may contain substantial errors.

Conclusion

The structures of $H_2SO_4 \cdot nH_2O$ clusters ($n = 1-7$) are much different from the structures of the corresponding bulk phases of the same composition. The $H_2SO_4 \cdot nH_2O$ ($n = 1-6$) clusters that are most stable are bound together by hydrogen bonds, some of which are extremely strong. The heptahydrate ($H_2SO_4 \cdot 7H_2O$) formed a single H_3O^+ ion and a HSO_4^- ion. These results should be compared to the bulk phase structures where H_2SO_4 and two H_2O's have been converted to two H_3O^+ ions and a free SO_4^- ion. It is important in the formation of larger clusters that the free energy of this ionization process is still available for increasing the size of the particle. This happens for larger particles when the dielectric properties of the cluster become sufficient to stabilize the ion pairs produced. At this stage the particle may grow by adding H_2SO_4. Finally, there is a contribution to the so-called surface free energy by the fact that in larger clusters, ions may be stable in the bulk parts of the particle but not near the surface. As the surface of the particle is approached, the amount of dielectric available to stabilize the ions rapidly decreases and a hydrogen-bonded molecular complex of H_2SO_4 and H_2O become favored. It is likely that most of the H_2O and H_2SO_4 near the surface of such particles are hydrogen-bonded molecular complexes.

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References and Notes

(1) Castleman, A. W., Jr.; Keesee, R. G. *Annu. Rev. Earth Planet. Sci.* **1981**, *9*, 227.

(2) Castleman, A. W., Jr. *Space Sci. Rev.* **1974**, *15*, 547.

(3) Mirabel, P.; Katz, J. L. *J. Chem. Phys.* **1974**, *60*, 1138.

(4) Clarke, A. D. *J. Geophys. Res.* **1993**, *98* (20), 633.

(5) Carslaw, K. S.; Peter, T.; Clegg, S. L. *Rev. Geophys.* **1997**, *35*, 125.

(6) Shugard, W. J.; Heist, R. H.; Reiss, H. *J. Chem. Phys.* **1974**, *61*, 5298.

(7) Perry, K. D.; Hobbs, P. V. *J. Geophys. Res.* **1994**, *99*, 22803.

(8) Hegg, D. A. *Geophys. Res. Lett.* **1990**, *17*, 2165.

(9) Hamill, P.; Kiang, C. S.; Cadle, R. D. *J. Atmos. Sci.* **1976**, *34*, 150.

(10) Hamill, P.; Toon, O. B.; Turco, R. P. *J. Geophys. Res., D: Atmos.* **1990**, 417.

(11) McMurry, P. H.; Friedlander, S. K. *Atmos. Environ.* **1979**, *13*, 1635.

(12) Hoppel, W. A. *Atmos. Environ.* **1987**, *21*, 1.

(13) Russell, L. M.; Pandis, S. N.; Seinfeld, J. H. *J. Geophys. Res., D: Atmos.* **1994**, *99*, 20989.

(14) Kreidenweis, S. M.; Penner, J. E.; Yin, F.; Seinfeld, J. H. *Atmos. Environ.* **1991**, *25A*, 2501.

(15) Hegg, D. A.; Radke, L. F.; Hobbs, P. V. *J. Geophys. Res.* **1990**, *95*, 13917.

(16) Kreidenweiss, S. M.; Seinfeld, J. H. *Atmos. Environ.* **1988**, *22*, 283.

(17) McMurry, P. H. *J. Colloid Interface Sci.* **1980**, *78*, 513.

(18) Shaw, G. E. *Atmos. Environ.* **1989**, *23*, 2841.

(19) Easter, R. C.; Peters, L. K. *J. Appl. Meteorol.* **1994**, *33*, 775.

(20) Molina, M. J.; Zhang, R.; Wooldridge, P. J.; McMahon, J. R.; Kim, J. E.; Chang, H. Y.; Beyer, K. D. *Science (Washington, D.C.)* **1993**, *261*, 1418.

(21) Koop, T.; Carslaw, K. S. *Science (Washington, D.C.)* **1996**, *272*, 1638.

(22) Zhang, R. Y.; Leu, M. T.; Keyser, L. F. *J. Phys. Chem.* **1994**, *98*, 13563.

(23) Zhang, R. Y.; Jayne, J. T.; Molina, M. J. *J. Phys. Chem.* **1994**, *98*, 867.

(24) Jaecker-Voirol, A.; Mirabel, P.; Reiss, H. *J. Chem. Phys.* **1987**, *87*, 4849.

(25) Jaecker-Voirol, A.; Mirabel, P. *J. Phys. Chem.* **1988**, *92*, 3518.

(26) Jaecker-Voirol, A.; Mirabel, P. *Atmos. Environ.* **1989**, *23*, 2053.

(27) Taleb, D.-E.; McGraw, R.; Mirabel, P. *J. Geophys. Res.* **1997**, *102*, 12885.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewsk, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(30) Gonzalez, L.; Mo, O.; Yanez, M. *J. Comput. Chem.* **1997**, *18*, 1124.

(31) Soliva, R.; Orozco, M.; Luque, F. J. *J. Comput. Chem.* **1997**, *18*, 980.

(32) Novoa, J. J.; Sosa, C. *J. Phys. Chem.* **1995**, *99*, 15837.

(33) Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **1995**, *246*, 40.

(34) Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.

(35) Hofmann, M.; Schleyer, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 4947.

(36) Planas, M.; Lee, C.; Novoa, J. J. *J. Phys. Chem.* **1996**, *100*, 16495.

(37) Lee, C.; Sosa, C.; Planas, M.; Novoa, J. J. *J. Chem. Phys.* **1996**, *104*, 7081.

(38) Lee, C.; Sosa, C.; Novoa, J. J. *J. Chem. Phys.* **1995**, *103*, 4360.

(39) Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451.

(40) Lee, C.; Fitzgerald, G.; Planas, M.; Novoa, J. J. *J. Phys. Chem.* **1996**, *100*, 7398.

(41) Kim, S. K.; Breen, J. J.; Willberg, D. M.; Peng, L. W.; Heikal, A.; Syage, J. A.; Zewail, A. H. *J. Phys. Chem.* **1995**, *99*, 7421.

(42) Rovira, M. C.; Novoa, J. J.; Whangbo, M. H.; Williams, J. M. *Chem. Phys.* **1995**, *200*, 319.

(43) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(44) Sodupe, M.; Oliva, A.; Bertran, J. *J. Phys. Chem. A* **1997**, *101*, 9142.

(45) Kjallman, T.; Olovsson, I. *Acta Crystallogr.* **1972**, *B28*, 1692.

(46) Taesler, I.; Olovsson, I. *J. Chem. Phys.* **1969**, *51*, 4213.