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Citation: *The Journal of Chemical Physics* **108**, 1031 (1998); doi: 10.1063/1.475496

View online: <http://dx.doi.org/10.1063/1.475496>

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***Ab initio* study of gas-phase sulphuric acid hydrates containing 1 to 3 water molecules**

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(Received 2 September 1997; accepted 10 October 1997)

Sulphuric acid has a tendency to form hydrates, small clusters containing a few water molecules, in the gas phase. Hydrate formation has a stabilising effect on the vapour as the pressure of sulphuric acid drops (relative to unhydrated vapor), decreasing the nucleation rate. In classical nucleation theories the hydration energies and the hydrate distribution are predicted assuming that hydrates can be described as liquid droplets having thermodynamic properties of bulk liquid. To obtain a better understanding of the structures and formation energies of the smallest clusters, we have performed *ab initio* density functional calculations of the mono-, di-, and trihydrates. The hydrogen bonds between the molecules are found to be strong. The more water molecules the hydrate contains, the clearer ring-like structure is formed. Comparison to classical values for the hydration enthalpies confirms that the properties of bulk liquid do not describe the properties of the smallest clusters too well. The energy barrier for proton transfer reaction $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{HSO}_4^- \cdot \text{H}_3\text{O}^+$ for mono- and dihydrate is high, and protonisation is unlikely to occur, but in trihydrate the protonisation has almost occurred and the barrier is very low. We also studied the singly protonised monohydrate, and found that while sulphuric acid forms H bonds with the OH parts, the hydrogen sulphate ion tends to bind with the O (S=O) part, and the second proton stays tightly in the ion. © 1998 American Institute of Physics. [S0021-9606(98)03103-1]

I. INTRODUCTION

Atmospheric sulphate particles scatter incoming solar radiation back to the space, and may therefore partially offset the warming of the Earth's climate.¹ It is therefore no surprise that the formation and growth of these particles has recently received considerable experimental and theoretical interest. It is believed that the sulphate particles are formed via homogeneous or ion-induced nucleation of sulphuric acid and water vapors, possibly aided by some other chemical species.² The quantitative and even qualitative aspects of such nucleation remain obscure, however. At the moment, the classical nucleation theory³ (including certain variants) is the only means of predicting sulphuric acid/water nucleation rates. Unfortunately, the predictions of the theory for this system have not been reliably tested so far, as the various laboratory measurements⁴ are not in quantitative agreement.

One of the special reasons for the theoretical difficulties of predicting sulphuric acid/water nucleation, compared with other binary systems, stems from the tendency of sulphuric acid to form hydrates (small clusters containing up to about 10 water molecules) in the gas phase. The hydrates stabilise the vapor, i.e., their formation energy is negative, and therefore it is energetically more difficult to form a critical nucleus out of hydrates than out of monomers. The ability of H_2SO_4 to form hydrates was recognised first by Doyle in 1961,⁵ but it took some 13 years before the first thermodynamical theory predicting the hydration energies and hydrate

distributions at given conditions appeared.⁶ A refined theory was later presented by Jacker-Voirrol *et al.*⁷ Their theory relies on the capillarity approximation, assuming that the hydrates can be described as liquid droplets having macroscopic properties such as liquid density and surface tension. This is, of course, very questionable with such small molecular clusters, although the study by Mirabel and Ponche⁸ seemed to indicate that the formation enthalpy of the monohydrate compares rather well with *ab initio* calculations.

To date there are few molecular studies of sulphuric acid/water clusters. Kurdi *et al.*⁹ performed an *ab initio* study of the monohydrate assuming rigid molecules, while Hale and Kathmann¹⁰ and Kusaka *et al.*¹¹ studied clusters of varying sizes using classical Monte Carlo simulation techniques. The purpose of this study is to investigate the first three sulphuric acid hydrates using *ab initio* density functional methods. All the atoms are freely let to relax to the energetically optimal structure. We were particularly interested in determining how many water molecules are needed to cause the proton transfer reaction $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{HSO}_4^- \cdot \text{H}_3\text{O}^+$. The energy barriers for this reaction were estimated for the mono-, di-, and trihydrates. The binding energies of the stabilised structures were compared with the enthalpies obtained from the simple liquid-drop model of hydration.

II. COMPUTATIONAL DETAILS

To study the behavior of sulphuric acid with 1–3 water molecules we have used a density functional theory (DFT)

TABLE I. Experimental values for O...O distance and H-bond energy of water dimer, and their optimised values calculated with LDA, Becke only and BLYP functional for exchange-correlation energy.

	LDA	H ₂ O·H ₂ O Becke	BLYP	Expt.
O...O distance	2.7 Å	3.0 Å	2.9 Å	3.0 Å
O...O distance ^a	2.70 Å	3.02 Å	2.95 Å	
O...O distance ^b	2.72 Å	3.00 Å	2.91 Å	
H-bond energy	-36.8 kJ/mol	-12.1 kJ/mol	-18.0 kJ/mol	-22.2 kJ/mol
H-bond energy ^a	-37 kJ/mol	-12 kJ/mol	-18 kJ/mol	
H-bond energy ^b	-42 kJ/mol	-14.3 kJ/mol	-22 kJ/mol	

^aFrom Ref. 15.^bUsing Biosym's DMol program Ref. 26.

based Car–Parrinello (CP) *ab initio* molecular dynamics method.¹² Even though the main advantage of the CP method is the possibility to perform dynamical simulations, in this work we have only optimised the geometries and investigated proton transfer barriers. For the barrier estimation we have implemented a standard SHAKE type constraint algorithm¹³ to our CP code.

The regularly used local density approximation (LDA) in DFT has turned out not to be accurate enough to describe hydrogen binding,¹⁴ whereas the gradient corrected LDA (GC–LDA) seems to work very well.^{14,15} In such schemes the exchange and correlation energy is assumed to depend on both the density and its gradient,

$$E_{xc} = \int \epsilon[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] d^3r. \quad (1)$$

The CP scheme we use has already proven to be successful for water,^{16,15} for proton transfer in water¹⁷ and for solution of hydrohalic acids, like HF and HCl, in water.^{18–20} One should add a word of caution here. All the gradient corrected functionals are very sensitive to numerical inaccuracies while calculating the derivatives of the density. This leads to certain inaccuracies with the binding energies. In our case these errors are of a few kJ/mol.

In this work we have used the Perdew–Zunger parametrization of the LDA²¹ and Lee–Yang–Parr²² gradient corrected approximation for the correlation energy and added a correction due to A. Becke²³ to the LDA exchange term. This BLYP approach seem to be particularly well suited for hydrogen bound systems.¹⁵

In the CP code the valence electronic wave functions are expressed with plane waves

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{G}} C_n(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}}, \quad (2)$$

where \mathbf{G} is a reciprocal lattice vector (we are using periodic boundary conditions). To control the size of the basis, only plane waves corresponding to \mathbf{G} vectors with lengths less than some cutoff $|\mathbf{G}| < G_{\text{cut}}$ are taken into account. In this calculation the cutoff energy, $E_{\text{cut}} = G_{\text{cut}}^2/2$, was 25 Ry.

To describe the chemical binding it is usually enough to take only the valence electrons into account. Thus the effect of nuclei plus their core electrons to valence electrons are described using Vanderbilt ultrasoft pseudopotentials^{24,25} for

all the heavy atoms (oxygen and sulphur) and a simple local pseudopotential for hydrogen. To perform consistent calculations the pseudopotentials have been constructed using the same LDA/LDA+GC scheme as used in the CP calculations. The use of soft pseudopotentials is mandatory due to the inefficiency of the plane waves to describe rapidly varying orbitals. Further technical details of such a pseudopotential *ab initio* molecular dynamics approach can be found in Refs. 16 and 25.

The plane wave basis has several advantages, but to its disadvantage, the periodic boundary conditions have to be used even when the system is not periodic as is clearly the case with clusters. To reduce the effect of the artificial boundary conditions the clusters have to be placed on a relatively large simulation box. In this simulation we used a cubic box with side length of 10.6 Å.

III. TEST CALCULATIONS

To test the accuracy of our pseudopotential DFT code we performed model calculations for water dimer and a single sulphuric acid molecule, for which experimental geometries are available. Table I shows the experimental values for the O...O distance and hydrogen bond energy for water dimer, and values calculated using different functionals for the exchange-correlation energy. We used standard LDA, LDA with Becke correction only, and BLYP. As one can see from Table I the gradient corrections are necessary for a realistic description of the H bond. We also compare our water dimer results to Sprik *et al.*¹⁵ and similar calculations using a DMol program.²⁶ Our results are identical to Sprik *et al.*, showing that the numerical accuracy is very good. Compared to DMol results the geometries we obtained are similar, but DMol gives binding energies 4–5 kJ/mol higher than our calculations.

Table II shows bond lengths and angles for optimised structure of sulphuric acid calculated with different exchange-correlation functionals, and their experimental values. In general the LDA predicts the S–O and S=O distances very well, while the other exchange-correlation functionals produce slightly less satisfactory values for these distances. Despite this, we use the BLYP exchange-correlation functional for water–sulphuric acid clusters,

TABLE II. Experimental values for bond lengths and angles of sulphuric acid, and their optimized values calculated with LDA, Becke only and BLYP functional for exchange-correlation energy.

	H ₂ SO ₄			Expt.
	LDA	Becke	BLYP	
S=O distance	1.43 Å	1.46 Å	1.46 Å	1.42 Å
S–O distance	1.59 Å	1.64 Å	1.64 Å	1.57 Å
O–H distance	0.99 Å	0.99 Å	0.99 Å	0.95 Å
S=O=S angle	122.8°	122.8°	123.7°	123.3°
S–O–S angle	99.6°	99.2°	101.4°	101.3°
S–O–H angle	108.9°	108.3°	108.5°	108.5°

since it is essential to have a realistic model for the hydrogen bonds.¹⁵

IV. RESULTS

A. Monohydrate

There are two possible configurations for the sulphuric acid monohydrate, shown in Figures 1(a) and 1(b). In structure a the water is bound to the OH part of the sulphuric acid and in b the water is bound to the S=O part.

We have optimized the geometries of both of these structures. In Table III the nearest neighbor distances, O···O distances in hydrogen bonds, binding angles and bond energies for both configurations are shown. Configuration a has a strong hydrogen bond with an O···O distance of 2.66 Å. This can be compared to the O···O distance in water dimer, which is ~3 Å, or to liquid water with an O···O distance of ~2.8 Å. The O···O distance in configuration b is 3.09 Å, indicating a much weaker hydrogen bond. This is seen in the bond energies as well: Configuration a is energetically favourable, having a H-bond energy of –38 kJ/mol, while the H-bond energy of configuration b is only –2 kJ/mol. Again, as comparison the H-bond energy in water dimer is –18 kJ/mol (using BLYP). Thus the H bond between sul-

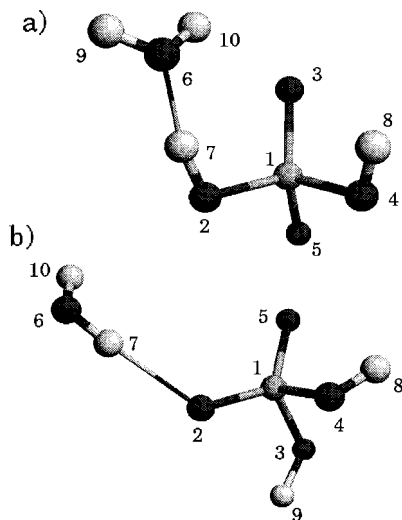


FIG. 1. Optimized geometries of two configurations of sulphuric acid monohydrate. White spheres represent oxygen atoms, black spheres hydrogen atoms and grey spheres sulphur atoms.

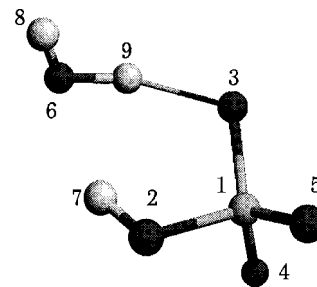


FIG. 2. Optimised geometry of HSO₄[–] · H₂O.

phuric acid and water is twice as strong as in water dimer! The hydrogen bond O–H···O angles in both configurations are around 170°. The optimization of configuration b was carried out without any constraints and it did not converge toward configuration a. Comparison of Tables II and III shows that the hydrogen bond does not affect the geometry of the sulphuric acid in configuration b, and in configuration a it affects only the bound S–O–H branch, where the S–O distance is shortened and the O–H distance lengthened. The water molecule remains symmetric. In configuration a a weak bond between O(3) and H(10) [the numbers refer to Fig. 1(a)] results in a slight unsymmetry between S=O bonds.

One of the interesting questions concerning the small sulphuric acid–water clusters is how many water molecules are needed to pull out a proton from the sulphuric acid mol-

TABLE III. Bond lengths and angles for two sulphuric acid monohydrate configurations. Atom numbers refer to Figures 1 (a) and (b).

BLYP	H ₂ SO ₄ · H ₂ O	
	Configuration a	Configuration b
d(1–2)	1.60 Å	1.46 Å
d(1–3)	1.48 Å	1.63 Å
d(1–4)	1.64 Å	1.63 Å
d(1–5)	1.45 Å	1.46 Å
d(2–6)	2.66 Å	3.09 Å
d(2–7)	1.04 Å	2.10 Å
d(3–9)	...	1.00 Å
d(3–10)	2.24 Å	...
d(3–6)	2.89 Å	...
d(4–8)	0.99 Å	1.00 Å
d(6–7)	1.64 Å	0.99 Å
d(6–9)	0.99 Å	...
d(6–10)	0.99 Å	0.99 Å
∠(1–2–7)	109.0°	128.6°
∠(1–3–9)	...	109.2°
∠(1–4–8)	108.5°	109.0°
∠(2–1–3)	109.0°	108.7°
∠(2–1–4)	102.9°	105.2°
∠(2–1–5)	108.1°	123.4°
∠(2–7–6)	165.7°	174.1°
∠(3–1–4)	107.5°	102.2°
∠(3–1–5)	122.2°	105.8°
∠(3–10–6)	125.5°	...
∠(4–1–5)	105.5°	109.6°
∠(7–6–10)	...	104.8°
∠(9–6–10)	107.9°	...
Total H-bond energy	–38 kJ/mol	–2 kJ/mol

TABLE IV. Bond lengths and angles for HSO_4^- . Atom numbers refers to Fig. 2.

BLYP	$\text{HSO}_4^- \cdot \text{H}_2\text{O}$	HSO_4^-
d(1–2)	1.69 Å	1.73 Å
d(1–3)	1.52 Å	1.49 Å
d(1–4)	1.49 Å	1.49 Å
d(1–5)	1.48 Å	1.49 Å
d(2–6)	2.97 Å	...
d(2–7)	1.00 Å	0.99 Å
d(3–6)	2.68 Å	...
d(3–9)	1.68 Å	...
d(6–7)	2.04 Å	...
d(6–8)	0.99 Å	...
d(6–9)	1.02 Å	...
$\angle(1-2-7)$	106.5°	104.4°
$\angle(1-3-9)$	112.6°	...
$\angle(2-1-3)$	103.6°	103.4°
$\angle(2-1-4)$	106.0°	104.7°
$\angle(2-1-5)$	103.2°	101.5°
$\angle(2-7-6)$	152.6°	...
$\angle(3-1-4)$	112.9°	114.1°
$\angle(3-9-6)$	163.1°	...
$\angle(3-1-5)$	113.8°	115.7°
$\angle(4-1-5)$	115.6°	115.1°
$\angle(8-6-9)$	104.8°	...
Total H-bond energy	–43 kJ/mol	...

ecule ($\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{HSO}_4^- \cdot \text{H}_3\text{O}^+$). To estimate this proton transfer barrier, the $\text{H} \cdots \text{O}$ [atoms 6 and 7 in Fig. 2(a)] distance was varied from 1.64 Å (optimised geometry) to 1.25 Å optimizing all the other coordinates. Pushing the $\text{O} \cdots \text{H}$ distance to even smaller values would force the monohydrate structure to change, and the barrier would no longer represent proton transfer. The calculated energies are shown in Figure 5. One water molecule is not able to cause a proton transfer reaction. The binding energy grows monotonously when the 6–7 distance is decreased, and no metastable protonised state is found. The barrier increases steeply, and at the $\text{O} \cdots \text{H}$ distance of 1.3 Å it is already ~ 18 kJ/mol.

Here we can also make comparisons to the HF calculations of Kurdi and Kochanski.⁹ The $\text{O} \cdots \text{O}$ distance they obtain was 2.656 Å and the binding energy 64 kJ/mol. The $\text{O} \cdots \text{O}$ distance agrees well with our results (2.66 Å), but the binding energy is much higher. We believe that the energy difference is due to the different treatment of the electron exchange-correlation. Kurdi and Kochanski used the Hartree–Fock approximation while we use GC-LDA. To further test our result, we performed a calculation of the monohydrate using the DMol program²⁶ with the BLYP scheme.

TABLE V. Effective point charges for sulphuric acid, calculated within LDA.

atom	H_2SO_4	HSO_4^-	SO_4^{2-}
S	0.81	0.89	0.89
O(H)	–0.49	–0.59	
O(S=O)	–0.37	–0.54	–0.72
H	0.45	0.37	

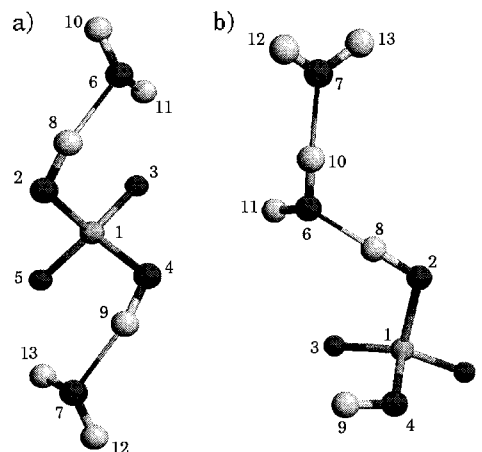


FIG. 3. Optimized geometries of two configurations of sulphuric acid dihydrate.

The difference between the binding energies given by the DMol and CP codes is about 20%, consistent with the water dimer case. Kurdi and Kochanski also estimated the proton transfer barrier by optimizing the $\text{O} \cdots \text{O}$ distance of the ionic system $\text{HSO}_4^- + \text{H}_3\text{O}^+$, keeping the geometry of the ions fixed. They find the ionic system has ~ 100 kJ/mol higher energy! Thus, neither of these calculations indicate proton transfer at the monohydrate level.

B. Protonised monohydrate

For sulphuric acid in aqueous solution, the acidity constant for the first proton is $\text{pK}_a = -2$, indicating almost complete dissociation, while for the second proton, $\text{pK}_a = 1.92$.²⁷ The sulphuric acid loses one proton readily, but it is much harder to get the other one out from the residual ion. To see if this phenomenon is present already at the monohydrate level we studied the protonised sulphuric acid monohydrate.

Figure 2 and Table IV show the optimised geometry for $\text{HSO}_4^- \cdot \text{H}_2\text{O}$. Table IV also shows the comparison to free hydrogen sulphate ion. It turns out that the HSO_4^- and water form a ring-like structure, where two hydrogen bonds are formed: A stronger one between a hydrogen atom (9, Fig. 2) of the water and an oxygen atom (3) of the hydrogen sulphate ion having an $\text{O} \cdots \text{O}$ distance of 2.68 Å, and a weaker one between the oxygen atom (6) of the water and the hydrogen atom (7) of the hydrogen sulphate ion with an $\text{O} \cdots \text{O}$ distance of 2.97 Å. The total H-bond energy is –43 kJ/mol, higher than in the monohydrate due to the double bond formation. The $\text{H}-\text{O} \cdots \text{H}$ angles are distorted from 180°, being 163° and 153°.

The $\text{S}(1)-\text{O}(2)$ distance of the hydrogen sulphate is shortened compared to the free ion case. The $\text{S}(1)-\text{O}(3)$ distance in hydrogen sulphate and $\text{O}(6)-\text{H}(9)$ distance in water are lengthened due to binding, but the $\text{O}(2)-\text{H}(7)$ distance is essentially the same as in the free ion case. It seems that the water is not pulling the proton out strongly, since the H bond between $\text{O}(6)$ and $\text{H}(7)$ is weaker than the $\text{O}(3)-\text{H}(9)$ bond. This is supported by the preliminary proton transfer barrier

TABLE VI. Bond lengths for sulphuric acid di and trihydrate. Atom numbers refer to Figs. 3(a) and 3(b) (dihydrate) and 4(a) and 4(b) (trihydrate).

BLYP	H ₂ SO ₄ ·2(H ₂ O)		H ₂ SO ₄ ·3(H ₂ O)	
	Configuration a	Configuration b	Configuration a	Configuration b
d(1–2)	1.61 Å	1.59 Å	1.55 Å	1.59 Å
d(1–3)	1.47 Å	1.47 Å	1.49 Å	1.47 Å
d(1–4)	1.61 Å	1.65 Å	1.65 Å	1.62 Å
d(1–5)	1.47 Å	1.45 Å	1.46 Å	1.48 Å
d(2–6)	2.66 Å	2.58 Å	2.46 Å	2.57 Å
d(2–8)	1.04 Å	1.06 Å
d(2–9)	1.22 Å	1.07 Å
d(3–6)	2.85 Å
d(3–8)	2.75 Å	...
d(3–11)	2.10 Å	3.08 Å
d(3–12)	2.78 Å
d(3–16)	1.77 Å	...
d(4–7)	2.66 Å
d(4–8)	2.69 Å
d(4–9)	1.04 Å	0.99 Å
d(4–10)	0.99 Å	1.03 Å
d(5–7)	2.85 Å
d(5–8)	2.83 Å
d(5–13)	2.10 Å
d(5–16)	2.02 Å
d(6–7)	...	2.77 Å	2.74 Å	2.76 Å
d(6–8)	1.64 Å	1.52 Å	2.63 Å	...
d(6–9)	1.24 Å	1.51 Å
d(6–10)	0.99 Å	1.01 Å
d(6–11)	1.00 Å	0.99 Å	1.01 Å	1.01 Å
d(6–12)	1.03 Å	0.99 Å
d(7–9)	1.64 Å
d(7–10)	...	1.77 Å
d(7–11)	1.74 Å	1.75 Å
d(7–12)	0.99 Å	0.99 Å
d(7–13)	1.00 Å	0.99 Å	0.99 Å	0.99 Å
d(7–14)	0.99 Å	0.99 Å
d(8–10)	1.69 Å
d(8–12)	1.63 Å	...
d(8–15)	0.99 Å	0.99 Å
d(8–16)	1.01 Å	1.00 Å
Total H-bond	–86	–67	–118	–114
Energy	kJ/mol	kJ/mol	kJ/mol	kJ/mol

calculations we made. Experimentally this is reflected to the equilibrium constants for dissociation reactions in sulphuric acid-water solution.

Another interesting phenomenon is that the S=O part of a normal sulphuric acid molecule *does not* form a hydrogen bond with water, but that of the protonated sulphuric acid does. Naturally the S=O part of doubly protonated sulphuric acid will form strong H bonds. To obtain some qualitative understanding to this, we analyzed the effective point charges on the atoms in H₂SO₄, HSO₄[–] and SO₄^{2–}. We used the GAUSSIAN-94 program²⁸ (at CSC, Espoo) within DFT-LDA. The basis set was 6-31G(d) and the charges were fitted to reproduce the electrostatic potential (FITCHARGE option). The results are shown in Table IV. The charges of the oxygens (S=O) increases from –0.37 to –0.72 when the charge of the whole cluster increases (H₂SO₄→SO₄^{2–}). This explains the stronger H bonds to these oxygens. Similarly, the reduction of the H-bond strength to the OH parts can be

“explained” with the lowering of the hydrogen charges from 0.45 to 0.37.

We have also constructed an empirical potential model for these molecules, but the results of these studies will be reported later.

C. Dihydrate

Figures 3(a) and 3(b) and Tables VI and VII show the optimised geometries for two configurations of the sulphuric acid dihydrate. The hydrogen bond energy for configuration a is –86 kJ/mol, and for configuration b –67 kJ/mol. If no interaction would occur between the waters in the opposite ends of configuration a, the binding energy would be two times the monohydrate binding energy (–76 kJ/mol). In linear approximation the binding energy of configuration b is obtained by summing the binding energies of a monohydrate and a water dimer, giving –56 kJ/mol. Thus, the correction

TABLE VII. Bond angles for sulphuric acid di- and trihydrate. Atom numbers refer to Figs. 3(a) and 3(b) (dihydrate) and 4(a) and 4(b) (trihydrate).

BLYP	H ₂ SO ₄ ·2(H ₂ O)		H ₂ SO ₄ ·3(H ₂ O)	
	Configuration a	Configuration b	Configuration a	Configuration b
∠(1–2–8)	108.8°	111.6°
∠(1–2–9)	117.5°	110.1°
∠(1–4–9)	108.8°	107.6°
∠(1–4–10)	108.4°	108.9°
∠(2–1–3)	108.9°	109.8°	110.7°	109.6°
∠(2–1–4)	103.8°	102.9°	104.1°	103.9°
∠(2–1–5)	106.9°	107.9°	111.6°	107.0°
∠(2–8–6)	163.9°	179.7°
∠(2–9–6)	179.2°	176.1°
∠(3–1–4)	106.9°	107.1°	105.9°	106.9°
∠(3–1–5)	120.2°	122.1°	118.8°	120.0°
∠(3–11–6)	131.0°
∠(3–16–8)	161.3°	...
∠(4–1–5)	109.0°	105.1°	104.3°	108.3°
∠(4–9–7)	164.3°
∠(4–10–8)	162.4°
∠(5–13–7)	130.8°
∠(6–10–7)	...	177.8°
∠(6–11–7)	176.0°	174.4°
∠(6–12–8)	161.6°	...
∠(10–6–11)	107.5°	108.5°
∠(11–6–12)	112.1°	109.3°
∠(12–7–13)	107.4°	107.2°
∠(13–7–14)	106.7°	106.4°
∠(15–8–16)	106.9°	107.1°

due to nonlinear effects is ~ -10 kJ/mol in both configurations. The large energy difference between the monohydrate configurations a and b shows that a structure in which one water is bound to an oxygen and the other to a hydrogen atom is unlikely.

The symmetric configuration a is the optimal structure for the dihydrate. The hydrogen bonds between the O–H parts of the acid and the oxygens of the water are strong with O...O distances of 2.66 Å and bond angle 164°. There are also weaker hydrogen bonds between the S=O parts of the acid and the hydrogens of the water having O...O distances of 2.85 Å and bond angles of 131°. The ring-like structure is clearer than in monohydrate. Compared to the free molecules, the S–O(–H) distances are slightly shortened, and the S=O and the O–H distances of the acid and the bound part of the water are lengthened due to bonding.

Both of the hydrogen bonds in configuration b are strong. The O...O (2–6, numbers refer to Fig. 3 (b)) distance of the acid–water bond is only 2.58 Å, shorter than in the monohydrate, and the O...O (6–7) distance of the water–water bond is 2.77 Å. Both O–H...O angles are close to 180°. The changes due to the hydrogen bonds in the geometries compared to free molecules are as follows: The S(1)–O(2) distance is shortened and the O(2)–H(8) distance is a bit longer than in monohydrate, and O(6)–H(10) distance in the first water molecule is lengthened. A very weak bond between O(3) and H(11) causes slight unsymmetry between the S=O bonds.

The O(6)...O(2) and the O(6)...H(8) distances are

shorter in configuration b than in configuration a. Thus, the geometry shown in Fig. 3 (b), although not the one with the lowest energy, is more interesting when investigating the proton transfer reaction. The hydrogen bond forming H₂SO₄–proton [8, Fig. 3(b)] is closer to the oxygen (2) belonging to the sulphuric acid than to the oxygen (6) belonging to the water cluster. Thus, spontaneous proton transfer does not take place.

The proton transfer barrier was estimated by varying the O(6)–H(8) distance of configuration b between the optimised value (1.5 Å) and the O–H distance in hydronium ion (1.1 Å). The results are shown in Figure 5. As in the monohydrate case there is no metastable minimum on the proton transfer curve, but the barrier is always well below the monohydrate barrier. The data indicate that proton transfer is very unlikely also at the dihydrate level.

D. Trihydrate

Figures 4(a) and 4(b) and Tables VI and VII show optimised geometries for two configurations of the sulphuric acid trihydrate. The bond energies of the two configurations are close to each other, -118 kJ/mol (a) and -114 kJ/mol (b). This indicates that the waters of trihydrate can bind on the *same* side of the acid molecule. This is opposite to the dihydrate case, where the structure in which both the O–H parts of the acid molecule bound to water, had clearly lower energy.

The bond energy of configuration a can be approximated

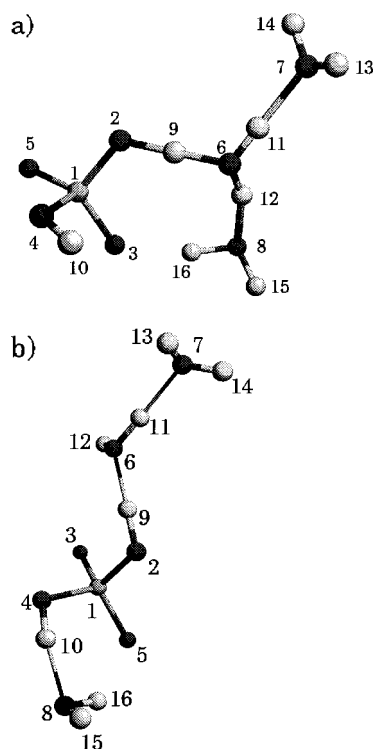


FIG. 4. Optimized geometries of sulphuric acid trihydrate.

by adding the binding energies of dihydrate configuration b and a water dimer, giving 85 kJ/mol. The correction due to nonlinear effect is as high as 33 kJ/mol. A linear estimate for the bond energy of configuration b is found by adding the bond energies of monohydrate configuration a and dihydrate configuration b or dihydrate configuration a and water dimer. Both of these approaches give about -105 kJ/mol. The correction due to nonlinear effects is about 10 kJ/mol as in dihydrate.

Configuration a is a clear ring-like structure with four hydrogen bonds. The $O(2)\cdots O(6)$ distance [numbers refer to Fig. 4(a)] is only 2.46 Å, shorter than in the di- and monohydrates. The $O(6)\cdots O(7)$ distance is 2.74 Å, the $O(6)\cdots O(8)$ distance 2.63 Å, and the $O(3)\cdots O(8)$ distance 2.75 Å, all indicating rather strong hydrogen bonds. The hydrogen bond forming proton H(9) is practically halfway between the oxygens of the sulphuric acid (2) and the water (6), and thus the proton transfer reaction has almost occurred. It is interesting to compare these $O\cdots O$ distances to a hydronium ion (H_3O^+) in water.¹⁷ For liquid water, the normal $O\cdots O$ distance is ~ 2.8 Å, while the hydronium water $O\cdots O$ distance is ~ 2.5 Å.¹⁷ Similarly the $O\cdots O$ distance at the $(H_5O_2)^+$ molecule is 2.4 Å. Thus the $O(2)-H(9)-O(6)$ structure we obtained is consistent with the structure of hydronium in water. The H-bond angles $\angle(2-9-6)$ and $\angle(6-11-7)$ are close to 180° , while the angles $\angle(6-12-8)$ and $\angle(3-16-8)$ are $\sim 160^\circ$. Compared to free molecules, the O–H distances 2–9, 6–11, 6–12 and 8–16 are longer due to bonding, as well as the S(1)–O(3) distance. Again, the S(1)–O(2) distance is shorter.

Configuration b is an elongated, less compact structure

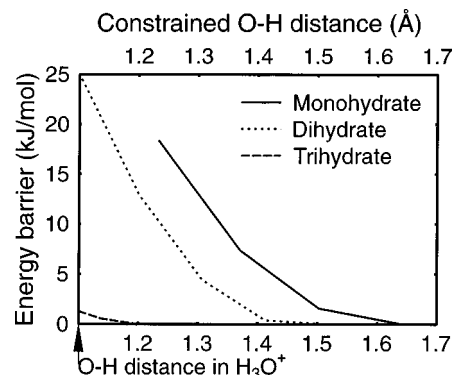


FIG. 5. Proton transfer barriers for mono-, di- and trihydrate. The points at which the curves intersect x axis correspond to optimized geometries.

than configuration a. The $O\cdots O$ distances are generally longer than in configuration a, 2.57 Å for bond 2–6 [numbers refer to Fig. 4(b)], 2.69 Å for bond 4–8 and 2.76 Å for bond 6–7. The end with one water molecule forms a clear ring (with a weak bond between atoms 5 and 16), but the other end is similar to the dihydrate configuration b with no ring structure. The H-bond angles $\angle(2-9-6)$ and $\angle(6-11-7)$ are close to 180° , while the angle $\angle(4-10-8)$ is $\sim 160^\circ$. Compared to free molecules, the O–H distances 6–11, 2–9, 4–10 and 8–16 and the S(1)–O(5) distance are longer due to bonding, the S(1)–O(4) distance is slightly shorter and the S(1)–O(2) distance clearly shorter.

The proton transfer barrier was once more estimated by varying the $O(6)-H(9)$ (configuration a) distance between the optimised value and the O–H distance in hydronium ion. The results are shown in Fig. 5. Because the proton transfer reaction has almost occurred the barrier is very low, only 1–2 kJ/mol.

The partial proton transfer explains also the preference of the three water molecules to bind to *one* side of the sulphuric acid molecule and not to both of the O–H parts. If we consider one of the O–H parts partly protonated to $O-H-OH_2$ it seems to be preferable to solvate the “ H_3O^+ ” molecule than two O–H parts. This is reasonable because the water binding energy to hydronium is much higher than to water.

V. COMPARISON WITH THE CLASSICAL HYDRATION MODEL

The classical theory formulated by Jaecker-Voirol *et al.* gives the standard free energy of addition of a water monomer to an $(n-1)$ cluster as

$$\Delta G_{n-1,n}^0 = kT \ln[P_w(sol)] + \frac{2\gamma v_w}{r}, \quad (3)$$

where $P_w(sol)$ is the equilibrium vapor pressure of water over a (flat) solution surface expressed in atmospheres, γ is the surface tension of the solution, v_w denotes the partial molecular volume of water, and the radius r is calculated assuming the hydrate to be spherical. Note that Eq. (3) is obtained by differentiating the free energy of an n hydrate.

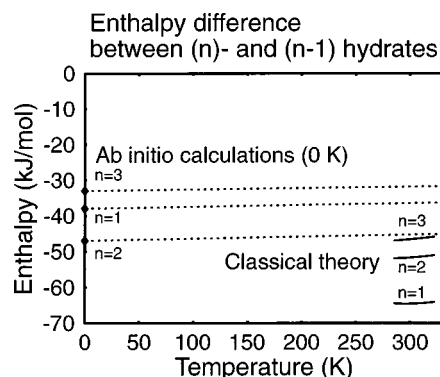


FIG. 6. Comparison of enthalpy differences between successive hydrates given by *ab initio* calculations and by the classical liquid drop model. See the text for details.

This continuum approximation brings about an ambiguity as to whether the solution composition and hydrate radius should be determined for an $(n-1)$ hydrate or for an n hydrate. For larger clusters the difference would be small, but this is not the case for the small hydrates considered here. With a monohydrate, the solution composition cannot be calculated for $n-1$, because the logarithmic term would diverge, and thus we take the reference state to be the n hydrate.

The enthalpy of the water monomer addition is obtained from the Gibbs–Helmholtz equation

$$\Delta H_{n-1,n}^0 = \frac{\partial(\Delta G_{n-1,n}^0/T)}{\partial(1/T)}. \quad (4)$$

In our numerical calculations, we used the equilibrium vapour pressures calculated with the sulphuric acid/water activity coefficients given by Taleb *et al.*,²⁹ and a surface tension fit based on the data of Sabinina and Terpugov.³⁰

Figure 6 shows a comparison between the enthalpy of H_2O addition for the first three hydrates given by the classical equations (3) and (4) and by the *ab initio* calculations (at 0 K the enthalpy is equal to the total bond energy of the cluster.) The classical values are calculated at temperatures between 283 and 323 K, which is the temperature interval at which the surface tensions of sulphuric acid solutions have been measured. At lower temperatures the slopes of the classical enthalpy curves become negative, which may sign the deviation of the extrapolated surface tension fitting function from the true values, and therefore we do not show the enthalpy differences at lower temperatures (note that the enthalpy is very sensitive to the temperature dependence of $\Delta G_{n-1,n}^0$). The difference between our classical values and those calculated by Mirabel and Ponche (for example, they calculate -53.5 kJ/mol for the monohydrate at 298 K) originates mostly in the different water activity coefficients used. The *ab initio* values are shown at 0 K, and the dashed lines indicate the 4%/300 K–temperature dependence found by Kochanski³¹ in a Monte Carlo study of Ca^{2+} hydrates (see also Mirabel and Ponche⁸). The classical values do not compare too well with the *ab initio* values. Even the order is wrong: Monohydrate is predicted to have the highest en-

thalpy difference and trihydrate the lowest. This reflects the fact that through the use of bulk liquid values for the thermodynamic parameters, it is implicitly assumed in the classical model that proton transfer has taken place already in the smallest hydrates.

From the point of view of nucleation calculations, a more interesting quantity to compare would be the free energy given by Eq. (3) rather than the enthalpy difference. Unfortunately, we are not able to produce a meaningful number at around 300 K from the *ab initio* results; for this the temperature dependence shown in Fig. 6 is much too uncertain both in magnitude and in shape. It is thus somewhat difficult to assess the success of the classical model in predicting the formation free energies of the smallest hydrates.

In the present nucleation theories, the stabilising effect of hydrates on nucleating vapor is accounted for using classical hydrate distribution that is based on Eq. (3). Although Fig. 6 indicates that the classical mono- and dihydrate enthalpies are somewhat overestimated, we feel that it is better to use the classical hydrate correction rather than to totally ignore hydration in nucleation calculations.

VI. CONCLUSIONS

Although the hydrates considered above are very small, we believe that we gained useful information on the sulphuric acid–water interactions. The hydrogen bonds between sulphuric acid molecule or hydrogen sulphate ion and water are generally strong. The binding energies are much larger and the $\text{O}\cdots\text{O}$ distances are shorter compared to pure water. Also the water–water bonds are stronger than in pure water due to the presence of the sulphuric acid molecule. The more water molecules in the hydrate, the clearer ring structure is formed.

The sulphuric acid–water binding is very different at the various protonization states (H_2SO_4 , HSO_4^- and SO_4^{2-}), due to quite different effective charges on oxygens and hydrogens. In the neutral sulphuric acid molecule, the OH parts formed much stronger H bonds than the O ($\text{S}=\text{O}$) parts, whereas in the HSO_4^- both O ($\text{S}=\text{O}$) and OH formed H bonds. It is interesting to note that in the trihydrate case, where the sulphuric acid molecule is partly protonated, a clear hydrogen bond is formed between the waters and the $\text{S}=\text{O}$ part.

Only few water molecules are needed to protonate the sulphuric acid molecule. According to our calculations, already 3–4 waters would be enough. In the trihydrate case the proton transfer from the sulphuric acid is not complete; however, the transferred proton is halfway between the H_2SO_4 oxygen and water, with very small $\text{O}\cdots\text{O}$ distance (2.45 Å). Such symmetric structures are not unusual. The simplest example is the H_5O_2^+ molecule, but similar structures are also observed in water.¹⁷ For the second proton to leave, a much larger amount of water is needed, because even in water the singly protonated sulphuric acid is a weak acid.

In the future, we are planning to study larger sulphuric acid–water systems using molecular dynamics and empirical

potentials. This will hopefully also enable us to give further assessments relating to nucleation theory.

ACKNOWLEDGMENTS

We would like to thank the Center for Scientific Computing (CSC) in Espoo, Finland for the computer time. K.L. would like to thank Juha Vaara for help in using the GAUSSIAN-94 program. Financial support by the Academy of Finland is gratefully acknowledged.

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