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Experimental Study of the Heterogeneous Interaction of SO₃ and H₂O: Formation of Condensed Phase Molecular Sulfuric Acid Hydrates

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Abstract: The interaction of SO_3 and H_2O at low temperatures upon an inert surface has been studied with infrared spectroscopy and compared to the predictions of recent computational studies. At low temperatures and low water partial pressures, amorphous deposits of molecular H_2SO_4 complexed with variable amounts of H_2O in a ratio of between 1:1 and 2:1 are formed. Upon annealing, this material ejects water and converts first to a 1:1 $H_2SO_4 \cdot H_2O$ complex and subsequently to anhydrous H_2SO_4. Adding water to the amorphous molecular hydrate results in the formation of a new species, which on the basis of its thermal behavior and by comparison to theoretical predictions can be attributed to a molecular polymer with a repeat unit of $(H_2SO_4 \cdot (H_2O)_2)_n$. Implications of these observations for the initial stages of the formation of sulfate aerosol in the atmosphere and their surface reactivity are discussed.

Introduction

Considerable interest has developed in the past decade on the role played by sulfuric acid in the chemistry and physics of the atmosphere and a range of experimental methods have been applied to develop a deeper understanding of the formation, stability, optical, and chemical properties of sulfuric acid aerosol.[1] However, there is still considerable uncertainty concerning the detailed physical chemistry of the acid at low temperatures and water partial pressures, particularly in the fundamental stages of the formation of atmospheric sulfate aerosols from the hydration of precursors such as SO_2 and SO_3. This paper addresses aspects of the low-temperature chemistry of sulfuric acid and compares experimental results to the predictions of recent computational studies. Spectroscopic evidence is presented of the structure and stability of molecular H_2SO_4 hydrates and their potential role as intermediates in atmospheric chemistry is discussed.

Spectroscopic and other methods applied to bulk samples of sulfuric acid/water mixtures have shown that condensed thin films exist as a range of hydrates, with compositions dependent on the temperature and partial pressure of water vapor.[2] These hydrates are ionic in nature, containing H_3O^+, $H_5O_2^+$, HSO_4^-, and SO_4^{2-} and in many cases readily interconvert upon variation of ambient conditions. In situations for which a comprehensive

database of vibrational spectroscopic fingerprints obtained under appropriate conditions exists, the presence and concentration of these ionic species can often be extracted. However, this process requires that each species shows a strongly characteristic pattern of absorption bands and is frequently complicated by the fact that the individual absorption features tend to vary in a complex way with temperature, environment and physical state. The bulk phase diagram is also well-understood and shows a variety of both stable and metastable compositions.[3] Of potential interest in the atmosphere are the stable monohydrate (SAM) and the tetrahydrate (SAT), whereas the dihydrate and trihydrate are metastable states and not currently thought to be significant components of atmospheric aerosol. It has been suggested that the octahydrate may be a high relative humidity form present in the stratosphere,[4] although this phase has only been observed in the laboratory in aerosol droplets which have been cooled to 166 K, significantly lower that that experienced in the stratosphere. Adding to the solid phase complexity, liquid sulfuric acid aerosols are known to strongly supercool[4] and are observed to show a strongly temperature-dependent affinity for water vapor and gaseous nitric and hydrochloric acids.[5]

In the atmosphere, sulfuric acid is believed to be formed from the hydration of SO_2 and SO_3. The gas-phase formation of H_2SO_4 has been extensively studied experimentally and theoreti-

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cally.[6,7] Although there are some discrepancies, there is reasonable agreement in the literature as to the nature of this process. Computational studies suggest that the reaction of SO_3 with one water molecule has an activation barrier of about 28 kcal mol^{-1}, with the high energy barrier being due to a sterically hindered four centered transition state. The introduction of a second water molecule reduces this energy barrier to about 13 kcal mol^{-1} through the formation of a six centered transition state. Additional water molecules continue to reduce the barrier either by acting as microsolvent stabilizing the transition state or by allowing alternative reaction mechanisms (i.e., stepwise rather than concerted proton transfers). The presence of 10 or more water molecules effectively removes the barrier for the reaction. These predictions are supported by experimental work. For example, the gas-phase $SO_3 + H_2O$ reaction has been shown experimentally by Jayne et al to be second order with respect to the partial pressure of water and to have a strong negative temperature dependence.[7] In the pressure range from 133 to 1000 mbar and temperature range from 283 to 370 K, Jayne et al observed Arrhenius behavior with $A = 3.90 \times 10^{-41}$ cm^{-6} molecule^{-2} s^{-1} and $E_a = -13.5$ kcal mol^{-1} for the reaction. However, at lower temperatures (243−268 K) and at SO_3 densities of $\sim 10^{12}$ molecules cm^{-3}, very fast decay rates showed a trend to first-order dependence in water vapor pressures, which may represent an efficient heterogeneous reaction between SO_3 and acid water particles at reduced temperature.

Theoretical studies predict reaction products which involve molecular sulfuric acid complexed with varying amounts of hydrogen bonded water in the gas phase. This behavior is confirmed in molecular beam experiments, with the principal product being an un-ionized monohydrate complex for which detailed structural parameters have been obtained.[8] In order for the ionic species observed in condensed films and aerosols to be formed, these complexes must further hydrate and coalesce during the formation of an aerosol particle. In this paper, spectroscopic observations of the molecular products of the heterogeneous hydration of SO_3 collected on a cold ATR element are presented, along with an analysis of the effects of temperature and water partial pressure upon the subsequent formation of intermediates and ionic hydrates.

Experimental Section

The experimental apparatus used in this study has been described previously.[9] Briefly, a germanium internal reflection element (IRE) is held on a thermostated sample mount in a high vacuum chamber. The temperature of the IRE, measured by a K type thermocouple, is controlled by the combination of liquid nitrogen cooling and resistive heating. Three high precision leak

valves with internal dosing tubes are directed at the open faced of the IRE; this enables co-dosing of reactive gases. The gases for dosing are prepared in separate gas lines to prevent pre-reaction, and films are deposited by simultaneous dosing of SO_3 and H_2O (or D_2O). SO_3 gas is prepared by sublimation of solid SO_3 (Aldrich, U.K.) into a preconditioned, evacuated gas line. Deionized H_2O or D_2O (Aldrich, U.K.) is vacuum distilled and degassed by repeated freeze/pump/thaw cycles.

SO_3 and H_2O are co-dosed on to the IRE between 190 and 200 K, which is above the deposition temperature for either ice or SO_3 at partial pressures of less than 10^{-5} mbar. The partial pressures of the reacting gases are monitored during deposition by a nude ion gauge and a residual gas analyzer. Calibration of the absolute pressures at the sample IRE face is performed by measuring the frost point of water vapor at a set temperature. The local pressures at the surface of the IRE are calculated from a knowledge of the relationship between the measured chamber pressure and the local pressure at the exit points of the dosing tubes.

Results

Formation and Structure of Amorphous Sulfuric Acid Films. At 190 K, neither SO_3 nor H_2O form stable single component films of appreciable thickness at partial pressures of less than 1×10^{-5} mbar. The deposition of material upon the IRE surface must therefore be due to either a rapid gas-phase reaction or a heterogeneous process with one or both components adsorbed prior to reaction. Extrapolating the reaction rate for $H_2O_{(g)} + SO_{3(g)}$ determined by Jayne et al.[7] down to 180 K gives a very long half-life for the reaction, and since the mean free path at pressures below 1×10^{-4} mbar is of the order of meters there is not a significant probability of the reaction occurring in the gas phase in the short distance between the ends of the dosing tubes and the face of the IRE. In their kinetic study, Jayne et al observed that at low temperatures and at relatively high SO_3 pressures ($> \sim 10^{12}$ molecules cm^{-3}) the reaction is very fast due to a heterogeneous reaction at the surface of the acid−water film. Further evidence for the likelihood of a heterogeneous process in these experiments comes from an observation during sample preparation. The Ge IREs used in this laboratory are cleaned prior to use by etching in dilute HF. This renders the surface extremely hydrophobic. Upon subsequent surface oxidation (either chemically or by standing in the atmosphere), the IRE becomes hydrophilic in nature. In vacuo uptake of water is observed to be retarded on the fresh hydrophobic surface, and the reaction between SO_3 and H_2O does not occur at pressures below 1×10^{-5} mbar. However, reaction is observed immediately upon exposure above the hydrophilic surface and a film of 5 nm thickness is deposited in ca. 5 min. This behavior is attributed to the immobilization of a thin (possibly monolayer) film of H_2O by interaction between gaseous H_2O and surface oxide and hydroxide functionalities which initiates the heterogeneous process. In these experiments, the hydrophilicity of the IRE surface increases the lifetime of surface-bound H_2O and permits the $SO_{3(g)} + H_2O_{(ads)}$ reaction to be studied in detail.

By variation of the ratio of the partial pressures of H_2O and SO_3 above the IRE, the composition of the film which is deposited on the cold IRE surface can be controlled. (NB, For the purposes of simplicity, hereafter this ratio is defined as R_p,

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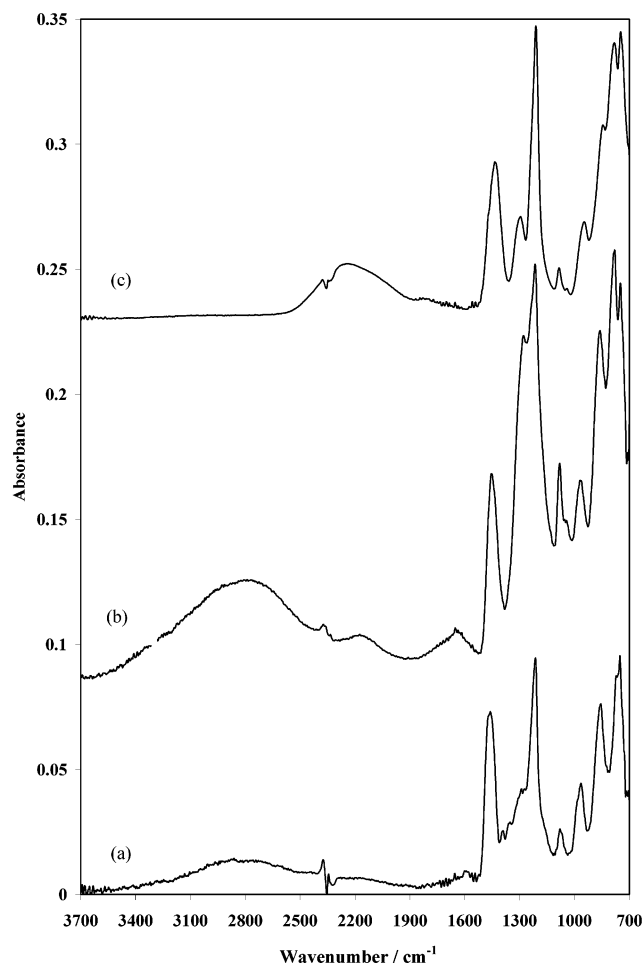(9) Horn A. B.; Sully, K. J. *J. Chem. Soc.: Faraday Trans.* **1997**, *93*, 2741.

Figure 1. ATR−IR spectra of the formation of sulfuric acid species from the reaction of gas-phase H_2O and SO_3 on a Ge ATR element at 190 K. (a) $H_2O = 1 \times 10^{-7}$ mbar, $SO_3 \approx 7 \times 10^{-6}$ mbar.; (b) $H_2O = 5 \times 10^{-7}$ mbar, $SO_3 \approx 7 \times 10^{-6}$ mbar; (c) $D_2O = 1 \times 10^{-7}$ mbar, $SO_3 \approx 7 \times 10^{-6}$ mbar. Spectra are offset for clarity.

where the subscript p denotes partial pressure ratio). For example, for an $H_2O:SO_3$ ratio of 1:5, $R_p = 5$]. At high values of R_p, the concentration of the surface film will tend to favor sulfate species over water-containing species. Figure 1 shows the ATR−IR spectra of films deposited at 190 K with $R_p = 70$ (specifically, pH_2O (and pD_2O) $\approx 1 \times 10^{-7}$ mbar and $pSO_3 \approx 7 \times 10^{-6}$ mbar as determined by the ion gauge) along with a more hydrated deposit. Film thicknesses, calculated using an optical property of the ATR process described elsewhere,[9] are ca. 11 nm.

In Figure 1a and 1c, the strongest peaks in the spectra below are seen at 2845(2262), 1460(1441), 1214(1213), 970(955), 864-(850), and 752(750) cm^{-1} (deuterated species in parentheses). Of these major bands, those at 1460 and 1214 cm^{-1} correlate well with those previously reported for sulfuric acid vapor spectra[10] and matrix isolated sulfuric acid, assigned to the antisymmetric and symmetric stretching modes of the O=S=O group, respectively. Furthermore, there appears to be some evidence of splitting of the peaks at 1460 and 1214 cm^{-1}, seen mainly as shoulders to the main features. This is likely to be due either to the presence of two separate species or to a difference in local environments within the deposited film

(similar to the effects seen in the matrix spectra of Givan et al.,[11] who report evidence for the presence of both stable and unstable environments for H_2SO_4 molecules held in a CO matrix giving rise to a multiplicity of bands from a single vibrational mode). These features confirm that the species involved is molecular H_2SO_4 because such high frequencies are not observed for any SO_4 core modes of either bisulfate or sulfate ions.

There are, however, a number of bands in the spectra which are significantly shifted from those observed in the vapor phase. In the high wavenumber region of the spectra where OH stretching vibrations of water and the SO−H groups are expected, the OH stretch appears at 3600 cm^{-1} in both the vapor phase and in an inert matrix for the anhydrous acid, whereas it occurs at ca. 2845 cm^{-1} in Figure 1. For comparison, this vibration occurs at about 2960 cm^{-1} in liquid H_2SO_4 and at 3010 cm^{-1} in condensed solid films.[12] The red shift of this mode implies there is a strong interaction with neighboring H_2SO_4 and/or H_2O molecules. There are a number of vibrational frequency calculations for molecular complexes such as (H_2-SO_4)·$(H_2O)_n$ which are discussed in more detail below which show this effect, typically yielding red shifts of the order of 10−17%. Furthermore, the visible features in the OH stretching region are very broad, also commensurate with strong hydrogen bonding. Although less easy to assign unequivocally, the lower wavenumber features are also shifted from the gas phase and matrix values. The main bands in this region in Figure 1 occur at 970, 864, and 752 cm^{-1}, and fall within the region where coupled and independent S−O stretches occur. Given that the H_2SO_4 is formed from gaseous SO_3 and H_2O, these spectral changes can be rationalized by considering the established reaction mechanism. Theoretical and experimental studies have shown that at least 2 water molecules are required per SO_3, with the result that any H_2SO_4 formed must initially be in the presence of at least one other water molecule. At the low temperatures utilized in these experiments, there is a significant likelihood that additional water molecules are also incorporated into the deposit. This is confirmed by Figure 1b, which shows an IR spectrum of a film formed at higher water pressures ($R_p = 14$). Compared to Figure 1a, the additional features present in this spectrum are seen at 1284, 1086, and 788 cm^{-1}. These bands are variable in intensity and are observed in both the normal and deuterated spectra. Their intensity relative to the acid bands shows a strong dependence on water content. It will be shown below that these features are due to the formation of a higher molecular hydrate of H_2SO_4 with a characteristic structure. Similarly, very little surface product is observed on the experimental time scale in the presence of only trace amounts of water, since the reaction is limited by water availability. At higher temperatures and higher water pressures (> 195 K, R_p < 1), extended ionized sulfuric acid monohydrate ($H_3O^+HSO_4^-$) films are formed directly on the time scale of the IR experiment. This is commensurate with the theoretical predictions of Larson et al., who observed a direct channel to the $H_3O^+HSO_4^-$ ion pair in their simulation of 4:1 $H_2O:SO_3$ clusters.[13]

The spectroscopic data presented above indicate that surface reaction of H_2O and SO_3 at cold temperatures (190 K) produces

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an amorphous film in which the individual acid molecules are associated with surrounding water molecules through hydrogen bonding and have many of the spectroscopic characteristics of the acid vapor and of matrix-isolated species. Such an environment clearly perturbs the S=O vibrations of H_2SO_4 very little compared to the gas phase, with the main influence being through the vibrational modes of the OH groups through which hydrogen bonding occurs, accompanied by a less marked effect on the S–OH modes. These amorphous sulfuric acid films are only formed when the conditions are very water limited although it is clear that more than one water molecule must be involved in the heterogeneous process as for the gaseous one. The material deposited on the ATR element surface under these conditions is clearly more closely related to the gas-phase products of the $SO_3 + H_2O$ reaction than a genuine condensed solid phase, producing species in a form analogous to that observed in a matrix isolation experiment. As will be shown, an increase in water pressure rapidly converts this film to other species. In the following sections, it will also be shown that the as-yet unassigned bands (1284, 1086, and 788 cm^{-1}) can be attributed to a number of the stable molecular hydrate species (for the moment labeled "species X") predicted by theoretical methods.

Thermal Behavior and $H_2SO_4 \cdot H_2O$ Complex Formation. To investigate the composition of the deposit, thin films of amorphous sulfuric acid were warmed slowly in vacuo from 190 to 225 K. Changes in the condensed film were followed by IR spectroscopy along with simultaneous monitoring of the partial water pressure in the chamber with a residual gas analyzer. Figure 2 shows spectra recorded at 190, 210, 217, and 225 K during such an annealing procedure. Figure 2a shows an initial amorphous film at 190 K. Above 205 K, a significant increase in water pressure in the chamber is observed as excess water is driven from the sample. The IR spectrum of the film at 210 K (Figure 2b) reveals a reduction in the bands at 1284, 1086, and 788 cm^{-1} attributed to the as-yet unidentified hydrates. The amorphous sulfuric acid bands at 1460 and 1214 cm^{-1}, attributed to the O=S=O antisymmetric and symmetric stretching modes, broaden and shift down to ca. 1400 and 1180 cm^{-1}. Similarly, strong broad features at ca. 965 and 802 cm^{-1} grow in along with a shoulder at 911 cm^{-1}. These new bands clearly have their origin in some new species. The broad O–H stretching peak at 2845 cm^{-1} shifts up to 2926 cm^{-1} as the concentration of sulfuric acid in the film increases.

Continued heating shows further transformation as the remainder of the excess water leaves the film and eventually the ejection of water ceases and the chamber pressure returns to background levels. The partial pressure of water during these experiments is shown in Figure 3, where the base pressure of water is 5×10^{-8} mbar. Inspection of the spectrum of the film at 217 K in Figure 2c during this process shows the film to be predominantly liquid sulfuric acid with characteristic broad peaks at 1359, 1164, 965, and 906 cm^{-1}. The peaks at 1400 and 802 cm^{-1} are still present but have diminished in intensity (the related bands at 1180 and 965 cm^{-1} cannot be discerned explicitly because of overlap). On heating to 225 K, these minor peaks disappear as the ejection of water vapor ceases and the liquid sulfuric acid peaks sharpen as the film crystallizes, as can be seen in Figure 2d.
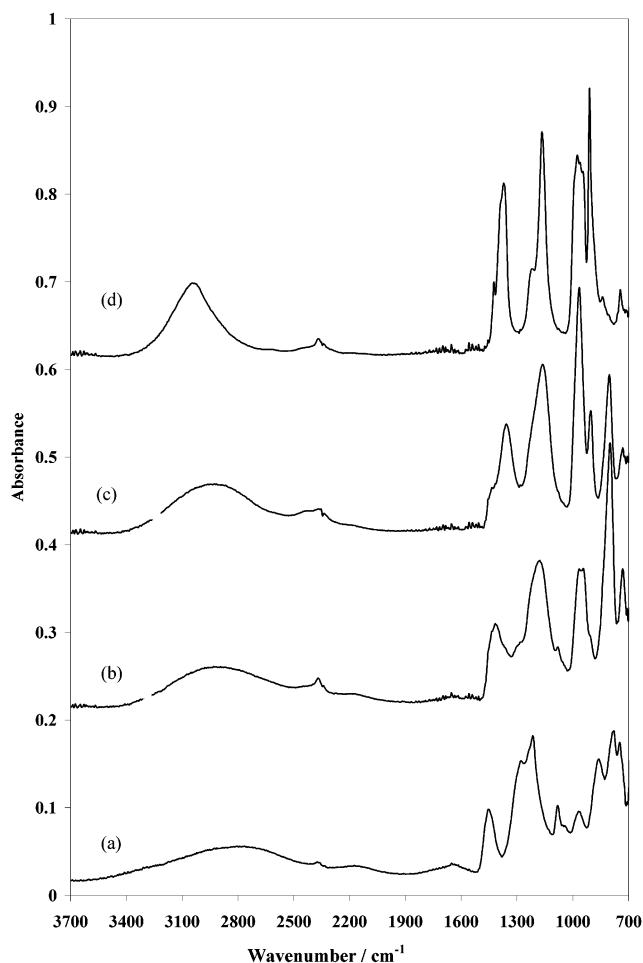

Figure 2. ATR–IR spectra showing the effect of annealing the as-deposited thin film to successively higher temperatures: (a) as-deposited, 190 K; (b) 210 K; (c) 217 K; (d) 225 K.

The material present upon the surface can now be identified using the above observations in conjunction with aspects of the theoretical work in the literature.[13] The work of Re et al.[14b] and Bandy and Ianni[14a] is based upon DFT methods, reputedly accurate for hydrogen bonded complexes. Both studies clearly identify a number of stable molecular hydrates, as shown in Figure 4, and both support the notion that spontaneous ionization is unfavorable for less that four water molecules per H_2SO_4. The most stable 1:1 $H_2O \cdot H_2SO_4$ complex has the H_2O hydrogen bonded across one HO–S=O angle in a six-membered ring, as shown in Figure 4a. Two possibilities exist for the 2:1 complex, with either two H_2O molecules across one HO–S=O angle in an eight-membered ring (Figure 4b) or one H_2O across each HO–S=O angle (Figure 4c). According to Re et al., the former is the more stable by 0.7 kcal, although at 190 K this barrier is likely to be insignificant. It therefore seems probable that the species initially formed upon reaction at the IRE surface is a mixture of these species, since the direct formation of anhydrous H_2SO_4 is not feasible. Because heating the initially formed material drives off a proportion of excess water to form a stable species still containing molecular H_2SO_4 and H_2O, it seems likely that the initial material consists of a mixture of the

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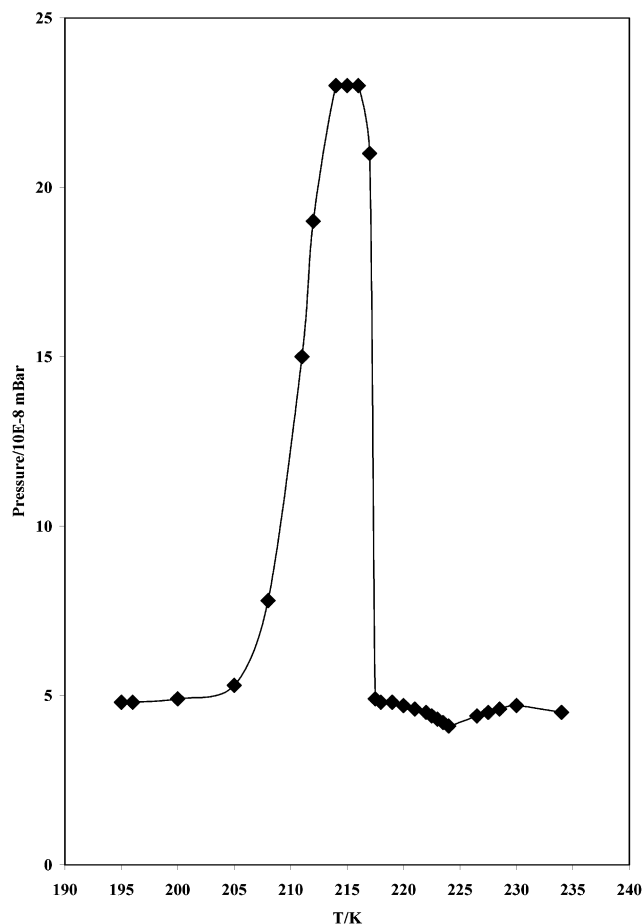
Figure 3 (left column, plot).

Figure 3. Partial pressure of H_2O in the vacuum chamber during film annealing from 190 K.

Figure 4 (right column, structures).

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

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

Figure 4. Structures for the theoretically predicted 1:1 and 2:1 $H_2O \cdot H_2$-SO_4 complexes from Re et al. (ref 14b) (a) 1:1 complex, (b) 2:1 complex: Isomer I, (c) 2:1 complex: Isomer II.

monohydrate and one or both of the dihydrate isomers. Taking the dihydrates as an example, the theoretical structures can then be used to guide the IR band assignments. As a result of the weak hydrogen bonding interaction between the S=O bonds and H_2O in either dihydrate structure, the S=O bonds are approximately the same length in both cases at ca. 0.146 nm. These two bonds couple to give the strong symmetric and antisymmetric stretching modes described above at 1214 and 1460 cm^{-1} for both isomers. However, the effect of hydrogen bonding between the water molecules and the SO−H bonds leads to rather different S−O bond lengths between the two isomers. For isomer I (Figure 4b), the interacting S−O bond shortens and the noninteracting bond lengthens, whereas for the symmetrically bonded isomer II (Figure 4c), both bonds are of equal length. Given that the bond lengths affect the vibrational frequencies, the resonances from these two isomers will therefore be different both from each other and from the free gas-phase molecule. In isomer I, the bonds are different lengths and will not necessarily couple, giving a high frequency for the vibration of the short bond and a lower one for the longer bond. For isomer II, the bonds are still very similar in length and strength to each other, so coupling to give a symmetric and antisymmetric doublet should occur. If both species are present, then up to four bands should be observed in the S−O stretching region provided that neither species possesses high symmetry (more will be expected if the monohydrate is also present, although considerable overlap is to be expected). On the basis of these observations, the bands at 970, 864, and 752
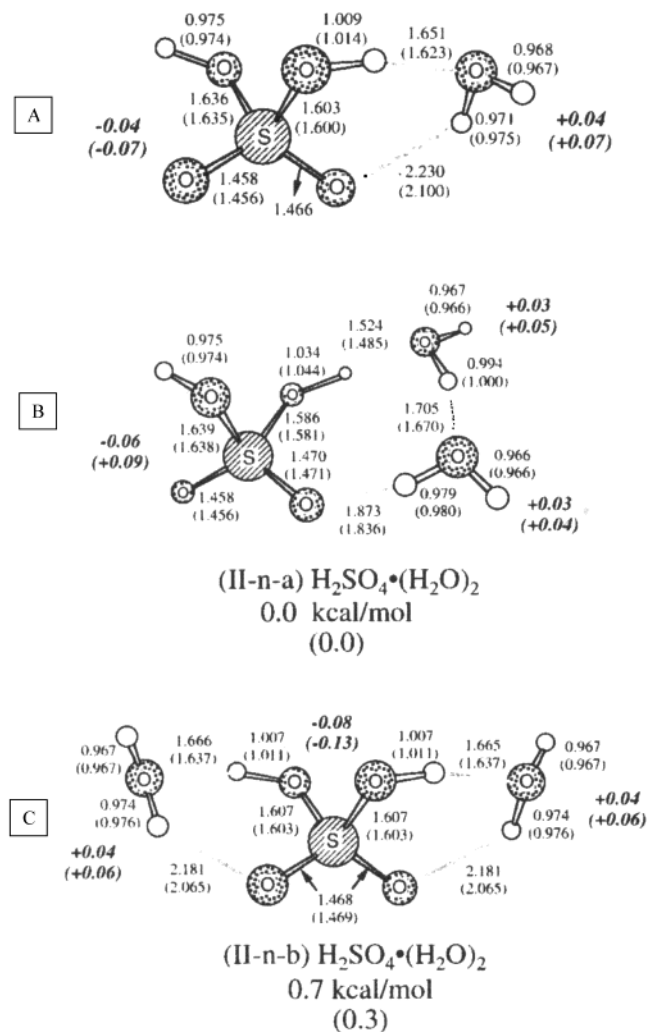
cm^{-1} can be assigned to stretching modes (coupled or individual bond displacement) of S−O bonds in a hydrogen bonded configuration. The pattern of three modes rather than four suggests that either there are coincidences or that one or more modes of the most symmetrical isomer (II) is IR-forbidden. That these modes are due to S−O vibrations is confirmed by the fact that they do not shift significantly upon full deuteration.

By analogous reasoning, the 1:1 complex of H_2O and H_2SO_4 as shown in Figure 4a can therefore be envisaged as a step in the dehydration process. Although it is also likely to be present at variable concentrations in the as-deposited film as discussed above, the material may not be sufficiently well-ordered to produce a characteristic spectrum. The microwave spectrum of this material in the gas phase[8] reveals that the single water molecule in the 1:1 complex is bound by two hydrogen bonds across the O=S−OH moiety, just as predicted by theoretical methods. As before, the S=O bonds are short and relatively free from hydrogen bonding, giving rise through coupling to the doublet at ca. 1400 and 1180 cm^{-1}. It is also likely that these modes are softened somewhat compared to the dihydrate isomers by virtue of increased long range order induced by annealing the film. The band at 802 cm^{-1} can be assigned to the librational mode (frustrated rotation) of the bound H_2O in

Table 1. Summary of Vibrational Frequencies and Assignments for the Initial Deposit at 190 K and Its Thermal Products at 210 and 217 K[a]

amorphous deposit 190 K (Figure 1a)	deuterated deposit 190 K (Figure 1c)	gas phase (anhydrous) (ref 10)	thermal product I 210 K (Figure 2b)	thermal product II 217 K (Figure 2c)	H_2SO_4 (s) 210 K (ref 12)	
2845 (m, br)	2262 (m, br)	3610	2926 (s, br)			OH stretch
1460 (s)	1441 (s)	1450	1400 (m)	1365 (s)	1358 (s)	ν_{as}(O=S=O)
1284	1302					species X
1214 (s)	1213 (s)	1223	1180 (s, br)	1170 (s)	1165 (s)	ν_s(O=S=O)
1086 (w)	1091					species X
970 (m)	955 (m)	883	965 (s, br)	969 (s)	965 (s)	ν_{as}(HO−S−OH)
864 (s)	850 (sh)	834	911 (w, sh)	907 (s)	905 (s)	ν_s(HO−S−OH)
			802 (vs)			complexed H_2O
788 (s)	780 (m)					species X
752 (s)	750 (s)		752 (m)			undefined O−S−O related

[a] (Peak intensities indicated by: (s) strong; (m) medium; (w) weak; (br) broad; (sh) shoulder).

a highly ordered system, analogous to the H_2O librational mode observed in crystalline ice at 810 cm^{-1}. The fact that this mode is due to an OH-related vibration is verified by deuteration experiments, in which it is absent (although it is not possible to identify this band at a shifted position in the deuterated sample as it lies below the low-wavenumber cutoff of the optical system used here). Fiacco et al.[8] observed a significant degree of rotational freedom for the H_2O molecule in this configuration, which lends weight to the assignment. The residual features in Figure 2b arise from the 2:1 isomers, and decrease as the reaction dehydration continues. Figure 2c represents further dehydration, i.e., water loss from the 1:1 complex as anhydrous sulfuric acid is formed. This IR spectroscopic evidence therefore supports predictions of the stability of the 1:1 complex, and that fact that a range of products are observed from the initial reaction also supports the assertion that the free energies of formation of the lower ratio isomers are similar. Under these conditions (i.e., reduced temperature and water concentration), the formation of the higher hydrates is favored energetically but the amounts actually formed are limited by the availability of H_2O.

On the basis of the above observations, it is proposed that the conversion of the as-deposited sulfuric acid hydrate film to condensed anhydrous sulfuric acid film proceeds largely from two isomers of molecular $H_2SO_4 \cdot (H_2O)_2$ through $H_2SO_4 \cdot H_2O$ (thermal product I) to molecular H_2SO_4 (thermal product II). Thus Figure 2a shows a mixture of the mixed dihydrates with a small amount of disordered 1:1 complex, Figure 2b is predominantly the 1:1 complex with some liquid sulfuric acid present and Figure 2c shows predominantly a film of liquid sulfuric acid. It was not possible in these experiments to stabilize a film of the 1:1 complex, suggesting that the structure is only weakly stable as a condensed film under vacuum conditions. Table 1 summarizes the vibrational frequencies and assignments presented above.

Hydration of Amorphous Sulfuric Acid at 190 K. To further investigate the structure and stability of the molecular complexes identified above, additional water was added. Given that the lower ratio hydrates are formed largely as a result of the restricted amount of water available for reaction, this would be expected to facilitate the formation of higher hydrates. When the water pressure above an amorphous sulfuric acid film is raised above 1 × 10^{-5} mbar, significant changes in the film spectra are observed as the condensate rapidly converts to a new species. Figure 5 shows IR spectra of this transition and Figure 6 shows examples of the hydration product and its
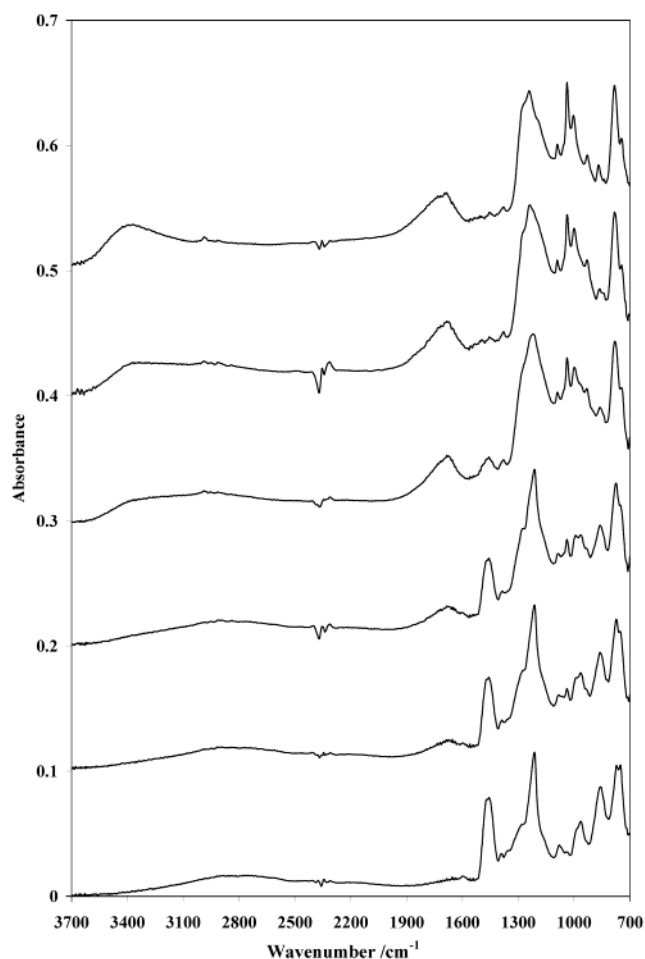

Figure 5. ATR−IR spectra of the product of exposing the film with spectra shown in 1(a) and 1(c) to 1 × 10^{-5} mbar H_2O at 190 K until complete conversion has occurred.

deuterated analogue. The spectra are characterized by a number of strong absorption bands in the SO_4 core region. Bands at ca. 1260(1275), 1092(1092), 1038(1039), 785(783), and 750(745) cm^{-1} are common to both normal and deuterated materials, with additional features of significant intensity at 1007, 931, and 873 cm^{-1} in the undeuterated film. Additionally, the OH stretching region is dominated by strong broad absorptions at ca. 3380 cm^{-1}, due to the addition of less strongly bound H_2O molecules in the deposit. At temperatures below 190 K, this transformation is not observed: upon water exposure, the amorphous acid peaks remain unchanged and molecular H_2O is observed to be
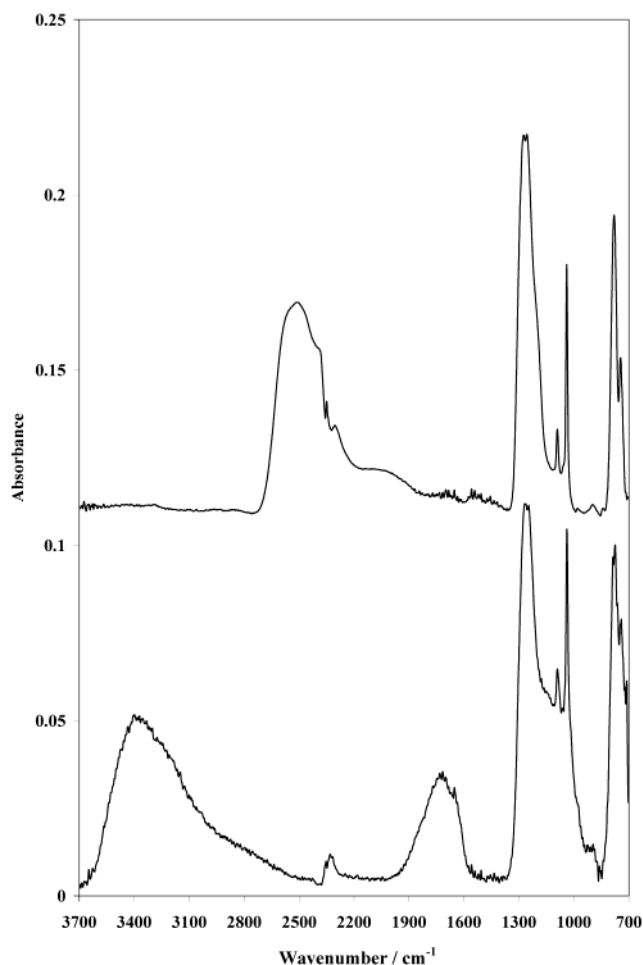
Figure 6. ATR−IR spectra of (a) normal and (b) deuterated hydration product at 190 K produced directly from gaseous SO_3 and H_2O at $R_p = 10$. Spectra are offset for clarity.

Figure 7. ATR−IR spectra showing the result of annealing the hydration product to successively higher temperatures. (a) 190 K; (b) 195 K; (c) 200 K; (d) 205 K; (e) 208 K; and (f) 210 K.

incorporated into the film as crystalline ice. By careful control of the water and SO_3 pressures around $R_p = 10$, this material can be deposited directly. Films produced by this method are generally free of lower hydrate contamination, as can be seen from the spectra presented in Figure 6.

Although the direct analysis of this material by assignment of the spectral features is difficult without reference materials, the approximate composition can be deduced by observation of its thermal behavior. Heating the undeuterated film slowly from 190 to 220 K results in an irreversible transformation to sulfuric acid monohydrate, as shown in Figure 7. Starting from the unidentified material in Figure 7a at 190 K to the end product SAM in Figure 7f at 210 K, several clear transformations are observed. The broad absorption at ca. 3380 cm^{-1} characteristic of liquidlike molecular H_2O is lost, to be replaced by the broad features at ca. 2860, 2202 and 1699 cm^{-1} characteristic of the H_3O^+ ion. Concomitantly in the sulfate region, the broad features at ca. 1260 and 785 cm^{-1} and the sharp features at 1092 and 1038 cm^{-1} are also gradually lost as the characteristically strong and broad features of the bisulfate ion at 1130, 1034, and 902 cm^{-1} grow in. Simultaneous monitoring of the gas phase above this film reveals the ejection of water during this transformation as shown in Figure 8. The rate of this ejection peaks at ca. 202 K, commensurate with the midpoint of the transformation from the unidentified species to crystalline SAM. No sulfur-containing species are ejected during this process. Furthermore, once the
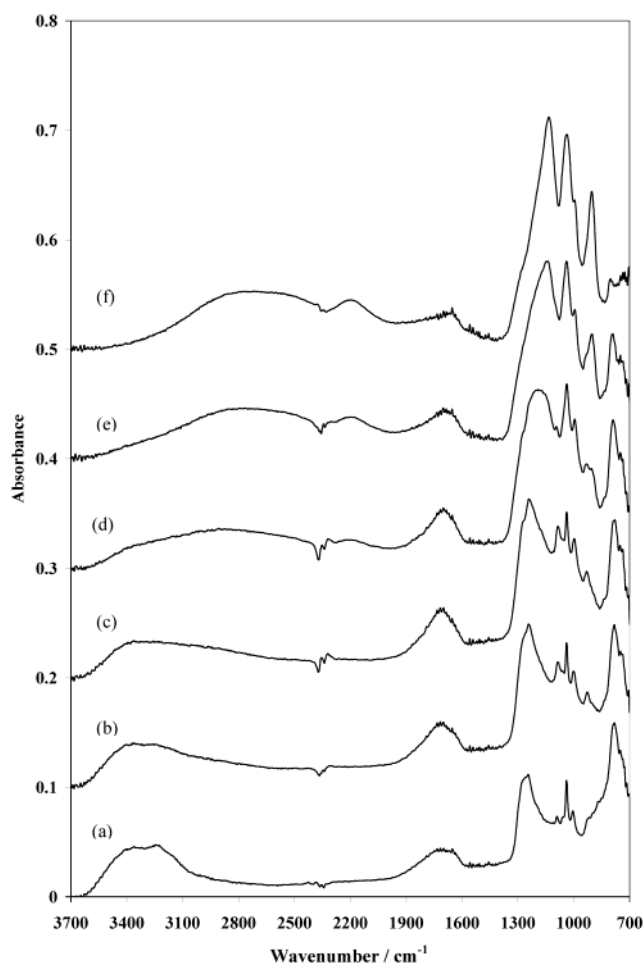
film has been converted to SAM, it is not possible to regenerate the original species.

Composition of the Hydration Product. The changes in the OH vibrations on conversion to SAM in Figure 7 along with the predictions from the computational studies give some clues as to the character of the new species. Comparison with reference spectra of sulfuric acid tetrahydrate[9] (SAT) suggest that the material does not contain tetrahedral SO_4^{2-}, which would give rise to an intense, sharp band at ca. 1070 cm^{-1}. Although the sulfate ion could be present in a different coordination environment, the spectral features are not compatible with any of its known distortions in complexes.[15] Furthermore, there is no convincing evidence in the initial spectrum (Figure 7a) for the presence of H_3O^+ (or higher proton hydrate) counterions which would necessarily accompany any ionized sulfur-containing anion. Figure 8 clearly shows that some water is driven off during the conversion to SAM, whereas Figure 7a−f show production of H_3O^+ simultaneous with this loss. This implies that some of the water associated with the hydrate is being converted to the hydronium ion and some is lost to the vacuum. Because SAM ($H_3O^+HSO_4^-$) is effectively an ionized form of the $H_2SO_4 \cdot H_2O$ complex, the product must contain more water than either of these materials (obviously, it has more than

(15) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley-Interscience, New York, 1997. (b) Yamaguchi, T.; Jin, T.; Tanabe, K. *J. Phys. Chem.* **1988**, *90*, 3148.
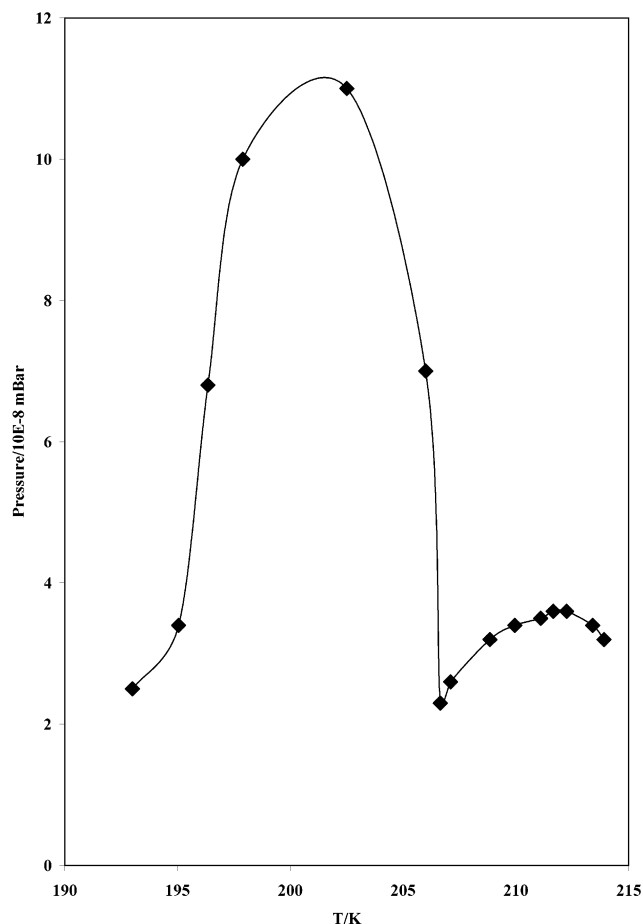
Figure 8. Partial pressure of H_2O in the vacuum chamber during annealing the hydration product from 190 K.

the latter because it was formed from hydration of the $H_2SO_4 \cdot (H_2O)_n$ ($1 < n < 2$) complex(es)). If the hydrated product contains intact molecular H_2SO_4, the SO_4 core is clearly not in the same form as in either the anhydrous condensed form (solid or liquid), the amorphous form ($1 < n < 2$) or the 1:1 complex. The spectroscopic evidence points to the fact that the hydrated product must therefore be a molecular complex of H_2SO_4 and H_2O in a ratio greater than 2:1

The DFT studies of Bandy and Ianni[14a] for the hydrates of sulfuric acid in small clusters of up to 7 water molecules and for the dimer of the trihydrate of sulfuric acid $(H_2SO_4 \cdot 3H_2O)_2$ point the way to possible structures for this material. As in the Re et al. work,[14b] they found that many neutral clusters of $H_2SO_4 \cdot nH_2O$ for $n = 1-6$, were stable in the form of hydrogen-bonded molecular complexes of H_2SO_4 and H_2O and contain no H_3O^+ ions. They also determined that there is no free energy barrier to the formation of larger hydrates below 248 K. The calculations suggest that the species $(H_2SO_4 \cdot 3H_2O)_2$ had the greatest Gibbs free energy of formation of the species studied and on the basis that water molecules may be coordinated between several H_2SO_4 molecules to produce an extended structure, the authors speculate that most atmospheric ultra-fine particles in the $1-100$ nm radius range might be entirely composed of long chains of $(H_2SO_4 \cdot 2H_2O)_n$. They also considered the probability of neutral clusters of $H_2SO_4 \cdot nH_2O$ isomerizing to form $H_3O^+HSO_4^- \cdot (n-1)H_2O$ by calculating the Gibbs free energy of isomerization of the hydrates of sulfuric acid (into the ionized form). In contrast to bulk solutions, these

studies suggest that the free energy of ionization of an acid complex is positive at room temperature even with $n = 6$. Consequently, it is probable that at least 5 water molecules are required before the spontaneous ionization is favorable, even at temperatures of 180 K. Re et al arrived at similar conclusions that several water molecules are required before ionization becomes favorable; although Larson et al have identified an alternative mechanism for $n = 4$. The spectroscopic observations presented here are therefore discussed in the light of these predictions.

Given the stability of hydrogen bonded molecular complexes of H_2SO_4 and H_2O, possibly comprising of loosely bound $(H_2SO_4 \cdot 3H_2O)_2$ dimers or higher chains with the form $(H_2SO_4 \cdot 2H_2O)_n \cdot 2H_2O$, the following observations can be made to propose a structure for the hydrated product and an assignment of its vibrational modes as seen in Figures 6 and 7a. In the OH stretching region, there is a strong, broad feature at 3380 cm^{-1} and a weaker (broad) shoulder centered at ca. 3000 cm^{-1}. The calculated lengths of the O–H bonds of both the SO–H and the H–O–H moieties in these higher ratio complexes are similar those observed in the 1:1 complex and are somewhat longer than those found in the isolated H_2O. The broad OH feature at ca. 3380 cm^{-1} is therefore due to the O–H stretching modes of complexed H_2O molecules and the broad shoulder at ca. 3000 cm^{-1} arises from the OH stretches of H_2SO_4. The intensity of the water-related OH stretches compared to those of H_2SO_4 support the assertion that the hydrate contains a significant amount of water. The OH-related features are also seen at appropriately shifted values in the spectrum of the deuterated compound. These assignments are supported by literature observations of the spectral signatures of thin films of vapor deposited ice, which are characterized by broad, structured absorption bands comprising of a number of overlapping resonances. These composite bands typically show maxima at ca. 3240 cm^{-1} with shoulders at ca. 3380 and 3160 cm^{-1} in the amorphous form. On heating such films, the features at 3240 and 3160 cm^{-1} increase in intensity at the expense of that at 3380 cm^{-1}, which implies that the shoulder at 3380 cm^{-1} is associated with H_2O in an environment where it is not fully coordinated in a regular ice lattice. The assertion that the 3380 cm^{-1} band may be due to weakly coordinated water is supported by recent experimental work by Schriver–Mazzuoli et al.,[16] who have deposited a thin ice film showing a asymmetric band with a maximum at 3380 cm^{-1} and a secondary maximum at 3230 cm^{-1}. This film was grown under slow deposition conditions and is similar is shape and position to that seen in the product hydrate.

Assignment of the SO_4 core modes is more problematical but can again follow similar reasoning to that invoked for the 1:1 and 2:1 complexes. For example, from the calculated structure of the $(H_2SO_4 \cdot 3H_2O)_2$ dimers, there are considerable changes in the lengths and inter-bond angles of the S=O and S–OH bonds. We propose the following assignments on the basis of the generalized structural features observed in the higher hydrates. Typically, both of the S=O bonds are lengthened through hydrogen bonds leading to considerable downward frequency shifts from the free acid. The broad, structured feature at ca. 1260 cm^{-1} (1275 cm^{-1} in the deuterated analogue) is

(16) Schriver-Mazzuoli, L.; Schriver, A.; Hallou, A. *J. Mol. Struct.* **2000**, *554*, 289.

Table 2: Summary of Vibrational Frequencies and Assignments for the Hydration Product at 190 K and for the Thermal Product at 210 K

hydration product (Figure 6a)	D_2O product (Figure 6b)	thermal product III (Figure 7f)	assignment
3380 (s, br)	2524 (s, br)		νH_2O
		2860 (br)	νH_3O^+
1723 (br)	-	1699 (br)	δH_3O^+
		1274 (sh)	$\delta O-H$ (bisulfate)
1260 (s)	1275 (s)		$\nu_{as}(O\!=\!S\!=\!O)$ (acid)
1246 (s)	1261 (s)		$\nu_s(O\!=\!S\!=\!O)$ (acid)
		1130 (s)	$\nu_{as}S-OH$ (bisulfate)
1092 (m)	1092 (m)		$\nu_{as}(O-S-O)-2$ (acid)
1038 (s)	1039 (s)		$\nu_{as}(O-S-O)-1$ (acid)
		1034 (s)	$\nu_{as}SO_3$ (bisulfate)
1007 (w)			
931 (w)			
		902 (s)	$\nu_s SO_3$ (bisulfate)
873 (w)			
785 (s)	783 (s)		$\nu_s(O-S-O)-1$ (acid)
750 (m)	745 (m)		$\nu_s(O-S-O)-2$ (acid)

therefore assigned to the overlapped symmetric and antisymmetric ($O\!=\!S\!=\!O$) stretches. There are clearly more than two bands under this profile, which is similar for both the normal and deuterated material: this is most likely due to the presence of at least two environments for the H_2SO_4 molecules within the polymeric structure. The shoulder at ca. 1200 cm^{-1} is also present in the deuterated analogue, confirming its association with the SO_4 core (although the broad δOD modes of D_2SO_4 and D_2O will also underlie this region of the spectrum).

The microwave study of the 1:1 $H_2SO_4 \cdot H_2O$ complex by Fiacco et al.[8] reveals evidence for changes in the inter-bond angles that might be expected as more water is added to the hydrate and the H_2SO_4 moiety experiences additional hydrogen bonding. These changes are particularly pronounced for the $HO-S-OH$ angles, in conjunction with the predicted shortening of the $S-O$ bonds in a hydrogen bonded chain, this effect would serve to increase the frequency spacing between the antisymmetric and symmetric stretching modes. Consequently, the strong sharp bands at 1038 and 785 cm^{-1} (1039 and 783 cm^{-1} in the deuterated material) are tentatively assigned to these modes (respectively). These bands are enveloped by weaker features at 1092 and 750 cm^{-1}, which are attributable to the same vibrational modes of a second H_2SO_4 molecule in a slightly different environment (probably with a slightly wider $O-S-O$ bond angle). These pairs of modes are always observed with a fixed relative intensity ratio with respect to each other in the spectra. Furthermore, it is unlikely that the lower frequency modes at ca. 780 cm^{-1} are due to $O\!=\!S\!=\!O$ deformation modes, given that the highest frequency modes of this type in the spectra of matrix isolated H_2SO_4 occurs at 554 cm^{-1}. Suggested vibrational assignments are given in Table 2.

In summary, although the above tentative assignment requires further theoretical work to ascertain the validity of the vibrational mode assignment, the hydrated product is clearly a higher ratio molecular H_2SO_4/H_2O complex. Upon heating, it thermally decomposes to ionic sulfuric acid monohydrate with the loss of water (but does not lose any sulfur-containing moiety). Upon overlaying the spectra of the molecular to ionic hydrate conversion shown in Figure 5, an isosbestic point is evident at ca. 800 cm^{-1}, indicating a straightforward conversion of one species to another (namely, H_2SO_4 to HSO_4^-). The diagram in
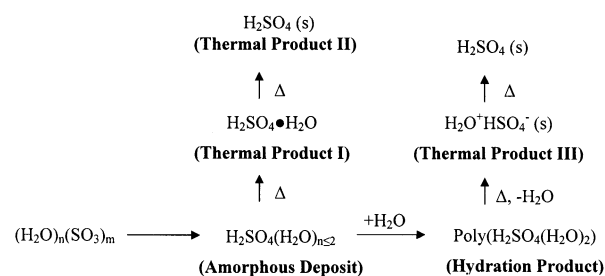
Figure 9. Reaction scheme and interconversion of sulfuric acid species with temperature and water exposure (ejection).

Figure 9 summarizes the observed forms of sulfuric acid and its hydrates and their interconversions.

Conclusions

By controlled variation of temperature and reaction conditions, various low-ratio H_2SO_4/H_2O species have been condensed and characterized. Amorphous mixtures of sulfuric acid and water can be formed at low temperatures under conditions of low water availability. These deposits show a vibrational spectrum very similar to that observed for H_2SO_4 in dilute inert gas matrixes. That anhydrous H_2SO_4 cannot be formed directly under these conditions (i.e., water is always present in the condensed film) and is only accessible by dehydration supports gas-phase experimental and theoretical observations that the reaction of SO_3 with H_2O requires at least two H_2O molecules, even when the reaction occurs heterogeneously. It would appear that the principal role of the surface in this reaction is to immobilize one or both of the reactants, thereby increasing the reaction efficiency. The stoichiometry of this heterogeneous process cannot therefore be determined directly from the gas-phase measurements without a knowledge of the temperature-dependent sticking probabilities of H_2O and SO_3.

Upon heating, this amorphous sulfuric acid/water mixture evolves the excess water trapped in the film and transforms first into an ordered 1:1 molecular complex of H_2O and H_2SO_4 and then into molecular sulfuric acid. The released water can be observed in the gas phase until there is complete conversion to the molecular acid. The 1:1 complex is characterized by H_2SO_4 vibrations which, although lower in frequency than those for the initially formed amorphous acid/water mixture, are clearly different from those observed for condensed anhydrous H_2SO_4. Additionally, this complex is characterized by a readily identifiable vibration of the coordinated H_2O molecule. The vibrational spectroscopic observation of such a complex provides further evidence in support of the conclusions of microwave and theoretical studies that such a complex is stable at low temperatures in clusters.

The addition of water to the amorphous H_2SO_4/H_2O mixture results in the formation of a new material with a reproducible and well-defined vibrational spectrum. Through the use of a combination of literature theoretical predictions, thermal behavior and spectroscopic arguments, this material is identified as a stable higher ratio molecular H_2SO_4/H_2O complex with a probable structure of poly($H_2SO_4(H_2O)_2$). Given additional energy, this material irreversibly transforms into an ionized sulfuric acid hydrate, namely the monohydrate $H_3O^+HSO_4^-$. Further heating produces the anhydrous molecular acid as seen in previous experiments. This study presents the first experiment observation of this un-ionized complex.

There are atmospheric implications as a result of the stability of these compounds. Because the majority of atmospheric sulfate aerosol are thought to be formed from both the gaseous nucleation of SO_3 and water and through the heterogeneous hydration of SO_3 on water droplets, it is likely that these species are involved directly in the process of aerosol formation, although it is unlikely that they are long-lived in the bulk aerosol under typical ambient conditions. However, the reproducibility and stability of formation of these materials gives experimental credibility to the suggestion by Bandy and Ianni[14a] that un-ionized acid hydrates may be important surface species on aerosols because these molecular species are potentially far more stable at the aerosol/vacuum interface than any ionic species. An understanding of the nature of the hydrate complexes, their ionization energetics and their thermal stability will clearly be essential for detailed models of aerosol formation in the atmosphere. The direct observation of these intermediates in sulfate aerosol formation processes provides a challenge for future experiments.

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