

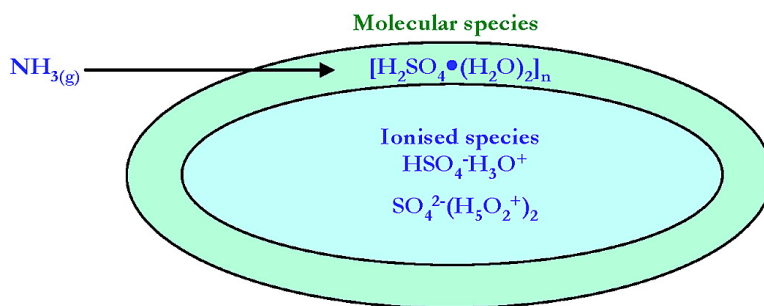
Communication

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## Identification of Surface Molecular Hydrates on Solid Sulfuric Acid Films

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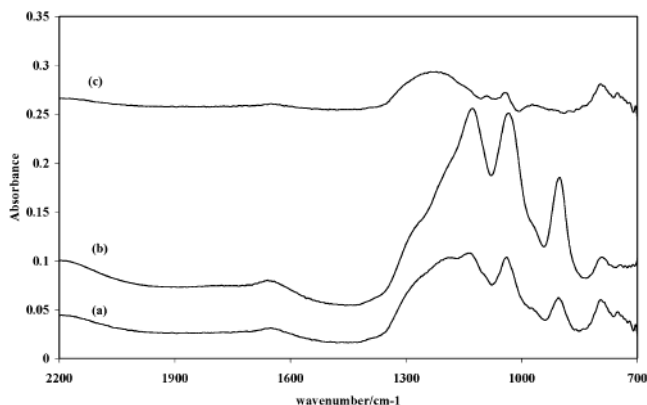
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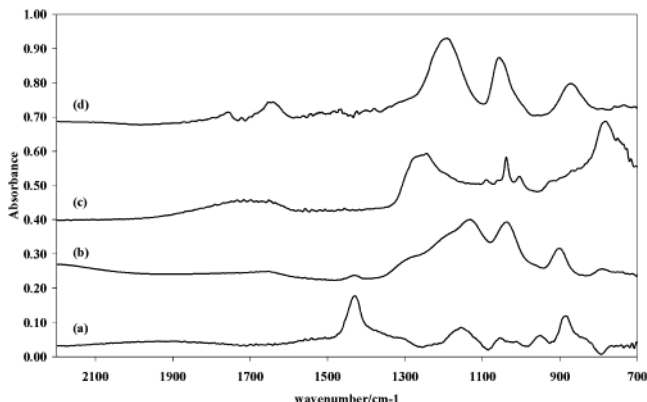
In this communication, we report observations of the presence of a surface molecular hydrate on condensed (solid) sulfuric acid hydrate films. The composition of this surface layer has been established through infrared spectroscopy and static secondary ion mass spectrometry (SSIMS). Such surface layers serve to insulate the ionic bulk of the hydrate and may play an important role in atmospheric reactions and nucleation processes.

The reactive uptake of atmospherically relevant species upon particulate material in the atmosphere is known to show a strong dependence upon surface composition, bulk mobility, morphology, and temperature.<sup>1</sup> Such experiments identify the availability of water as one of the main parameters influencing reactivity through both physical and chemical effects. For condensed aerosol particles such as those containing sulfuric acid, the availability of water at the interface (and the rate at which it can be replaced from the bulk) is the rate-limiting factor in heterogeneous hydrolysis processes relevant to the upper troposphere and lower stratosphere. To parameterize the reactivity of a range of aerosol materials for inclusion in atmospheric models, it is essential that the mechanisms of the surface processes involved are understood. For example, although surface reactivity often relates directly to bulk composition, there are frequent examples in the literature where reactivity varies with time as a result of surface depletion or poisoning in a way that is not reflected in the overall bulk composition. In recent years, the application of spectroscopic<sup>2,3</sup> and surface mass spectrometric<sup>4,5</sup> methods have enabled detailed examination of such surface-specific chemistry, leading to observations such as the saturation reaction of ice particles with ClONO<sub>2</sub>, where reactivity ceases once the surface is fully covered with nitric acid hydrates. Saturation effects have also been observed in kinetic studies in coated wall flow tubes, although the surface products or intermediates could not be directly identified. It is only from the synergy between mechanistic and kinetic observations and theory that a detailed understanding of such systems has been obtained.

Figure 1 shows IR spectra of thin (100 nm) and thick (250 nm) films of sulfuric acid monohydrate (SAM) deposited at ca. 210 K from the reaction between SO<sub>3</sub> and H<sub>2</sub>O, obtained in an attenuated total internal reflection geometry.<sup>6</sup> Given the nature of the optical configuration, the thick films are largely representative of the bulk composition, whereas the thin film shows both surface and bulk features. Scaled subtraction of the bulk spectrum from that of the bulk + surface (Figure 1c) reveals the presence of a second material which has a spectrum characteristic of a recently identified molecular hydrate<sup>7</sup> (Figure 2c). The main IR absorption bands of this material which distinguish it from other sulfuric acid hydrates are the strong, broad resonances at ca. 1260 and 780 cm<sup>-1</sup>. Thus this material, predicted to be stable by theoretical studies,<sup>8</sup> is also



**Figure 1.** ATR-IR spectra of films of SAM at 200 K. (a) Thin (100 nm); (b) thick (>250 nm); (c) scaled subtraction: [(a) - 0.36(b)].



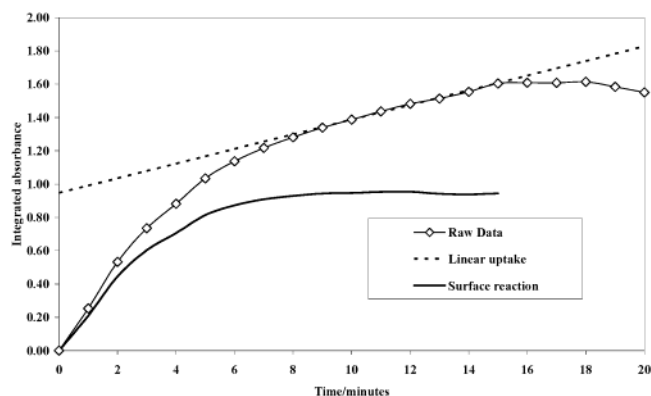
**Figure 2.** Infrared spectra of sulfuric acid hydrates and reference spectra. (a) Absorbance difference spectrum of SAM exposed to  $1 \times 10^{-7}$  mbar NH<sub>3</sub> for 300 s versus clean SAM; (b) bulk SAM; (c) molecular hydrate; (d) sodium bisulfate reference.

clearly present on the surface of SAM films. SSIMS analysis, including depth profiling, of SAM films deposited in a similar manner also demonstrates the existence of a surface layer over the bulk films. Spectra recorded of the film surface indicate a mixture of acid species, with water availability during deposition representing the primary influence on the composition of this interface. SIMS depth profiles of thin films provide evidence that at deposition temperatures of 200 K the surface layer is not mobile.<sup>9</sup> That these molecular surface layers play a role in the surface chemistry of condensed sulfate hydrates is confirmed by observations of the interaction of such films with gaseous NH<sub>3</sub>. Exposure of a 100 nm thick SAM film at 220 K to a flux of NH<sub>3</sub> results in the formation of the characteristic absorption bands of NH<sub>4</sub><sup>+</sup> along with overlapping gains and losses in the sulfate core region (1400–800 cm<sup>-1</sup>) as shown in Figure 2. By comparison to reference spectra recorded

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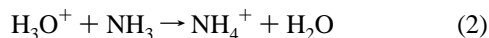
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**Figure 3.** Plot of the typical integrated intensity of the  $\delta(\text{NH}_4^+)$  band vs time (constant  $\text{NH}_3$  exposure of  $1 \times 10^{-7}$  mbar to 15 min). Traces are raw data ( $\diamond$ ), a linear absorbance vs time fit (dashed line) and the (raw data – linear uptake) residual due to the saturating surface reaction (solid line).

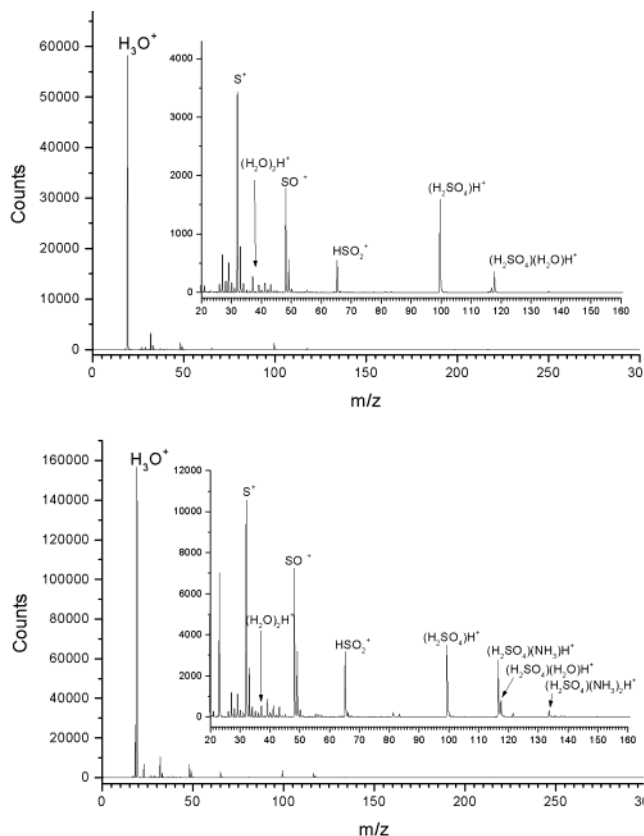
under similar conditions, these gains and losses are attributed as follows.<sup>10</sup> Besides  $\text{NH}_4^+$ , the other main gain is the characteristic absorption pattern for the bisulfate ion in a salt (as opposed to SAM). The loss features are attributed to  $\text{H}_3\text{O}^+$ , SAM-related bisulfate ions, and the surface molecular hydrate. A plot of the integrated intensity of the  $\text{NH}_4^+$  deformation mode absorption with  $\text{NH}_3$  exposure (Figure 3) reveals two distinct processes, namely an initially rapid reaction, which appears to saturate, and a continuous linear uptake. The former can be associated with the reaction between  $\text{NH}_3$  and the surface molecular hydrate, while the latter is attributed to the reaction between  $\text{NH}_3$  and  $\text{H}_3\text{O}^+$  ions in the SAM structure. The fact that the surface process saturates is due to the loss of the molecular hydrate during reaction and its replacement by a capping layer of ammonium bisulfate. The rate of the continuous reaction is likely to be controlled by the diffusion of  $\text{H}_3\text{O}^+$  from the bulk.

A significant amount of water ejection from the surface is observed by mass spectrometry during exposure to  $\text{NH}_3$ . This is also accompanied by an increase in the SIMS signal attributable to surface  $\text{NH}_4^+\text{HSO}_4^-$ . Both reactions produce water:



Much of the  $\text{H}_2\text{O}$  released during these reactions is likely to be retained as water of crystallization by the product ammonium bisulfate. However, reaction 1 produces significantly more  $\text{H}_2\text{O}$  than reaction 2: moreover, the  $\text{H}_2\text{O}$  produced is already at the surface and thus is readily released into the vacuum.

SSIMS analysis of SAM films following exposure to ammonia provides additional evidence supporting reaction 1 as the dominant process occurring on the surface. Spectral features are observed associated with sulfuric acid/ammonium clusters without any evidence for the formation of ammonium/water clusters (Figure 4). The reaction results in the formation of a layer of ammonium bisulfate on the surface of the SAM film. Depth profiling by SIMS, used to monitor the extent of reaction of ammonia with the bulk material, reveals a very short penetration distance (a few monolayers only) on the time scale of the experiment. Furthermore, reaction of the film with  $\text{ND}_3$  as opposed to  $\text{NH}_3$  shows extensive proton/deuterium exchange with new peaks appearing for SD, SOD,  $\text{SO}_2\text{D}$ , and  $\text{H}_2\text{SO}_4\text{D}$ .



**Figure 4.** SSIMS spectra of SAM film as deposited (top), and following exposure to  $8 \times 10^{-10}$  mbar  $\text{NH}_3$  for 5 min (bottom) both at 200 K.

In summary, although sulfuric acid monohydrate is not believed to be a major component of atmospheric particulate materials, the observations described above are relevant to the atmosphere insofar as they support the theory first expounded by Ianni and Bandy that molecular hydrates are potentially stable under atmospheric conditions and are likely to play a role in the surface chemistry of sulfuric acid aerosol. Furthermore, Couling et al. have recently reported the direct observation of the 1:1 and polyhydrate  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$  molecular complex in sulfuric acid aerosols, which provides further evidence for the stability of molecular hydrates.<sup>11</sup> These species are not included or described in current models of aerosol reactivity.

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