

Chemistry at the Surfaces of Ice and Sulfuric Acid: Toward an Understanding of Adsorption at Molecular Solids

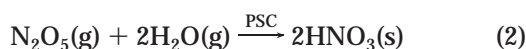
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Introduction

In 1985 the British Antarctic Survey published evidence for a dramatic, seasonally recurring depletion of the south polar ozone layer.¹ The data, which were met with some skepticism, soon were confirmed by a U.S. scientific team,² and the phenomenon has since been the subject of intense international scrutiny. Over the past few years, evidence for what has come to be called the “ozone hole” has accumulated to such an extent that it is now accepted by virtually all credible atmospheric scientists as real, serious, and anthropogenic in origin. Among the explanations originally advanced to account for the ozone hole, the one now accepted to be correct involves chemical transformations that take place at or near the surfaces of polar stratospheric cloud (PSC) particles.³ Many reactions have been identified as important or potentially important, among the most significant of which are:^{4–8}



Equation 1 causes the conversion of the photolytically stable chlorine reservoirs HCl and ClONO₂ into Cl₂, which readily photodissociates to form ozone-reactive Cl. The effect of eq 2 (and related reactions) is to remove certain gaseous nitrogen oxides from the atmosphere, which affects the ozone level because the same nitrogen oxides are Cl scavengers.

Several classes of PSC particles have been identified.^{9–12} So-called type I particles are made up of mixtures of nitric acid and water. Type II particles, found in the coldest regions of the stratosphere, consist of ice. Finally, there are sulfate particles, which are mixtures of sulfuric acid and water. Sulfate particles may be solid or liquid, depending on their composition, temperature, and ther-

mal history. Although the kinetics and product distributions of PSC-mediated reactions are now reasonably well established, it is fair to say that the detailed mechanisms of many important reactions remain undefined. The reactions are often the result of complex, multistep transformations, involving at least some of the following phenomena: gas-phase diffusion, accommodation at the surface, bulk and surface diffusion, the reaction itself, and product release into the gas phase. This extraordinary complexity has made deep mechanistic understanding elusive.

Ice, nitric acid, and sulfuric acid are of interest for reasons beyond their relevance to the atmosphere because they exemplify a class of substances, namely molecular solids, whose surfaces are poorly understood compared to those of metals, oxides, and semiconductors. For chemists interested in the gas–solid interface, molecular solid surfaces present a wide array of fascinating and unexplored questions. For instance, in a molecular solid at equilibrium with its gas phase, evaporation and recondensation rates at the surface can be extraordinarily high. As we shall see, the consequences, both structural and kinetic, of such a surface are only beginning to be realized. A second, largely unconsidered issue in molecular solid surface chemistry relates to the fact that the adsorption energy of many substances is a significant fraction of the cohesion energy of the solid itself. A good guess for the adsorption enthalpy of HCl on ice is ~25 kJ·mol⁻¹ (roughly the strength of a hydrogen bond), or approximately 50% of the ice sublimation enthalpy.¹³ Compare these values to those of the well-studied system, CO on Pt, for which the CO adsorption enthalpy (approximately 100 kJ·mol⁻¹, depending on the surface plane and coverage)¹⁴ is only 20% of the Pt sublimation enthalpy. What, one might ask, are the chemical consequences of such a situation? Possibly, adsorbate-induced surface reconstruction and faceting are more significant than they are in more conventional chemisorption systems. Could other effects come into play as well?

In this Account, I describe some of our recent studies of the surface chemical properties of ice and sulfuric acid. Our approach involves the application of high-vacuum surface analysis methods to ultrathin films, typically between 20 and 100 monolayers (ML) thick, of ice and sulfuric acid. The paper is divided into several parts, beginning with a justification of the experimental approach, moving on to a description of various aspects of the ice and sulfuric acid surfaces, and concluding with an assessment of the state of understanding of this important scientific problem.

Experimental Approach

The surfaces we study are those of ultrathin ice and sulfuric acid films deposited on a single-crystal metal

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substrate, generally Pt(111). To grow the films, we use low deposition rates, typically $1 \text{ ML}\cdot\text{s}^{-1}$ or less. Ultrathin films are in many respects good laboratory surrogates for the micron-sized particles on which most ice- and sulfuric acid-mediated reactions occur. Their bulk properties, for instance, their sublimation energies and infrared optical constants, are indistinguishable from those of macroscopic samples of the same temperature and composition.^{13,15–17} Also, for films of nominal thickness greater than $\sim 5 \text{ ML}$, the substrate is completely masked from the gas phase, and beyond $\sim 10 \text{ ML}$ the substrate has no discernible influence on the structure or properties of a film.^{15,18}

There are several reasons for studying the surfaces of ultrathin films rather than those of macroscopic samples. The most important is related to the intrinsically high surface area-to-volume ratio of a film that is several tens of monolayers thick. By virtue of the fact that there are comparable numbers of molecules at the surface and in the bulk of an ultrathin film, analytical probes normally thought of as bulk-sensitive (e.g., infrared spectroscopy and mass spectrometry) can be used to interrogate adsorbed and bulk phases *simultaneously*. This point is critical because evidence accumulates that many PSC-mediated reactions are multistep, some of the steps occurring at a cloud particle surface and others within a bulklike phase in the near-surface region.¹⁹

A critical issue that arises in any study of thin film surfaces is surface area, which can be an exceptionally sensitive function of deposition conditions. Particularly for ice films, the subject is the source of some controversy.²⁰ Extensive characterization of the films discussed herein has shown that the adsorbate-accessible surface areas are very nearly equal to those of the underlying single-crystal substrates, or roughly 10^{15} adsorption sites/ cm^2 . These exceedingly low surface areas (the macroscopic and microscopic surface areas are essentially equal) are a result of the growth conditions, especially the low deposition rate.²¹

Amorphous and Crystalline Ice. An obvious question to be asked regarding the ice surface is this: What functional groups are available for interaction with an adsorbate? In models of surface structure that are based upon simple truncation of the crystalline bulk lattice, half of surface water molecules are oxygen terminated and half terminate in “dangling” OH groups that are perpendicular to the microscopic surface plane.²² Although such a model is a good starting point for a consideration of ice surface structure, there is no reason to expect that it adequately describes a real surface. Surface reconstruction is a well-known phenomenon in metals and semiconductors, and recent simulations of the infrared spectra of ice nanocrystals have suggested that reconstruction may be important for ice as well.²³

In Figure 1 are shown the OD stretching regions of the infrared spectra of two 20 ML ice films made of fully deuterated water (ice- d_2) deposited on Pt(111). The upper spectrum was obtained after allowing room-temperature water vapor to condense on the 130 K substrate, and the

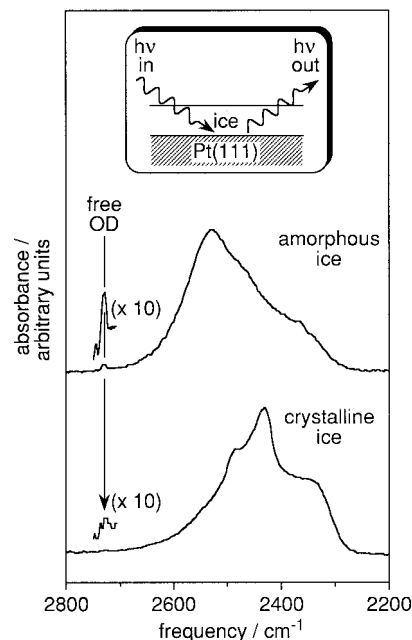


FIGURE 1. Infrared spectra of amorphous and crystalline ice- d_2 on Pt(111). Spectra were obtained with Fourier transform infrared reflection absorption spectroscopy (FTIRAS), as shown schematically at the top of the figure. The intensity of the free OD stretch on the amorphous surface is roughly 0.0006 absorbance units.

bottom spectrum after briefly heating the same ice film to 173 K.²⁴ The broad absorption bands between 2300 and 2700 cm^{-1} are attributed mostly to the OD stretching vibrations in hydrogen-bonded D_2O in the thin film bulk. Differences between the two spectra in this frequency region are associated with bulk structure: D_2O condenses at 130 K as an amorphous, metastable phase, while heating to 173 K induces crystallization to hexagonal or cubic ice. The amorphous and crystalline spectra also both exhibit a sharp feature at 2727 cm^{-1} , a frequency which is near that of the O–D stretch in gaseous D_2O . The mode is assigned to $\nu(\text{O–D})$ of a dangling OD group at the ice- d_2 surface. That the dangling OD group is associated with surface D_2O has been demonstrated by the following experiment: exposure of an amorphous ice- d_2 film to 1 ML equiv²⁵ of gaseous H_2O results in the complete disappearance of the OD mode and in the corresponding appearance of the dangling OH vibration.²⁶ The frequency of the mode is close to those reported by Devlin et al. for the dangling OD group at the surfaces of crystalline and amorphous ice nanoparticles.²⁷ In that work, the dangling OH/OD group was shown to be associated with surface water molecules that are hydrogen-bonded to three other water molecules.

A notable aspect of the spectra in Figure 1 is that the intensity of the dangling OD stretch of an amorphous film is greater than that of a crystalline film by a factor of approximately six. The phenomenon is not associated with a surface area effect, since the adsorbate-accessible surface areas of the two types of film do not differ by more than 20%.²¹ The implication of the spectroscopic data is therefore that the crystalline and amorphous surfaces are structurally different in a way that is related to the number

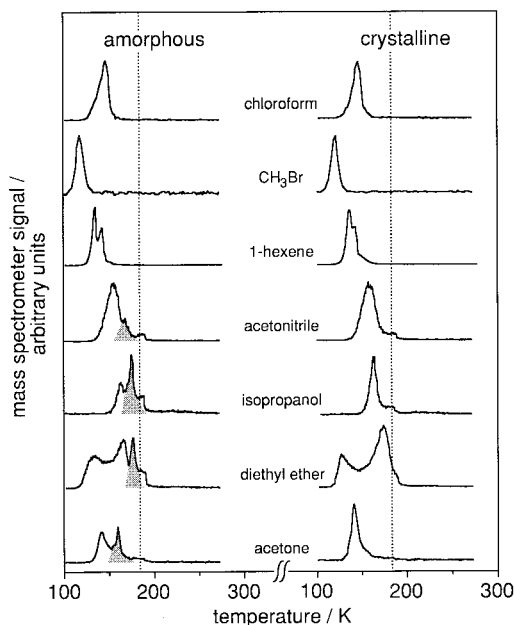


FIGURE 2. Temperature-programmed desorption (TPD) spectra of several compounds from ~ 80 ML films of amorphous and crystalline ice. In all cases, exposures were sufficient to saturate the ice surface. The spectra were collected at heating rates between 3.5 and $5 \text{ K}\cdot\text{s}^{-1}$.

of dangling OH or OD groups. Inferences based on mode intensity must be made with care, however. In fact, the strongest evidence for a greater dangling OH coverage on amorphous ice is based on an analysis of the different chemical properties of the amorphous and crystalline surfaces. As we shall see, the amorphous surface is a significantly better net hydrogen bond donor.

Hydrogen Bonding Ability of the Ice Surface. In Figure 2 are shown data from a series of temperature-programmed desorption (TPD) experiments designed to probe the surface chemical properties of ice.²¹ The experiments were carried out in the following way. Ice films, crystalline and amorphous, were deposited on Pt-(111), cooled to 100 K , and exposed to roughly 1 ML equiv of an adsorbate, either acetone $[(\text{CH}_3)_2\text{CO}]$, acetonitrile (CH_3CN) , 2-propanol $[(\text{CH}_3)_2\text{CHOH}]$, diethyl ether $[(\text{C}_2\text{-H}_5)_2\text{O}]$, 1-hexene $[\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3]$, methyl bromide (CH_3Br) , or chloroform (CHCl_3) . The films were heated at a rate of $\sim 5 \text{ K}\cdot\text{s}^{-1}$, and the gas-phase products were detected with a mass spectrometer. Dashed lines correspond to the temperature by which 1 ML equiv of the underlying ice film has sublimated into the gas phase. Thus, in most cases desorption occurs from a surface that is quiescent with respect to the solid-vapor equilibrium.

For every compound studied, desorption occurs from one or more well-defined states. For example, there are two 1-hexene desorption states, at 135 and 145 K . They have been shown to be associated with condensed hexene multilayers and with hexene adsorbed to the ice surface, respectively. Hexene is one of a class of compounds for which the desorption spectra from amorphous and crystalline ice are indistinguishable. Other substances in this class are methyl bromide, chloroform, and carbon tetrachloride. A second class of compounds, represented in

Figure 2 by acetone, acetonitrile, 2-propanol, and diethyl ether, exhibit desorption states that are unique to the amorphous surface. For instance, acetone desorbs from crystalline ice at 133 K ; the state is associated with physisorption to the ice surface. Physisorbed acetone forms on amorphous ice as well but only after the surface is saturated by another state that desorbs at 157 K .

What is the origin of these unique desorption states, which are highlighted in Figure 2? They are associated with hydrogen bonding to the amorphous surface via interactions of the type $-\text{OH}\cdots\text{X}$. The TPD studies provide some of the evidence for hydrogen bonding. For example, qualitatively different TPD spectra on amorphous and crystalline ice are manifest only for adsorbates that are good hydrogen bond acceptors. Also, the desorption temperatures of the unique states usually are higher than those of the states common to both types of ice. A higher desorption temperature implies a more strongly adsorbed state, which should be the case when hydrogen bonding accompanies or replaces weaker, less specific physisorption interactions. Finally, the unique states exhibit different desorption rates from ice- d_2 and $-d_2$, whereas there are no desorption isotope effects for states that are common to the amorphous and crystalline surfaces.²⁸ The magnitudes of the isotope effects are substance-dependent, with the value of $k_{\text{H}}/k_{\text{D}}$ (where k_{H} and k_{D} indicate the first-order desorption rate constants from ice- d_2 and ice- $-d_2$) sometimes greater than and sometimes less than unity. The reasons for this phenomenon are under scrutiny in our laboratory. Nevertheless, the very observation of a kinetic isotope effect for *only* these states clearly points to an interaction with the OH group of water.

Infrared spectroscopy provides further evidence that the unique desorption states are associated with hydrogen bonding. Figure 3 shows a series of infrared difference spectra, which illustrate how the vibrational spectrum of an amorphous ice- d_2 film changes as it is exposed to successively greater amounts of acetone.²⁹ Significantly, acetone adsorption is accompanied by a reduction in the intensity of the free OD stretch, presumably because the mode becomes part of the broad envelope associated with hydrogen-bonded water. Complexation of the free OH group to acetone accounts as well for some of the changes in the broad region of the OH stretching band. Other changes in this region of the spectrum may be related to acetone-induced modifications of environment in hydrogen-bonded water molecules at and near the surface. The most prominent spectral feature of adsorbed acetone is the carbonyl stretching band, which at low coverages appears at 1703 cm^{-1} . This is 13 cm^{-1} below the $\text{C}=\text{O}$ stretching frequency in liquid acetone but extremely close to that of acetone in an ice matrix,³⁰ a system for which hydrogen bonding between the carbonyl oxygen and the OH group of water has been unequivocally demonstrated. The band at 1703 cm^{-1} , which initially increases in intensity with exposure, saturates at roughly 0.20 ML . Instead, a new band associated with physisorbed acetone

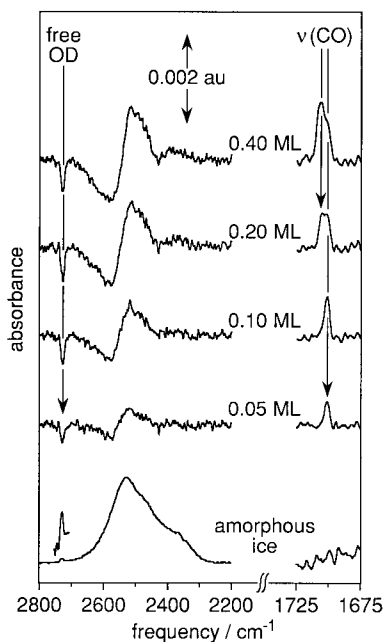


FIGURE 3. Bottom: Infrared spectrum of a 50 ML amorphous ice- d_2 film. The top four other spectra are difference spectra, recorded following various exposures of acetone on the amorphous surface at 100 K. Spectra were obtained with FTIRAS.

appears at 1716 cm^{-1} . It is that state which grows in intensity as the acetone exposure is increased above 0.20 ML.

To further correlate the acetone desorption states with specific features in the infrared spectra, experiments were conducted in which FTIRAS spectra were collected during TPD of acetone on amorphous ice- d_2 .²⁹ As expected, the higher frequency carbonyl stretch, i.e., that attributed to physisorbed acetone, disappears before the lower frequency, hydrogen bonded, one. Also, there is a close correspondence between the temperatures at which the physisorbed and hydrogen-bonded carbonyl stretches begin to disappear and the temperatures at which the two acetone desorption states appear in the TPD spectra.

Difference infrared spectra recorded after adsorption of acetone on crystalline ice are similar to those recorded after adsorption on amorphous ice with one crucial exception: the exposure required to saturate the hydrogen-bonded state on crystalline ice is roughly one-eighth of that required to saturate the state on amorphous ice.²⁹ On both surfaces, acetone adsorption results in quantitative titration of the dangling OH group, since the free OH stretch is absent in normal FTIRAS spectra recorded after adsorption of 1 ML equiv of acetone.

The infrared spectra of other adsorbed hydrogen bond acceptors on amorphous ice can also be interpreted as evidence formation of complexes of the type $\text{--OH}\cdots\text{X}$. The hydrogen-bonded and physisorbed states of adsorbed acetonitrile can be spectroscopically distinguished via the $\text{C}\equiv\text{N}$ stretch.³¹ The $\text{C}\equiv\text{N}$ stretching frequency of adsorbed acetone increases upon hydrogen bond formation, from 2255 to 2266 cm^{-1} . The direction and magnitude of the shift are in line with what is expected for the conversion from physisorbed to hydrogen-bonded aceto-

nitrile. In fact, the $\text{C}\equiv\text{N}$ stretching frequencies and mode assignments are similar to those given by Eisenthal and co-workers in sum frequency generation (SFG) studies of nitriles adsorbed at the air-liquid water interface.³²

In summary, the amorphous surface is a much better net hydrogen bond donor than the crystalline surface. Given the very different intensities of the dangling OH stretching vibration on the two surfaces, it is difficult to avoid the conclusion that the enhanced hydrogen-bonding ability of the amorphous surface originates in a greater coverage of dangling OH groups. In this context, it is interesting that Shen's SFG-based estimate of 0.25 ML as the dangling OH coverage on the liquid water surface³³ is equal, within 20%, to the minimum acetone coverage required to quantitatively titrate the dangling OH group on amorphous ice. Nevertheless, it must be pointed out that the evidence linking surface hydrogen-bonding ability with dangling OH coverage is at present circumstantial. A deeper understanding of the connection between surface chemistry and structure awaits more experimental results.

Nature of a PSC Particle Surface. Taking into account the data presented above, the question naturally arises whether PSC ice particles are crystalline or amorphous. Stratospheric particles have not been collected and analyzed in the laboratory, but there is ample reason to believe that the bulk phase is crystalline. The nature of the surface, however, is far less clear. At stratospheric temperatures, the equilibrium evaporation and recondensation rates of water at the surface of an ice particle are enormous: $\sim 50\text{ ML}\cdot\text{s}^{-1}$ at 188 K, the low-temperature limit of the Antarctic stratosphere, and nearly $2000\text{ ML}\cdot\text{s}^{-1}$ at 210 K.³⁴ There are numerous potentially important and unexplored consequences of such a rapidly changing surface. One is structural. Most models for crystal growth invoke at least three elementary steps: (i) adsorption from the gas phase to a mobile, disordered phase, (ii) migration of disordered molecules (or atoms) across the surface, and finally (iii) trapping at crystalline sites.³⁵ Depending on the time scales of steps ii and iii, which for ice are unknown, it is possible that few surface water molecules actually "crystallize" under short residence time conditions. The surface of a PSC particle may therefore be disordered and perhaps structurally similar to that of amorphous ice. Interestingly, the rate of at least one stratospherically important process, namely HCl adsorption, is structure-sensitive: The HCl adsorption probability on amorphous ice surface at 120 K is approximately twice that on a crystalline surface at the same temperature.³⁶

Another potentially important consequence of the dynamic surface is that it could provide a mechanism for nondiffusive transport of material from surface to bulk. If the residence time of an adsorbed molecule is long compared to the time required for the condensation of a water monolayer, it may be possible for adsorbed material to be "buried" beneath the ice surface. Obviously, material could not penetrate deeply into the bulk via this mechanism, because water evaporation would bring previously buried material back to the surface. Rather,

burial would lead to the formation of a boundary layer of reactants in a matrix. Heterogeneous chemistry could then occur in this region. This model differs in some respects from the quasi-liquid layer proposed by Molina et al.,¹⁹ but both models are in agreement in their assertion that much PSC-mediated chemistry takes place in a phase of bulklike properties.

At present, there are no direct experimental measurements of a boundary layer formed by the burial mechanism described above. However, it is known that the desorption rates of many adsorbed compounds (acetone, HCl, CCl₄) from ice are greatly suppressed when they are covered by a *single* water monolayer.^{13,15,29} Thus, the potential importance of burial in stabilizing reactants with respect to desorption is demonstrated. Whether burial actually occurs on a PSC particle is undoubtedly a sensitive function of the molecule in question and the temperature of the system. We determined the desorption rate parameters for one atmospherically abundant substance, OCIO, from ice.^{37,38} The parameters were used to estimate the OCIO residence time at 189 K. The value, 0.001 s, is too low for significant burial to occur, since approximately 0.01 s are required for 1 ML of water to condense at the same temperature. Other substances may have much longer adsorbed lifetimes on ice, however, and for these substances burial may be important. For instance, recent molecular dynamics simulations carried out by Gertner and Hynes suggested that burial is an elementary reaction step in the ionization of HCl on stratospheric ice.³⁹

Sulfuric Acid. Stratospheric cloud particles that consist of sulfuric acid and water mixtures are exceedingly common. The study of ultrathin sulfuric acid films presents an experimental challenge: How can monolayer quantities of this corrosive and nonvolatile material be introduced into a controlled and reproducible fashion? One solution is to synthesize H₂SO₄ in situ, by codepositing H₂O and SO₃ at 100 K and then annealing at a temperature between 180 and 260 K.^{16,40} By variation of the annealing temperature and the initial SO₃/H₂O ratio, the composition of the resulting H₂SO₄ + H₂O mixtures can be varied, from approximately 10 mol % H₂SO₄ in water to pure, crystalline sulfuric acid. Infrared spectra of the mixtures (Figure 4) are highly suggestive of homogeneous, amorphous solids. The composition assignments, which are based upon the line shapes of the OH stretching regions, have been independently confirmed with X-ray photoelectron spectroscopy.¹⁶

The surface chemical properties of solid sulfuric acid and ice are qualitatively different in surprising ways. For example, HCl is readily adsorbed (probably molecularly) and absorbed (ionically) by ice at 120 K,^{13,36} whereas on pure sulfuric acid no measurable uptake occurs, even at adsorption temperatures as low as 100 K (Figure 5).⁴¹ The situation on a water-rich film is very different, and exposure of such a film to HCl results in significant adsorption and absorption. The lack of HCl incorporation into pure H₂SO₄ is perhaps not unexpected in light of its low solubility in concentrated sulfuric acid.⁴² However,

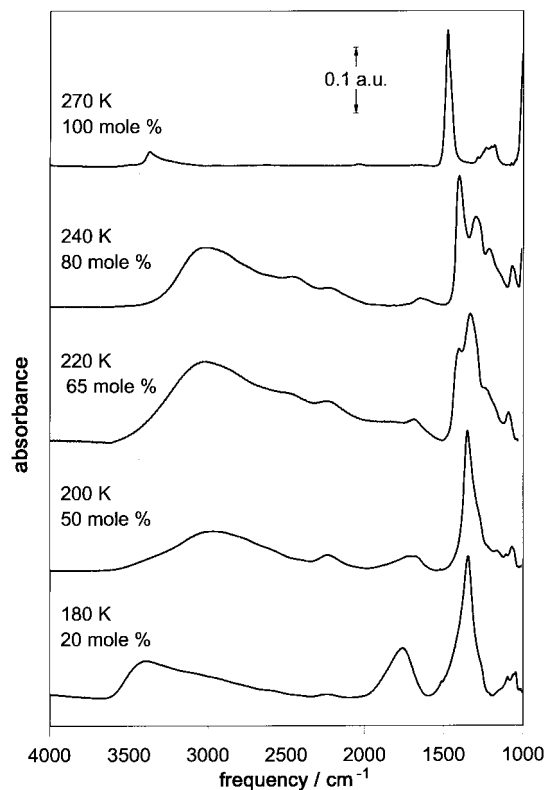


FIGURE 4. Infrared spectra of solid H₂SO₄ + H₂O mixtures deposited on Pt(111). The concentrations refer to the mole percentage of H₂SO₄. All films were roughly 50 ML thick. Spectra were obtained with FTIRAS.

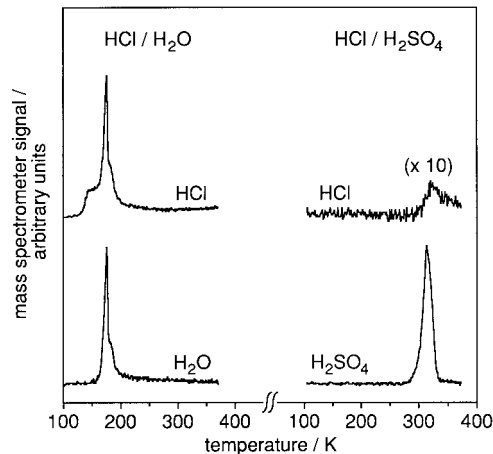


FIGURE 5. Comparison of HCl desorption from 50 ML thick films of amorphous ice and pure, crystalline sulfuric acid. The HCl desorption traces are shown in the top part of the figure, and the H₂O and H₂SO₄ sublimation features in the bottom. The small HCl signal in the H₂SO₄ desorption data is an artifact, derived from the displacement of HCl from the reactor walls during evaporation of the H₂SO₄ film. The TPD spectra were collected at heating rates between 3.5 and 5 K·s⁻¹.

chemisorption wells as shallow as 25 kJ·mol⁻¹ may be accessed at adsorption temperatures of 100 K. Something about the pure H₂SO₄ surface must therefore make it inert to HCl adsorption. Interestingly, there are no spectral features attributable to the free OH or OD groups in the infrared spectra of ultrathin H₂SO₄ and D₂SO₄ films. Perhaps HCl adsorption at these temperatures requires

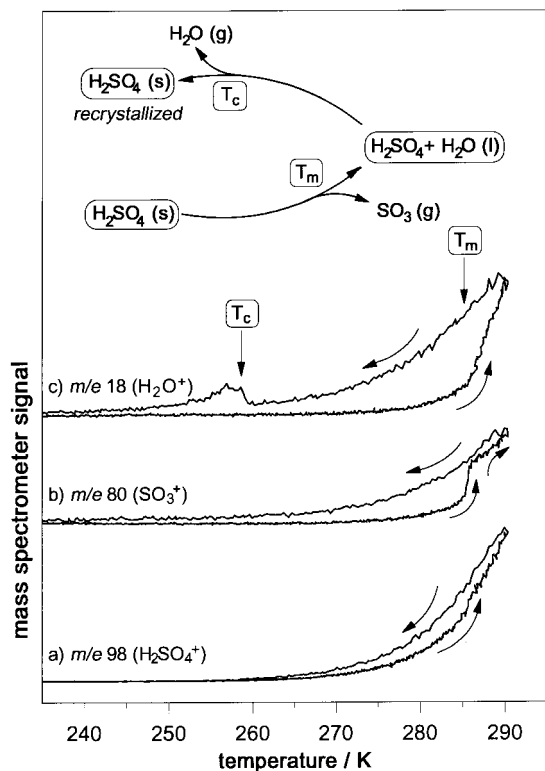


FIGURE 6. Gas-phase composition, monitored mass spectrometrically, during the heating and cooling of an ultrathin sulfuric acid film deposited on Pt(111).

the presence of a free OH or OD group for hydrogen bonding. The apparent absence of free OH groups is consistent with a suggestion that pure sulfuric acid crystallizes as long chains held together by strong, intermolecular hydrogen bonds.⁴³ Because H_2SO_4 has twice as many hydrogen bond acceptors (the S=O group) as donors (the OH group), termination of the bulk lattice need not lead to the formation of free OH.

Although pure H_2SO_4 is inert toward HCl adsorption, it is exceptionally active for certain organic transformations, especially when the reactant in question is able to undergo dehydration.^{16,44} Ethanol is dehydrated to ethene, and 2-propanol is dehydrated to propene. Under certain conditions, acetone undergoes a remarkable series of condensation and dehydration reactions, ultimately to form trimethylbenzene. It is at this point unclear whether the reactions are true surface-mediated processes or whether they occur in the sulfuric acid bulk.

As a result of sulfuric acid's low vapor pressure, ultrathin films of pure H_2SO_4 can be made to melt before they evaporate.¹⁷ Melting is incongruent, i.e., the solid melts to form an azeotrope of roughly 98 mol % H_2SO_4 and 2 mol % H_2O . The liquid films recrystallize but only after passing through a metastable supercooled region. Melting and recrystallization have been monitored with infrared spectroscopy and mass spectrometry. Figure 6 shows some results of the latter type of experiment, in which a crystalline sulfuric acid film was heated above its melting point ($T_m = 285$ K) and cooled below its recrystallization temperature ($T_c = 255$ K). During heating ($0.5 \text{ K}\cdot\text{s}^{-1}$) and cooling ($2 \text{ K}\cdot\text{s}^{-1}$), the mass spectrometer

was tuned to m/e 98 (H_2SO_4^+), m/e 80 (SO_3^+), and m/e 18 (H_2O^+). Note that there is a burst in the SO_3^+ signal at 285 K during heating but not during cooling. An analogous increase is observed in the water signal, but it occurs at 255 K and only during the cooling part of the cycle. The pressure bursts occur at the temperatures at which infrared spectra show that a film melts or recrystallizes, and they are associated with the fact that the solid and liquid compositions differ. When the pure solid melts, some H_2SO_4 decomposes to H_2O and SO_3 ; H_2O remains in the film as part of the $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ azeotrope, and SO_3 is expelled into the gas phase. When the liquid crystallizes, H_2O is expelled to form pure H_2SO_4 .

The stability of the liquid $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ films with respect to evaporation is remarkable. At 260 K, over 90 min is required for a 100 ML thick film to evaporate. Under ultrahigh vacuum, the composition of the liquid is approximately 98 mol % H_2SO_4 . However, by introducing water into the gas phase, we are able to prepare considerably more dilute films, as low as 20 mol % H_2SO_4 . The ability to prepare stable ultrathin liquid films opens innumerable opportunities for studying chemistry at the gas-liquid interface, especially since the films are amenable to infrared spectroscopic studies. Preliminary work in this laboratory has concerned the proton exchange reaction between $\text{HCl}(\text{g})$ and $\text{D}_2\text{SO}_4(\text{l})$, as a well as a comparison of the reactivities of the solid and liquid surfaces.⁴⁴

Conclusions

The central finding of these studies is that the surface chemical properties of ice (certainly) and sulfuric acid (probably) are strongly influenced by structure. The statement may seem obvious to the casual reader, but it was by no means obvious at the beginning of our work on the problem. Its implications for our understanding of the chemical properties of "dynamic," high vapor pressure surfaces, like those of PSC particles, are possibly significant. Nonlinear optical probes, e.g. SFG, have the potential of providing more insight into such critical structural issues as surface functionality, but the experiments are challenging to implement and the data are often difficult to interpret.^{30,32,33,45} Molecular beam studies of gas-surface dynamics may shed light on the dynamical aspects of ice- and sulfuric acid-mediated reactions, but they are limited to fairly low vapor pressure systems ($\sim 10^{-6}$ Torr or less).^{46,47} In the end, a deep mechanistic understanding of PSC chemistry is most likely to require many approaches, especially those seeking to measure^{19,46,48,49} and model^{46,50} overall heterogeneous reaction kinetics.

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