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Interactions of Atmospheric Trace Gases with Ice Surfaces: Adsorption and Reaction

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1. Introduction

Considerable interest in the interactions of trace gases with ice surfaces has only developed of late, in large part prompted by the discovery of the Antarctic Ozone Hole and the recognition that atmospheric ice particles can play a dominant role in determining the chemical composition of the atmosphere. The substantial loss of ozone in the Antarctic springtime stratosphere is a phenomenon where gas-phase, “reservoir” species of chlorine are converted over to more photochemically active forms by the catalytic action of polar stratospheric cloud (PSC) particles.[1] Prior to the detection of the Ozone Hole, it was thought that PSCs could be composed of ice.[2] However, it was soon realized that, more commonly, they are either supercooled aqueous solutions of nitric and sulfuric acid, or solid nitric acid hydrates (Type I PSCs).[1] Ice is only stable when the temperatures are below the frost point of ice, i.e., between 185 and 190 K for the Antarctic stratosphere, and in these conditions Type II PSCs form.

Jon Abbatt obtained his B.Sc. in chemistry from the University of Toronto in 1984. He joined the atmospheric chemistry field during his Ph.D. (Harvard University, 1984–1990, Research Supervisor, J. G. Anderson), for which he studied the kinetics and mechanisms of gas-phase radical–molecule reactions. His current interest in atmospheric heterogeneous chemistry started during his postdoctoral appointment (MIT, 1990–1992, Research Supervisor, M. J. Molina), where he investigated polar stratospheric cloud chemistry. Subsequently, he has focused largely on tropospheric chemistry as a faculty member at the University of Chicago (Assistant and Associate Professor, Department of the Geophysical Sciences, 1992–2000) and the University of Toronto (Professor, Department of Chemistry, 2000 to present). His current research interests include the rates of gas–surface chemistry, mechanisms for the formation of both liquid water and ice clouds, and the partitioning of species between the gas phase and atmospheric particulate matter.

Although ice forms only in the winter/spring polar stratosphere, it is a widespread component of the troposphere. In particular, at the cold temperatures of the upper troposphere and tropopause region, cirrus ice clouds are widely prevalent, roughly 50% of the time in equatorial regimes and 25% of the time at mid-latitudes.[3] Interaction of gas-phase species with these clouds has the potential both to promote reactive heterogeneous chemistry and to scavenge semivolatile gas-phase species.[4,5] In the lower troposphere, both precipitating and nonprecipitating glaciated clouds are also common. At the Earth's surface, there is now evidence that snow and sea ice are involved in the chemistry of the boundary layer, acting as sources of reactive bromine, small oxygenated organics, and NO_x,[6] and as sinks for organic pollutants.[7] Many of the first studies of gas–ice interactions were motivated by the need to understand the rate of deposition of species such as SO_2 to snow.[8,9]

From a molecular-level perspective, the interactions of gases with ice surfaces represent a largely

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unexplored discipline, quite unlike the interactions of gases with refractory surfaces such as dry salts and metals. The chemistry is interesting for a number of reasons. First, over atmospheric time scales the ice surface is highly dynamic, with many monolayers of water molecules evaporating and condensing under equilibrium conditions. Second, as has been pointed out previously,[10] the heat of adsorption of gas-phase species can frequently be comparable to, or larger than, the heat of condensation of water molecules to solid ice. This implies that substantial surface reconstruction/modification may arise via the adsorption interaction. And third, under all atmospheric conditions the surface exhibits a degree of disorder which is significantly higher than that of the bulk crystal. Together, these factors make the gas−surface interface region and the nature of the adsorption interactions not as easily defined as they are with a metal or dry salt. To complicate matters from an experimental perspective, the high vapor pressure of ice under tropospheric and stratospheric conditions precludes the use of some traditional ultrahigh-vacuum analytical techniques that have been successfully applied to the study of gas−surface interactions with refractory solids.

The physical chemistry of the interactions of atmospheric trace gases with ice surfaces will be reviewed in this paper. The focus is on experimental, laboratory-based studies that have increased our understanding of atmospheric chemistry, either through elucidation of the gas−surface interaction mechanism or through measurement of quantitative information that can be incorporated into atmospheric models. Many interesting studies at temperatures significantly lower than those prevalent in the troposphere and stratosphere will not be discussed to the same degree as those performed at warmer temperatures. The paper starts with a discussion of the ice surface and then separately discusses nonreactive and reactive interactions.

2. The Surface of Ice

When the temperature is higher than about 180 K, as it always is in the troposphere and stratosphere, the hexagonal form of ice (I_h) is stable.[11] In this crystalline form, the oxygen atoms are arranged in a cyclohexane-type structure so that each is tetrahedrally coordinated on average with two O−H bonds and two H bonds. As shown in Figure 1, a side view of the crystal emphasizes the hexagonal structure and illustrates that the water molecules arrange themselves in bilayers. The open structure of the ice lattice results in a relatively low density solid. This is the reason that ice floats on water. When ice is generated from the vapor phase at lower temperatures, different crystal structures, such as cubic ice (I_c), or amorphous forms can arise. The degree of crystallinity depends on both the temperature and the deposition rate.

The structure of the ice surface is not nearly as well defined as that of the bulk. From the earliest work on this topic, done by Michael Faraday in the middle part of the 19th century, there has been a suggestion that a liquid-like layer resides on the surface of crystalline ice that grows progressively thicker as the temperature approaches the melting point. Faraday showed that if two ice cubes were allowed to contact each other when immersed in water at the freezing point, they would fuse together with ice forming at the junction.[12] The strength of attraction increased as the contact time lengthened.

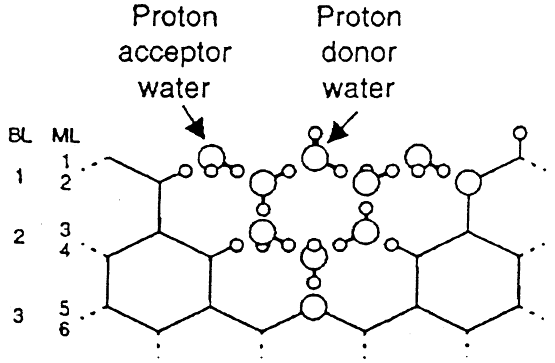

Figure 1. Side view of the ice lattice. BL refers to bilayer and ML to monolayer. Reprinted with permission from ref 58. Copyright 1996 American Association for the Advancement of Science (http://www.aaas.org).

Concern was raised that the pressure due to contact between the ice bodies in Faraday's experiments gave rise to melting, but the effect was confirmed in later studies conducted with very little force exerted on contact.[13] The adhesion phenomenon, referred to as sintering, is thought to arise from the thermodynamically unfavored region that exists where the two solid bodies meet. In particular, surface melting occurs when the free energy lowered having both a solid−liquid and a liquid−vapor interface instead of a single solid−vapor interface. The high surface mobility of water molecules in the liquid-like layer provides the mechanism for the flow of water molecules and the formation of a less stressed junction between the two ice bodies. For a more detailed discussion of early work on the liquid-like layer on the surface of ice, the reader is referred elsewhere.[11,14]

More recently, a variety of experimental techniques, including neutron scattering,[15] ellipsometry,[16] optical reflection,[17] surface-sensitive X-ray diffraction,[18] LEED experiments,[19] and nonlinear vibrational spectroscopy,[20] have provided direct evidence that there is indeed disordering of water molecules on the ice surface, in a layer that grows increasingly thick as the temperature approaches the melting point. To highlight two of these studies, neutron scattering experiments have been performed on ultrathin films of water adsorbed onto MgO microcrystalline surfaces.[15] These studies show clear evidence for mobility and disorder in the films. From the data, a translational diffusion coefficient of 1.5×10^{-5} cm^2 s^{-1} at 265 K has been determined, very similar to that for liquid water molecules at 273 K.[21] As the temperature was increased from 265 to 270 K, the disordered layer increased in thickness, and there was an increase in the rotational mobility of the surficial water molecules. A second example is the sum-frequency vibrational spectroscopy of ice in the

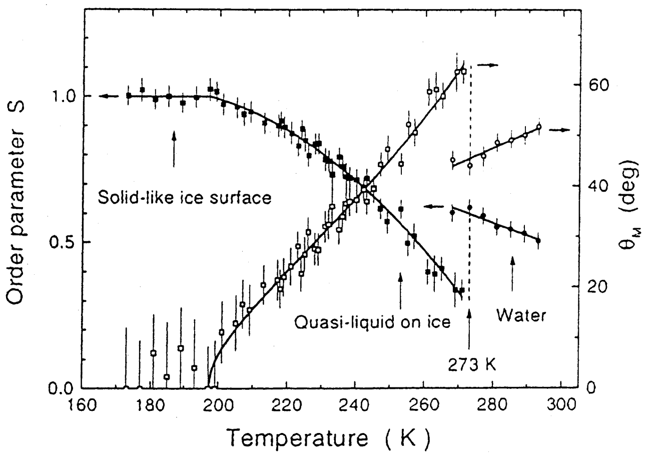

Figure 2. Properties of the free OH bonds on ice (squares) and water (circles) surfaces, as measured by sum-frequency vibrational spectroscopy. The orientational order parameter S and the maximum tilt angle θ_M are measures of orientational order on the surface: $\theta_M \rightarrow 0$ and $S \rightarrow 1$ for perfect ordering (see original source for details). Reprinted with permission from ref 20. Copyright 2001 American Physical Society.

OH stretch region of the spectrum.[20] It was observed that the shape of the mode arising from free OH bonds at the surface (vide infra) was strongly temperature dependent. In particular, an orientational order parameter and the maximum tilt angle of this bond were determined from the spectra and are shown in Figure 2. Below 200 K, there is no temperature dependence to these quantities, but as the temperature increased above 200 K both parameters changed in size. These changes are consistent with increasing disorder on the ice surface due to liquid-like layer formation.

Molecular dynamics simulations using both classical and first-principles approaches support the presence of substantial disordering of water molecules on the surface of ice.[15,22−25] For a detailed discussion the reader is referred to a recent review.[26] Briefly, these calculations show the onset of disorder at the surface occurring around 200 K. At higher temperatures, the disorder is enhanced so that at 250 K, a disordered interfacial region had become three to four bilayers thick. Snapshots in time from a set of dynamical simulations are shown in Figure 3, where the three frames demonstrate the increasing degree of disorder that arises as the temperature increases.[26] At 190 K, the hexagonal structure extends to the outermost water layer, at 235 K the outmost bilayer is disordered, and at the highest temperature, 270 K, the disorder extends much deeper into the film. The simulation imposes rigidity upon the lowermost two layers.

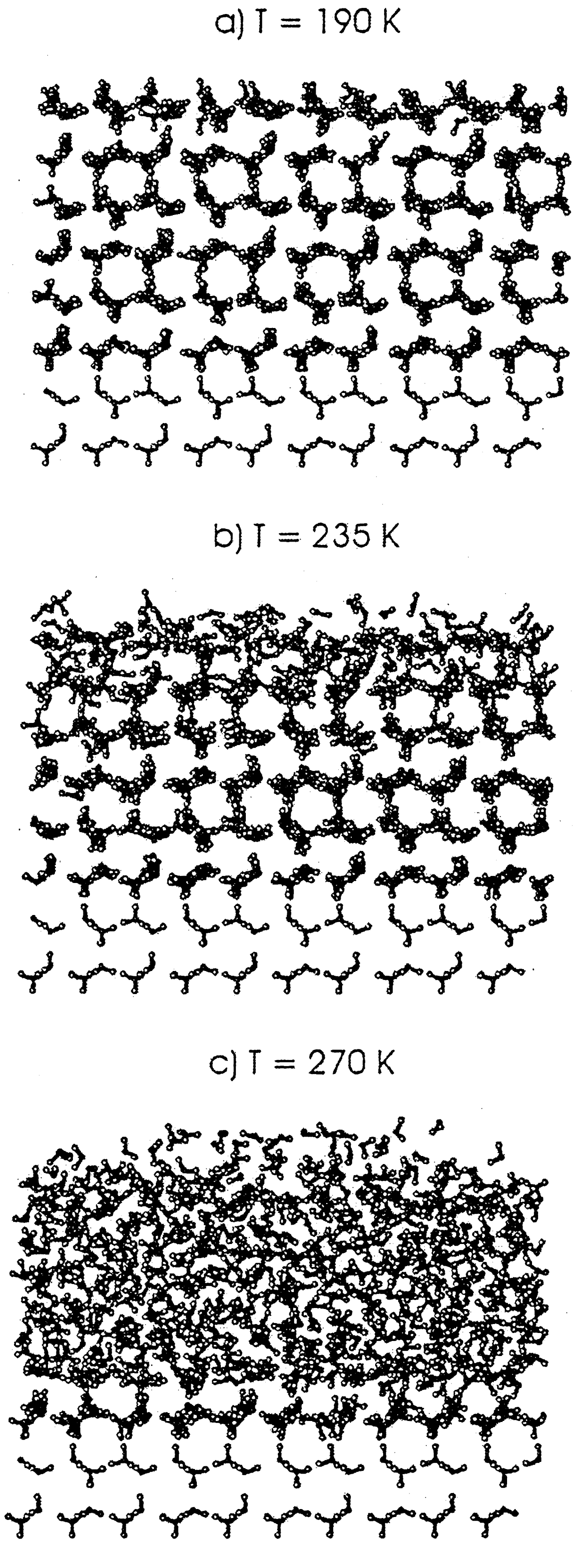

Figure 3. Side-view snapshots of thin hexagonal ice film from classical dynamical simulations at three temperatures. The simulations fix rigid bilayers at the bottom of the film. Note that the hexagonal structure at the surface at 190 K is lost at 235 K and that the disorder extends through the film at 270 K, except for the rigid support layers. Reprinted with permission from ref 26. Copyright 2001 Elsevier.

It is not surprising that ice has a different structure at its surface than in the bulk. For most solids, the asymmetric electronic environment for interfacial molecules compared to the environment felt in the bulk gives a driving force for surface structure modification.[27] For example, even for a refractory solid such as NaCl, where the ions are held rigidly in the ionic lattice, a small amount of distortion at the surface is thought to occur to reduce the high chemical potential of surficial ions. In comparison, ice is a molecular solid with fairly weak intermolecular forces: the sublimation enthalpy is 11.8 kcal/mol, or roughly the equivalent of two standard H bonds.[28] As a result, water molecules are significantly more mobile, and this dynamic nature facilitates the surface melting that results in the formation of the liquid-like surface.

Ice has a high vapor pressure: 2.5×10^{-4} Torr at 190 K, 7×10^{-2} Torr at 230 K, and 3.5 Torr at 270 K. Using a precise optical interference technique, both evaporation and condensation rates for ice have been measured.[28] Under atmospheric conditions at equilibrium, these growth/evaporation rates are extremely rapid, with 10^2-10^4 monolayers of ice evaporating and recondensing per second between temperatures of 180 and 240 K, respectively. At such a fast rate, it is not clear whether a newly deposited water molecule on the surface has the time to crystallize before evaporating again.[10] In this regard, the dynamic nature of the ice surface with respect to mass exchange with the gas phase may be coupled to the degree of surface disorder that exists on ice.

Of importance to interactions with gas-phase molecules is the polarity and the nature of the chemical bonds on the ice surface. If an ice crystal were cleaved and no surface reconstruction occurred, there would be a high degree of “dangling” OH bonds, as portrayed in Figure 1. This surface would have a high polarity. However, classical Brunauer−Emmett−Teller (BET) adsorption experiments on the affinity of N_2 for ice surfaces at 77 K imply the surface of ice does not behave in a highly polar manner, particularly if it has been annealed at 203 K.[29] A more direct measure of the polarity of the surface comes from direct spectroscopic observation of these free OH groups on the surface of ice. In particular, these surface OH groups offer spectroscopically distinct signals from bulk OH stretch modes, largely because they are not participating in H-bonding. As described above, these dangling OH groups have been studied by nonlinear optical spectroscopy.[20] They have also been observed with Fourier transform infrared reflection−absorption spectroscopy (FTIRAS) of ultrathin ice films, both amorphous and crystalline in nature.[10,30] The prevalence of these modes in amorphous ice at low temperatures, around 130 K, is close to a factor of 6 times higher than in crystalline ice which has been annealed by raising the temperature to 173 K and then lowering it again 130. This is evidence for surface reconstruction leading to a less polar surface on crystalline solids under these conditions.

These observations suggest that the surface of crystalline ice may be only moderately polar, particularly at higher temperatures. However, is this the correct way to describe the environment that an adsorbing molecule experiences? At low temperatures, the adsorbing species may primarily experience bonding interactions with the surface OH groups, but under atmospheric conditions, where the mobile, disordered layer becomes a few monolayers thick, the adsorbing species may experience considerably more hydration by molecules in the liquid-like layer. For example, it was observed in classical BET adsorption experiments that nonpolar organics interact with warm ice as they do with liquid water.[31] This issue will be addressed again in section 3.

The specific surface area of different ice samples, i.e., the surface area that can be sampled by adsorbing gaseous species, is of importance to measurement of nonreactive and reactive uptake in both the laboratory and the field.[32] When ice is deposited from the vapor at low temperatures, highly structured dendritic ice can be formed.[11,33,34] This ice has a specific surface area orders of magnitude larger than the macroscopic, geometric surface area.

To what degree does structure at the smallest distance scales, i.e., on the order of nanometers, affect the specific surface? Given that the Kelvin effect is felt strongly on such small scales and that the water molecules on ice surfaces are somewhat mobile, some level of annealing of such structures will occur under atmospheric conditions. Indeed, it has been shown that the enhancement of the specific surface area over the geometric area is thought to come from structures that can be viewed by optical microscopy and not from smaller nanoscale features. In particular, the specific surface area of highly dendritic snow has been measured by BET adsorption experiments with CH_4 and by scanning electron microscopy, techniques which both measure surface area at the nanoscale, and by optical microscopy, which measures surface area at the micron scale or so.[35] To within the precision of the three techniques, the specific surface areas are equal, implying the absence of nanoscale structures. A similar conclusion was also reached on ice films formed by vapor deposition that had been annealed at temperatures above 200 K.[36]

This model suggests that nondendritic ice, such as that formed by freezing liquid water, will have a specific surface area similar to the geometric surface area of the sample. Laboratory evidence to this effect is presented in more detail in section 3 but is mentioned here because it also confirms the absence of very fine scale structure. Briefly, it has been shown for this type of ice that a variety of molecules − small *n*-alcohols, HCl, HNO_3, acetic acid, and acetone − all have saturated surface coverages of $1 \times 10^{14}-3 \times 10^{14}$ molecules/cm^2, where the uptakes have been referenced to the geometric area of the ice.[37−42] For small molecules which have molecular surface areas of ∼20 Å^2/molecule, a full monolayer coverage on a smooth surface is 5×10^{14} molecules/cm^2. We can infer from this that ice films formed by freezing water are extremely smooth at the molecular level.

3. Adsorption of Atmospheric Trace Gases to Ice Surfaces

From an atmospheric perspective, it is important to know both the degree to which a gas partitions to the surface and the mechanism by which the partitioning occurs. In this way, estimates can be made of the extent of gas-to-ice scavenging and of the chemical form the molecule converts to upon adsorption. Determining the full adsorption isotherm, i.e., the surface coverage as a function of both temperature and partial pressure, is central to addressing both issues. An appropriate isotherm can be incorporated into atmospheric models, permits laboratory measurements to be related to atmospheric conditions, and gives information on the uptake mechanism. Additional mechanistic understanding comes from theoretical calculations and direct spectroscopic experiments on adsorbed species.

This section focuses primarily on the uptake of three classes of molecules that exhibit atmospherically significant partitioning: strong acids, weak acids, and hydrogen-bonding organics. Central themes include the following: What properties of molecules make adsorption likely? To what degree does the ice surface facilitate adsorption? Can empirically based models be developed that predict the degree of adsorption?

3.1. Adsorption of Strong Acids: HCl and HNO_3

Soon after the discovery of the Antarctic Ozone Hole, studies of the interaction of relatively high partial pressures of gas-phase HCl with ice surfaces showed substantial, irreversible gas-to-solid uptake.[43,44] Indeed, the uptake corresponded to the formation of an ice solution with up to a few weight percent HCl. This finding was incongruent with earlier studies, performed by freezing HCl solutions, that had shown HCl to have considerably lower solubility in ice.[45] The findings were also at odds with later experiments that showed that monolayer-like surface coverages prevail when the HCl partial pressure is considerably reduced and closer to atmospheric values.[39,46−50]

It is now clear that the large uptake behavior arises when the HCl partial pressures thermodynamically force the system to the HCl aqueous solution regime (see Figure 4).[47] That is, the HCl uptake causes the ice to melt, and a thermodynamically stable HCl solution forms on the surface. Note that this solution layer, being determined by the degree of HCl exposure, can be quite thick; it should not be confused with the thin liquid-like layer that exists on the surface of pure ice. When HCl partial pressures are employed that are lower than those corresponding to the coexistence of HCl aqueous solution and ice, then uptakes are orders of magnitude smaller.[47,48,51]

The finding that dramatically different observed behavior can result when different condensed phases are thermodynamically constrained by the experimental conditions is crucial to the design and interpretation of experiments attempting to study gas-to-condensed phase partitioning experiments under atmospheric conditions. In addition to temperature, it is imperative that atmospherically relevant partial pressures and the appropriate relative humidity be employed.

The surface coverage of HCl to ice films under low-partial-pressure conditions has been reported to be between roughly 10^{14} and 10^{15} molecules/cm^2, where the reference surface area is the geometric area of the ice film and the temperature is between 180 and 230 K.[39,47−51] These experiments have been conducted in flow tubes and Knudsen cells, where the ice films were formed either by deposition from the gas phase or by rapid freezing of liquid water. The uptake is determined by integrating the time-dependent loss of gas-phase HCl upon its exposure to the surface on time scales of up to a few minutes. The experiments are designed to have stable ice films not experiencing net evaporation or growth. In this manner, the measured surface coverages represent quasi-equilibrium partitioning to the (highly dynamic) ice surface but are not sensitive to diffusion of the adsorbate very deep into the bulk, a process which occurs over considerably longer time scales. Similarly, experiments performed with a laser-induced thermal desorption technique have measured surface coverages of about one monolayer on the smoothest films prepared.[52] Experiments with ice aerosol, consisting of single crystals, also show substantial uptake of greater than 2×10^{13} molecules/cm^2.[50]

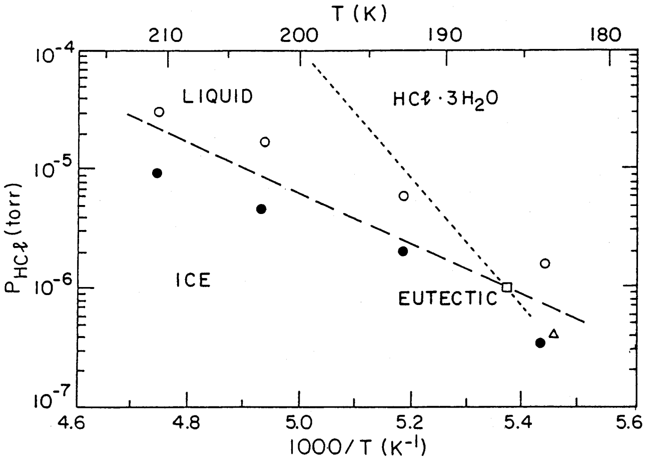

Figure 4. Results of uptake experiments for exposure of gaseous HCl to ice films. Open circles represent significant uptakes yielding films with greater than 0.5 wt % HCl, whereas closed circles exhibited significantly smaller uptake, in the monolayer regime. Dashed curves represent solution−solid coexistence curves. Reprinted with permission from ref 47. Copyright 1992 American Geophysical Union.

In general, the reported uptakes are largest on the thickest, dendritic films formed by vapor deposition and smallest on films formed by freezing water. This is consistent with there being considerable surface roughness in thick vapor-deposited films.[34] There have been no experiments performed on films that have had their surface areas directly determined by inert gas BET adsorption experiments at the same temperature. However, at temperatures between 205 and 230 K, the surfaces have been shown[39] to be saturated with HCl at values of $(2 \pm 0.7) \times 10^{14}$ molecules/cm^2 on the same frozen liquid-water surfaces for which saturated surface coverages of $2 \times 10^{14}-3 \times 10^{14}$ molecules/cm^2 of geometric surface area have been observed for a suite of polar organics and HNO_3 (see below). Given that a monolayer coverage represents about 5×10^{14} molecules/cm^2 and that two very different classes of molecules reach saturation at similar surface coverages, it seems likely that this HCl uptake corresponds to a large fraction of a monolayer. Similar uptake measurements of between 10^{14} and 10^{15} molecules/cm^2 at low partial pressures provide evidence that micron-thick films formed by vapor deposition can also be formed without substantial roughness.[48,53]

Because of the small amount of HCl on the surface in the “monolayer-uptake” regime, direct observation of the form of adsorbed HCl by surface spectroscopy is experimentally challenging and has not yet been convincingly demonstrated. Infrared experiments conducted under higher partial pressures and/or lower temperatures clearly illustrate HCl dissociation and hydrate formation.[51,54] That being said, there are a number of reasons to believe that a dissociative mechanism also prevails in the low-partial-pressure, monolayer-uptake regime at temperatures above 190 K or so.[55] This is a reasonable suggestion, given the liquid-like nature of the ice surface and that HCl is such a strong acid. Experimental evidence for this comes indirectly from the fact that the amounts of HCl that adsorb are far larger than those predicted by interactions proceeding with a single H bond to the surface.[56] Also, the dramatic enhancement over gas-phase rates that arises in the kinetics of the heterogeneous reactions of HCl with $ClONO_2$ and HOCl (see section 4.2) is consistent with an ionic mechanism involving an adsorbed chloride moiety.

Theoretical support for dissociation comes from calculations that have shown strong interaction of HCl with H_2O molecules.[57−61] Ab initio results imply that the barrier to dissociation is largely removed when HCl clusters with four water molecules. Molecular dynamics calculations have shown that it is energetically favorable for the formation of a contact-ion pair, i.e., $H_3O^+{\cdot}Cl^-$, on an ice surface if a small degree of water molecule mobility is permitted.[58] More specifically, the calculations "bury" an HCl molecule in the uppermost bilayer of ice by removing a H_2O molecule and replacing it with HCl. If that mobility/burial is not permitted and HCl is only able to interact with the ice surface via a single H bond to the ice surface, then the degree of partitioning to the surface is calculated to be orders of magnitude smaller than that observed.[56] Recent molecular dynamics work at polar stratospheric temperatures also shows that dissociation is favorable, particularly in the environment of dangling OH bonds.[61] Nevertheless, it is clear that at significantly lower temperatures HCl can adsorb in a molecular state,[62,63] and so the precise fraction of molecular versus ionic adsorption as a function of temperature still remains to be well determined.

The observed uptake behavior of HNO_3 is similar to that of HCl. Under low-temperature conditions and high partial pressures, the ice surface is converted to HNO_3 supercooled solutions.[64,65] Indeed, under sufficiently high nitric acid supersaturation, nitric acid hydrates can also be generated. It is at higher temperatures and/or lower nitric acid partial pressures that ice remains thermodynamically stable.[66] Under these conditions, monolayer surface coverages similar to those for HCl have been measured.[37,38,40,65,67] Two sets of flow-tube experiments on ice films formed by freezing liquid water have yielded similar results, with there being little dependence to the uptake over the partial pressure regime from 10^{-7} to 10^{-5} Torr and only a weak, negative temperature dependence.[37,40] As with HCl, it is observed that a sizable fraction of the HNO_3 that adsorbs to the ice surface does not desorb on the time scale of the experiment. The vapor pressure of the HNO_3 that does not readily desorb is particularly low, e.g., $<3 \times 10^{-8}$ Torr at 218 K.[37] In these experiments, only the initial, short-term uptake has been quantified and a longer term, largely irreversible uptake has not been, although it has been shown to have a time dependence typical of a diffusive process of a diffusive process, presumably into the disordered surficial layers of ice.[37] Recent results from a Knudsen cell experiment show considerably more dependence of the surface coverage on temperature than the flow-tube measurements, with larger uptake at lower temperatures. The reason for the discrepancy between the flow-tube and the latest Knudsen cell experiments is not fully clear but may be that the latter focused more on the long-term, diffusive-like uptake.[67] Finally, saturated HNO_3 surface coverages of 1×10^{14} molecules/cm^2 have been measured at 230 K on ice single crystals a few tenths of a micron in radius that were formed by freezing of supercooled water droplets.[38] This saturated coverage is the same as that on frozen water films to within a factor of 2, providing additional support that the film measurements are not compromised by high surface porosity or by uptake to grain boundaries.

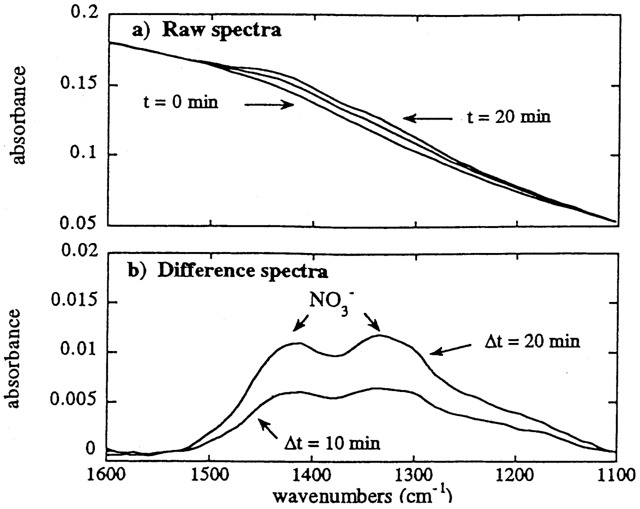

Figure 5. Infrared spectra of 211 K ice films exposed to gaseous HNO_3 in the monolayer-uptake regime where ice is thermodynamically stable. The upper frame shows the raw spectra at different times, and the lower frame the difference spectra. Features due to condensed-phase nitrate are present. Reprinted with permission from ref 65. Copyright 1997 American Geophysical Union.

Using low-partial-pressure conditions where ice is thermodynamically stable, the mechanism of nitric acid uptake onto ice has been directly studied using grazing-incidence, infrared reflection−absorption spectroscopy. An important result is that the spectral features of nitrate, and not molecular nitric acid, have been observed (see Figure 5).[65] This is consistent with a dissociative uptake mechanism.

Studies using low partial pressures have shown that the initial uptake coefficient, i.e., the ratio of the loss rate of a gas-phase species to the surface relative to the collision rate, of HCl and HNO_3 onto ice is larger than about 0.1 if the temperature is roughly 205 K or below.[39,47,48,64,67−69] A number of studies indicate the uptake coefficient is smaller than 0.1 at higher temperatures,[40,67,69] although one flow-tube study at 218 K reports a value of greater than 0.2.[37] The full temperature dependence of the initial uptake coefficient can be modeled with a physisorbed precursor model, but a single set of parameters for a single precursor does not represent the results well when high-temperature data (for example, above about 210 K) are also included.[40,69,70] This may not be surprising, given that the ice surface starts changing, i.e., becoming more disordered, at such temperatures. Note that the inverse temperature dependence has also been observed for the condensation coefficient of water molecules to ice surfaces.[71,72]

With regard to the temperature dependence, it is important to note two issues. First, the lifetime of the adsorbed species shortens with increasing temperature. Thus, these measurements of the "initial" uptake coefficient do not necessarily reflect the value of the mass accommodation coefficient. That is, with the limited time resolution of some experiments, significant desorption of adsorbed species to the gas phase may be lowering the observed uptake coefficient. Second, the measurement of large initial uptake coefficients can be problematic in both flow tubes and Knudsen cells, with complications arising that lead to erroneously low values. In Knudsen cells, desorption of sticky adsorbents, such as HNO_3, from chamber walls can occur after exposure of the ice surface to the gas flow. In flow tubes, desorption of adsorbents from previously exposed surfaces connecting the ice surface to the detector can occur when the injector is withdrawn, and gas-phase diffusion limits accurate uptake coefficient measurements to values less than about 0.2 or so.

For adsorption of both HCl and HNO_3 under atmospheric conditions, the general model that arises is of efficient dissociative uptake driven by the strong acidity of the adsorbate, mobile surficial water molecules, and a polar ice surface. To what degree do the adsorbed species diffuse into the bulk after adsorption? Taking HNO_3 as an example, it is easy to show, using literature values for the diffusion constant in single-crystal ice,[73] that nitric acid will diffuse from the rich-surface layers to some degree over experimental time scales: 10^{-4} cm over 1000 s at 228 K, for example. However, the solubility of HNO_3 in ice at 228 K[73] is sufficiently small that 2 orders of magnitude less HNO_3 will dissolve in this volume of ice as will adsorb at about 10^{-6} Torr partial pressure. Thus, diffusion into a micron-thick layer is not a viable explanation for the long-term component to the uptake of HNO_3 that has been observed by a number of workers.[37,40,67] It is possible, however, that diffusion into the disordered upper bilayers or grain boundaries is occurring or, perhaps, that adsorption is leading to enhanced disorder at the surface.

The uptakes of HF, HBr, and HI have also been studied. Briefly, it is thought that HF is not a sufficiently strong acid to dissociate on ice and so it exhibits little uptake and reactivity upon exposure from the gas phase.[57,74] On the other hand, in all experiments so far, both HBr and HI have been shown to undergo extremely large (i.e., many monolayers), continuous uptake, similar to that exhibited by HCl in its high-partial-pressure regime.[51,68,74−80] In the case of HBr, there is evidence that both amorphous solutions and stable hydrates form.[51,79] It is likely that the hydrates crystalize from supercooled solutions that form initially.

3.2. Adsorption of Weak Acids: SO_2

In the aqueous phase it is well known that SO_2 associates with water molecules and then dissociation occurs to form bisulfite (HSO_3^-) and a hydronium ion:

$$SO_2 + H_2O \leftrightarrows SO_2{\cdot}H_2O \qquad (1)$$

$$SO_2{\cdot}H_2O + H_2O \leftrightarrows H_3O^+ + HSO_3^- \qquad (2)$$

Does this acid dissociation occur on an ice surface, as has been previously suggested?[81]

Indirect evidence for a strong interaction comes from a suite of experiments that demonstrated considerable uptake of SO_2 to bare ice surfaces.[43,82−90] These experiments were conducted on a variety of ice substrates, including ice crystals and ice films formed by both vapor deposition and freezing liquid water. One study of note used chromatographic-type columns packed with 0.1-mm-sized ice spheres at temperatures from 243 to 268 K.[82,84] The time-resolved "breakthrough" of low partial pressures of SO_2 through these packed columns was observed and then converted to an adsorption amount. The time scale for uptake has been shown to be consistent with diffusion along the contact regions (e.g., grain boundaries, veins) of different ice crystals in the column.[91]

Other indirect evidence for dissociation came from the observation that the uptake of SO_2 could be enhanced by an oxidation reaction forming sulfate on natural ice surfaces that presumably contain some level of H_2O_2 (or other peroxides) or on laboratory ice doped with H_2O_2.[83,86,88,92,93] Assuming that the oxidation occurs via the same mechanism that it does in aqueous systems, HSO_3^- must be formed to a considerable degree after SO_2 is taken up by the ice surface.

Most recently, using a flow tube with ice surfaces formed by freezing liquid water, the surface coverages of SO_2 at 228 K have been quantified as a function of partial pressure, P_{SO_2}.[90] The uptake is reversible and, unlike in the packed-column studies using highly polycrystalline ice, rapid. As shown in Figure 6, the surface coverage on the pure ice scales precisely with the square root of P_{SO_2}, a strong indication that dissociation takes place on the surface. As confirmation, the uptake was considerably reduced on acidified ice surfaces and the isotherm had a more linear dependence on partial pressure, whereas the uptake was significantly enhanced on alkaline surfaces. This behavior would not be observed if SO_2 did not react with water and then dissociate on the ice surface. Indeed, given the very much higher acidity of HCl and HNO_3 relative to SO_2, the evidence that this occurs on ice surfaces with SO_2 is additional support for a dissociation mechanism prevailing for the strong acids as well.

The packed-column and the flow-tube measurements yield a consistent view of the temperature dependence of the surface coverage for partial pressures around 4 × 10^{-5} Torr.[84,90] As can be seen in Figure 7, the surface coverage shows a positive dependence on temperature, unlike the reported behavior for any molecule other than CO_2.[94] This

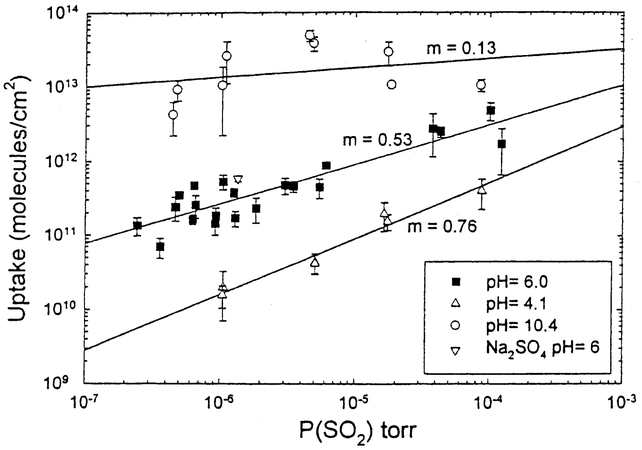

Figure 6. SO_2 uptake to ice surfaces as a function of SO_2 partial pressure at 228 K. The slopes of the lines are given the label *m*, and the pH of the solutions from which the ice was formed is indicated (pH = 6.0 represents deionized water). Reprinted with permission from ref 90. Copyright 2001 American Chemical Society.

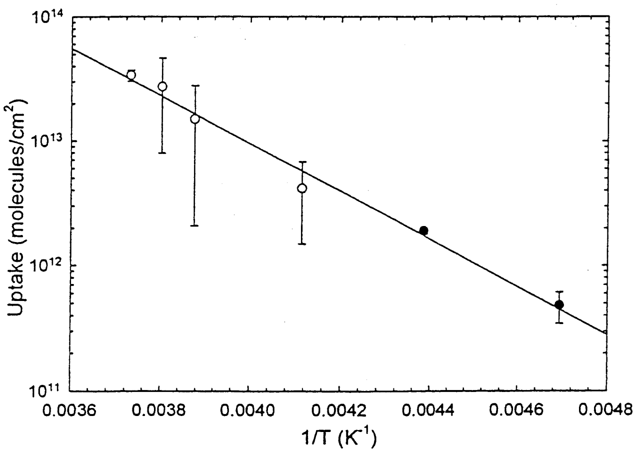

Figure 7. SO_2 uptake to ice surfaces at 4×10^{-5} Torr partial pressure, where the solid circles were measured using an ice-coated-wall flow tube and the open circles come from a frontal chromatographic approach with 0.1-mm ice spheres.[84,90] Reprinted with permission from ref 90. Copyright 2001 American Chemical Society.

behavior is likely due to the presence of the liquid-like layer on the ice surface. Either the greater thickness of this layer at higher temperatures provides a larger reservoir for HSO_3^-, or the increased mobility of surficial water molecules facilitates the dissociation process. Attempts to quantitatively model the observed uptake of SO_2 using aqueous-phase equilibrium constants for reactions (1) and (2) yield an unrealistically thick liquid-like layer hundreds of nanometers thick at temperatures close to 273 K.[81] This is not surprising, given that the nature of molecular interactions will be distinctly different in aqueous solutions compared to those occurring in uptake to a solid, albeit one with liquid-like surface properties.

A detailed BET adsorption study of the adsorption of CO_2 to ice reports a strong positive temperature dependence of the uptake, very similar to that displayed by SO_2.[94] Given that H_2CO_3 can dissociate also, this is probably not a coincidence. The mechanism of the uptake has not been probed, but if dissociation in the liquid-like layer on the surface of ice is occurring, it is postulated here that "pure" atmospheric ice surfaces may be somewhat acidified, as are liquid cloud droplets. This could have impact, for example, on the rates of acid-catalyzed reactions such as those involving hypohalous acids (see section 4.2).

With SO_2 and CO_2 as examples, it is intriguing to inquire whether other weak acids or bases also dissociate on ice surfaces. For the case of acetic acid (see section 3.3), the uptake scales linearly with partial pressure over the temperature range of 228−245 K.[41] Thus, the H-bonding interactions that the undissociated molecules experience with the ice surface appear to dominate the dissociative uptake, to the extent that it occurs, over this temperature range. Weak acids such as HOCl also adsorb to ice surfaces, although the studies have been performed only at low temperatures close to 200 K or below.[48,95−98] The experimentally measured adsorption enthalpies (−9 to −14 kcal/mol)[48,95,97,98] are similar to those theoretically calculated using models where HOCl acts as a proton donor in H-bonding interactions.[59,99,100] Therefore, there is no need to invoke a dissociative adsorption mechanism for HOCl at these temperatures. Similar adsorption behavior has been observed for HONO as well.[101]

It should be noted that the initial uptake coefficient for HOBr on ice also shows a negative temperature dependence up to 240 K,[70,75,102−104] analogous to that exhibited by HNO_3 in some studies. This may arise from a physisorbed-precursor state[102,103] but, as with HNO_3, a single-parameter model does not represent the data well at high temperatures, perhaps because the ice surface is changing and becoming significantly disordered.[70,104] Also contributing may be the fact that the uptake of HOBr is nonreversible, indicative of an unidentified reactive process on the ice, e.g., self-reaction or hydrate formation.

3.3. Adsorption of Hydrogen-Bonding Species: Oxygenated Organics

Motivated by observations of oxygenated organics throughout the troposphere,[105−107] including the upper troposphere where cirrus clouds are widely prevalent, there has been recent interest in measuring the interactions of small alcohols, aldehydes, acids, and ketones with ice surfaces.[41,42,108−111] The observed uptake behavior is distinctly different from that of strong acids on ice. In particular, for temperatures between about 200 and 240 K and for the same partial pressure, the uptakes are not as substantial. Also, they are fully reversible on the time scale of the experiments.[41,42] The adsorption isotherms show a strong partial pressure dependence that is well described by a nondissociative Langmuir model.[41,42,110,111] This is shown in Figure 8, which illustrates the temperature-dependent surface coverages for acetone on ice surfaces formed by freezing liquid water. The uptakes are linearly dependent on partial pressure at low pressures, but they move into the saturated regime at higher pressures. Similar behavior has been demonstrated for a suite of *n*-alcohols where multilayer uptake can be observed if

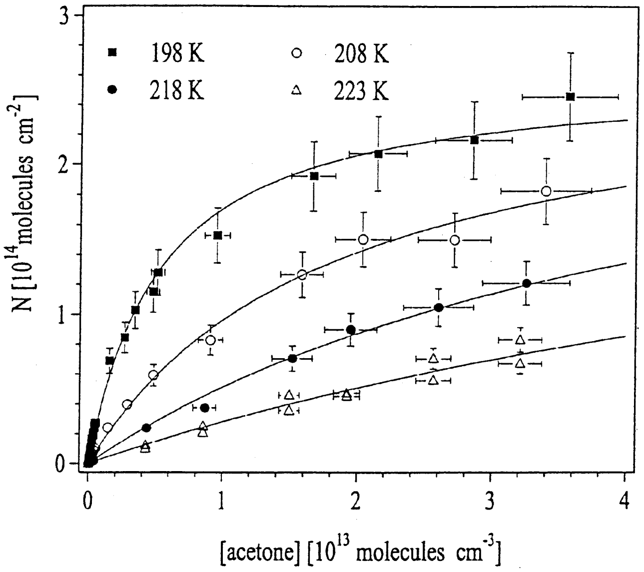

Figure 8. Uptake of acetone to ice as a function of partial pressure at different temperatures. Solid lines are Langmuir isotherm fits. Reprinted with permission from ref 42. Copyright 2002 The Royal Society of Chemistry on behalf of the PCCP Owner Societies.

the partial pressures are raised sufficiently high.[41] The fact that a Langmuir model describes the data so well at submonolayer coverages is probably a reflection of the nature of the ice surface. The high water mobility ensures that one of the critical assumptions of the model, that all surface sites are equal, is satisfied.

On ice surfaces of this type and at temperatures between about 200 and 240 K, the saturated surface coverages that come from Langmuir isotherm fits to the data are all within ±50% of 3.0×10^{14} molecules/cm^2 for a remarkably wide range of molecules: methanol, ethanol, propanol, 1-butanol, 1-pentanol, acetone, and acetic acid.[41,42] As mentioned above, this value is the same as that observed for HCl and HNO_3 uptake for partial pressures larger than 10^{-7} Torr and is a strong indication that this represents monolayer-like surface coverages for these adsorbates. Given the very different chain lengths for the five alcohols and that the saturated coverages are within ±10% of each other, it also suggests that the alkyl chains are aligned perpendicular to the surface in this regime.[41] For submonolayer coverages, the alcohols are not necessarily oriented in this manner.

For the same partial pressure, the larger alcohols partition to the surface more efficiently than do the smaller ones. This trend is the reverse of that for dissolution in liquid water. From this, it can be concluded that at temperatures close to 228 K, the alcohols are not fully solvated when they are taken up by ice surfaces.

To gain insight into the forces that drive uptake, the gas-to-surface equilibrium constant (or partition coefficient), determined from the slope of the unsaturated portion of the adsorption isotherm, is plotted versus the standard free energy for condensation of the organic (see Figure 9). There is a strong correlation between these quantities, not only within the *n*-alcohol homologous series, but also when a carboxylic acid (acetic acid) and an aldehyde (1-hexanal) are included in the trend analysis. Condensation is clearly not occurring at these partial pressures, but apparently the molecules experience similar intermolecular forces upon adsorption as they do when the pure organics condense. The trend in Figure 9 represents the starting point of a semiempirical model that could facilitate incorporation of adsorption data into atmospheric models, particularly so if it is shown to hold across an even larger set of molecular types.

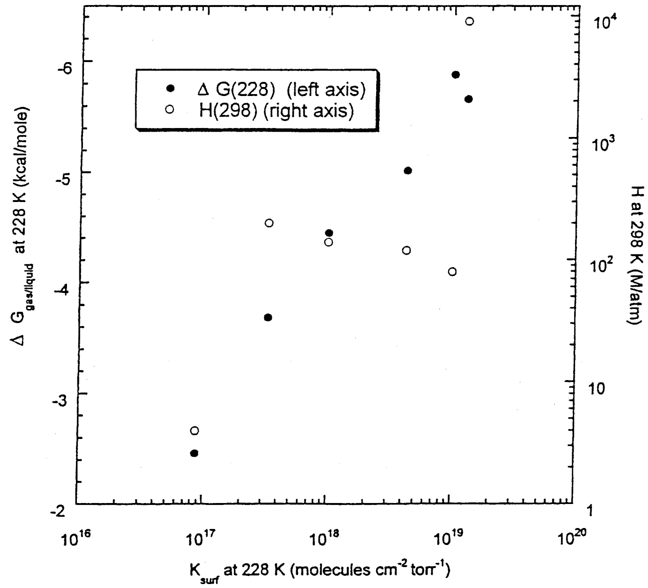

Figure 9. For a set of six oxygenated organics, correlation of 228 K gas-to-surface equilibrium constant (K_{surf}) with free energy for condensation of the liquid at 228 K (left axis, filled circles) and Henry's law constant at 298 K (right axis, open circles). From left to right, the symbols are data for hexanal, ethanol, propanol, 1-butanol, 1-pentanol, and acetic acid. Note the strong correlation with $\Delta G_{gas/liquid}$ but not with H. Reprinted with permission from ref 41. Copyright 2002 American Chemical Society.

The enthalpy of adsorption in the unsaturated regime, as determined from a van't Hoff analysis, is substantial for all species studied to date (see Table 1).[41,42,110,111] Note that the enthalpies of adsorption are all negative, indicating that the degree of adsorption is largest at lowest temperatures. This is a common finding in most adsorption studies, and it further highlights the unusual behavior that prevails for SO_2 and CO_2. With a standard hydrogen bond strength of about 5 kcal/mol, it appears that these oxygenated organics adsorb via a number of H bonds and interact with more than one water molecule on the surface. Theoretical calculations support this model.[112] Taking acetic acid as an example, molecular dynamics simulations confirm that there are interactions with a number of water molecules upon adsorption and the calculated enthalpy of adsorption is in very good agreement with the experimental value.[41,112] Note that most values in Table 1 are significantly larger than the enthalpy of gas–liquid condensation, indicative of a strong adsorptive interaction.

Finally, it should be noted that nonpolar organics also interact with ice significantly at temperatures close to the melting point, presumably via interaction

Table 1. Experimental Enthalpies of Adsorption of Oxygenated Organics to Ice[a]

molecule	Sokolov and Abbatt[41]	Winkler et al.[42]	Hudson et al.[111,b]	Domine and Rey-Hanot[110]	enthalpy of condensation to liquid
methanol		−12.2	−10.8/−9.9		−9.1
ethanol	−14.8				−10.3
1-butanol	−16.2				−12.2
1-pentanol	−17.1				−13.6
acetone		−11.0	−6.8/−9.4	−13.1	−7.5
acetaldehyde			−5.3/−8.3		−6.2
hexanal	−15.5				−10.3
acetic acid	−17.5				−12.4

[a] Values are in kcal/mol. [b] Dual values refect different manner by which the enthalpy of adsorption was extracted from the data.

with a number of water molecules.[31,113,114] Indeed, the degree of adsorption is similar to that exhibited on liquid water close to 273 K. For alkanes, the strength of the interaction is considerably weaker at temperatures where the liquid-like layer is less dominant, e.g., below 238 K.[31]

3.4. Adsorption of Other Species

Although this article has focused on the three classes of atmospheric molecules where the physical chemistry of adsorption has been most extensively studied, a number of other species have been studied as well. Their chemical behavior in the presence of ice will be briefly described.

Species that are relatively nonpolar and nonacidic, such as O_3, NO, NO_2, and Cl_2, all exhibit sufficiently little adsorption to pure ice surfaces that the interaction in its own right, i.e., without the presence of coadsorbed species that are potentially reactive, is atmospherically unimportant.[101,115,116] For example, it is only with the presence of high concentrations of an ozone chemical scavenger, such as SO_3^{2-}, that ozone loss to ice surfaces can be observed.[116]

An important NO_x reservoir species, peroxy acetyl nitrate (PAN), adsorbs considerably less efficiently to ice than do other NO_y reservoirs (i.e., HNO_3) but more so than the NO_x species themselves (i.e., NO and NO_2).[101] It is possible that ice scavenging of PAN could be important in high latitudes where the surface area in the snowpack is considerable.

Last, the adsorption of radical species such as ClO, BrO, OH, and HO_2 has not been quantified, although no reversible adsorption has been observed when relatively high partial pressures between 10^{-6} and 10^{-5} Torr are employed in coated-wall flow tubes.[115,117−120] Instead, it is noteworthy that reactive loss of these radicals has been observed on ice, particularly for BrO, OH, and HO_2.[117,119,120] This probably arises due to heterogeneous self-reaction between the radicals, which implies that some degree of adsorption is occurring. These effects need to be studied again at lower partial pressures, to better predict behavior under atmospheric conditions.

3.5. Adsorption: Atmospheric Implications

Given the progress in laboratory studies of gas-to-ice adsorption, what can we conclude about the extent to which this partitioning occurs in the atmosphere, particularly in the upper troposphere where many studies have been recently performed?

Starting with nitric acid, a number of field programs have attempted to measure the degree to which it partitions to the surfaces of cirrus cloud particles. These studies have been conducted from high-altitude aircraft that have both forward- and backward-facing detectors, either for total NO_y or HNO_3 itself. The backward-facing detector samples only the gas phase, whereas the sensitivity of the forward-facing unit is significantly enhanced to particulate species due to inertial effects. The difference in the signals from the two detectors can be related to the total amounts of particulate HNO_3 (or NO_y).

As suggested by the initial laboratory experiments,[37,65] these field measurements have confirmed that an adsorbed form of HNO_3 is present on cirrus cloud surfaces.[121−123] That is, when the aircraft fly through an ice cloud, the levels of particulate HNO_3 (or an NO_y species that is generally assumed to be HNO_3) are significantly enhanced. There is considerable variability from experiment to experiment, however, in the amounts of condensed-phase nitric acid and the partitioning between different phases. In some cases, the measurements come close to the monolayer coverages of between 10^{14} and 10^{15} molecules/cm^2 (referenced to the geometric surface area of the ice particles) that have been observed in a number of laboratory studies.[37,38,40,65] However, in most cases, somewhat smaller amounts are detected and there is a tendency for the amount of nitric acid on the cloud particles to be considerably enhanced when the temperatures are low, particularly as 200 K (and the NAT stability regime) is approached. This is more in agreement with the most recent low-temperature laboratory studies.[67]

Full interpretation of the results is complicated by considerable uncertainties, including the impact that arises from interstitial aerosol particles in the clouds[122] and the dynamics of the cloud, i.e., whether it is experiencing growth or evaporation. In particular, is there potential for nitric acid to be buried within an ice crystal after it has been experiencing growth? From the laboratory side, if the uptake coefficient of nitric acid to the cloud surfaces is indeed between 10^{-2} and 10^{-3},[67] then it may not be safe to assume rapid equilibrium between the gas-phase nitric acid and the cloud surface, and the amount of nitric acid on the cloud particles may be under kinetic rather than thermodynamic control. Similarly, in laboratory studies there are as yet no measurements of the uptake isotherm at close to 10^{-8} Torr partial pressure of nitric acid, i.e., close to typical values in the upper troposphere. Does the surface retain a monolayer surface coverage at these partial pressures? To date, dissociative Langmuir models that have been applied to the laboratory data predict there is substantial falloff in the uptake at these lower partial pressures.[40,124] However, these extrapolations remain somewhat poorly constrained by the lack of laboratory data. If substantial falloff does occur, this could be an explanation for the submonolayer coverages inferred from the aircraft measurements.

In the upper troposphere, one measure of the ability of ice to scavenge gas-phase molecules comes from the measurement of the convective enhancement factor (CEF), which is the ratio of the abundance of a trace gas in a region of outflow divided by the abundance of the gas in a background region unaffected by convection. Thus, it is a measure of the ability of convection to transport trace species from the boundary layer and of the degree to which they are depleted during transport. In the TRACE-A field campaign, conducted in equatorial regions, the CEFs for HNO_3 and H_2O_2 were measured to be less than 1 and larger than 1, respectively.[125] During convection, supercooled water droplets form from cooling moist air, and then these droplets freeze to form ice. Noting that both HNO_3 and H_2O_2 are highly soluble in liquid water but that only the former adsorbs strongly to ice,[90] the CEF observations can be explained. In particular, when the supercooled water freezes, the dissolved nitric acid is retained by the ice particle surface, the ice particles gravitationally settle, and little nitric acid is delivered to the upper troposphere. By contrast, hydrogen peroxide will be retained poorly by the frozen droplets. It will then be carried aloft by the rising air to produce the CEF larger than 1.

For other species, such as SO_2 and small oxygenated organics, which adsorb relatively weakly under these conditions, it is likely that they too will be effectively transported to the upper troposphere.[125] Indeed, the reason that SO_2 can be delivered by a large volcano to the stratosphere, whereas HCl cannot, may be due to the relative ice scavenging efficiencies of these gases.[126] The conclusions of a number of workers is that SO_2 and small oxygenates adsorb sufficiently weakly that partitioning to ice particles in the upper troposphere is unlikely to significantly affect their gas-phase abundance.[41,42,90,110,111]

Although this section has focused on processes occurring in the upper troposphere, it is important to point out that this last conclusion is most probably not correct for boundary layer conditions where ice surface areas are so high, both in the form of precipitating ice and snow groundcover. In this regard, a review article, now 20 years old, details a wealth of organic species that have been detected in snow particles in the atmosphere, whereas more recent work has focused on the uptake of toxic organics, such as PAHs and PCBs to snow surfaces.[7,127] Indeed, it is now known that high-latitude, snow-covered regions act as major repositories for toxic species of this type.[128]

3.6. Adsorption: Needs for Laboratory Research

To date, there has been considerable emphasis placed on understanding the adsorption of trace gases to ice surfaces under the particularly cold temperatures of the polar stratosphere and upper troposphere regions. However, crucially lacking are studies at substantially higher temperatures more typical of the free troposphere and the high-latitude planetary boundary layer. Indeed, in this regime where the liquid-like surface of ice is considerable, only a few studies have been performed for SO_2, CO_2, and a few nonpolar organics.[31,84,94,113,114] At high temperatures, does aqueous solubility become a better predictor of uptake or do surficial processes still dominate? More specifically, does the trend presented in Figure 9 continue to hold? Is the scavenging capacity for atmospheric trace gases significantly increased?

Given that bare ice surfaces frequently do not exist in the atmosphere, studies of competitive adsorption are also lacking. Initial investigations indicate competition in the saturated adsorption regime between pairs of molecules such as HCl/HNO_3 or acetic acid/1-butanol.[40,109] However, the degree of competition cannot be quantitatively described with a simple, competitive Langmuir model. For the case of HOCl, the presence of coadsorbed HNO_3 has been observed to lengthen its adsorption lifetime.[97] Also, the degree of crystallinity and the role of grain boundaries as reservoirs for adsorbed species should be more fully explored, in particular with regard to uptake to snow surfaces at the ground.[91,129]

From a mechanistic perspective, adsorption experiments should be conducted over as wide a range of partial pressures as possible so as to determine the nature of the adsorption isotherm. For example, precise measurements in the lower partial pressure ($<10^{-7}$ Torr), unsaturated portion of the isotherm are crucially needed for the strong acids so as to better define the uptake mechanism. Such studies could address the following questions: Do the isotherms indicate dissociation, as they do for SO_2? Do they confirm predictions based on uptake data close to the saturated region that the binding energy of HNO_3 to ice is about -13 to -14 kcal/mol?[40,124] Is there a temperature at which the adsorption mechanism switches over from a predominantly molecular process to one involving ionic dissociation? Also, increased utilization of surface-specific spectroscopic techniques for the direct identification of the chemical form of the adsorbed species is needed.

Last, this review has focused on the quasi-equilibrium that arises between gas-phase species and ice surfaces not experiencing substantial net growth (or evaporation). No systematic uptake studies have been conducted with growing ice. This situation frequently arises in the atmosphere, and it could provide a mechanism for the formation of a thermodynamically metastable mixture where the adsorbate is buried in the ice. If so, are gases incorporated at a rate more closely proportional to their initial uptake coefficients to the ice surface[130] or to their equilibrium surface coverages? In this regime, to what degree does the rate of solid-state diffusion control the bulk composition?

4. Reactions of Atmospheric Trace Gases on Ice Surfaces

A number of features of an ice surface distinguish its reactivity. One is that water is available as a reactant, raising the following questions: To what degree does the mobility of water molecules at the ice surface promote heterogeneous reactivity? Is the reactivity similar to that which occurs on a liquid water surface? A second characteristic is that adsorption can modify the chemical structure of a reactant so as to make it more reactive. The prime example here is the ionic dissociation of HCl, thought to drive a number of heterogeneous reactions in the atmosphere. However, this is not a unique process. S(IV) oxidation is also promoted by the formation of ions arising from the adsorption of SO_2 to ice. Thus, this section of the review focuses on hydrolysis reactions, halogen activation processes, and S(IV) oxidation. In the halogen activation section, the focus is on selected HCl activation processes and the reactivity of frozen halide solutions.

4.1. Hydrolysis Reactions

After the discovery of the Antarctic ozone hole, it was shown that both $ClONO_2$ and N_2O_5 can be hydrolyzed on surfaces at atmospherically significant rates,[43,44,115,131,132] whereas the gas-phase reactions are exceedingly slow:

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (4)$$

These studies were conducted in Knudsen cells and in ice-coated flow tubes at cold, polar stratospheric temperatures (~185−200 K) with relatively high partial pressures of reactants (≈mTorr). The reactive uptake coefficient (γ^{react}) was measured to be large for both reactions, e.g., between 0.01 and 0.06 for reaction (3)[43,44,131] and about 0.03 for reaction (4).[115,132,133] Gas-phase HOCl and condensed-phase HNO_3 were observed as reaction products. In one experiment, Cl_2O was identified as a gas-phase product for reaction (3), although this secondary product almost certainly arose from the HOCl primary product reacting with itself at the relatively high concentrations at which it was formed.[132] For all these studies, ice was deposited as a relatively thick film by vapor deposition.

Subsequently, an important set of coated-wall flow-tube experiments was conducted at similar temperatures that utilized low reactant partial pressures ($\sim10^{-7}$ Torr), similar to those prevalent in the polar stratosphere.[134] The N_2O_5 hydrolysis reaction probability was similar to that measured under the higher partial pressure conditions ($\gamma^{react} = 0.024$) but that for $ClONO_2$ hydrolysis was significantly larger, with a measured value of $\gamma^{react} = 0.3^{+0.7}/_{-0.1}$. For reaction (3), it was shown that the surface was readily deactivated by the HNO_3 product, possibly by the formation of nitric acid trihydrate (NAT) on the surface. This could explain the lower values for γ^{react} reported in the earlier work, given the high partial pressures used. The measured reaction probability for the N_2O_5 hydrolysis would not be so sensitive to this effect because its rate is considerably slower than that for $ClONO_2$.

Detailed studies involving vapor pressure measurements and infrared characterization of the condensed phase have since shown that supercooled solutions of nitric acid initially form on ice surfaces as a result of reactions (3) and (4).[64,135] These thin films inefficiently nucleate to nitric acid hydrates, only doing so when they are concentrated and the supersaturation level above the hydrate is extremely high. Deactivation of fresh ice surfaces via exposure to either $ClONO_2$ or N_2O_5 has been observed by a number of other research groups and experimental techniques.[133,136−139]

There has been considerable effort expended, in particular on reaction (3), to validate these measurements and understand the mechanism at the molecular level. Experimentally, the large uptake coefficient for reaction (3) was confirmed by low-pressure Knudsen cell measurements conducted in both a steady-state and pulsed manner, e.g., $\gamma^{react} = 0.2$ from 180 to 200 K.[137] Other flow-tube measurements conducted with low partial pressures at similar temperatures report a slightly lower uptake coefficient, $\gamma^{react} \approx 0.1$.[140] In addition, it has been shown that $BrONO_2$ hydrolyzes just as efficiently as $ClONO_2$, forming HOBr.[137,141]

Given that a molecule will experience more collisions with a rough surface than with a flat one, concern has been raised that significant ice porosity may lead to reported uptake coefficients that are too large.[142] For highly porous surfaces, this is undoubtedly a significant effect, most important for relatively slow gas−surface reactions that sample a large fraction of the available pore space. However, accurate implementation of a theory to take this into account is not straightforward, requiring a variety of input including the specific surface area, particle size, particle density, and a tortuosity factor related to the ease of diffusion through the porous solid.[143] This is particularly difficult for ice, given the different morphologies that ice can assume. One set of kinetic measurements on vapor-deposited ice films in flow tubes was shown to be largely independent of ice thickness and not in accord with the model that incorporates porosity corrections to the observed kinetics.[53] In laboratory experiments, one way to avoid this complication is to perform kinetics studies on nonporous ice, as is likely the case for ice formed by freezing liquid water. In the environment, these porosity corrections will invariably be important for snow at the ground, whereas in the atmosphere ice particles are frequently single crystals, albeit sometimes with high specific surface areas.

Mechanistically, by exposing $ClONO_2$ to ^{18}O-labeled ice it was shown that $H[^{18}O]Cl$ is produced.[144] Thus, it is the $Cl-ONO_2$ bond that breaks upon hydrolysis, driven by nucleophilic attack of a water's oxygen on the Cl atom. This finding is not consistent with an

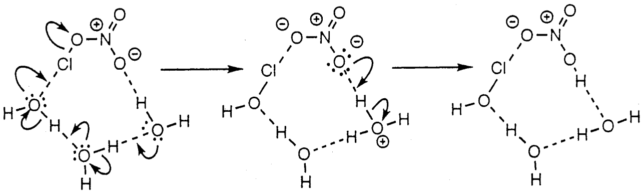

Figure 10. Schematic reaction diagram for reaction (3). Reprinted with permission from ref 147. Copyright 1998 American Chemical Society.

acid-catalyzed mechanism for reaction (3), proposed on the basis of gas-phase, ion−molecule kinetics studies,[145] that predicted the formation of NO_2^+ subsequent to the attack of H^+ on the O atom between Cl and N. Under this mechanism, NO_2^+ would then have reacted with water molecules on the ice to form $HNO_2[^{18}O]$ instead.

Motivated by the assignment of an infrared absorption band in cold (180 K), low water-content $ClONO_2/H_2O$ films to H_2OCl^+,[146] there has been considerable discussion in the literature concerning the mechanism of reaction (3) and whether this, or any other, ionic species is a stable intermediate. Some researchers claim this absorption band is due to molecular nitric acid instead.[147,148] In particular, ab initio calculations have shown that the pathway involving H_2OCl^+ is not energetically favorable and predict that a concerted electron- and proton-transfer process is more likely due to stabilization provided by bonding to water molecules in the ice lattice.[147,148] In this calculation, nucleophilic attack is carried out by a $HO^{\delta-}$ entity, a better nucleophile than H_2O. A reaction diagram is shown in Figure 10. Other calculations support the role of as few as three water molecules on the ice surface greatly lowering the barrier to reaction, not only for reaction (3) but for (4) as well.[149−151] Subsequent infrared experiments conducted with more atmospherically appropriate, water-rich $ClONO_2$ films do not show spectroscopic evidence for the H_2OCl^+ intermediate.[96,135]

Although $ClONO_2$ reacts with ice surfaces on time scales faster than a second or so,[134,137] the appearance of gas-phase HOCl is delayed by tens of seconds.[43,48,137,152] Knowing that HOCl reversibly adsorbs and desorbs to ice surfaces (see section 3.2), this delay has been quantitatively accounted for in flow-tube experiments.[48] In particular, the HOCl product from reaction (3) did not appear fully in the gas phase until the surface coverage came into equilibrium with the prevalent HOCl partial pressure. When the $ClONO_2$ exposure was stopped, the amount of HOCl inferred to adsorb was subsequently observed to desorb.

These conclusions are not in agreement with a recent model for reaction (3) which attributes the delay to the autocatalytic nature of the reaction, driven by the formation of the HOCl product.[152] This model is based on the temporal profiles of second harmonic, laser spectroscopic measurements of the HOCl surface coverage after $ClONO_2$ is exposed to ice at 185 K.[152] Doping of the ice with HOCl prior to exposure shortened the delay, which is given as evidence of the autocatalytic nature of the reaction.

It is striking that reactions (3) and (4) proceed on ice at ~200 K as rapidly as they do on aqueous liquids. For example, $\gamma^{react}(N_2O_5) \approx 0.036$ on liquid water at 282 K and $\gamma^{react}(ClONO_2) \approx 0.1$ on 40 wt % sulfuric acid solutions at temperatures approaching 200 K.[153] Given that only a few water molecules are necessary to dramatically lower the energy barrier to reaction,[147−151] it appears as though the mobile nature of the surficial water molecules, even at these cold temperatures, is sufficient to efficiently catalyze these reactions.

4.2. Halogen Activation Reactions

As with the hydrolysis reactions, the following HCl activation reactions do not proceed in the gas phase at an atmospherically significant rate but do so on surfaces:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (5)$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \qquad (6)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (7)$$

$$HOBr + HCl \rightarrow BrCl + H_2O \qquad (8)$$

In the first attempts to study (5) and (6) on ice, the reactions were shown to proceed efficiently and gas-phase Cl_2 and $ClNO_2$ products were observed.[43,44,115,131,132] However, knowing that HCl efficiently melts ice surfaces under low-temperature, high-partial-pressure conditions (see section 3.1), these experiments were probably measuring the reactivity of $ClONO_2$ and N_2O_5 with HCl aqueous solutions instead of ice.

Experiments on (5), (7), and (8) conducted with low HCl partial pressures (i.e., below those of the ice/HCl solution coexistence curve) have indicated that the monolayer amounts of HCl present on the surface are sufficient to promote highly efficient reactions. For example, when HCl is the excess reagent, the reported values for the reaction probability corresponding to reactant loss are nearly all greater than 0.1.[48,50,75,95,134,137,140,141] One exception is a report that the reaction probability for reaction (8) is significantly below 0.1 at 222 K with HCl partial pressures of 10^{-6} Torr and below.[102]

Considering the reaction between $ClONO_2$ and HCl in detail, a variety of studies have been conducted. In particular, it has been shown that the rate of the reaction is independent of HCl partial pressure over the range from about 10^{-7} to 10^{-5} Torr.[48,50,140] This is fully consistent with the ice surface being saturated with HCl for these conditions. In addition, the kinetics are as fast on ice crystals, formed by rapid cooling of supersaturated vapor, as they are on films formed by freezing liquid water and by vapor deposition.[50] The Cl_2 reaction product is observed promptly upon exposure of $ClONO_2$ and HCl to an ice surface, on a time scale less than a second or so.[48,137] No formation of gas-phase HOCl is observed when HCl is present. In flow-tube experiments, the loss rate of $ClONO_2$ on fresh ice due to reaction (3) was not enhanced when

HCl was added to the flow,[134] though it was in a Knudsen cell experiment.[137]

Two mechanisms have been proposed for reaction (5), both involving an adsorbed ionic chloride species. Whether the chloride exists as a contact ion-pair or whether the proton is considerably separated from the halide ion is not known. The rationale for invoking ionic mechanisms comes from the evidence for HCl ionic dissociation on ice surfaces presented in section 3.1. In the first mechanism, a direct reaction occurs between Cl^- and $ClONO_2$. Knowing that chloride ions react with $ClONO_2$ at collision rates in the gas phase provides support for this mechanism.[154] Indeed, this mechanism must proceed on NAT because, on this surface, the reaction probability for reaction (3) is much smaller than that for reaction (5).[134,136] Ab initio calculations predict a low barrier to reaction when HCl is ionically dissociated, and the ice lattice is playing an active role in the stabilization of the transition state.[155−157]

In the second mechanism, $ClONO_2$ hydrolyzes to form HOCl, which then resides sufficiently long on the surface to react with dissociated HCl. Support for this mechanism comes from the knowledge that HOCl has a high affinity for ice and that it reacts with adsorbed HCl as efficiently as does $ClONO_2$.[48,95,140] This is consistent with there being no enhancement in the loss rate of $ClONO_2$ on ice surfaces when HCl was added in a flow-tube experiment.[134] At present, both mechanisms remain viable.

For the case of reaction (6), the loss rate of N_2O_5 ($\gamma^{react} = 0.024$) in ice-coated flow tubes and Knudsen cells does not significantly increase when low partial pressures of HCl are added.[134,158] However, the gas-phase $ClNO_2$ product is observed.[158] In this manner, the mechanism of reaction (6) on ice appears to be similar to that on aqueous surfaces, where there is also little enhancement in the kinetics of N_2O_5 loss on sodium halide surfaces relative to pure water.[153] The reaction rate appears to be limited by the accommodation of N_2O_5 by the surface or by its reaction with surficial water, i.e., by reaction (4).

Given that hypohalous acids and HCl both adsorb to ice surfaces to a significant degree (see sections 3.1 and 3.2), it is likely that reactions (7) and (8) proceed through a Lindemann−Hinshelwood-type reaction scheme where both reactants are adsorbed for some time on the ice surface prior to reacting. Indeed, the results from one kinetics study of reaction (8), that indicated a dependence of the HOBr loss rate on both temperature and HCl partial pressure, have been interpreted in this manner.[102] However, it should be noted that it is not easy to distinguish between this mechanism and an Eley−Rideal mechanism (where a gas-phase reactant collides with an adsorbed one) with kinetics measurements of this type. Other techniques, perhaps involving time-resolved surface spectroscopy, are needed to more definitively determine which general mechanism is operating.

In addition to experiments where all the reactants are delivered to the ice surface from the gas phase, there have been recent studies where a single gas-phase reagent is exposed to ice films prepared by freezing halide-containing solutions.[159−162] These experiments are complicated by rapid depletion of reactants at the surface. Their interpretation is also challenging because the spatial distribution of the reactants in the ice film has not yet been determined. Indeed, recent NMR studies surprisingly indicate that frozen NaCl solutions have considerable liquid present at temperatures well below the eutectic.[163] The reactivity of substrates of this type is relevant to the chemistry of the high-latitude boundary layer where sea ice and frozen marine aerosols are present.

As an example, it has been shown that when Cl_2 is exposed to a frozen NaBr aqueous film, gas-phase Br_2 is formed with very little production of gas-phase BrCl:[160]

$$Cl_2 + Br^- \rightarrow BrCl + Cl^- \tag{9}$$

$$BrCl + Br^- \rightarrow Br_2 + Cl^- \tag{10}$$

It has been inferred that the rate of the reaction increases as the amount of bromide at the ice surface increases, until saturation is reached. At this point, the reaction probability for Cl_2 loss ($\gamma^{react} \approx 0.1$) is similar to that for Cl_2 loss on ice films exposed to gas-phase HBr, where Br_2 was also the only product observed.[74] In this sense, the reaction set (9) and (10) is similar to that where both reactants are delivered from the gas phase.

Reactions involving HOBr or HOCl interacting with halide/ice films proceed at a steady rate, independent of whether the films are mildly acidic or alkaline, suggesting that the weakly acidic HOCl/HOBr may be acting as the proton source:[160−162]

$$HOX + H^+ + Y^- \rightarrow XY + H_2O \qquad (X,Y = Br, Cl) \tag{11}$$

However, when the films are made highly acidic by freezing pH 2 solutions, a pronounced increase in reactivity is observed. Interestingly, the maximum reaction probability for HOBr loss, $\gamma^{react} \approx 0.02$,[161,162,164] observed by a number of research groups at close to 250 K, does not approach the larger values observed when HOBr reacts with either HBr or HCl delivered from the gas phase at lower temperatures.[75,102,137,141] It is possible that this is due to the physical separation of the H^+ and X^- reactants on the surface of the film.

It has been shown that fresh NaCl/NaBr ice films with Cl^-/Br^- ratios close to those in seawater yield gas-phase Br_2 as a reaction product when reacted with low partial pressures of HOBr.[162] However, the yield of Br_2 decreases and that of BrCl increases as the small amounts of bromide at the surface are depleted by reaction with HOBr. It is probably for this reason that BrCl was observed in other studies of the same chemistry that used considerably higher HOBr partial pressures.[161,164] The production of Br_2 is important as part of the proposed autocatalytic production of photochemically active bromine in the high-latitude marine boundary layer.[165]

Finally, it has been shown that ozone can oxidize bromide on frozen seawater in the dark, giving rise to Br_2 formation via the following reaction sequence:[159]

$$O_3 + Br^- + H^+ \rightarrow HOBr + O_2 \qquad (12)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (13)$$

This process may also play an important role in the formation of active bromine in the boundary layer.

4.3. Sulfur(IV) Oxidation Reactions

As mentioned previously, there is now considerable evidence that sulfur dioxide can react on ice surfaces in both field and laboratory settings. The first indications of this came from studying the dry deposition of SO_2 to snow in the field, where it was found that S(VI) was efficiently formed.[83] It was speculated that reaction of SO_2 could be occurring with H_2O_2, which is known to be prevalent in freshly fallen snow:[166]

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \qquad (14)$$

Soon thereafter, laboratory experiments confirmed that reaction (14) proceeds.[86,92] In particular, it was shown that substantially more SO_2 could be taken up by snow/ice surfaces in the presence of H_2O_2 than in its absence down to temperatures as low as 213 K, and sulfate was detected as a reaction product.

In the past few years, the reaction has been studied again to better quantify the kinetics and mechanism of gas-phase SO_2 interacting with an H_2O_2-containing ice surface. In one study, ice films with a few weight percent H_2O_2 were formed on the inner walls of a flow tube by co-condensing H_2O and H_2O_2.[88] At temperatures around 200 K, the initial uptake coefficient of gas-phase SO_2 onto a fresh surface was shown to be considerably larger on an H_2O_2–ice film than on one without H_2O_2. It was also shown that the amount of SO_2 adsorbed by the ice surface increased with increasing SO_2 partial pressure.

Subsequently, the kinetics of gas-phase SO_2 loss were measured under conditions where gas-phase H_2O_2 was delivered in excess to the ice-coated walls of a flow tube.[93] In this case, the ice had been formed at 228 K by freezing liquid water, and the surface coverages of H_2O_2 were known as a function of partial pressure from previous adsorption studies.[90] As with the hydrolysis reaction of $ClONO_2$ on ice, the reaction kinetics were shown to be time-dependent, with the largest reactive uptake coefficients measured on fresh ice surfaces (see Figure 11). The initial SO_2 uptake coefficients were linearly dependent on the partial pressure of H_2O_2, as expected because the H_2O_2 surface coverage scales linearly with partial pressure for the range of experimental conditions.[90] However, at a constant H_2O_2 surface coverage, the SO_2 uptake coefficients decreased with increasing SO_2 partial pressure, indicating that the process is not first-order. This behavior was shown to be quantitatively consistent with HSO_3^- as the adsorbed species, and not adsorbed SO_2, involved in the rate-determining step of the reaction. It was hypothesized that the same chemistry that occurs in cloudwater droplets was proceeding on the surface of ice. The observed deactivation of the ice with time (see Figure 11) is related to the formation of H_2SO_4 on the surface. The increasing acidity will decrease the concentration of HSO_3^- and thereby slow the reaction, but it is also possible that the deactivation arises from the surficial water molecules becoming strongly associated with, or coated by, sulfate.

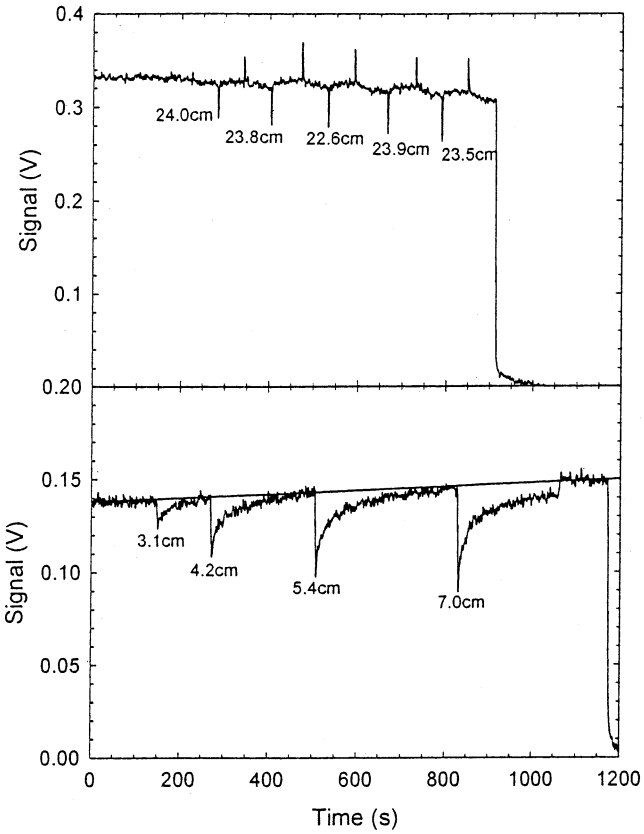

Figure 11. Typical profiles of SO_2 uptake to ice in the absence (upper frame) and presence (lower frame) of gas-phase H_2O_2. For the upper frame the injector is withdrawn and pushed back in five times, with the exposure distances shown. In the lower frame, the data illustrate an irreversible, time-dependent loss of gas-phase SO_2 where the injector is withdrawn over four different distances of fresh ice. Note that much smaller withdrawal distances in the lower frame lead to significantly more SO_2 loss than in the upper frame, indicative of reaction. Reprinted with permission from ref 93. Copyright 2001 European Geosciences Union.

Reaction (14) is another example of a reaction that proceeds efficiently through an ionic mechanism on ice surfaces but does not proceed in the gas phase.

4.4. Reactions: Atmospheric Implications

As with the scavenging of gases to ice, this section attempts to briefly highlight atmospheric observations related to the ice chemistry discussed above. As far as the HCl activation reactions are concerned, the reactions clearly go very fast under the conditions of the polar stratosphere, where the prevalent HCl partial pressures produce monolayer-like HCl surface coverages on ice surfaces. It is important to note, though, that polar ozone chlorine activation is predominantly driven by Type I PSCs, i.e., clouds composed of nitric acid hydrates and ternary solutions, and that Type II PSCs will be important in this regard to a less frequent degree.

Motivated by the need to better explain lower stratospheric ozone depletion and by observations of low ozone in cirrus cloud regions,[3,167] it has been suggested that heterogeneous chlorine activation may also proceed close to the tropopause via reactions involving chlorine reservoir species.[4] This region is characterized by cold temperatures, cirrus cloud surface areas that are frequently very high, and relatively low levels of inorganic chlorine. Some studies have found indirect evidence for chlorine activation in the lower stratosphere and for ClO spikes in cirrus cloud regions.[168,169] However, a separate study has reached a different conclusion, that there is no evidence for chlorine activation in this manner. In particular, using detailed observations of ClO, particle surface area, and water vapor taken on board the ER-2 aircraft over a number of flights, it was found that ice saturation conditions did not extend above the tropopause and ClO levels were very low, i.e., no more than about 1 pptv in this region.[170] From a laboratory perspective, it is not known whether $ClONO_2$ or HOCl continue to react with high efficiency on ice surfaces that may be undersaturated with HCl, given the low partial pressures that will be prevalent in this part of the atmosphere.

In the upper troposphere, areas that have not received much consideration include the possibility for fast bromine heterogeneous ice chemistry, especially in light of recent observations of BrO in the free troposphere. This chemistry could provide a mechanism for recycling of bromine in HOBr back to radical forms, via reactions such as (8).[104] Also, it is likely that the rate of SO_2 oxidation will be dominated in ice clouds by this heterogeneous process and not by gas-phase reaction with OH.[93]

Although there is uncertainty pertaining to the role of ice chemistry in the tropopause region, it is clear that it occurs in the boundary layer albeit at rates that are as yet not fully quantified. In the case of SO_2, dry deposition to snow gives rise to sulfate via oxidation processes of the type discussed above.[83] This SO_2 oxidation may also proceed on low-altitude ice clouds. In particular, inclusion of an S(IV) oxidation process in a Global Circulation Model (GCM) simulation of the sulfur cycle shows far better agreement with ground-level measured sulfate deposition rates at high latitudes than do simulations when this chemistry is not included.[171] Perhaps the most dramatic evidence for ice chemistry is the phenomenon of almost complete boundary layer ozone depletion that occurs in the high-latitude springtime, driven by very high levels of BrO radicals.[172] Although the mechanism for bromine formation has not been conclusively demonstrated, the chemistry is commonly believed to involve oxidation of bromide that concentrates to the surface of ice when either seawater freezes or frost flowers form. An autocatalytic release of bromine can result if Br_2 is released from the interaction of HOBr with the surface,[165] as has been observed in experiments described above.[162]

4.5. Reactions: Needs for Laboratory Research

With the vast majority of experimental work driven by the need to understand the Ozone Hole phenomenon, studies of ice heterogeneous chemistry are lacking at the higher temperatures of the lower and middle troposphere. Reaction (14) is a good example. Although the reaction proceeds efficiently at temperatures between 190 and 228 K,[88,93] detailed kinetic studies have not been performed at higher temperatures where the liquid-like layer is thicker and the surface coverage of S(IV) is higher. It will also be interesting to measure the sensitivity of the kinetics to the acidity of the surface, perhaps by preadsorbing a species like HNO_3. Last, by analogy to cloudwater chemistry, it will be interesting to examine whether a reaction proceeds between adsorbed SO_2 and O_3.

For the high-latitude boundary layer, the greatest uncertainties arise from the lack of high-temperature laboratory experiments and from the uncertainty in the nature of the reactive surfaces. To what degree does HOBr activate sea-ice bromide if many other species are present at the surface, such as sulfate, nitrate, or semivolatile organics? From both a laboratory and a field perspective, it is important to know the degree to which reactive anions come to the surface of snow and frozen seawater. This will affect the relative rates of chloride and bromide oxidation. What is the pH of the ice surfaces? To what degree does polycrystallinity affect reaction kinetics? This is a good opportunity for the application of advanced analytical techniques to better characterize the chemical nature of ice/halide surfaces.

Given the propensity for organic vapors to adsorb to ice (see section 3.3), heterogeneous oxidation reactions involving OH and O_3 will undoubtedly occur, although they have yet to be studied. Initial studies of organic heterogeneous chemistry on ice show interesting reactivity.[173]

5. Summary

In the past two decades, we have learned that the ice surface is chemically active. The dynamic and mobile nature of surficial water molecules promotes hydrolysis reactions that do not proceed in the gas phase and lead to efficient adsorption of a wide range of atmospheric trace gases, including strong acids, weak acids, and polar organics. In many cases, adsorption leads to ionic dissociation that drives a set of atmospherically important heterogeneous reactions via ionic mechanisms. Research needs for the future include the study of reactions at higher temperatures where the liquid-like layer is thicker, and application of surface-specific analytical techniques to better define the detailed mechanisms of these processes. For all these studies there remains the need to perform the experiments under thermodynamic conditions similar to those in the atmosphere.

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