Uptake of Gas-Phase SO_2 and H_2O_2 by Ice Surfaces: Dependence on Partial Pressure, Temperature, and Surface Acidity

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The uptakes of gas-phase SO_2 and H_2O_2 by ice surfaces have been investigated at temperatures from 213 to 238 K and from 10^{-7} to 10^{-4} Torr partial pressure. These experiments have been conducted in a low-temperature, coated-wall flow tube coupled to an electron-impact, quadrupole mass spectrometer which monitors changes in the SO_2 and H_2O_2 partial pressure. The ice surfaces are formed by freezing liquid water. Unlike the uptakes of strong acids such as HNO_3 and HCl, the SO_2 and H_2O_2 uptakes are fully reversible on the time scale of the experiment and the surface coverages are roughly a thousandth of a monolayer at 10^{-6} Torr partial pressure and 228 K. The SO_2 uptakes scale with the square root of the partial pressure of the SO_2 gas, indicating that dissociation of the hydrated form of adsorbed SO_2 is occurring on the surface. The H_2O_2 uptakes scale linearly with the H_2O_2 partial pressure, indicating that dissociation does not occur. The uptakes are driven by H-bond interactions in this case. Support for these conclusions comes from uptake measurements with ice surfaces which were formed by freezing either acidic or basic aqueous solutions. Although the H_2O_2 uptakes are independent of pH, the acidic ice surfaces considerably inhibit the SO_2 uptake and the basic surfaces enhance the SO_2 uptake. The results in this paper are consistent with atmospheric observations which show that both S(IV) and H_2O_2 have low retention efficiencies after supercooled cloud droplets freeze, whereas the retention efficiency of HNO_3 is high. The uptakes are sufficiently small that scavenging of SO_2 and H_2O_2 by ice clouds will not be significant.

Introduction

Although it is well-known that atmospherically important gases such as HNO_3 and HCl interact to a significant extent with ice surfaces,[1−5] our understanding of the nature of these interactions with other important atmospheric trace species is not nearly as well advanced. This arises in part because the HNO_3 and HCl uptakes are large, thought by many to represent a large fraction of a monolayer under typical atmospheric conditions, whereas other gases interact to a significantly smaller degree. For the strong acids, the driving force for the uptake is believed to be the dissociation and subsequent hydration of the newly formed ions on the ice surface. Indeed, high-level molecular dynamics calculations support the formation of a contact-ion pair at the ice surface with a large degree of hydration.[6] Additional support for the dissociation mechanism comes from infrared spectroscopy studies of HNO_3 adsorbed on ice, which show the formation of nitrate on the surface.[5]

As part of an effort to study the interactions of atmospheric gases with ice, we present in this paper uptake studies of SO_2 and H_2O_2 at temperatures encountered in the free troposphere. These experiments were designed to investigate several of the physical characteristics associated with the adsorption of chemically dissimilar gases. For example, it is unclear what happens when a weak acid such as SO_2 interacts with ice. Furthermore, the degree to which these species dissociate is also unknown, and the surface acidity of the ice may significantly impact this process. In particular, does SO_2 adsorb more strongly to an alkaline surface than to an acidic one? As a second example, how large is the uptake of a molecule that cannot dissociate, but can participate in H-bonding? Hydrogen peroxide is an interesting candidate in this regard because it is an extremely weak acid but has the ability to bind via either one or two hydrogen bonds.

A second motivation to perform these uptake studies is to assess the extent to which these gases will be scavenged by ice clouds, and the impact that gas uptake may have on the surfaces of the ice particles. If the uptakes are comparable to those exhibited by HNO_3 and HCl, then the possibility for scavenging of these gases by cirrus clouds is quite strong.[4,5] Lawrence and Crutzen have predicted that there can be significant effects on the atmospheric distribution of H_2O_2 if ice scavenging occurs in a manner similar to that exhibited by HNO_3.[7] A third motivation is that the uptakes and their dependence on partial pressure and temperature can help us to study the rate of the reaction that occurs between adsorbed SO_2 and H_2O_2 on ice surfaces.[8−10]

SO_2 interactions with ice have been studied previously by a number of workers.[8−18] Most notably, ice spheres of known size packed into a column have been exposed to a controlled flow of SO_2.[11,12] In this chromatographic-type experiment, the signal of SO_2 was monitored as a function of time, which allowed the SO_2 uptake at “infinite” exposure time (i.e., for a saturated surface) to be estimated. SO_2 uptakes were measured as a function of temperature and reveal that the uptake was largest at the highest temperatures, which was taken as indirect support for the presence of a liquid−water-like layer on the surface of ice close to its melting point. Subsequent studies have confirmed that SO_2 uptake onto ice occurs and that it is enhanced at high temperatures.[8−9,13−18] However, the ice surfaces used

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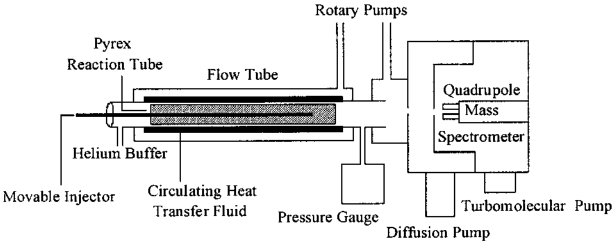

Figure 1. Diagram of the low-temperature, coated-wall flow tube coupled to an electron-impact quadupole mass spectrometer.

in these studies were for the most part rough and the surface areas were not quantified, so surface coverages could not be readily determined. Finally, it should be mentioned that in flow tube studies, similar in nature to those presented here, Chu et al. have recently reported uptake measurements for SO_2 on ice at temperatures close to 200 K.[10]

An interesting observation is that SO_2 uptakes onto real-world snow samples lead to S(VI) formation, indicating that an oxidant capable of reacting with SO_2 is present in the snow.[14] It is possible that the oxidant is either hydrogen peroxide or an organic peroxide. H_2O_2 has been detected directly in snow and ice core samples, at levels which are sufficient to oxidize adsorbed S(IV) species.[19,20] An additional motivation for this work is that, in contrast to the numerous studies of the adsorption of SO_2 to ice, we are not aware of any studies of hydrogen peroxide/ice interactions.

Experimental Section

Figure 1 contains a diagram of the experimental apparatus which couples a low-temperature, coated-wall flow tube to an electron-impact quadrupole mass spectrometer. Ice films were prepared by coating the inner walls of a Pyrex reaction tube (2.5 cm inner diameter) with approximately 1 mL deionized water (pH = 6.0), or aqueous solutions of H_2SO_4, Na_2SO_4, or NaOH. The reaction tube was inserted into the cold flow tube and allowed to cool at atmospheric pressure for several minutes before the flow tube was pumped out. At the temperatures used in these experiments, 238 to 213 K, the film would begin to form within 1 to 2 min. The ice film completely covered the inner wall of the reaction tube and appeared to the eye to be smooth. For reasons described elsewhere, we believe that films prepared in this manner are relatively smooth at the molecular level.[21] Given the highly dynamic nature of the ice surface at these relatively warm temperatures, it is important to note that the overall roughness of the film may not be determined solely by the manner by which it is prepared. Ice films were maintained by a flow of wet helium regulated by calibrated mass flow controllers. Total carrier gas flows were approximately 300 sccm and the flow tube pressure was about 0.75 Torr.

Known amounts of SO_2 and H_2O_2 were delivered to the flow tube in a helium buffer gas also regulated by calibrated mass flow controllers. Dilute samples of SO_2 (Matheson, Anhydrous Grade) in He (UHP Grade) were prepared without further purification. The SO_2 partial pressure in the flow tube was calculated from changes in the bulb pressure as a function of time. Aqueous solutions of hydrogen peroxide (Aldrich, 50 wt %) were concentrated by bubbling dry nitrogen through a H_2O_2 sample for approximately 2 weeks. Density measurements indicated that greater than 95 wt % H_2O_2 samples were prepared and maintained when used daily. H_2O_2 was introduced to the flow tube by bubbling a controlled flow of He through the H_2O_2 bubbler and then through a 10 cm-long UV−vis absorption cell. Variations in the H_2O_2 partial pressure were obtained by adjusting the He flow rate. The concentrations in the absorption cell were determined by transmission measurements at 220 nm where the optical cross section is 2.58×10^{-19} cm^2.[22]

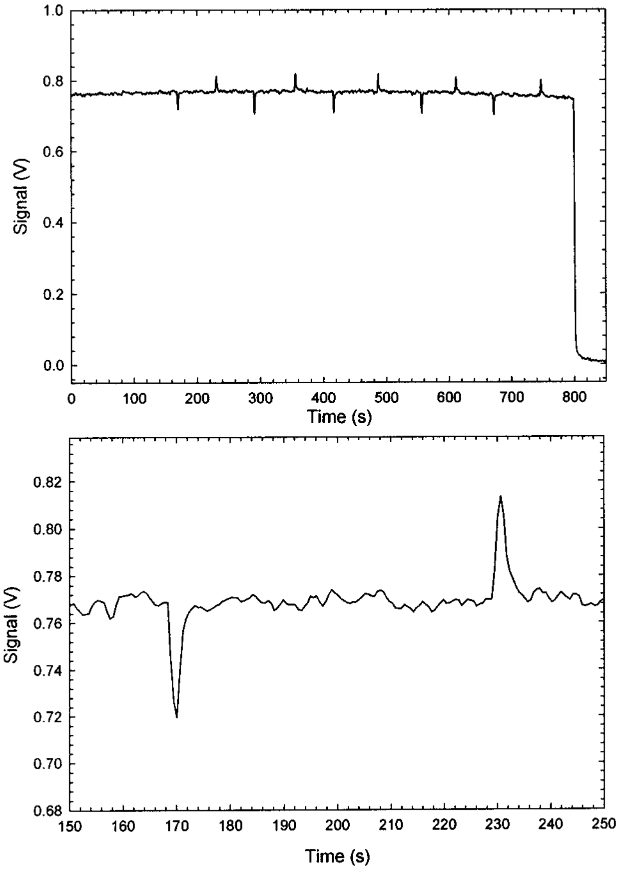

Figure 2. Uptake experiment where 3.5×10^{-6} Torr SO_2 is exposed to ice at 228 K and monitored by the mass 64 spectrometer channel. The lower plot is a signal enhanced view of the first uptake experiment. For approximately the first 160 s, the end of the moveable injector (Figure 1) is positioned beyond the ice film while a steady signal is obtained. As the moveable injector is pulled back 15−20 cm, SO_2 is adsorbed onto the ice and a decrease in the signal is recorded. A surge in the spectrum is observed as the injector is pushed back to the original position and SO_2 desorbs from the surface. In this case, five uptakes were recorded using the same ice film and the average uptake is $(4.6 \pm 0.8) \times 10^{11}$ molecules/cm^2.

To illustrate the experimental method, an uptake experiment involving the exposure of 3.5×10^{-6} Torr SO_2 to ice at 228 K is displayed in Figure 2. Both an absolute scale (top) which illustrates a number of uptake cycles and a signal enhanced scale (bottom) which illustrates just one cycle are shown. The samples enter the flow tube through a moveable injector as depicted in Figure 1. The end of the injector is initially positioned beyond the ice covered reaction tube while a steady mass spectrometer signal (at mass 64) is obtained, as shown in the first 160 s of the data in Figure 2. As the moveable injector is pulled back on the time scale of a second or so, SO_2 adsorbs onto the surface of ice and a momentary decrease in the mass spectrometer signal is observed. When the injector is pushed back to the original position, SO_2 desorbs from the surface and a surge in the mass spectrometer signal is observed. As described below, the integrated area of these peaks is proportional to the amount of SO_2 adsorbed onto or desorbed from the ice surface.

Uptakes of H_2O_2 on ice were performed by monitoring the mass 34 channel. The mass spectrometer sensitivity to H_2O_2 was low at this mass, presumably because ionization leads to the dissociation of most of the H_2O_2 into two OH. Unfortunately,

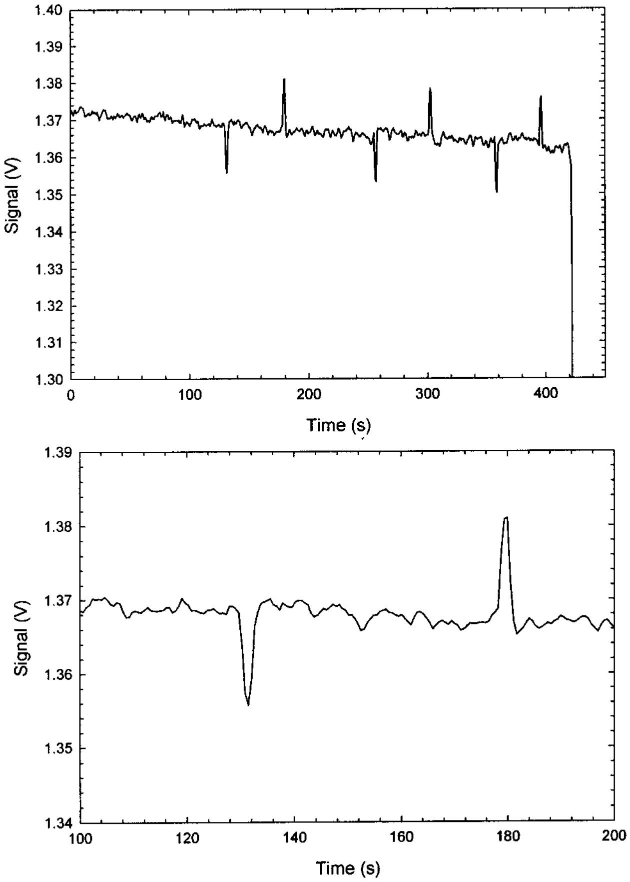

Figure 3. Experiment where 5.6 × 10^{-5} Torr Ar is exposed to a dry room temperature flow tube. Upper frame shows the Ar signal observed as the injector was withdrawn and pushed back in to its starting position three times. For the first experiment (see lower frame), the injector is withdrawn 15 cm at approximately 130 s and pushed back in at 180 s. The bulk flow velocity for this experiment was 1129 cm/s.

the OH signals at mass 17 could not be used due to the large amount of water involved in the experiment. Furthermore, highly concentrated H_2O_2 is unstable and breaks down into O_2, H_2 and H_2O. The natural abundance of the $^{34}O_2$ isotopic component of O_2 is about 0.2%, which significantly increased the baseline signal at this mass. Fortunately, measurements indicated that O_2 does not adsorb strongly to ice and that our uptakes were due to H_2O_2 only. H_2O_2 signals were corrected for the component arising from $^{34}O_2$ by subtracting the appropriate fraction (i.e., the natural abundance ratio of $^{34}O_2$ to $^{32}O_2$) of the $^{32}O_2$ signal, which was monitored during each H_2O_2 experiment.

Given that the SO_2 and H_2O_2 uptakes on ice were small, we wanted to evaluate the smallest uptakes that could be measured with this technique by performing uptake experiments on dry Pyrex surfaces at room temperature. In particular, some experiments were done with Ar, a typical example of which is shown in Figure 3. There is clearly a reversible loss and recovery of Ar signal each time the injector is withdrawn and pushed back in to the starting position. Aside from interactions that Ar may experience with the wall surface, we believe that some of the loss in signal is due to the injector being withdrawn into a flow which has no Ar within it. To explain, consider a hypothetical experiment where a trace gas is delivered to the flow tube through an injector that could be pulled back instantaneously. Given the bulk flow velocity for typical experimental conditions, it would require tens of milliseconds for the gas to reach the mass spectrometer detector. As the gas travels the additional distance to the detector, the detector would observe an analyte-free “plug”, and the mass spectrometer signal would go to zero. The fraction of signal loss due to this injector motion can be readily calculated from the change in the signal level times the time for the gas to travel the additional distance (i.e., change in signal times change in injector position divided by flow velocity). The observed loss of signal was within a factor of 2 of the calculated “plug” area for the Ar experiments. As an example, for the uptake experiment in the lower frame of Figure 3 the calculated loss of signal was 47% of the observed value. The discrepancy between the observed and the calculated values is not obvious but in theory could arise from adsorption of Ar to the flow tube surface. Later in the paper, we will also present results from a few control experiments with H_2O_2 in a warm, dry flow tube, where we found that the observed change in signal very closely matched the calculated value.

The SO_2 and H_2O_2 uptakes are considerably larger than the amount of signal loss that may be due to this “plug”. Nevertheless, corrections were applied to all the SO_2 and H_2O_2 data presented in this paper by subtracting the calculated intensity of the SO_2- and H_2O_2-free plugs from the observed uptakes. The magnitude of this correction is illustrated for both SO_2 and H_2O_2 in the Results and Discussion section.

Results and Discussion

SO_2 Studies. The upper frame of Figure 2 shows a typical sequence of uptake experiments performed with a single ice film at 228 K. As described above, each momentary loss of signal corresponds to the injector being pulled back over a fresh ice surface, and each surge arises when the injector is pushed back to its starting position. The integrated loss (or gain) of signal arising from moving the injector is proportional to the amount of SO_2 which has adsorbed to (or desorbed from) the surface. To within 20%, the adsorption amounts are the same for repeated exposures of one film to SO_2. This is an indication of the relatively small errors that arise from integrating the rapidly changing SO_2 signal. From the lower frame of Figure 2, it is clear that the desorption amounts are the same as the adsorption amounts, to within experimental error. The shapes of the adsorption and desorption curves are also similar, with perhaps just a small amount of ‘tailing’ on the latter. This indicates that the uptake is a fully reversible process and the kinetics involved are faster than the time scale of the experiment.

From the mass flow rate of SO_2 down the flow tube, which can be calculated from the SO_2 partial pressure in the flow tube and total flow rate of He buffer gas, the adsorption areas in Figure 2 can be quantified in terms of the number of molecules of SO_2 lost from the flow. This quantity is then converted to a surface coverage by referencing it to the geometric surface area of the Pyrex reaction tube. For the conditions shown in the figure, the average surface coverage (or uptake amount) is (4.6 ± 0.8) × 10^{11} molecules/cm^2, where the uncertainty is a $1 - \sigma$ precision error. The “plug” correction is 20% of the observed loss of signal for this set of data. Given the uncertainties of up to a factor of 2 associated with making this correction (see the Experimental section), we believe this is the largest source of systematic uncertainty in the reported surface coverages. The precision errors observed in the scatter in the data are at least as large as the systematic uncertainties and are likely due to the differences in the ice films from experiment to experiment.

This surface coverage is very much lower than a full monolayer, which would correspond to roughly 5 × 10^{14} molecules/cm^2 for a molecule the size of SO_2 if the molecules are packed on the surface next to each other. The measurements of surface coverages derived in this manner for a wide range

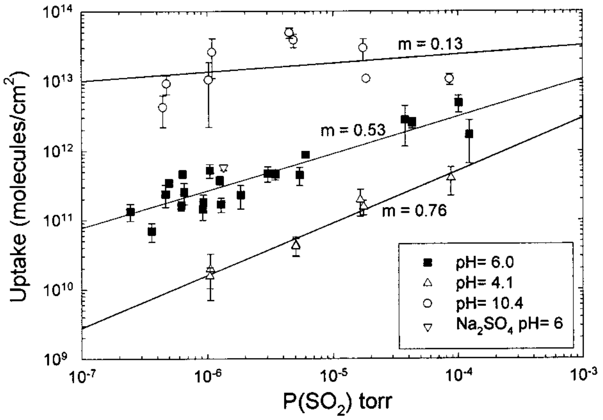

Figure 4. SO_2 uptake (molecules/cm^2) plotted as a function of SO_2 partial pressure (Torr), at 228 K. The data sets represent experiments where ice films were prepared with deionized water (pH = 6) and aqueous solutions of H_2SO_4 (pH = 4.1), NaOH (pH = 10.4), and Na_2SO_4 (pH = 6). The slope of the best fit line for each data set is indicated in the figure.

of conditions are shown in Figure 4. In particular, the solid squares and the line-of-best-fit to those points represent uptake measurements as a function of the SO_2 partial pressure performed on an ice film generated by freezing neutral (pH = 6) water. There is a clear dependence of the uptake upon the partial pressure, indicating that the surface is not saturated under these conditions. This is in agreement with the magnitude of the uptake itself, which is very much smaller than that of a saturated monolayer coverage.

Interestingly, the surface coverage varies with the square root of the SO_2 partial pressure (the slope of the log−log plot in Figure 4 is 0.53). This is different from the linear dependence that is predicted by a simple Langmuir-type adsorption isotherm. We believe that this dependence indicates the manner by which SO_2 adsorbs to an ice surface. Consider a model where SO_2 interacts with an ice surface via chemical interactions which are analogous to, but not the same as, those of an SO_2 molecule dissolving in liquid water

$$SO_2(g) \Leftrightarrow SO_2(ads) \tag{R1}$$

$$SO_2(ads) + H_2O \Leftrightarrow H^+(ads) + HSO_3^-(ads) \tag{R2}$$

where the (g) and (ads) symbols denote gas-phase and adsorbed-phase, respectively. SO_2(ads) represents the adsorbed form of SO_2, which is likely to involve hydration via a small number of water molecules on the ice surface. We do not consider the dissociation of HSO_3^- into SO_3^{2-} because the acidity of our pH-neutral water was 6.0, and the pK_a of HSO_3^- is 7.2,[23] i.e., we expect little dissociation of the bisulfite ion. For these two reactions we can write equilibrium constant expressions

$$K_{R1} = [SO_2(ads)]/P_{SO2} \tag{E1}$$

$$K_{R2} = [H^+(ads)][HSO_3^-(ads)]/[SO_2(ads)] \tag{E2}$$

and define a quantity [S^{tot}(ads)] which represents the total amount of S(IV) species adsorbed on the surface

$$[S^{tot}(ads)] = [SO_2(ads)] + [HSO_3^-(ads)] \tag{E3}$$

Note that the concentration quantities in E1 to E3 may be viewed either as surface coverages or as a concentration of adsorbed species in the top few monolayers of an ice surface which are accessible on the time scale of the experiment. For the analysis below, either definition is appropriate. If we assume that [H^+(ads)] = [HSO_3^-(ads)], i.e., the acidity is determined by the dissociation process, eqs 1 to 3 can be solved to give

$$[S^{tot}(ads)] = K_{R1}P_{SO2} + (K_{R1}K_{R2}P_{SO2})^{1/2} \tag{E4}$$

where the first term on the right-hand-side represents the quantity of surface S(IV) in the form of undissociated SO_2 and the second term represents S(IV) on the surface as HSO_3^-. Equation 4 predicts that, if the amount of HSO_3^- on the surface is much larger than the amount of undissociated SO_2, the surface coverage should be proportional to the square root of the SO_2 partial pressure. This is the behavior demonstrated in Figure 4.

Thus, the observations imply that SO_2 uptake by a neutral ice surface is driven by the dissociation of adsorbed SO_2 and the subsequent hydration of the product ions. The dissociation presumably takes place in the uppermost few monolayers of the ice surface, given that diffusion times into bulk ice are long. It is important to note that elements of this aqueous-like model for the interaction of SO_2 with ice surfaces have been presented before.[16] However, it is our belief that although the chemistry appears qualitatively similar to that which occurs in aqueous solutions, it seems unlikely that at a quantitative level the aqueous model will be accurate, given the very different types of interactions that take place between molecules in a liquid and those on a solid. At a minimum, the values of the equilibrium constants K_{R1} and K_{R2} will be different.

Support for this model involving dissociation and chemical interactions with surface water comes from two directions. First, the uptakes of SO_2 from the gas phase were greatly enhanced on films formed by freezing basic solutions (see pH 10.4 data in Figure 4) and greatly reduced on acidic films (pH 4.1 data). For the basic case, the R2 equilibrium is pulled over to the right as the protons formed in the reaction are consumed by hydroxide ions on the surface. Indeed, the lack of dependence of the uptake on the SO_2 partial pressure is consistent with the number of accessible hydroxide ions being the sole factor which determines the uptake capacity of the film. For a pH 10.4 film and with the volumes of solution that we use to make the films, we can calculate the maximum number of OH^- ions that could be available for reaction, assuming that they all come to the surface when freezing of the solution occurs. The SO_2 uptakes are roughly 5 to 10% of this maximum uptake amount. If the number of accessible hydroxide ions determine the uptake capacity, then it would suggest that 5 to 10% of OH^- moves to the surface upon freezing.

For the acidic films, SO_2 uptakes are considerably smaller than those on neutral surfaces and their dependence on the SO_2 partial pressure is closer to being linear (the slope of the line-of-best-fit in the log−log plot in Figure 4 is 0.76). These observations are consistent with the surface protons inhibiting the dissociation of adsorbed SO_2, which makes the uptakes smaller, and with the first term in E4 becoming more important. It is also possible that the sulfate ions that are part of the sulfuric acid solution used to acidify the water could have influenced the uptake of SO_2. To test for this, we performed uptake experiments with a pH-neutral 0.1 M Na_2SO_4 solution, and observed that the uptake is the same as on pure ice surfaces. Thus, we feel confident that it is the protons close to the surface which inhibit the uptake of SO_2 on the acidified ice surfaces.

The second line of evidence, albeit indirect, that a substantial chemical interaction with water is occurring is given by the temperature dependence of the SO_2 uptake. In Figure 5, we present our uptake data on neutral ice surfaces for a SO_2 partial

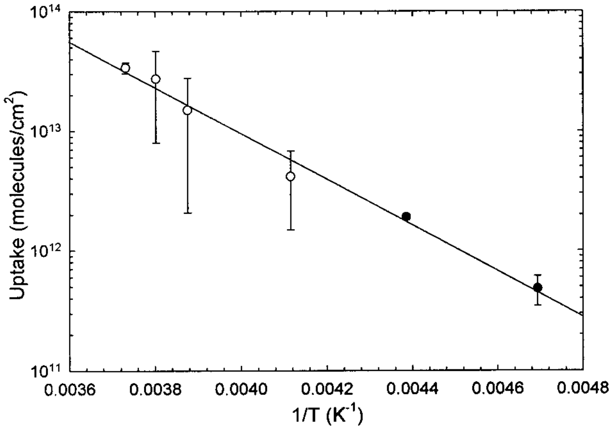

Figure 5. SO_2 uptake (molecules/cm^2) at 4×10^{-5} Torr partial pressure vs T^{-1} (K^{-1}) where the open and closed circles are from Clapsaddle and Lamb[12] and this work, respectively. At 228 K, our data point is taken from our line-of-best-fit in Figure 4, whereas the point at 213 K is the average of 5 uptake experiments on a single film. The other points in the figure represent values interpolated for the same partial pressure from the Clapsaddle and Lamb uptake measurements made at four different temperatures.

pressure of 4×10^{-5} Torr for two temperatures, 228 and 213 K. We also include data points from another experiment which measured the uptake in a very different manner and at higher temperatures.[12] Specifically, Clapsaddle and Lamb formed small spheres of ice by spraying water droplets into a liquid nitrogen bath and then used these spheres to pack a chromatographic column. SO_2 flowed through the column for periods of hours, and a surface coverage was calculated from the "breakthrough" curve of SO_2 coming through the column. Experiments were performed at a small number of partial pressures for a range of relatively warm temperatures. To make the most appropriate comparison to our data, we have interpolated the data sets in Reference 12 for each temperature and determined the uptake at a SO_2 partial pressure of 4×10^{-5} Torr. Quite remarkably, given the very different nature of the two experimental approaches, the Clappsaddle and Lamb data set and ours appear to be consistent with each other. Specifically, when the logarithm of the uptake is plotted versus the inverse temperature, the data fall on the same line-of-best-fit within experimental uncertainties.

Comparison to other uptake studies is not as fruitful. In particular, a number of studies involving uptake to snow do not report snow surface areas and the surfaces are undoubtedly rough. We believe this may be the reason that Chu et al. report SO_2 surface coverages which are approximately 1 order of magnitude larger (2.4×10^{12} molecules/cm^2 for 1.3×10^{-6} Torr SO_2) than those reported here.[10] The primary difference between the Chu et al. experimental approach and our own is that the former uses water vapor deposition to form the ice film, which may lead to a high surface-area film. Indeed, we have found that HCl uptakes on vapor-deposited films to be considerably larger than on films formed by freezing liquid water.[1,4] Given that the Chu et al. uptakes were performed at even lower temperatures (191 K) than our own, we would have expected, if anything, the uptakes to be somewhat smaller than ours had the areas of the films been similar.

There is a temptation to interpret Figure 5 in a van't Hoff manner, where the slope would be related to an energy of adsorption. But to do so may be incorrect, or at least incomplete, given the various processes that will determine the magnitude of the uptake as a function of temperature. Consider the first step in the process, the adsorption of gas-phase SO_2. One would expect this process to be exothermic, and that lower temperatures would push the equilibrium to the right, contrary to the trend shown in Figure 5. Similarly, the dissociation of adsorbed SO_2 should also be an exothermic process. What, then, is driving the increased uptakes at higher ice temperatures? As has been previously suggested,[12,16] a possibility is that the quasi-liquidlike layer that has been hypothesized to exist on the surface of ice[24] is more developed at higher temperatures and thus more capable of accommodating SO_2 in the manner described above. In particular, the increased mobility of water molecules that would be part of a quasi-liquid layer could facilitate the dissociation of adsorbed SO_2 by enhancing the ability of water molecules to hydrate the H^+ and HSO_3^- ions. Or, the layer may be simply thicker at higher temperatures, and thus able to accommodate more S(IV) species.

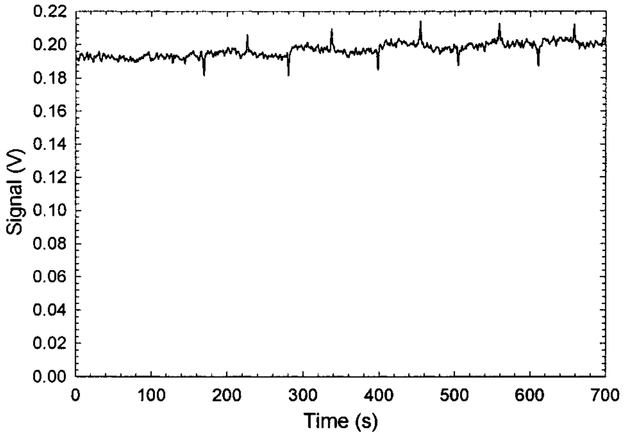

Figure 6. Uptake experiment, analogous to that in Figure 2, where 2.8×10^{-5} Torr H_2O_2 is exposed to ice at 228 K.

H_2O_2 Studies. Analogous experiments to those just described were also performed with hydrogen peroxide. In Figure 6, a typical set of uptakes on an ice film at 228 K and a H_2O_2 partial pressure of 2.8×10^{-5} Torr is shown. Note that the issues associated with detecting H_2O_2 in electron-impact mode give rise to somewhat poorer signal-to-noise than in the case of SO_2, but the uptakes are easily measurable nevertheless. As with SO_2, the uptakes are small—for this set of data the average surface coverage is $(2.2 \pm 0.4) \times 10^{12}$ molecules/cm^2—representing a small fraction of a monolayer.

The dependence of the uptakes upon the H_2O_2 partial pressure and upon the acidity of the ice film indicate a different type of chemical interaction occurs between ice and H_2O_2 than with ice and SO_2. First, the dependence of the H_2O_2 uptake upon its partial pressure is linear from 4×10^{-8} Torr to 3×10^{-5} Torr (see Figure 7, where the slope of the log−log plot is 0.94), indicating that the uptake is in the portion of the adsorption isotherm where the surface is unsaturated. The linear dependence is also an indication that H_2O_2 is not dissociating on the surface, as expected given that H_2O_2 is an exceedingly weak acid. Uptake studies were performed with both acidic and basic films, as shown in Figure 7, which demonstrate that there is no dependence on the extent of surface acidity. This supports our contention that there is little dissociation of H_2O_2 on the surface. Rather, the uptake is much more likely being driven by the formation of either one or two H-bonds between H_2O_2 and the ice surface.

Also shown in Figure 7 are the calculated quantities of the H_2O_2-free "plug" (see Experimental section) which were subtracted from each of the uptakes. The "plug" values agree very well with the "uptakes" measured in three control experi-

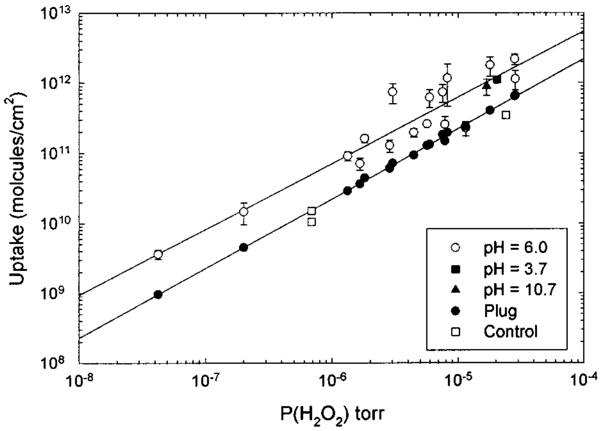

Figure 7. H_2O_2 uptake (molecules/cm^2) plotted as a function of H_2O_2 partial pressure (Torr). As discussed in the text, the uptakes (open circles) were corrected by subtracting the H_2O_2 free plug (closed circles) from the integrated signals. The figure includes data points from control experiments (open squares) performed by measuring the uptake on room-temperature Pyrex surfaces. Uptake experiments were also performed on ice surfaces that were prepared from aqueous solutions of H_2SO_4 (pH = 3.7) and NaOH (pH = 10.7). The best fit line reflects only the pH = 6.0 data (open circles) and the slope is 0.94.

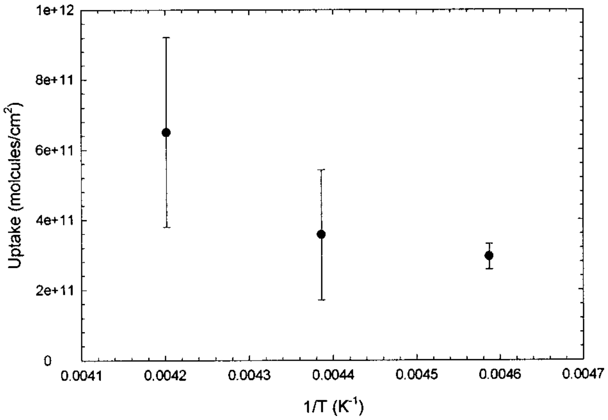

Figure 8. The H_2O_2 uptake (molecules/cm^2) vs T^{-1} (K^{-1}). Each data point was the average between 5 and 15 uptakes (5 uptakes per film) where the H_2O_2 partial pressures were 5.2 (±0.6) × 10^{-6} Torr.

ments performed with dry Pyrex surfaces at room temperature. The plug correction is on average 35% of the reported uptake.

The temperature dependence of the uptake at 2.8 × 10^{-5} Torr partial pressure is considerably weaker than that exhibited by SO_2 and sufficiently small that there is no statistically significant trend over the temperature range from 238 to 213 K (see Figure 8). Assuming an adsorption energy of 5 kcal/mol (i.e., a typical H-bond), a van't Hoff dependence would predict that the uptake would increase by a factor of 2.6 from 238 to 218 K. The fact that we do not observe such an increase may be an indication that additional factors determine the temperature dependence of the uptake, e.g., the thickness of the quasi-liquid layer.

Comparison of Uptake Behavior of Different Gases. In an earlier study, we have shown that strong acids, such as HNO_3 and HCl, exhibit ice uptakes at partial pressures of 1 × 10^{-6} Torr which are very much larger (~2 × 10^{14} molecules/cm^2)[4] than those measured here for SO_2 and H_2O_2 (~2 × 10^{11} molecules/cm^2 and 8 × 10^{10} molecules/cm^2, respectively). Given that the aqueous physical solubilities of H_2O_2 and HNO_3 are both extremely large and similar to each other[23] is an indication that the uptake of gases by ice is driven by an additional factor. As in aqueous solutions, the primary determining factor for ice appears to be whether the species is able to readily dissociate, a capability which both HNO_3 and HCl have but which H_2O_2 does not. H_2O_2 is likely to bind via H-bonding and, as a result, the uptakes observed are very much smaller. An intermediate case is that of SO_2. SO_2 is a substantially weaker acid than either HNO_3 or HCl, and the uptakes are substantially smaller, roughly comparable to those of H_2O_2. Interestingly, when the dissociation channel of adsorbed SO_2 is shut down by acidifying the ice surface, the uptakes of SO_2 become considerably lower than those of H_2O_2, probably because the intermolecular forces which drive the uptake of molecular SO_2 will be considerably weaker than the H-bonding in which H_2O_2 can participate.

An additional indication that the uptakes of SO_2 and H_2O_2 differ in nature from that of strong acids is that they are largely reversible on the time scale of the experiment, i.e., the amount of gas which desorbs from the surface closely matches that which adsorbs. On the other hand, only a small fraction of HNO_3 desorbs under similar conditions, presumably an indication of the strong binding strength of the hydrated products to the ice surface.

Atmospheric Implications. The results from these studies are in general agreement with field studies that examine the chemical content of both supercooled water and ice droplets in order to determine the extent to which chemicals are retained by cloud particles when freezing occurs. General conclusions from these studies are that strongly acidic species, such as HNO_3, are very strongly retained, whereas both SO_2 and H_2O_2 have low retention efficiencies.[25,26] Given that the solubility of each of these gases in ice is low, it is likely that freezing of a supercooled water droplet transports the dissolved species to the surface of the newly formed ice particle. If there is a strong affinity of the molecule for the surface, as in the case of HNO_3, the observed retention will be high. Conversely, if the molecules are not strongly bound to the surface, as in the case of SO_2 and H_2O_2, they will readily desorb and the retention will be low.

This behavior can have considerable impact on atmospheric trace gas abundances, particularly in the upper troposphere where deep convection is an important transport process taking chemically active species up from the boundary layer. For example, in a field campaign (TRACE-A) conducted in equatorial regions, the convective enhancement factors (the ratio of gas abundances in convective outflow relative to levels in the absence of convection) were less than one for HNO_3, indicating efficient scavenging, and larger than one for H_2O_2, an observation which has been interpreted as being consistent with inefficient scavenging of H_2O_2 by ice clouds.[27]

Aside from interactions in convective systems, it has been hypothesized that the interaction of HNO_3 with ice surfaces could give rise to substantial scavenging of HNO_3 in the upper troposphere if the surface areas of cirrus clouds are sufficiently high.[4,5] This suggestion has been confirmed by some field measurements which show that a fraction of NO_y, presumably in the form of HNO_3, is taken up by ice particles.[28] In addition, a 3-D modeling study predicts that substantial effects on the spatial distribution of nitric acid through the free troposphere could arise through scavenging effects of this type.[7] This modeling study also predicts similar effects for H_2O_2, assuming that the affinity of H_2O_2 for ice is roughly the same as that for HNO_3. The results in this paper, which show that the surface coverages are in fact orders of magnitude smaller under typical atmospheric partial pressures, suggest that such scavenging in unlikely to be important. To illustrate, consider that the thickest cirrus clouds have surface areas of about 10^{-4} cm^2/cm^3. A typical mixing ratio of H_2O_2 at 8 km in the free troposphere is 500 pptv, or 10^{-7} Torr.[29] The surface coverage for this partial pressure (see Figure 7) will be 8×10^9 molecules/cm^2, which corresponds to scavenging just 0.02% of gas-phase H_2O_2 (i.e., in one cm^3 of air, amount of H_2O_2 on ice surfaces $= 8 \times 10^9$ molecules/cm^2 $\times$ 10^{-4} cm^2/cm^3 $= 8 \times 10^5$ molecules; amount of H_2O_2 in gas phase is 10^{-7} Torr, or 4.2×10^9 molecules, assuming 228 K).

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