Uptake and Interaction of HI on Ice Films

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The uptake of HI and co-uptake of HI + HCl on water-ice have been studied in a flow reactor at polar stratospheric temperature. The uptake of HI on ice is determined to be in the range of 1.1×10^{14}−1.8×10^{16} molecules/cm^2. The HI uptake thermodynamics is also investigated. The nature of higher uptake and the effect of acidity on the HX uptake are studied and discussed. The HI + HCl co-uptake experiment reveals that the uptake of HI on ice is about a factor of 10 more efficient than that of HCl at 188 K.

I. Introduction

The interaction of HCl and HBr on ice has stimulated a number of studies on this subject. The significance of this process is the conversion of photochemically inactive halogen species such as HCl into reactive forms via heterogeneous reactions on polar stratospheric cloud (PSC) surfaces.

$$HOCl + HCl(s) \rightarrow Cl_2 + H_2O(s) \qquad (1)$$
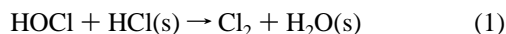
The photochemically active halogen will then enter into catalytic cycles to deplete polar ozone. The uptake and interaction of hydrogen halides (HXs) on ice is fundamentally important in understanding polar ozone chemistry, and its study would reveal the nature of the chemical interaction between HXs and ice surfaces.

Recent laboratory studies have shown that the uptake of HF on ice is very low: $\sim 10^9$ molecules/cm^2 at 200 K.[1] The uptake of HCl on ice has been studied by a number of groups and is about 5×10^{14} molecules/cm^2 at $\sim$190 K and $P_{HCl} = 5 \times 10^{-7}$ Torr.[2−4] The uptake of HBr on ice is reported to be 3×10^{15} at about 4×10^{-7} Torr.[1,5] Hanson and Ravishankara[1] suggested that the lower uptake of HF on ice may be associated with the fact that HF molecules do not dissociate on ice. Both HCl and HBr are believed to be ionically bound on ice,[6] and this results in higher uptake on ice. HBr forms hydrates at the PSC temperature and that strongly affects the uptake of HBr on ice.[5,7] Robertson and Clary[8] also suggested that the ionic solvation process is energetically feasible for HCl and HBr but not for HF. Ionic solvation may be a critical factor in understanding the uptake and interaction of HXs on ice at PSC temperatures. Interestingly, the polarizability of hydrogen halides increases in the same trend as the uptake of HX on ice, *i.e.*, HI > HBr > HCl > HF.[9] This indicates that the gas−surface (physical) interaction increases in the same order. Currently, very little is known about the interaction of HI on ice at about 190 K. Pickering determined that HI forms hydrates HI·4H$_2$O, HI·3H$_2$O, and HI·2H$_2$O in the temperature range of 190−230 K and measured the freezing points of the hydrates.[10,11] In this study, we will explore the trend of hydrogen halide uptake and the nature of the interaction of HI on ice.

In this paper, we report a new measurement of uptake of HI on ice and co-uptake of HI + HCl on ice at PSC temperatures. In the following sections, we will briefly describe the experimental procedures used in the determination of uptake and present the experimental results. We then discuss and compare the uptake of HI versus HBr and HCl on ice at PSC temperatures.

II. Experimental Section

The uptake measurement was performed in a flow reactor. The loss of HI on ice was monitored by a differentially pumped quadrupole mass spectrometer (QMS). The details of the apparatus have been discussed in our previous publications, and we will only briefly describe it in this article.[5,7,12]

Flow Reactor. The cylindrical flow reactor was constructed of Pyrex glass, and its dimensions were 1.70 cm inner diameter and 35 cm in length. The temperature of the reactor was regulated by a liquid-nitrogen-cooled methanol circulator and measured with a pair of J-type thermocouples located in the middle and at the downstream end. During the experiment, the temperature was maintained at either 188 or 195 K and the stability of the temperature was better than 0.3 K. The pressure inside the reactor was monitored by a high-precision baratron gauge (MKS Instrument, 690A), which was located at the downstream end of the flow reactor; stability of the pressure was better than 0.001 Torr.

Ice-Film Preparation. The ice film was prepared as follows: Helium carrier gas was bubbled through a water reservoir, which was kept in a constant-temperature, 293.2 ± 0.1 K, circulator, and the helium saturated with water vapor was admitted to the inlet of the sliding Pyrex injector. During the course of ice deposition, the sliding injector was slowly pulled out at a constant speed and a uniform ice film was deposited on the inner surface of the reactor, which was normally at 188 K. After the film was prepared, the injector was further pulled out and kept at the upstream end to prevent warming of the ice film. The ice-film length was measured both just after the deposition and several minutes after the deposition. The latter length was shorter because the ice film evaporated and recondensed in the flow tube, and we used this length to calculate the ice-film thickness. The typical ice-film length was 15 cm. The average thickness of the ice film was calculated by using the geometric area of the ice film, the mass of ice deposited on the wall, and the bulk density of the vapor-deposited ice, 0.63 g/cm^3.[2,13]

The HCl-containing ice film was prepared by bubbling helium through HCl solution (2.5 or 5.5 M) at 293.2 ± 0.1 K, and the helium gas saturated with the vapors of the HCl solution was admitted to the inlet of the sliding Pyrex injector. The film-deposition procedure was identical to that for the ice film as described above. The pH of the film is about 0.12 or 1.2. These

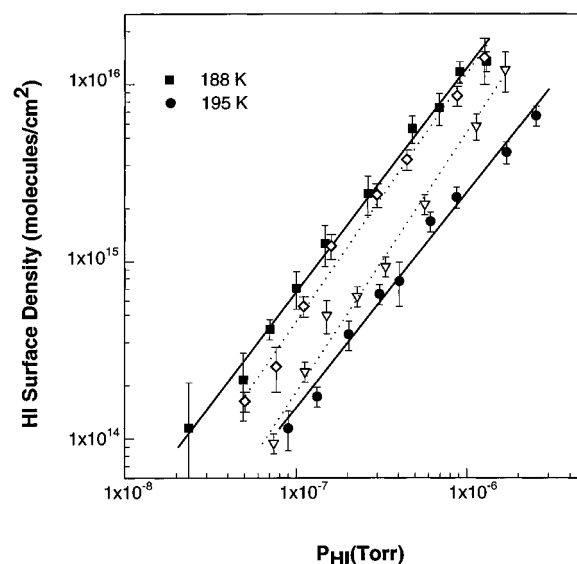* To whom correspondence should be addressed. E-mail, lchu@cnsvax.albany.edu; fax, (518) 473-2895.
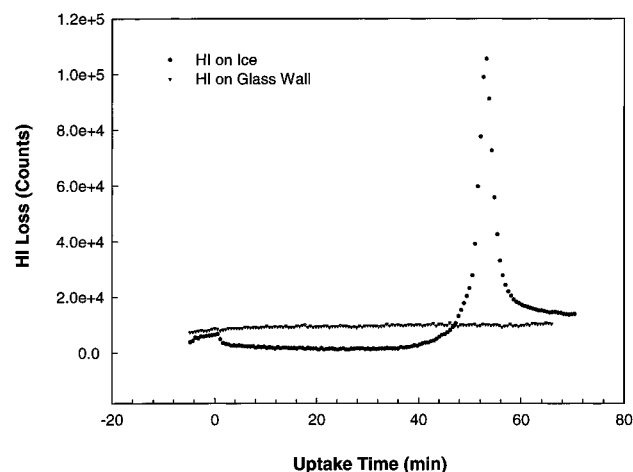
Figure 1. Uptake of HI on an ice film at $P_{HI} = 5.1 \times 10^{-7}$ Torr and 188 K. The total pressure in the flow reactor is 0.40 Torr. ● represents the HI loss onto the ice film. The uptake starts at $t = 0$ min, and desorption occurs at $t = 52$ min (the uptake time). ▽ is the HI uptake over the cold glass wall under the same conditions in a separate experiment.

Figure 2. Plot of HI uptake versus partial HI pressures at 188 K (■) and 195 K (●). Two solid lines are curve-fitting results as described in the text. Also included in this plot is the uptake of HI on HCl-containing ice films at 188 K, and they are shown by symbols ◇ and ▽ with pH values of 1.2 and 0.12, respectively. The total pressure in the reactor is 0.4 Torr. Dotted lines are the least-squares fits for these data. The error bars included on the data represent 1 standard deviation.

are relatively weakly acidic films. Under such pH conditions, the ice film should belong to the HCl/ice phase.[14] The HCl hydrates start to form at molarity values of 9 and higher. Further, the purpose of this set of experiments is to test the effect of substrate acidity on the HI uptake amount. The pH cannot truly reflect the acidity on the ice-film surface; however, we can show the difference in uptake by comparison of the uptake of HI on pure ice versus HI on the acidic ice film. The pH of ice films (bulk acidity) was determined by condensing the vapors of HCl solutions into a U-tube at liquid-nitrogen temperature. Then the pH of condensed solutions at room temperature was measured with a pH meter (Orion).

HI Mixtures and Uptake Measurements. HI−He mixtures were prepared by mixing HI (Matheson, 1.08% HI balanced with 99.9999% purity of He, calibrated gas) and helium (MG, Scientific grade 99.9999%) in an all-glass manifold, which had been previously evacuated to 10^{-6} Torr. The typical HI-to-helium mixing ratio is $10^{-4}-10^{-5}$. HI along with additional helium carrier gas was introduced into the flow reactor via the glass tubing and stainless steel metering valve, and the amount was monitored with Monel flow meters (Teledyne-Hastings). Before the uptake experiment, the HI mixture was allowed to flow through the glass tubing until saturation, which was monitored by the QMS. This ensures an accurate amount of HI flow into the reactor. The measured HI signal was proportional to the concentration of HI admitted into the flow tube. This HI signal from a known concentration was used as a calibration standard for the HI signal in the measurement. The estimated uncertainty for the HI calibration is about 5%. The loss of HI onto the ice film was measured by the QMS at $m/e^- = 128$ and is shown in Figure 1 for a typical experiment. The total amount of HI loss onto the ice film just before the desorption is defined as the uptake of HI on ice films. Neither was heating applied nor was water vapor pressure adjusted during the course of the experiment. The desorption feature was observed in nearly all experiments conducted. The ice vapor pressure could be measured at $m/e^- = 18$ simultaneously during the uptake experiment.

The HI−HCl mixture was prepared by mixing HI and HCl (Matheson semiconductor, 99.999%) gases at different pressures in the glass manifold, which was already evacuated to 10^{-6} Torr. The amount of both HI and HCl before the mixing was calibrated at STP conditions. The mixture was further diluted with helium in the glass manifold. To minimize the error in

the pressure measurements for HI and HCl gases, we kept the HCl-to-HI mixing ratio in the range of 1−20.

III. Results

Uptake of HI on Ice. The uptake of HI as a function of partial HI pressures and ice-film temperatures of 188 and 195 K is shown in Figure 2. The ice-film thickness is 1.8 ± 0.4 μm. The results indicate that the HI uptake increases with HI partial pressure. The uptake amount is higher at 188 K than at 195 K. The uptake time changes slightly from one experiment to another. It is mainly influenced by the ice-film length and thickness. The desorption peak was observed in every experiment conducted (see Figure 1). By analogy to the HBr uptake on ice,[5] we attribute the desorption to the formation of hydroiodic acid hydrates (see below). The desorption amount is compared with the uptake amount in Table 1 along with other information.

The uptake of HI was also conducted on ice films containing a small amount of HCl, pH = 0.12 and 1.2. The thickness of the film is about 1.9 ± 0.4 μm, if we assume that the density of the film is the same as the density of ice film. The uptake is lower than that HI on pure ice at 188 K, and the result is also shown in Figure 2 by the symbols ◇ (pH = 1.2 ± 0.1) and ▽ (pH = 0.12 ± 0.02).

Co-uptake of HI and HCl on Ice Films. In these experiments, the HCl molecules reach saturation quickly (typically about 10−20 min) and the HI uptake time in the co-uptake experiment resembles that in the HI uptake experiment (about 50−60 min) as shown in Figure 1. The desorption of HI molecules toward the end of the co-uptake was observed in all experiments. The changes in ice vapor pressures near the end of uptake process forced the HCl molecules to desorb as well. For HI and HCl pressures ranging from 1.0×10^{-6} to 5.7×10^{-8} Torr, the HI + HCl co-uptake at 188 K and at a film thickness of 1.8 ± 0.3 μm is shown in Figure 3a. In this plot, the vertical axis is the uptake amount of either HI or HCl at a given partial HI and HCl pressure. The detailed experimental information, uptake, and errors are listed in Table 2. The two planes in Figure 3a are the least-squares fitting of the experi-

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TABLE 1: Uptake of HI on the Ice Films as a Function of HI Partial Pressures and Total Pressure[a]

P_{HI} (Torr)	P_{total} (Torr)	temp (K)	flow speed (cm/s)	U time[b] (min)	uptake (molec/cm^2)	desorption/uptake
1.3×10^{-6}	0.405	188.4	2.34×10^3	51 ± 3	$(1.4 \pm 0.2) \times 10^{16}$	0.97
9.1×10^{-7}	0.400	188.5	2.36×10^3	56 ± 2	$(1.2 \pm 0.2) \times 10^{16}$	0.77
6.9×10^{-7}	0.399	188.2	2.26×10^3	48 ± 2	$(7.4 \pm 1.5) \times 10^{15}$	0.66
4.8×10^{-7}	0.405	188.5	2.30×10^3	67 ± 16	$(5.6 \pm 1.0) \times 10^{15}$	0.75
2.6×10^{-7}	0.400	188.4	2.32×10^3	50 ± 7	$(2.4 \pm 0.6) \times 10^{15}$	0.55
1.5×10^{-7}	0.404	188.2	2.41×10^3	52 ± 9	$(1.3 \pm 0.3) \times 10^{15}$	0.50
1.0×10^{-7}	0.400	188.5	2.37×10^3	80 ± 26	$(7.1 \pm 1.2) \times 10^{14}$	0.40
7.0×10^{-8}	0.402	188.2	2.38×10^3	60 ± 4	$(4.1 \pm 0.5) \times 10^{14}$	0.44
4.9×10^{-8}	0.400	188.5	2.35×10^3	50 ± 9	$(2.1 \pm 0.9) \times 10^{14}$	0.52
2.4×10^{-8}	0.395	188.5	2.37×10^3	70 ± 10	$(1.2 \pm 1.0) \times 10^{14}$	0.22
2.5×10^{-6}	0.402	195.4	2.72×10^3	15 ± 1	$(6.6 \pm 0.9) \times 10^{15}$	1.0
1.7×10^{-6}	0.397	195.2	2.70×10^3	11 ± 0	$(4.1 \pm 0.6) \times 10^{15}$	1.0
8.7×10^{-7}	0.398	195.0	2.63×10^3	11 ± 2	$(2.3 \pm 0.3) \times 10^{15}$	1.1
6.1×10^{-7}	0.404	195.1	2.69×10^3	13 ± 3	$(1.7 \pm 0.2) \times 10^{15}$	0.79
4.0×10^{-7}	0.405	195.2	2.72×10^3	18 ± 1	$(7.7 \pm 2.2) \times 10^{14}$	0.71
3.1×10^{-7}	0.398	195.2	2.68×10^3	15 ± 4	$(6.5 \pm 0.8) \times 10^{14}$	0.87
2.0×10^{-7}	0.400	195.2	2.69×10^3	16 ± 2	$(3.9 \pm 0.7) \times 10^{14}$	0.56
1.3×10^{-7}	0.392	195.0	2.74×10^3	26 ± 12	$(1.7 \pm 0.2) \times 10^{14}$	0.52
8.9×10^{-8}	0.406	195.3	2.48×10^3	15 ± 1	$(1.1 \pm 0.3) \times 10^{14}$	0.55

[a] The error in the table represents 1 standard deviation. The individual error for the temperature is ± 0.3 K, and P_{total} is ± 0.001 Torr. [b] Uptake time is as defined in Figure 1, and the mean values are listed in the table. The uptake time depends on the total available ice surface area. The ice-film surface area is affected by the deposition length, ice-film thickness, and roughness.

TABLE 2: Co-uptake of HI + HCl on Ice[a]

P_{HI} (Torr)	P_{HCl} (Torr)	temp (K)	HI uptake (molec/cm^2)	HCl uptake (molec/cm^2)
1.00×10^{-6}	1.00×10^{-6}	189.0	$(9.7 \pm 1.3) \times 10^{15}$	$(1.4 \pm 0.7) \times 10^{15}$
6.68×10^{-7}	6.70×10^{-7}	188.8	$(4.4 \pm 0.6) \times 10^{15}$	$(7.2 \pm 0.9) \times 10^{14}$
4.75×10^{-7}	9.56×10^{-7}	189.4	$(3.9 \pm 1.2) \times 10^{15}$	$(4.3 \pm 1.2) \times 10^{14}$
3.38×10^{-7}	3.46×10^{-7}	188.9	$(2.1 \pm 0.3) \times 10^{15}$	$(3.6 \pm 0.5) \times 10^{14}$
3.30×10^{-7}	6.63×10^{-7}	188.9	$(2.2 \pm 0.3) \times 10^{15}$	$(3.1 \pm 0.4) \times 10^{14}$
2.27×10^{-7}	2.32×10^{-7}	188.7	$(1.2 \pm 0.5) \times 10^{15}$	$(1.9 \pm 0.6) \times 10^{14}$
1.94×10^{-7}	9.72×10^{-7}	188.2	$(1.6 \pm 0.4) \times 10^{15}$	$(3.7 \pm 0.5) \times 10^{14}$
1.70×10^{-7}	3.42×10^{-7}	189.3	$(7.6 \pm 2.8) \times 10^{15}$	$(2.3 \pm 0.4) \times 10^{14}$
1.32×10^{-7}	6.56×10^{-7}	189.1	$(7.7 \pm 1.3) \times 10^{14}$	$(2.7 \pm 0.6) \times 10^{14}$
1.17×10^{-7}	1.18×10^{-7}	188.9	$(6.7 \pm 1.0) \times 10^{14}$	$(1.5 \pm 0.2) \times 10^{14}$
1.15×10^{-7}	2.32×10^{-7}	189.5	$(5.3 \pm 0.7) \times 10^{14}$	$(1.8 \pm 0.3) \times 10^{14}$
1.00×10^{-7}	2.02×10^{-7}	189.6	$(3.6 \pm 0.6) \times 10^{14}$	$(1.5 \pm 0.2) \times 10^{14}$
9.71×10^{-8}	9.56×10^{-7}	188.3	$(2.5 \pm 0.3) \times 10^{14}$	$(3.4 \pm 1.5) \times 10^{14}$
9.40×10^{-8}	4.69×10^{-7}	189.5	$(2.4 \pm 0.5) \times 10^{14}$	$(1.9 \pm 0.4) \times 10^{14}$
8.58×10^{-8}	8.53×10^{-8}	189.1	$(4.2 \pm 0.6) \times 10^{14}$	$(1.3 \pm 0.2) \times 10^{14}$
8.02×10^{-8}	7.92×10^{-7}	188.7	$(1.6 \pm 0.6) \times 10^{14}$	$(1.8 \pm 0.3) \times 10^{14}$
6.77×10^{-8}	1.36×10^{-7}	188.7	$(2.4 \pm 0.3) \times 10^{14}$	$(1.4 \pm 0.2) \times 10^{14}$
6.35×10^{-8}	6.19×10^{-7}	188.4	$(9.6 \pm 3.6) \times 10^{13}$	$(1.9 \pm 0.9) \times 10^{14}$
6.16×10^{-8}	3.07×10^{-7}	188.7	$(1.6 \pm 0.2) \times 10^{14}$	$(2.1 \pm 0.7) \times 10^{14}$
5.70×10^{-8}	5.66×10^{-8}	188.2	$(1.8 \pm 0.9) \times 10^{14}$	$(8.8 \pm 1.2) \times 10^{13}$
5.34×10^{-8}	5.27×10^{-7}	188.2	$(6.6 \pm 0.9) \times 10^{13}$	$(2.4 \pm 0.3) \times 10^{14}$
2.80×10^{-8}	2.72×10^{-7}	188.5	$(5.4 \pm 1.0) \times 10^{13}$	$(1.9 \pm 0.3) \times 10^{14}$

[a] The error represents 1 standard deviation. The error for the temperature is ± 0.3 K.

mental data in terms of

$$\log \theta = f'_{HI} \log P_{HI} + f'_{HCl} \log P_{HCl} + K'' \qquad (2)$$

where θ is the uptake of either HI or HCl. The results indicate that the HI uptake increases with HI partial pressures and decreases with HCl partial pressures. The HCl uptake increases with partial HCl pressure and also increases slightly with partial HI pressures. The HI uptake is about a factor of 10 higher than HCl for the same partial HI and HCl pressures.

IV. Discussion

HI Uptake on H$_2$O Ice Films. *Uptake Amount.* The experimental results show that HI uptake in water ice is in the range of $(1.1 \times 10^{14})-(1.4 \times 10^{16})$ molecules/cm^2 if the geometric area of the ice film is used in calculating the uptake. It is known that vapor-deposited ice films are porous and that the surface area would be larger than the geometric area.[13] This would affect the uptake. In this study, we want to compare the differences in uptake among HF, HCl, HBr, and HI, where most

of published results were based on the geometric surface areas. For ease of comparison, we choose to use the geometric surface area in the uptake calculations and assume that the ice film is smooth. On the other hand, uptake determined based on the geometric surface should be considered as an upper limit owing to the evidence that ice films can have large internal surface areas that are accessible to HI molecules. These issues will be addressed in a future study.

Bulk Diffusion of HI in Ice. The larger ionic radius of iodide means the diffusion of HI in ice should be slower than that of HCl.[15] The amount of HI dissolved in the bulk ice depends on the exposure time and the diffusion coefficient of HI in ice. Using a simple equation $z = (tD)^{1/2}$,[16] where z is the HI diffusion length, t is the exposure time, and D is the diffusion coefficient, we can estimate z. On the basis of the diffusion coefficient of HCl in ice, which is in the range of $10^{-13}-10^{-17}$ cm^2/s at 190 K,[2,17,18] we can estimate the diffusion length to be in the range of $0.2-0.002$ μm provided that $t \sim 60$ min. The diffusion length of HI tends to be in the short end; thus, we conclude that HI molecules predominately remain near the ice-film surfaces for the duration of our experiments.

Desorption of HI. Desorption of HI is a possible indication of the formation of HI hydrates on ice, which is known.[10] We measured simultaneously both the water vapor pressure and HI partial pressure in some uptake experiments. If we assume the hydrate composition to be HI·nH$_2$O, the water composition n can be determined from the slope of the log P_{HI} versus log P_{H_2O} plot.[5,19] The n value is determined to be 2.0 ± 0.2 at $P_{HI} = 1 \times 10^{-6}$ Torr and 188 K. Hydrate crystals, HI·2H$_2$O, are believed to be formed over the ice surface, and the number of HI molecules per unit ice surface area is higher than that in the adsorption of HI on ice. That explains the higher HI uptake. The formation of hydrate alters the water vapor pressure near the point of formation of hydrate. The partial water vapor pressure is being preferentially flushed out by the helium gas, thus leading to the desorption of HI in the flow reactor.

Temperature and Pressure Dependence. On the basis of the ideal adsorption isotherm, we can treat the pressure-dependent HI uptake data in terms of[5,20]

$$P_{HI} = K\theta^f \qquad (3)$$

where P_{HI} is the HI partial pressure and θ is the HI uptake on ice in terms of surface density. The parameter f indicates

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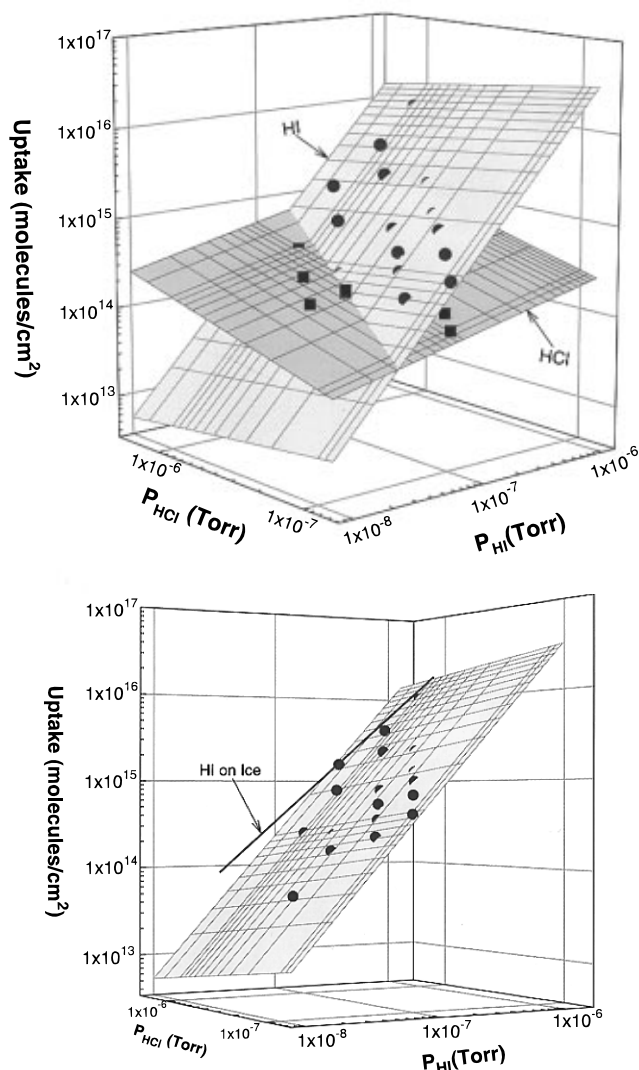
Figure 3. (Top) Plot of HI (●) and HCl (■) co-uptake as a function of partial HI and HCl pressures at 188 K and total pressure of 0.40 ± 0.01 Torr. The planes through the data are the best fits as described in the text. The HI uptake increases with partial HI pressure and is affected by the presence of HCl on ice. (Bottom) Comparison between the HI (solid line) uptake versus HI (●) co-uptake on ice. The HI uptake data set is placed at a constant HCl concentration region (1 × 10⁻⁶ Torr). The HI uptake amount in the co-uptake experiment is slightly lower than the HI uptake on pure ice. The error bars are not plotted on the figure for the ease of viewing the plots. The typical deviation of the measurement is about 20%.

associative adsorption if it is 1 and dissociative adsorption if it is 2. We can fit our data to

$$\log P_{HI} = \log K + f \log \theta \tag{4}$$

and obtain the parameter f. If we know f, K can be obtained by refitting the data to eq 3. We found that $f = 0.79$ for 188 K data and $f = 0.82$ for 195 K data. The value $f = 0.805 \pm 0.050$ can represent our data very well, and it is shown in Figure

2 as the solid lines. The value $f = 0.8$ indicates that the HI adsorption depends on surface sites of the ice film.[21]

The uptake of HI on ice increases by a factor of ∼5 as the temperature decreases by 7 K. The surface area of the ice film at 188 K is ∼25% larger than at 195 K.[13] Therefore, a reasonable explanation for the increase in uptake is an exothermic adsorption process. If so, the enthalpy of the uptake can be derived from our data. By analogy to the vapor-solution equilibria, one can write the following expression at constant pressure[22]

$$\left(\frac{\partial \ln(P_{HI}/\theta)}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \tag{5}$$

where ΔH is the enthalpy change of HI uptake into the ice film. We have obtained $P_{HI}/\theta = K\theta^{-0.2}$ (eq 3) at 188 and 195 K. By substituting eq 3 into eq 5, ΔH can be calculated using the fitted data set. We obtained $\Delta H = -17 \pm 3$ kcal/mol.

Co-uptake of HI + HCl on Ice. The co-uptake results show that the uptake of HI decreases as partial HCl pressure increases. This indicates that both HI and HCl are competing for available ice−surface sites. In these experiments, the concentration of HCl is always greater than or equal to the HI concentration. We noted that the initial loss rate of HI and HCl on ice was very similar (*i.e.*, the normalized net signal change in the first couple of data points at $t = 0$ min in Figure 1);[23] thus, we expect that the sticking probability of both HI and HCl is similar, as is the rate of adsorption. When a surface site adsorbs HCl, the site may not be available to HI. The influence of HCl on HI uptake depends on many factors; mainly the gas−surface interaction potentials and interactions between HI and HCl. Unfortunately, we cannot derive this information from the experimental results without theoretical calculations.

We may compare the uptake of HI on ice versus the HI + HCl co-uptake. The comparison is shown in Figure 3b. The HI uptake on ice is shown by a dark solid line, and it is placed over a constant HCl pressure region (*i.e.*, in the middle of the plot). It indicates that the HI uptake in the co-uptake experiment is close to the HI uptake on ice in a higher P_{HI} region. However, the HI uptake on ice is slightly higher than the HI uptake in the co-uptake experiment when the partial HI pressure is below ∼2 × 10⁻⁷ Torr, where HCl is generally in excess. This clearly shows that, with the presence of (excess) HCl, the HI uptake in the co-uptake experiment is reduced. This can be simply surface-site blocking, or HI solvation on ice is affected by HCl. This is also reflected in the f parameter in both eqs 2 and 3. The results are summarized in Table 3. The value $f_{HI} = 0.62$ of the co-uptake is slightly lower than $f_{HI} = 0.80$ of HI uptake on ice. The value $f_{HI} = 0.62$ shows that uptake process strongly depends on the surface site and agrees with competition of both HI and HCl for the available surface sites.

The uptake of HI on acidic ice shows a lower uptake in Figure 2. The purpose of this experiment is to show that a small amount of HCl in ice slows down the HI uptake process especially at lower P_{HI}. This may alter the proton solvation process for HI, which resembles the common-ion effect in

TABLE 3: List of the f Parameters[a]

		f'_{HI}	f_{HI}	f'_{HCl}	f_{HCl}	f_{HBr}	reference
co-uptake	HI	1.63 ± 0.08	0.62 ± 0.03				this work
	HCl			0.42 ± 0.08	2.3 ± 0.5		this work
uptake	HI		0.81 ± 0.05				this work
	HBr					0.80 ± 0.06	ref 5
	HCl				0.86, 2.4		refs 20, 27
	HCl				1.8, 2.0		refs 2, 7

[a] $f'_{HI} = 1/f_{HI}$ and $f'_{HCl} = 1/f_{HCl}$.

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solutions, or Cl^- reduces the active ice surface sites. A similar process may very well occur for the HI + HCl co-uptake experiment.

HCl uptake in the co-uptake experiment increases as partial HCl pressure increases. It also increases slightly as the partial HI pressure increases. The nature of the latter process is not very clear. The fitted HCl uptake has a fairly large error, and this increases the uncertainty. One possible explanation is that the presence of both HI and HCl on ice surfaces modifies the solvation process for both HCl and HI. HI has a higher $-pK_a$ value and easily yields hydronium ion.[24] The proton transfer between adsorbed HI and HCl at 188 K is perhaps controlled by a quantum tunneling pathway.[8] The solvated HI easily transfers a proton to HCl, which leads to an eased HCl solvation process on ice, and that may result in slightly higher HCl uptake.

Comparison of HXs Uptake on Ice. The uptake of HCl on ice has been studied extensively. A summary list[2] for the HCl uptake on ice in the partial HCl pressure range of (7×10^{-8})–(2×10^{-6}) Torr and temperature of 188–201 K is available on the basis of several groups' work.[2-4,25] The HCl uptake amount is in the range of (8×10^{13})–(3×10^{15}) molecules/cm^2, dependent on the experimental conditions. Our HCl uptake in the co-uptake experiment falls exactly in this range (see Table 2). As was discussed in the previous section, the effect of HI on the HCl uptake is relatively small, and thus the HCl uptake amount in the co-uptake experiment is very close to that of HCl on ice.

To our knowledge, there have been no reported data for the HI uptake on ice under similar experimental conditions. It is useful to compare the trend of HX uptake on ice at 188–201 K. The uptake of HF on ice is $\sim 10^9$ molecules/cm^2 at $P_{HF} = 10^{-7}$ Torr,[1] HCl uptake is about 5×10^{14} molecules/cm^2 at $P_{HCl} = 5 \times 10^{-7}$ Torr,[2-4] HBr uptake is 4×10^{15} molecules/cm^2 at $P_{HBr} = 5 \times 10^{-7}$ Torr,[1,5] and HI uptake is 5×10^{15} molecules/cm^2 at 5×10^{-7} Torr. Thus, the uptake of HX on ice has the following trend: HI $\approx$ HBr > HCl > HF. As a first-order approximation, the gas–surface interaction can be associated with polarizability of the molecules, which is inconsistent with the uptake trend. We believe the chemical nature of system has a large impact on the uptake, namely, dissociation and solvation of HX on ice. The uptake trend can be associated with the acidity of HX well. The $-pK_a$ of HX follows HI $\leq$ HBr > HCl > HF.[24] This strongly supports the effect of acidity on the HX uptake and is consistent with the suggestion of ionic solvation process energetically feasible for HCl and HBr.[8] Whether HX forms a hydrate at the PSC temperature may depend on the thermodynamic stability of the HX hydrates. In general, HF,[26] HCl,[3,14] HBr,[5,7] and HI[10] form hydrates, but this is not necessary at the PSC temperature.

The f parameter in eq 4 could potentially indicate the bonding nature of HX on ice. We may compare the f parameter for HCl,[2,20,27] HBr,[5] and HI. The f value for HBr and HI on ice is almost the same, 0.8, and the f value for HCl is about or less than 2 (see Table 3). This shows that both HBr and HI on ice

at 188 K are not in a "free" ionic form and is consistent with hydrates near the ice–film surface. For f to be less than unity indicates that the uptake rate depends on the HX surface coverage. HCl exhibits an ionic form on ice surfaces, and a molecular-dynamic calculation clearly show this ionic nature.[6]

The short photochemical lifetime of HI indicates that the heterogeneous HI reaction itself in the polar stratosphere may not play a significant role in ozone depletion.[28] With the higher HI uptake on ice, the removal of HI on clouds and aerosols may very well influence the budget of iodine in the stratosphere.

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