

# Morphology and Surface Areas of Thin Ice Films

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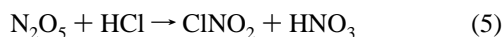
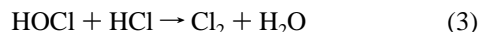
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Received: October 11, 1996; In Final Form: March 24, 1997<sup>⊗</sup>

Thin ice films formed by deposition from the vapor phase in flow-tube reactors have been used to simulate polar stratospheric cloud surfaces in order to obtain laboratory data on uptake and heterogeneous reaction rates. In the present study, ice films are formed in such a reactor, and their surface areas are determined *in-situ* from BET (Brunauer, Emmett, and Teller) analysis of gas adsorption isotherms. The measured surface areas are found to be strongly dependent on the total mass of ice deposited. The specific surface areas of ices prepared at 77 or 196 K are consistent with previous data obtained by using thicker nonuniform ice films. In a separate apparatus, environmental scanning electron microscopy (ESEM) is used to obtain particle sizes and shapes and to investigate the morphology of the ices prepared on borosilicate, aluminum, and silicon substrates. Ice films on borosilicate substrates are found to comprise micron-sized granules randomly packed in layers. The uptake of HCl in ice films prepared at 196 K using the same flow-tube reactor is also measured to be approximately  $1 \times 10^{14}$  molecules/cm<sup>2</sup> when a partial pressure of HCl of about  $5 \times 10^{-7}$  Torr is used. Similar to the surface areas, the total uptake is strongly proportional to the mass of ice deposited. The combined evidence suggests that even for thin ice films (1) surface areas are greater than the geometric area of the flow-tube reactor and (2) interaction of pore diffusion with surface reaction should be accounted for in the determination of uptake and heterogeneous reaction rates.

## Introduction

The loss of ozone in the Antarctic stratosphere is well-known to be initiated by heterogeneous reactions occurring on the surface of ice clouds that form when temperatures drop during the winter.<sup>1,2</sup> In the laboratory the ice clouds have been simulated by condensing the vapors onto cold substrates, for example, borosilicate glass and silicon. The resulting ice films have been used to obtain HCl uptake parameters<sup>3–5</sup> and reaction probabilities for the following reactions:<sup>6–11</sup>



In order to use these probabilities in atmospheric models, we need to know the area of the film surface that actually participates in the reaction. It is important to know not only the total surface area but also the film morphology in order to determine where and how the surface is situated and, thus, what fraction of surface is available for uptake or reaction.

Total surface area measurements have been previously reported<sup>12</sup> for nonuniform ice films prepared in a separate apparatus with thicknesses 120–540  $\mu\text{m}$ . These earlier experiments showed that the total area of these thick films is much larger than the geometric area of the underlying substrate. Currently there is a controversy concerning the thin (1–50  $\mu\text{m}$ ) ice films actually used in flow reactors. The disagreement centers on whether to use the geometric area or a value between

the geometric area and the the total surface area of these films.<sup>11</sup> The uptake of HCl on ice has also been investigated<sup>8</sup> in the absence of simultaneous ice surface area measurements. In this article we report *in-situ* measurements of ice surface areas and HCl uptake on thin ice films deposited in a flow reactor.

Preliminary results on the morphology of ice films investigated by environmental scanning electron microscopy (ESEM) without a micromanipulator have been published.<sup>13</sup> In this article a detailed study of the morphology of ice films using ESEM and a micromanipulator is discussed. The use of a micromanipulator is essential to discern the internal structure of these films.

## Experimental Methods

**Morphology Measurements.** The morphology of ice films was investigated by using ESEM. Ice films were formed by passing a mixture of H<sub>2</sub>O vapor and nitrogen over polished borosilicate, silicon, or aluminum plates which were cooled to about 77–190 K. Total pressure was about 2.0 Torr with H<sub>2</sub>O vapor partial pressures near 0.04 Torr. The silicon plate was extremely smooth; surface irregularities such as cracks or pits were smaller than 0.1  $\mu\text{m}$ , the highest resolution at which the microscope was operated. However, the surfaces of the aluminum and borosilicate plates were found to have hairline cracks and/or machining tool marks. As discussed below, the smoothness of these plates affects the morphology of ice films. A micromanipulator was used to remove some of the large ice granules situated at the top of the ice film so that the internal packing structure of these films could be observed.

**Surface Area Measurements.** A U-shaped fast-flow reactor was used to measure surface areas of ice films deposited from water vapor in a helium carrier using a sliding injector. The reactor was made of borosilicate tubing 40 cm in length and 2.50 cm inside diameter. The injector, also made of borosilicate tubing, was 100 cm in length and 1.25 cm outside diameter; it was heated by passing a large flow of nitrogen gas through an

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, July 1, 1997.

outside jacket in order to prevent ice condensation inside the injector. The ice film was prepared by moving the injector from the bottom to the top of the flow tube. Temperature was measured by using a pair of thermocouples attached to the wall. In this study either a solid  $\text{CO}_2$  plus methanol slurry or liquid nitrogen was used as a refrigerant. Flow rates of water vapor in helium were controlled by using a stainless steel needle valve and read on a Hastings mass flowmeter. The mass of ice deposited in the flow reactor was calculated from the flow rate and the duration of deposition. The thickness,  $h$ , of ice films ranged from 1.04 to  $47.4\ \mu\text{m}$  and was calculated from the mass,  $M$ ; the underlying geometric area of the flow tube,  $A_{\text{geom}}$ ; and the bulk density,  $\rho_b = 0.63\ \text{g/cm}^3$ ;  $h = M/(\rho_b A_{\text{geom}})$ .<sup>12</sup>

Surface areas were measured by using the Brunauer, Emmett, and Teller (BET) method to analyze adsorption isotherms obtained at a temperature of 77 K.<sup>14</sup> The U-tube was submerged in liquid nitrogen, and isotherms were determined volumetrically by expanding from a calibrated volume of  $519.6\ \text{cm}^3$  maintained at room temperature. The adsorptive gas used in these experiments was Kr. The saturation pressure ( $P_0$ ) of Kr was measured to be 1.70 Torr, which agrees exactly with the literature value for the vapor pressure of the solid at 77 K.<sup>15</sup> A value of  $20.2\ \text{\AA}^2$  was used as the average area occupied by Kr atoms on the surface.<sup>16,17</sup> The pressure measurements were corrected for thermal transpiration between the cold adsorption cell and the room-temperature section of the apparatus. Nonideal gas corrections were negligible. The surface area measurements were corrected for the surface area of the blank cell, which was determined in a separate experiment. The error limit of these measurements was estimated to be about  $\pm 100\ \text{cm}^2$ .

**HCl Uptake Measurements.** The uptake of HCl in water ice was investigated in the same flow-tube reactor interfaced with a differentially pumped quadrupole mass spectrometer. HCl–He mixtures were prepared by mixing HCl (Matheson semiconductor-purity, 99.995%) and He (Matheson-purity, 99.9999%) in a glass manifold which was previously evacuated to less than  $10^{-6}$  Torr. Flow rates of the mixture were monitored by a Hastings mass flowmeter. At first the HCl–He mixture was admitted to the flow reactor through an inlet located at the downstream end; this bypassed the ice film and allowed the vacuum lines to be conditioned with HCl. At the start of a typical uptake measurement, the flow was redirected through another inlet at the upstream end of the ice film.

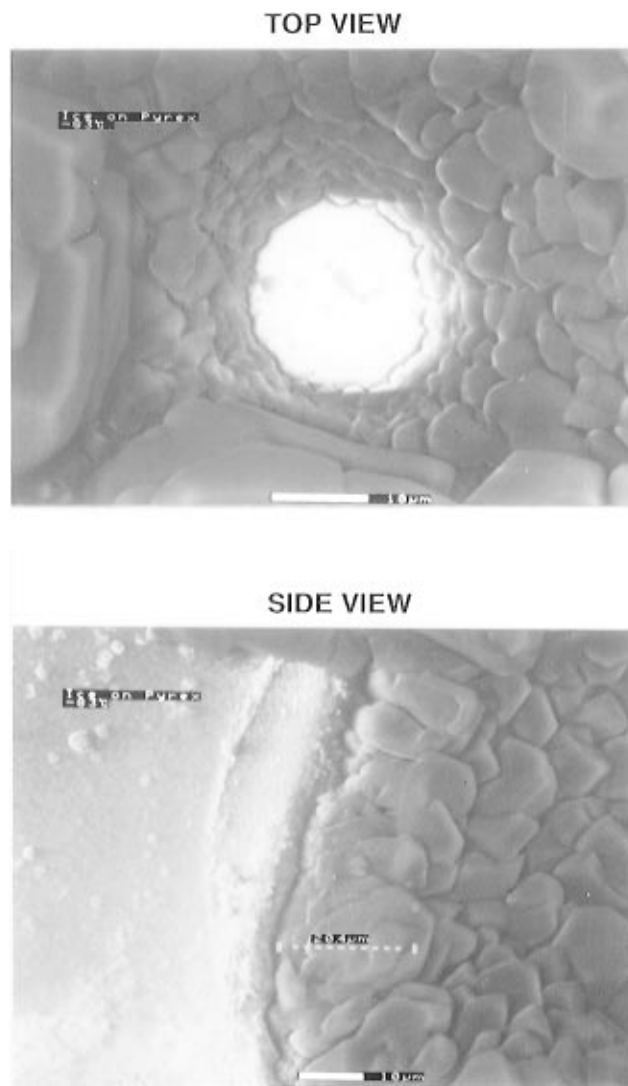
## Results and Discussion

**Morphology Measurements.** The morphology of ice films deposited on a borosilicate plate at 190 K is shown in Figure 1. In the top-view panel a micromanipulator was used to remove a large ice granule in order to make the underlying structure clearly discernible. In the side-view panel the thickness of ice film can be measured; again, the layered packing is evident.

A silicon plate was also examined by the ESEM; no cracks, scratches, or pits were discernible. Water ice deposited on this plate exhibited nearly perfect hexagonally shaped crystals which were surrounded by much smaller crystals ( $d < 1\ \mu\text{m}$ ). This is in contrast to the data obtained for the ice films deposited on a borosilicate plate, as shown in Figure 1.

We have also performed some experiments by depositing ice films on borosilicate or silicon plates at 93 K. By using a resolution of about  $0.1\ \mu\text{m}$ , we find that the films are comprised of very small amorphous particles (not crystalline). Moreover, as discussed in a previous article,<sup>12</sup> micropores may be present inside the particles at this temperature.

**Surface Area Measurements.** 1. *Ice Films Deposited at 77 K.* In order to compare the results for ice films deposited at



**Figure 1.** Electron micrographs of an  $\text{H}_2\text{O}$  ice film formed by vapor deposition onto a borosilicate substrate.

warmer temperatures, we performed some experiments at 77 K. The ice film was formed over a period of 40 min by moving the injector from the bottom to the top of one arm of the U-shaped flow tube. The tip of the injector was about 0.5 cm above the liquid nitrogen level, which was raised as the injector was moved upward. The length of the flow reactor covered by ice was about 20 cm. The mass of ice was 63.9 mg and the thickness was  $5.78\ \mu\text{m}$ . The BET plot is linear over a relative pressure ( $P/P_0$ ) range, 0.05–0.4; this is typical of many BET plots and implies that krypton adsorption on these ice films is well behaved. The ratio of the ice surface area to the geometric area of the underlying flow tube was calculated to be 928, and the specific surface area was determined to be  $256.2\ \text{m}^2/\text{g}$ .

We also performed a series of experiments by varying the mass from 19.7 to 119.1 mg (thickness =  $1.78$ – $10.8\ \mu\text{m}$ ). The results are summarized in Table 1. The ratio of the ice surface area to the geometric area increases from 305 at a thickness of  $1.78\ \mu\text{m}$  to an average of about 2500 at  $10.8\ \mu\text{m}$ . The increase in this ratio with thickness was also observed for ice films at 196 K (see below). The specific surface area was also calculated, and the results are shown in Table 1. The specific surface area is independent of the thickness within experimental error; this differs from ice deposited at 196 K and suggests that the morphology of ice films formed at the two temperatures may be significantly different (see below). The specific surface area of thin ice films at 77 K reported in this article is in

**TABLE 1: Summary of Measurements of Ice Surface Areas at 77 and 196 K**

<i>T</i> (K)	mass (mg)	rate (mg/min)	<i>h</i> <sup>a</sup> (μm)	<i>A</i> (m <sup>2</sup> )	<i>S<sub>g</sub></i> (m <sup>2</sup> /g)	ratio <sup>b</sup>
77	19.7	2.0	1.78	6.9	350.2	305
	39.4	2.0	3.56	12.7	321.3	724
	63.9	1.6	5.78	17.4	273.1	928
	93.9	2.4	8.49	24.1	256.2	1300
	118.5	2.4	10.7	48.9	411.7	2778
	119.1	2.4	10.8	40.0	336.2	2269
av =					324.8 ± 56.1	
196	18.7	1.9	1.69	0.028	1.50	1.6
	41.2	1.9	3.73	0.021	0.51	1.2
	66.5	2.0	6.01	0.043	0.65	2.4
	92.4	2.1	8.35	0.051	0.55	2.9
	100.2	2.0	9.06	0.089	0.89	5.1
	103.0	2.1	9.31	0.113	1.10	6.4
	204.8	2.0	18.5	0.043	0.21	2.4
	211.0	2.1	19.1	0.064	0.30	3.6
	328.8	2.0	29.7	0.109	0.33	6.2
	379.2	2.5	34.3	0.084	0.22	4.8
	210.0	3.5	19.0	0.067	0.32	3.8
	10.3	6.4	1.04	0.061	5.92	3.5
	30.6	6.4	3.09	0.040	1.31	2.3
	33.1	6.4	3.35	0.066	1.99	3.8
	130.0	6.4	11.8	0.108	0.83	6.2
	132.0	6.4	11.9	0.073	0.55	4.2
	199.3	6.4	18.0	0.108	0.54	6.2
	260.4	6.4	23.5	0.142	0.55	8.1
	268.2	6.4	24.2	0.102	0.38	5.8
	360.5	6.4	32.6	0.163	0.45	9.3
	400.0	6.4	36.2	0.085	0.21	4.8
	443.1	6.4	44.8	0.129	0.29	7.3
	524.6	6.4	47.4	0.129	0.25	7.3

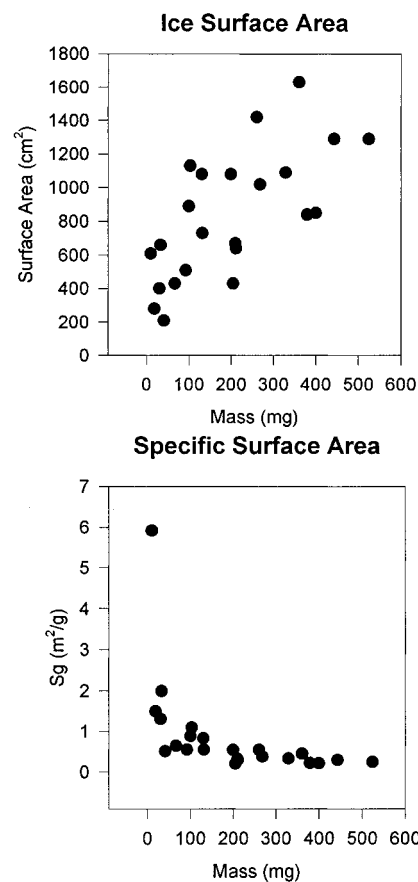
<sup>a</sup> Calculated from the sample mass, the geometric area, and the bulk density (0.63 g/cm<sup>3</sup>) measured near 200 K.<sup>12</sup> <sup>b</sup> Ratio of ice surface area/geometric area.

excellent agreement with previous results (100–400 m<sup>2</sup>/g) for thicker films.<sup>12,18–21</sup>

**2. Ice Films Deposited at 196 K.** In these experiments ice films were prepared similarly to those at 77 K. Deposition rates were varied from 1.9 to 6.4 mg/min, and the flow tube was cooled to 196 K by submerging it in a dry ice/methanol slush. After the deposition, the flow tube was cooled to 77 K for the BET measurement by immersing it in liquid nitrogen. The linearity and intercept in the BET plot imply that the adsorption isotherm is well behaved. After subtracting the surface area of the glass wall (determined in a blank experiment), we obtain a value of 6.2 for the ratio of the ice surface area to the geometric area in one of these experiments. The result suggests that ice films prepared in this manner are not smooth, nonporous solids and the use of the geometric area for the determination of the uptake coefficients or reaction probabilities in some previous studies is not valid.

A series of experiments were performed for ice mass ranging from 10.3 to 524.6 mg (thickness = 1.04–47.4 μm). The results are listed in Table 1 and plotted in Figure 2. The deposition rate was varied from 1.9 to 6.4 mg/min. The ratio of the ice surface area to the geometric area was found to vary from 1.6 to 9.3. In addition, the ice surface area is linearly proportional to the ice mass deposited as shown in the top panel of Figure 2. The specific surface area (*S<sub>g</sub>*) was found to vary from 5.92 m<sup>2</sup>/g for thinner ices to about 0.21 m<sup>2</sup>/g for thicker ices (as shown in the bottom panel); these values are in good agreement with previous results (0.40–10.8 m<sup>2</sup>/g) obtained for thicker ice films in a separate apparatus.<sup>12</sup>

As seen in Figure 2, *S<sub>g</sub>* decreases markedly as the mass (or thickness) increases, especially below 50 mg. This is in contrast to the results for ices deposited at 77 K (see above).

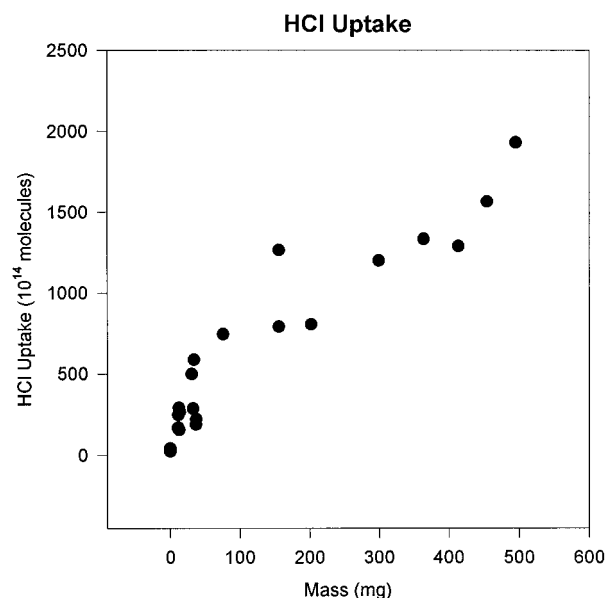


**Figure 2.** (a) Total ice surface areas vs mass for films deposited at 196 K. (b) Specific surface areas vs mass for films deposited at 196 K.

The average particle size, *d*, is inversely proportional to *S<sub>g</sub>*:  $d = 6/(\rho_t S_g)$ , where  $\rho_t$  is the true density of the ice. The observed decrease in *S<sub>g</sub>* suggests that the ice particle size increases as the film becomes thicker and the total area does not increase linearly with the mass. This increase in granule size with thickness has been observed previously by using ESEM to examine ice films forming near 200 K.<sup>13</sup>

**HCl Uptake Measurements.** The uptake of HCl in the ice films characterized above was measured at 196 K. The total amount of HCl adsorbed was obtained by integrating the HCl flow rates and calibrating HCl signal intensities over the observation time. The mass was varied from 11.3 to 496 mg (thickness = 1.04–44.8 μm). The HCl partial pressure was held at about  $5 \times 10^{-7}$  Torr in a total pressure of 0.47 Torr. The average flow velocity was 625 cm/s. The results are shown in Figure 3, which displays the HCl uptake as a function of mass. The uptake increases linearly with the ice mass deposited in the reactor. This suggests that the ice films are not smooth and ice surface areas should be greater than the geometric area. The average uptake was measured to be about  $1.0 \times 10^{14}$  molecules/cm<sup>2</sup> for thicker ice films (>100 mg). The amount of HCl adsorbed on borosilicate substrates (less than  $1 \times 10^{13}$  molecules/cm<sup>2</sup>) was found to be much smaller than on ice films; we have corrected for this contribution.

In earlier work we used a layer model to estimate the HCl surface density and obtained a value of  $2 \times 10^{13}$  molecules/cm<sup>2</sup> at 188 K and an HCl pressure of  $2.1 \times 10^{-7}$  Torr.<sup>8</sup> As noted in our previous study the HCl uptake is a complex function of temperature, HCl partial pressures, and ice film thickness. In addition, ice surface areas are very sensitive to the deposition temperature. Our previous investigation was performed at temperatures of 188 and 193 K. The variation of 3–8 K may result in significant differences in surface areas. Considering



**Figure 3.** Summary of HCl uptake measurements for ice films formed by vapor deposition at 196 K.

the simplicity of the model used, the sensitivity to experimental parameters, and the combined experimental errors, the HCl uptake reported here is in reasonably good agreement with the earlier estimate. Finally, it is noted that the nature of the HCl uptake on ice surfaces as a function of temperature, film thickness, and the HCl partial pressure has been discussed more fully in a previous publication.<sup>8</sup>

## Conclusions

In this article we report a set of three measurements of ice films used in the laboratory: (1) environmental scanning electron microscopy, (2) *in-situ* ice surface areas using BET analysis, and (3) *in-situ* uptake of HCl. The morphology of ice films clearly depends upon the substrate and the deposition temperature used. Nearly perfect hexagonal ice crystals have been observed on a silicon window at a deposition temperature of 190 K. However, a layer of irregular micrometer-sized ice granules forms on aluminum or borosilicate plates. Much smaller ice granules are clearly present when the deposition temperature is reduced to 77 K. BET measurements show that ice surface areas are significantly greater than the geometric area of the flow-tube reactor at 196 and 77 K. This observation

is further supported by the measurement of the HCl uptake, which increases linearly with the ice mass (film thickness). The combined evidence suggests that, even for thin ice films, the surface areas are greater than the geometric area of the flow-tube reactor and that the mathematical model of surface reaction and pore diffusion we have previously developed should be used in the determination of uptake and heterogeneous reaction rates on these surfaces.<sup>10,11</sup>

**Acknowledgment.** The research described in this article was performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. We thank Tom A. Hardt of ElectroScan Corp. for his assistance in obtaining scanning electron micrographs. R.S.T. gratefully acknowledges the financial support from Maj and Tor Nessling Foundation.

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