

### 5.3 *Solid Morphology Measurements* (L. F. Keyser and M-T. Leu)

#### 5.3.1 Introduction

In the laboratory, ice films formed by freezing from the liquid or more frequently by deposition from the vapor phase have been used to simulate stratospheric cloud surfaces for measurements of reaction and uptake rates. To obtain intrinsic surface reaction probabilities that can be used in atmospheric models, the area of the film surface that actually takes part in the reaction must be known. 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 it is available for reaction. Information on the structure of these ice films has been obtained by using several experimental methods. In the sections that follow, these methods will be discussed, then the results will be used to construct a working model of the ice films, and finally the model will be applied to an experimental study of HCl uptake by H<sub>2</sub>O ice.

#### 5.3.2 Experimental Techniques

5.3.2.1 Environmental Scanning Electron Microscopy. ESEM utilizes gaseous secondary electron detection, which allows operation at total pressures between 1 and 50 torr. By using this technique, it is possible to form and study ice films under conditions (temperature, pressure, supersaturation, deposition rate, sample size, film thickness and substrate) similar to those used in many uptake and surface reaction measurements.<sup>5.3-1</sup> In the experiments described here, the films are formed on a cold borosilicate substrate mounted on a cold stage within the specimen chamber of an ESEM instrument (ElectroScan Corp., Wilmington, MA). During the cool down period, the chamber is either evacuated or purged with a stream of dry nitrogen. When the temperature is below about 200 K, a mixture of H<sub>2</sub>O vapor in air or a 3:1 mixture of H<sub>2</sub>O and HNO<sub>3</sub> vapors in N<sub>2</sub> are directed at the substrate through an injector positioned parallel to and about 2.5 cm away from its surface. Micrographs are recorded during the

deposition process and during subsequent warming of the films. The very earliest stages of condensation are difficult to observe; but after several minutes, individual granules are clearly observable. Average granule size increases with deposition time and, hence, with thickness. A micrograph of H<sub>2</sub>O ice at 190 K is shown in Figure 1. The film is composed of loosely packed individual granules with some agglomerates near the outer surface. A few of these surface agglomerates have been moved aside to reveal the film's interior, which is made up of almost uniformly sized granules stacked in layers. When the ice films are warmed to 215 - 220 K, the granules increase slowly in size and some sintering is observed.

The ESEM experiments provide direct information on the sizes of the granules that comprise the ice films. These sizes can be used to estimate the total area contributed by the external surfaces of the individual granules by using eq 5.3-1.<sup>5.3-2</sup>

$$S_g = 6/\rho_l d \quad (5.3-1)$$

where  $S_g$  is the specific surface area in cm<sup>2</sup> g<sup>-1</sup>,  $\rho_l$  is the true density of the solid in g cm<sup>-3</sup>, and  $d$  is the granule size in cm. In Figure 2 surface areas calculated from ESEM experiments by using equation 5.3-1 are compared with areas obtained from the BET analysis discussed in the next section.

5.3.2.2 BET Surface Areas. Total surface areas can be measured by using the Brunauer, Emmett and Teller (BET) model to analyze gas adsorption isotherms.<sup>5.3-3</sup> The surfaces sampled by this method include the outer surfaces of the micrometer-sized granules as well as any internal pores of the granules themselves down to about 2 nm in size. Details of the BET method applied to vapor-deposited ice films have been discussed previously.<sup>5.3-4,5.3-5,5.3-6</sup> The ices used for the BET measurements are prepared under conditions similar to those used for the ESEM measurements discussed above. The films are deposited near 200 K; in some of the runs, the ice is then warmed or annealed at higher temperatures. In Figure 2 the BET surface areas are compared with the areas

calculated from the ESEM measurements. The open symbols give the results for annealed ices. The good agreement between the two types of experiment shows that the total surface area of the annealed films can be fully accounted for by the external area of the ice granules. That is, the granules composing the annealed films exhibit no significant internal porosity.

The filled symbols give data for unannealed ices. In this case the BET areas are much larger than the values calculated from the ESEM experiments. This suggests a more complicated morphology in which the unannealed ice granules are themselves porous. In the case of cubic H<sub>2</sub>O ice, the ESEM areas lie between the BET value and the best fit of the annealed data. Large reductions in surface areas have been observed previously in studies of the cubic-to-hexagonal phase change of H<sub>2</sub>O ice.<sup>5.3-7</sup> These results show that the film morphology can be simplified and the surface area reduced by annealing the ices above the deposition temperature; however, the annealing does not entirely remove the film porosity.

5.3.2.3 Bulk Densities. An ice film can be further characterized by its bulk density, which is defined as the weight of the ice per unit apparent volume of the film, that is, the weight per unit volume including all voids. The true density is the weight per unit volume of actual solid material. X-ray structure data give values of 0.925 and 1.625 g cm<sup>-3</sup> for the true density of H<sub>2</sub>O ice and NAT ice, respectively.<sup>5.3-8,5.3-9</sup> Because of possible random and irregular solid packing, the bulk density of vapor-deposited ice is expected to be less than the true density. To obtain bulk densities, ice-film profiles are recorded photographically and the volumes are then calculated by measuring the differences between film heights during the deposition process. Total weights are determined after collecting the sample by vacuum distillation. Details have been discussed earlier.<sup>5.3-6</sup> The resulting bulk densities, 0.63 g cm<sup>-3</sup> for H<sub>2</sub>O ice and 0.84 g cm<sup>-3</sup> for NAT ice, are much lower than the true solid densities. The results are independent of

temperature between 200 and 230 K. The low bulk densities found are consistent with the ESEM results, which show that these films are composed of loosely packed granules.

### 5.3.3 Working Model of Porous Ice Films

To convert a loss rate measurement into a surface-reaction or uptake probability, the area of the reactive surface must be known. For films that are smooth and nonporous, the geometric area of the underlying substrate may be used. However, the characterization studies outlined above show that these films can have surface areas much larger than the geometric area and that they are composed of loosely consolidated granules with diameters of a few micrometers. The large internal areas of such films consist of the surface areas of the individual ice granules. The loose packing of the granules makes these films highly porous and allows rapid gas-phase diffusion into the interior of the film. For porous films, the observed loss rates are affected by the internal surface area; and corrections, which account for the interaction of surface reaction and pore diffusion, are required in order to extract intrinsic probabilities.

In order to carry out these corrections, a working model of a porous ice film has been developed.<sup>5.3-10,5.3-11</sup> In this approximation, the film comprises spherical granules stacked in layers and any change in reactivity or uptake capacity with thickness depends only on the number of layers,  $N_L$ . For a porous H<sub>2</sub>O-ice film approximated by hexagonal close packing, the relation between the observed reaction probability,  $\gamma(\text{obs})$ , which is calculated by using the geometric area, and the true value,  $\gamma_t$ , is given by<sup>5.3-10</sup>

$$\gamma(\text{obs}) = \gamma_t \pi^{3/2} \{1 + \eta[2(N_L - 1) + (3/2)^{1/2}]\} \quad (5.3-2)$$

where  $\eta$  is an "effectiveness factor" or the fraction of the total film surface that participates in the reaction;  $\eta$  is determined by the relative rates of surface reaction to pore

diffusion.<sup>5.3-10,5.3-12</sup> To apply eq 5.3-2 to an ice film of given thickness, the relation between  $N_L$  and thickness,  $h$ , is needed. This can be obtained by fitting the model to an observed change in reactivity or uptake capacity with thickness. An example of this method as applied to the reaction of  $N_2O_5$  on ice and NAT<sup>5.3-13</sup> has been discussed in detail.<sup>5.3-10</sup> The relation between  $N_L$  and  $h$  that best fits the data can be approximated by:  $N_L = 2 + 9 \log_{10}h$ , where  $h$  is in  $\mu\text{m}$ . Another example is the application of the layer model to the change in HCl uptake with ice thickness; this is discussed in the next section. This method provides an internal calibration of the model to ice films formed under specified conditions. Once the relation between  $N_L$  and thickness is known, it can be used to approximate similarly formed films and applied to correct observed uptake capacities and loss rates on these surfaces.

The ratio of total film area to the geometric area of the underlying substrate can be estimated by using the layer model:<sup>5.3-10</sup>

$$A_{\text{total}}/A_{\text{geom}} = (6\rho_b/\rho_t)[1 + (N_L-1)(2/3)^{1/2}] \quad 5.3-3$$

Using the relation between  $N_L$  and  $h$  given above, the area ratio for a  $H_2O$  ice film 1  $\mu\text{m}$  thick is 7.4. This suggests that even for thin films the total surface area can be much greater than that of the substrate.

#### 5.3.4 Application to HCl Uptake by $H_2O$ Ice

The layer model can be used to analyze HCl uptake data by  $H_2O$  ice. The data are obtained by using a flow reactor interfaced with a differentially pumped quadrupole mass spectrometer.<sup>5.3-11</sup> The HCl partial pressure is  $2.1 \times 10^{-7}$  torr and the temperature of the flow tube is 188 K. Observed HCl uptake capacities vary from  $2 \times 10^{14}$  to  $1 \times 10^{15}$  molecules/ $\text{cm}^2$  (based on the geometric area of the flow reactor) for film thicknesses between 0.5 to 15.7  $\mu\text{m}$ . The data can be analyzed in terms of the layer model outlined in

the previous section; in this case the relation between  $N_I$  and  $h$  is modified to include films down to  $0.5 \mu\text{m}$  in thickness. The results are shown in Figure 3. The HCl surface density that best fits the data is  $\sim 2 \times 10^{13}$  molecules/cm<sup>2</sup>. This surface density value accounts for the total surface area of the ice film; it is a factor of 25 less than the average surface density obtained from the data by using the geometric area of the flow reactor. These results confirm that the vapor-deposited ice films used in the experiments are highly porous and have large surface areas. A similar procedure can be used to analyze the HCl uptake data obtained recently by Abbatt et al.<sup>5,3-14</sup>

## REFERENCES

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## FIGURE CAPTIONS

**Figure 5.3-1.** Micrograph of a H<sub>2</sub>O ice film deposited from the vapor phase onto a borosilicate substrate at 190 K. The partial pressure of H<sub>2</sub>O is about 0.05 torr in 2 torr of air. Environmental secondary electron detection is used with an accelerating voltage of 12 kv and a specimen distance of 9.6 mm; total observation time is about 30 minutes. In order to reveal the interior of the film, a micro-manipulator is used to move aside some of the surface agglomerates.

**Figure 5.3-2.** Comparison of surface areas obtained by using ESEM and BET techniques with ice films vapor-deposited onto borosilicate substrates. The temperature plotted is the deposition temperature for unannealed ice samples; otherwise the maximum annealing temperature is used. Annealing times are between 15 and 60 minutes. The ESEM areas are calculated from average granule sizes by using equation 5.3-1; the BET areas are obtained by analyzing gas-adsorption isotherms. The error bars represent one standard deviation at a given temperature; for the BET results, this is about the average of several separate runs; for the ESEM results, this is about the average of one run and is due to granule growth during the observation time. (a) HNO<sub>3</sub>-H<sub>2</sub>O ice obtained by depositing a 3:1 mixture of H<sub>2</sub>O and HNO<sub>3</sub> vapors: ▼, ESEM unannealed; ▽, ESEM, annealed; ●, BET unannealed; ○, BET annealed. The line is a linear least-squares fit of all the ESEM data and the annealed BET data. (b) H<sub>2</sub>O ice: ■, ESEM unannealed, cubic ice; ▼, ESEM unannealed, hexagonal ice; ▽, ESEM annealed; ●, BET unannealed; ○, BET annealed. The line is a linear least-squares fit of the annealed BET data and all the ESEM data, except cubic ice.



**Figure 5.3-3.** HCl uptake vs ice film thickness at  $P(\text{HCl}) = (2.1 \pm 0.1) \times 10^{-7}$  torr and  $T = 188$  K. The line through the data is the best fit obtained by using a layer model for the ice film. See text for details.



1030 Pyrex

50µm

12kV ESD X465

D=9.6mm P=2.0T

ElectroScan

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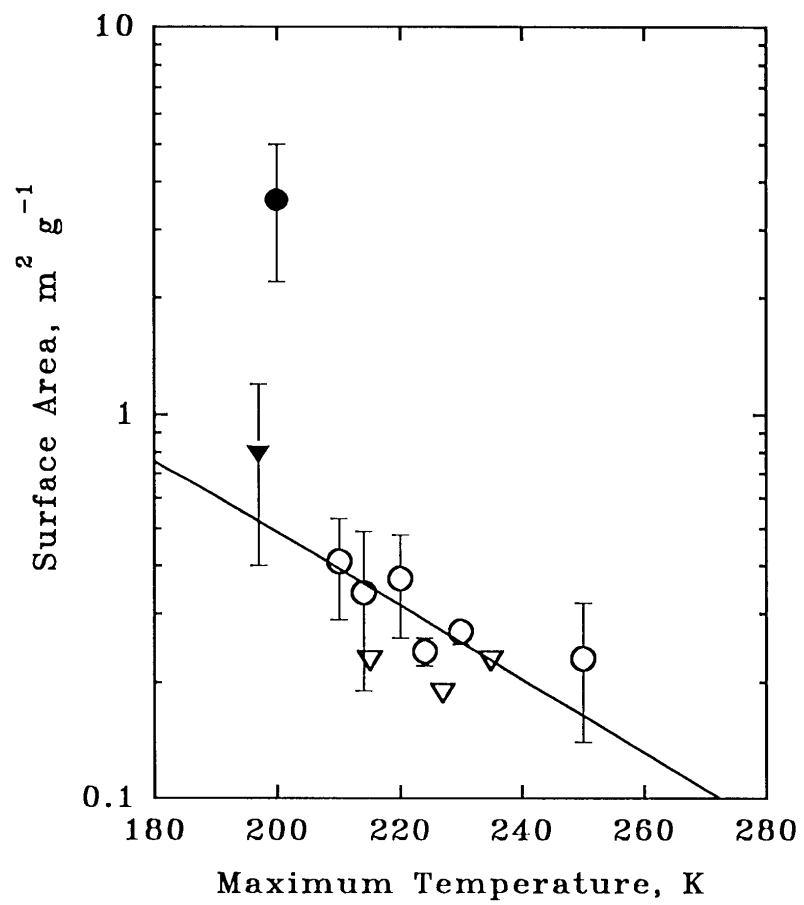


Figure 5.3-2a

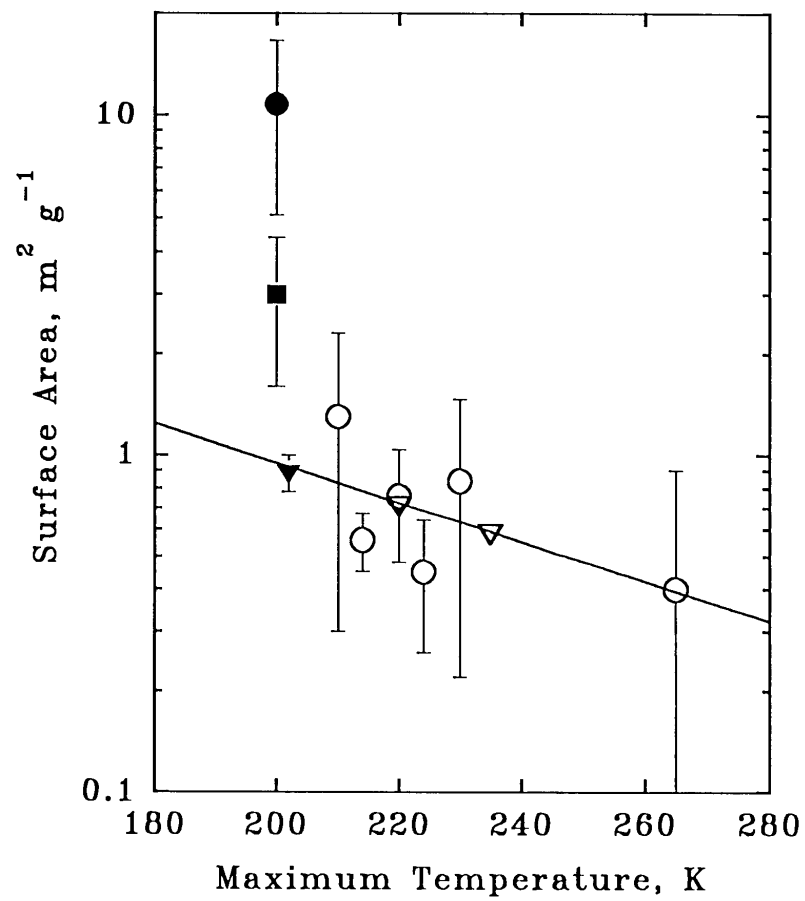


Figure 5.3-2b

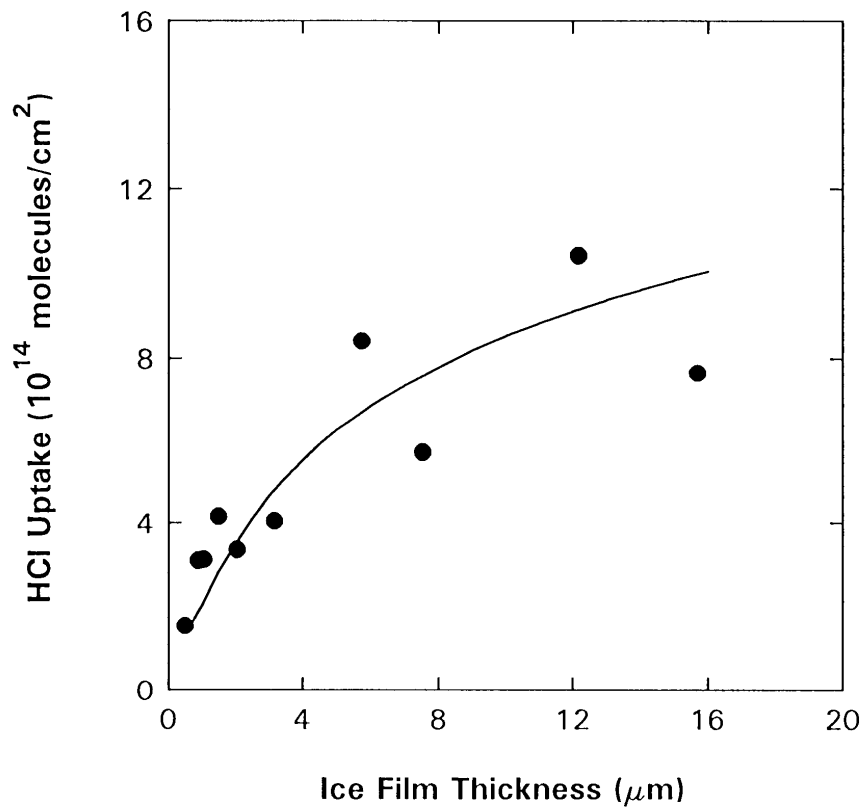


Figure 5.3-3