

# Hydrogen chloride-induced surface disordering on ice

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**Characterizing the interaction of hydrogen chloride (HCl) with polar stratospheric cloud ice particles is essential for understanding the processes responsible for ozone depletion. We studied the interaction of gas-phase HCl with ice between 243 and 186 K by using (i) ellipsometry to monitor the ice surface and (ii) coated-wall flow tube experiments, both with chemical ionization mass spectrometry detection of the gas phase. We show that trace amounts of HCl induce formation of a disordered region, or quasi-liquid layer, at the ice surface at stratospheric temperatures. We also show that surface disordering enhances the chlorine activation reaction of HCl with chlorine nitrate (ClONO<sub>2</sub>) and also enhances acetic acid (CH<sub>3</sub>COOH) adsorption. These results impact our understanding of the chemistry and physics of ice particles in the atmosphere.**

chlorine activation | ice chemistry | ozone depletion | stratosphere

To explain the catalytic role polar stratospheric cloud particle surfaces play in chlorine activation reactions (1–6), we proposed previously that HCl could induce the formation of a disordered region, or quasi-liquid layer (QLL), on the ice surface at stratospheric conditions (7). Surface disorder is known to exist on ice at temperatures near 273 K, but its existence has not been confirmed at stratospheric temperatures (188–203 K) (8–23). Surface disorder on hexagonal ice has been characterized by a variety of experimental and theoretical techniques, all of which agree that it does form below the bulk melting temperature, and that its thickness increases with increasing temperature. However, reported values of the onset temperature for surface disorder vary between 173 K, as determined by NMR (11), and 263 K, as measured by glancing angle x-ray scattering (12). Similarly, the measured thickness of the disordered surface region and its temperature dependence vary. Possible sources of discrepancy include the ice sample preparation method (24) or whether the QLL is at equilibrium or evaporating (22, 25). Inorganic and/or organic surface and bulk impurities are known to modulate the QLL thickness (14, 21), although to date they have not been shown to induce QLL formation. Furthermore, the experimental techniques used vary in sensitivity to surface properties (e.g., atomic force microscopy or sum-frequency generation vs. linear spectroscopies that show a higher sample penetration depth), and each intrinsically uses a different definition of “disorder.” For x-ray scattering, disorder means a structure factor that is different from the structure factor of crystalline material, i.e., it is mainly determined by the O-O radial distribution function. By contrast, in the case of NMR or sum-frequency generation, disorder means rotational disorder of dangling surface H bonds. In this study we use the refractive index,  $n$ , as a measure for distinguishing between order and disorder, and we track these changes via ellipsometry. For reference, at 632 nm  $n = 1.308$  for an ordered ice surface, whereas  $n = 1.333$  for liquid water (15).

Our goal in this study was to test the hypotheses that HCl induces surface disordering on ice at stratospheric conditions and that the presence of the QLL leads to enhanced chlorine activation. To this end, we studied the HCl–ice system by using the complementary approach of (i) ellipsometry to monitor the ice surface and (ii) coated-wall flow tube experiments, both with chemical ionization mass spectrometry (CIMS) detection of the

gas phase. We find that trace amounts of HCl induce surface change, which we interpret to be formation of a disordered surface region, on ice at a range of conditions that includes stratospherically relevant temperatures and HCl partial pressures. We show that the chlorine activation reaction of HCl with ClONO<sub>2</sub> on ice is enhanced in the presence of surface disorder, as is the uptake of gas-phase CH<sub>3</sub>COOH. These results impact our understanding of the chemistry and physics of ice particles in the atmosphere.

## Results

Figs. 1 and 2 show the ellipsometry signals during two studies of ice in the presence of HCl in the gas phase, (i) at constant HCl partial pressure ( $P_{\text{HCl}}$ ) but varying temperature (Fig. 1) and (ii) subject to a step change in  $P_{\text{HCl}}$  at constant temperature (Fig. 2). In agreement with earlier ellipsometry studies (15, 16), we observed strong surface disorder above  $\approx 271$  K on bare ice. Surface disorder was still measurable down to  $243 \pm 5$  K, below which the signal remained constant, implying the disappearance of the disordered surface region, i.e., a gas–solid interface. In the presence of  $\approx 10^{-6}$  torr HCl (1 torr = 133 Pa) in the gas phase (see Fig. 1), while we observed a response qualitatively like that observed on bare ice for  $273 \text{ K} > T > 210$  K, the ellipsometer signal changed significantly within a few seconds upon lowering the temperature to 207 K. At time = 0 (221 K) we observed 2D surface uptake of HCl onto the ice (adsorption) via CIMS and continued to cool the ice sample. The discontinuity in the ellipsometer signal when the temperature reached 207 K indicated a transition from a 2D system of HCl adsorbed on ice to a 3D system of HCl dissolved in a thin surface layer. The magnitude and the direction of the signal change resembled that observed when heating the basal ice face from 230 to 273 K, conditions at which it is commonly accepted that surface disordering exists (10–19). Therefore, these results are consistent with the rapid formation of a surface overlayer at  $\approx 10^{-6}$  torr HCl and 207 K. Other possibilities for the observed state such as a 2D adsorbed phase, hydrates, or a bulk solution showed significantly different ellipsometry traces based on our observations and can be excluded on this basis. We observed hydrate formation and bulk melting at experimental conditions corresponding to the “hexahydrate” (HCl·6H<sub>2</sub>O) and “liquid” regions of the phase diagram. Furthermore, 2D adsorption leading to a monolayer of HCl caused only a slight change in the refractive index, which is clearly shown in Fig. 2. For the experiment in which an ice sample was held at a constant temperature of 218

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Abbreviations: QLL, quasi-liquid layer; CIMS, chemical ionization mass spectrometry;  $P_{\text{HCl}}$ , HCl partial pressure.

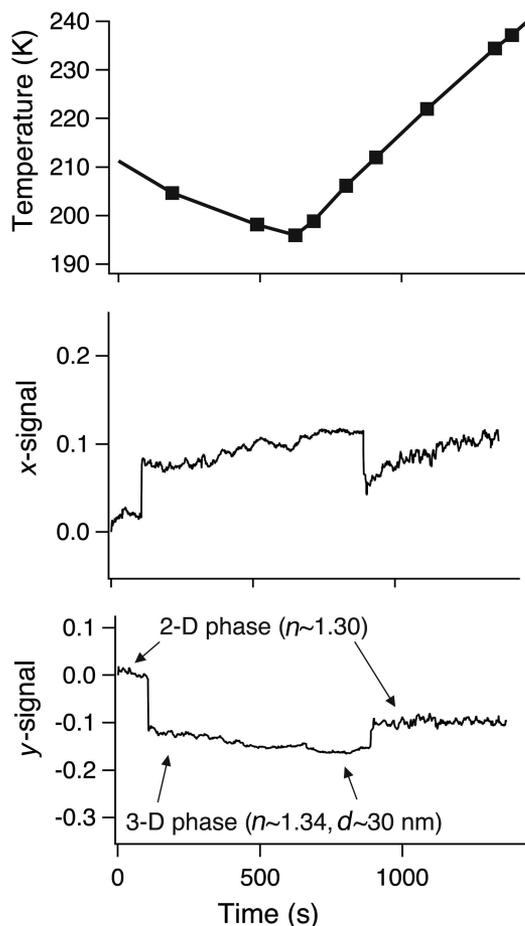
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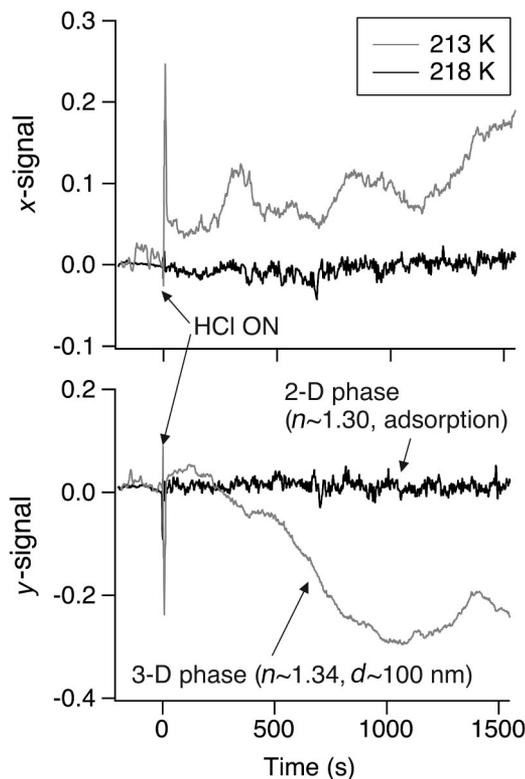
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**Fig. 1.** Time study of phase-modulated ellipsometry signals for a temperature-scanning experiment. Temperature (Top), the  $x$  signal (Middle), and the  $y$  signal (Bottom) are shown. An ice sample was exposed to  $5 \times 10^{-7}$  torr HCl and  $196 \text{ K} < T < 221 \text{ K}$ . As the temperature decreased from 221 to 196 K, there was a discontinuity in the signals corresponding to a surface change at 207 K. When the sample was returned to 221 K, another discontinuity was observed, with the signals returning to their previous levels at 209 K.

K (Fig. 2, black curve) and exposed to  $2 \times 10^{-6}$  torr HCl at  $t = 0$  s, the  $x$  and  $y$  signals remained unchanged, i.e., we did not observe surface change upon exposing the sample to HCl (“nondisordered conditions”). There was little change in the refractive index throughout the experiment, even though approximately a monolayer of HCl had been adsorbed. For the same exposure experiment at 213 K (Fig. 2, gray curve), pronounced signal changes occurred upon exposure to HCl and could clearly be attributed to surface change rather than 2D adsorption. Note that the ellipsometry signals change nonlinearly with increasing overlayer thickness (26). The coated-wall flow tube studies (described below) provided additional confirmation of the liquid-like behavior of the observed surface phase.

Lekner’s three-layer model (26), which describes the optical properties of an air–interfacial layer–crystal system, can be used for the interpretation of ellipsometry data. Applying this model to the data shown in Fig. 1, we found  $n \approx 1.34 \pm 0.01$  and layer thickness  $d \approx 30 \pm 10$  nm. Although  $n$  was similar in all experiments where overlayer formation was observed, the thickness varied between 10 and 100 nm for different  $P_{\text{HCl}}$  and different ice crystals. This estimate is in agreement with a recent study showing that HCl is available on ice for reaction with  $\text{ClONO}_2$  as deep as  $\approx 100$  nm (27–29). The measured index of refraction of  $\approx 1.34$  for the surface layer clearly exceeded that of



**Fig. 2.** Time study of phase-modulated ellipsometry signals for two constant temperature experiments. The  $x$  signal (Upper) and the  $y$  signal (Lower) are shown. Ice samples were held at constant temperatures of 213 K (gray curve) and 218 K (black curve) and exposed to  $2 \times 10^{-6}$  torr HCl at  $t = 0$  s. At 218 K, the  $x$  and  $y$  signals remain unchanged, but at 213 K, pronounced signal changes occur upon exposure to HCl. The spikes in the signal at  $t = 0$  s are caused by the movement of the injector. Note that the ellipsometry signals change nonlinearly with increasing overlayer thickness (26).

ice, indicating that the observed transition was not a roughening transition. Overlayer formation can also be distinguished from monolayer coverage of HCl on ice, i.e., 2D adsorption (see Fig. 2). These results suggest that the surface overlayer resembles liquid water or an aqueous solution of HCl in its optical properties, and therefore may be termed QLL.

In addition to varying the temperature at constant HCl partial pressure, we carried out constant-temperature studies in which the ice sample was exposed to a step change in  $P_{\text{HCl}}$  (see Fig. 2). A comparison of Figs. 1 and 2 shows that the rate of signal change was slower in the constant-temperature experiments than in the constant- $P_{\text{HCl}}$  experiments. However, the fact that the net refractive index change in both sets of experiments was comparable suggests that this change is independent of the thermodynamic pathway. Regarding the reversibility of overlayer formation, we observed a slight hysteresis (up to 4 K) when reheating the ice sample (see Fig. 1).

In Fig. 3 we summarize our ellipsometry measurements, superimposed on the HCl–ice phase diagram. The results of HCl step-change experiments such as those shown in Fig. 2 are depicted as follows: if, after  $\approx 1,000$  s of HCl exposure, the  $x$  and  $y$  signals had not changed by more than two times the noise (as in the 213-K,  $2 \times 10^{-6}$  torr HCl case), the temperature and HCl partial pressure of that experiment were designated “non-QLL” and are marked with a red circle in Fig. 3. If a large signal change ( $\geq$  five times the noise) was observed (as in the 218-K,  $2 \times 10^{-6}$  torr HCl case), corresponding in the three-layer model to a surface layer with refractive index of  $n \approx 1.34$  and a finite thickness, the conditions were designated “QLL”



temperatures expected to sample the conditions where we did (196 K) and did not (218 K) observe surface disordering with ellipsometry.

At 196 K, HCl was readily available for reaction and the reaction was efficient ( $\gamma > 0.1$ ), as previously observed (2–6). At 218 K, with the same reactant concentrations (nondisordered conditions), Cl<sub>2</sub> production was low and decreased with time. Analysis of the maximum portion of the Cl<sub>2</sub> signal (see *Methods* for more details) yielded a reactive uptake coefficient 10 times smaller than that observed under disorder-forming conditions ( $\gamma = 0.014 \pm 0.005$ ).

As an additional probe of the state of the ice surface in the presence of HCl, the coadsorption of HCl and CH<sub>3</sub>COOH was investigated on zone-refined ice cylinders by using the flow tube–CIMS technique. Sokolov and Abbatt (31) observed that CH<sub>3</sub>COOH uptake on bare ice was well described by the Langmuir model <243 K, but that saturation surface coverage increased  $\approx 2$ -fold >243 K, conditions where we observed surface disorder on ice even in the absence of HCl. We observed a similar enhancement of CH<sub>3</sub>COOH uptake at a temperature  $\approx 30$  K lower, in the presence of surface disorder-inducing levels of HCl. At a constant temperature of 212 K,  $P_{\text{CH}_3\text{COOH}} = 4.2 \times 10^{-6}$  torr and an HCl partial pressure where no surface change was observed with ellipsometry ( $P_{\text{HCl}} = 7 \times 10^{-7}$  torr), our measured CH<sub>3</sub>COOH uptake was  $1.4 \pm 0.2 \times 10^{14}$  molecule·cm<sup>-2</sup>. At the same temperature and  $P_{\text{CH}_3\text{COOH}}$ , but at HCl partial pressures leading to surface disordering ( $P_{\text{HCl}} = 2 \times 10^{-6}$  torr), we observed a 2-fold enhancement in CH<sub>3</sub>COOH adsorption ( $2.9 \pm 0.6 \times 10^{14}$  molecule·cm<sup>-2</sup>).

## Discussion and Conclusions

Our observation that HCl-induced surface changes extend only part way into the interior of the ice stability envelope is consistent with work by Hynes *et al.* (32), who observed in coated-wall flow tube experiments at  $10^{-6}$  torr HCl that the HCl uptake coefficient,  $\gamma$ , on ice decreased from  $\gamma > 0.1$  at 200 K (conditions for which we observed surface change) to  $\gamma < 0.01$  at  $T > 205$  K (conditions for which no surface change was observed in our experiments). This unusually strong and abrupt decrease of uptake with increasing temperature can be rationalized in view of our results by surface disorder disappearing upon heating from 200 to >205 K. Ullerstam *et al.* (33) studied nitric acid (HNO<sub>3</sub>) uptake on polycrystalline ice films in a coated-wall flow tube with gas-phase HNO<sub>3</sub> detection. They observed enhanced uptake of HNO<sub>3</sub> at low temperatures and high HNO<sub>3</sub> partial pressures in the vicinity of the ice-nitric acid trihydrate equilibrium line on the HNO<sub>3</sub>/ice phase diagram, which they attributed to the formation of a supercooled HNO<sub>3</sub> solution at the surface. Further experiments with a surface-sensitive probe such as ellipsometry are necessary to evaluate whether the observed enhancement was caused by surface disordering induced by HNO<sub>3</sub>.

To interpret our observations, we modeled the coated-wall flow tube HCl uptake experiments numerically, using an approach similar to that of Behr *et al.* (34). In our model, HCl uptake on zone-refined ice under disorder-inducing conditions can be described at long times by absorption to a surface overlayer and diffusion from that overlayer into the bulk ice. The best agreement with our observations was obtained with a value of HCl solubility in the overlayer that was intermediate between that of a true liquid layer and that of bulk ice. We assumed an HCl–ice diffusion coefficient of  $10^{-12}$  cm<sup>2</sup>·s<sup>-1</sup>, which was measured by Thibert and Domine (35) for single crystals of ice at 258 K. This interpretation is consistent with those of Huthwelker *et al.* (36) and Rossi and coworkers (27–29). Molecular-level details regarding uptake under nondisordered conditions, including the location of the adsorbed HCl and the state of the adsorbate, are currently unknown.

It should be noted that an inverse temperature dependence for the ClONO<sub>2</sub> + HCl reaction was observed by Oppliger *et al.* (6) using a Knudsen cell at 180 and 200 K; however, the HCl partial pressures used by Oppliger *et al.* are not known, so it is difficult to identify the region of the phase diagram that their experimental conditions lie in and thus draw a comparison to this work. In all cases their measured values of reactive uptake coefficient,  $\gamma$ , were  $\geq 0.1$ . Because of diffusion limitations in the coated-wall flow tube (37), we are not able to accurately measure values of  $\gamma$  that are  $> 0.1$  and thus can only provide a lower limit for the efficiency of the reaction in the presence of surface disordering.

Solomon *et al.* (1) argued that for the HCl + ClONO<sub>2</sub> heterogeneous chlorine activation reaction “to alter the balances between the catalytic species and their reservoirs, which occur on a time scale of a few days, this reaction must proceed in Antarctic spring on a comparable time scale, requiring an equivalent two-body reaction rate of  $\approx 2 \times 10^{-14}$  cm<sup>3</sup>·s<sup>-1</sup>.” An estimate of the equivalent heterogeneous processing rate in the polar stratosphere based on our experimentally measured values of  $\gamma$  for the reaction of ClONO<sub>2</sub> + HCl on ice and the polar stratospheric cloud properties of Turco *et al.* (38) appears to meet this chlorine activation rate criterion at least within a factor of two under disorder-inducing conditions ( $10^{-7}$  torr HCl,  $10^{-8}$  torr ClONO<sub>2</sub>, and 196 K). At projected polar stratospherically relevant nondisorder conditions ( $2 \times 10^{-7}$  torr HCl,  $10^{-8}$  torr ClONO<sub>2</sub>, and 205 K) the processing rate falls  $\approx 20$  times below the criterion. Therefore, the ClONO<sub>2</sub> + HCl reaction on ice can account for the observed chlorine activation only if surface disorder is present.

To illustrate the enhancement of CH<sub>3</sub>COOH adsorption by the presence of surface disorder, we applied a Langmuir model of CH<sub>3</sub>COOH/HCl competitive adsorption by using parameters from this study and an extrapolation of the data available in Sokolov and Abbatt (31). The model predicts the measured CH<sub>3</sub>COOH surface coverage under nondisordered conditions reasonably well to within a factor of  $1.9 \pm 0.3$ , but underestimates the measured coverage under disorder-inducing conditions by a factor of  $10 \pm 2$ . It is not surprising that the Langmuir model, which is applicable only to an unchanging, refractory surface, fails if surface disorder is present. The affinity of CH<sub>3</sub>COOH for the ice surface appears to increase in the presence of surface disorder.

In conclusion, we have shown via several experimental approaches that HCl does induce the formation of a 3D quasi-liquid solution of HCl in the surface layer of ice, at temperatures and HCl partial pressures in the vicinity of the phase equilibrium line on the HCl–ice phase diagram (including stratospherically relevant conditions).

We have confirmed that formation of a disordered region at the ice surface explains the role played by type II polar stratospheric cloud particles in catalyzing chlorine activation reactions. In addition, these findings, along with those of Sokolov and Abbatt (31), suggest that the presence of surface disorder on cirrus cloud ice particles may enhance their scavenging ability at temperatures >243 K.

## Methods

Ellipsometry measures the change in polarization upon reflection at the sample, which is characterized in terms of a polarization ellipse defined by a real and an imaginary part. The  $x$  and  $y$  signals shown in Figs. 1 and 2 were calculated from the measured voltages at 50 kHz (Y) and 100 kHz (X) and are related to the real and the imaginary parts of the reflectivity, respectively (26). The phase-modulated ellipsometer used in these measurements (Beaglehole Instruments, Wellington, New Zealand) uses a photoelastic birefringence modulator, allowing high-sensitivity measurements. The light source was a 50-mW



