Hydrogen chloride-induced surface disordering on ice

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Contributed by Mario J. Molina, May 4, 2006

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 (CIONO₂) and also enhances acetic acid (CH₃COOH) adsorption. These results impact our understanding of the chemistry and physics of ice particles in the atmosphere.

chlorine activation | ice chemistry | ozone depletion | stratosphere

o 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).

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 ClONO₂ on ice is enhanced in the presence of surface disorder, as is the uptake of gas-phase CH₃COOH. 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_{HCl}) but varying temperature (Fig. 1) and (*ii*) subject to a step change in $P_{\rm HCl}$ at constant temperature (Fig. 2). In agreement with earlier ellipsometry studies (15, 16), we observed strong surface disorder above ≈ 271 K on bare ice. Surface disorder was still measurable down to 243 ± 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 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·6H₂O) 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

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

Conflict of interest statement: No conflicts declared.

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

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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 5×10^{-7} torr HCl and 196 K < 7 < 221 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 2×10^{-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_{HCI} and different ice crystals. This estimate is in agreement with a recent study showing that HCl is available on ice for reaction with ClONO₂ as deep as ≈ 100 nm (27–29). The measured index of refraction of ≈ 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 2×10^{-6} forr 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_{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_{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, 2×10^{-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, 2×10^{-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"





Fig. 3. Summary of ellipsometer–CIMS study results: the HCl–ice phase diagram adapted from Molina (7). Thermodynamically stable phases are shown as a function of temperature and P_{HCl} . Ice is the stable phase under polar stratospheric conditions (circled area). Liquid refers to a liquid solution, and HCl·3H₂O and HCl·6H₂O refer to the crystalline hydrate states. Blue squares indicate conditions where a change in signal consistent with formation of a disordered region at the ice surface was observed, and red circles indicate conditions where no surface change was observed. Arrows represent constant P_{HCl} (temperature scanning) experiments. Bars represent temperatures at which cease/onset of surface changes were observed. Phase transitions are indicated by open triangles.

and are marked with a blue square in Fig. 3. Temperature-scan experiments such as those shown in Fig. 1 are represented by arrows in Fig. 3. The criterion for assigning the transition between no disorder (Fig. 3, red circles) and disorder (Fig. 3, blue squares) and vice versa for these experiments was that an abrupt change in the x and y signals with a magnitude \geq five times the noise must be observed during heating or cooling.

Clearly, we observed an increased refractive index, which we interpret as formation of a disordered region on the ice surface, at conditions in the vicinity of the phase equilibrium line, including conditions encountered in the polar stratosphere during polar stratospheric cloud events. To the best of our knowledge, no prior direct experimental observations of HCl-induced surface disordering at stratospheric conditions exist, although we had predicted this phenomenon theoretically (7, 30). In the range of conditions on the interior of the ice stability envelope on the HCl-ice phase diagram, surface changes were not observed far from the phase equilibrium line. For example, exposing an ice surface to 10^{-7} torr HCl was observed to induce surface disorder only for T > 238 K and T < 208 K and not for 238 K > T > 208 K.

This trend is also reflected in the results of our flow tube–CIMS studies of HCl uptake on zone-refined ice cylinders (Fig. 4), which further showed that the nature of the interaction of HCl with the ice samples was different under conditions for which surface change was or was not observed with ellipsometry (see *Methods* for details on zone-refined ice cylinder preparation). We also investigated the ClONO₂ + HCl reaction on zone-refined ice cylinders by using the flow tube–CIMS technique. As shown in Fig. 5, Cl₂ production, and thus the ClONO₂ + HCl reaction efficiency, was enhanced in the presence of surface disorder. Referring to Fig. 3, if we were

Fig. 4. HCl adsorption on zone-refined ice at $\approx 7 \times 10^{-7}$ torr HCl. Shown is the HCl mass spectrometer signal (normalized to the baseline signal) vs. time. (*Upper*) At 214 K (nondisordered conditions), 20% of adsorbed HCl (total uptake = $1.2 \pm 0.1 \times 10^{15}$ molecules·cm⁻²) is desorbed after removal of the source. (*Lower*) Under disorder-inducing conditions (196 K), we observed a nearly constant HCl flux (5×10^{11} molecules·cm⁻²·s⁻¹) from the surface to the interior of the isource, >80% of the molecules taken up are released to the gas phase.

to traverse the phase diagram along the 10^{-6} torr HCl partial pressure line from 273 to 180 K, we would expect to start with a liquid HCl/H₂O solution, transitioning through a region where HCl coexists with ice in the presence of surface disorder until 243 K, then HCl adsorbed on ice with no surface disorder from 243 to 210 K. At 210 K, we would expect surface disordering to return, and then possibly see formation of the metastable HCl hexahydrate phase at ≈ 188 K. This experiment was performed at constant reactant concentrations (10^{-6} torr HCl and 5 $\times 10^{-7}$ torr ClONO₂), at two different



Fig. 5. The reaction of ClONO₂ with adsorbed HCl on zone-refined ice at $\approx 10^{-6}$ torr HCl and 5 $\times 10^{-7}$ torr ClONO₂ and temperatures where we did (196 K; *Right*) and did not (218 K; *Left*) observe surface disordering with ellipsometry. For each temperature, the ClONO₂ (*Upper*) and Cl₂ (*Lower*) mass spectrometer signals (normalized to the baseline signal) are shown vs. time. The production of Cl₂, and thus the efficiency of the reaction, was enhanced under conditions where surface change was observed with the ellipsometer.

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), Cl₂ production was low and decreased with time. Analysis of the maximum portion of the Cl₂ 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 CH₃COOH was investigated on zone-refined ice cylinders by using the flow tube-CIMS technique. Sokolov and Abbatt (31) observed that CH₃COOH 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 CH₃COOH 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, $P_{\rm CH_3COOH} = 4.2 \times$ 10⁻⁶ torr and an HCl partial pressure where no surface change was observed with ellipsometry ($P_{\rm HCl} = 7 \times 10^{-7}$ torr), our measured CH₃COOH uptake was 1.4 \pm 0.2 \times 10¹⁴ molecule·cm⁻². At the same temperature and P_{CH_3COOH} , but at HCl partial pressures leading to surface disordering ($P_{\rm HCl} = 2 \times$ 10^{-6} torr), we observed a 2-fold enhancement in CH₃COOH adsorption (2.9 \pm 0.6 \times 10¹⁴ molecule·cm⁻²).

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, γ , 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 (HNO₃) uptake on polycrystalline ice films in a coated-wall flow tube with gas-phase HNO₃ detection. They observed enhanced uptake of HNO3 at low temperatures and high HNO₃ partial pressures in the vicinity of the ice-nitric acid trihydrate equilibrium line on the HNO₃/ice phase diagram, which they attributed to the formation of a supercooled HNO₃ solution at the surface. Further experiments with a surfacesensitive probe such as ellipsometry are necessary to evaluate whether the observed enhancement was caused by surface disordering induced by HNO₃.

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 cm²·s⁻¹, 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 ClONO₂ + 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, γ , were ≥ 0.1 . Because of diffusion limitations in the coated-wall flow tube (37), we are not able to accurately measure values of γ 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 + $ClONO_2$ 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 $\approx 2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$." An estimate of the equivalent heterogeneous processing rate in the polar stratosphere based on our experimentally measured values of γ for the reaction of ClONO₂ + 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 $(10^{-7} \text{ torr HCl}, 10^{-8} \text{ torr ClONO}_2, \text{ and } 196 \text{ K})$. At projected polar stratospherically relevant nondisorder conditions (2 \times 10^{-7} torr HCl, 10^{-8} torr ClONO₂, and 205 K) the processing rate falls ≈ 20 times below the criterion. Therefore, the $CIONO_2 + HCl$ reaction on ice can account for the observed chlorine activation only if surface disorder is present.

To illustrate the enhancement of CH₃COOH adsorption by the presence of surface disorder, we applied a Langmuir model of CH₃COOH/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 CH₃COOH surface coverage under nondisordered conditions reasonably well to within a factor of 1.9 ± 0.3 , but underestimates the measured coverage under disorder-inducing conditions by a factor of 10 ± 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 CH₃COOH 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 quasiliquid 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

He/Ne laser, and the laser spot size was ≈ 1 mm. Because we observed true melting when we crossed the solid-liquid equilibrium boundary, and did not see any signal change at nondisordered conditions, we infer that the laser does not melt the ice surface because of local heating. Ice samples for the ellipsometry study were cut from ice cylinders ≈ 2.5 cm in diameter, which were slowly grown from the liquid by using an adaptation of the Bridgman technique (39). Samples ≈ 1.3 cm thick were cut from the cylinders by melting with a razor blade perpendicular to the c axis, exposing the atmospherically relevant {0001} basal surface (40). Unlike the {1010} prism face, the {0001} basal face does not show a roughening transition close to the melting point, which would interfere when tracking the QLL (15). The ice samples were observed by using crossed polaroids to have grain sizes on the order of centimeters. After cutting, the sample was placed in a precooled aluminum sample holder and housed in a vacuum-jacketed flow tube fitted with quartz windows that allowed the laser beam to pass through the cooling jacket and flow tube walls. Ice was placed upstream of the main sample to ensure that the sample was in equilibrium with water vapor. The sample was then annealed by heating to ≈ 272 K for 1 min, and then cooled at a rate of ≈ 1 K/min to the desired temperature.

The flow tubes used in the ellipsometry and coated-wall flow tube experiments were operated in the laminar flow regime (Re < 100) with He as a carrier gas, at a constant total pressure of ≈ 2 torr. In the HCl uptake experiments, the ice sample was exposed to a dilute mixture of HCl in He that was introduced to the main He flow through a moveable injector positioned near the centerline of the flow tube (an additional injector was used for the ClONO₂ and CH₃COOH experiments). The injectors were heated to prevent adsorption of HCl to the injector walls, creating a temperature gradient of <1 K in the flow tube. The temperature inside the flow tube was monitored with a thermocouple. The flow tube was interfaced with a CIMS system (Extrel C50, Pittsburgh) to monitor the gas-phase composition. Detection occurred via chemical ionization using SF_6^- ions generated by using a corona discharge or α -particle bombardment by flowing an SF_6/N_2 mixture through a ²¹⁰Po source attached perpendicularly to the flow tube. HCl, ClONO₂, Cl₂, and CH₃COOH were monitored as SF₅Cl⁻, ClONO₂F⁻, Cl₂⁻, and CH₃CO₂HF⁻, respectively.

Hollow zone-refined ice cylinders $\approx 2 \text{ mm}$ thick were prepared for the coated-wall flow tube experiments by using a modification of the Bridgman technique (39) as follows: A 20-cm section of 0.74-cm (i.d.) Plexiglas tubing was plugged and filled with HPLC-grade water, with a cylindrical mask to form the central flow channel. The filled tube assembly was placed inside a freezer, and the water was allowed to solidify. The ice sample was then zone-refined by using a heated ring that advanced slowly (1) μ m·s⁻¹) to the top of the cylinder, locally melting and refreezing the sample. Ice samples prepared in this manner were observed by using crossed polaroids to have grain sizes on the order of several millimeters. Fig. 6 is a photograph of ice cylinder fragments before and after zone-refining, lit from behind, and viewed through crossed polaroids. The zone-refined ice fragment consists of a few large crystals of ice, and therefore acts as a prism, visibly separating the white light into its constituent colors. The unrefined fragment, having smaller crystal domains, does not.

For an adsorption experiment, the flow tube was first precooled to 233 K. The finished cylinder was inserted into the flow tube, and then the system was slowly cooled to the operating temperature to minimize cracking. He flow was maintained during insertion to create an overpressure in the flow tube and the injector to prevent condensation of water vapor from the ambient air inside the cold flow tube or the injector. Full pumping was not resumed until the temperature in the flow tube



Fig. 6. Ice cylinder fragments before (a) and after (b) zone refining. The fragments are lit from behind and viewed through crossed polaroids. The zone-refined ice fragment consists of a few large crystals of ice, and therefore acts as a prism, visibly separating the white light into its constituent colors. The unrefined fragment, having smaller crystal domains, does not.

reached at least 213 K to prevent pumping away the sample. The sample thickness (\approx 2 mm) could be measured directly outside the flow tube with calipers.

In the ClONO₂ + HCl experiments, the surface was first equilibrated with HCl, and then the uptake of a constant flow of ClONO₂ and the associated Cl₂ evolution was monitored. A pseudo first-order rate constant was obtained from measurements of Cl₂ product formation at several exposed ice lengths (and thus reaction times) as in Chu *et al.* (5), and then corrected for diffusion by using the Brown algorithm (37). The reactive uptake coefficient, γ , is related to the diffusion corrected pseudo first-order rate constant, k_{corr}^{I} , according to:

$$\gamma = \frac{2Rk_{corr}^{I}}{\omega},$$
 [1]

where *R* is the radius of the flow channel and ω is the molecular velocity. Values reported here were calculated by using a ClONO₂ diffusion coefficient in He of 176 cm²·s⁻¹·torr at 200 K, assuming a *T*^{1.76} dependence (4). Reported uncertainties reflect a 20% uncertainty in diffusion coefficient and the uncertainty in observed loss rates. ClONO₂ was prepared via the method of Schmeisser *et al.* (41).

In the CH₃COOH/HCl coadsorption experiments, the surface was first equilibrated with HCl, and then the uptake of CH₃COOH and the associated HCl desorption was monitored. Dimerization of gas-phase CH₃COOH was accounted for as in Sokolov and Abbatt (31) when determining the CH₃COOH sample concentration.

We thank the reviewers for improving the manuscript through their suggestions and comments. This research was supported by a grant from the National Aeronautics and Space Administration, a National Aeronautics and Space Administration Graduate Student Fellowship in Earth System Science (to V.F.M.), an Austrian Science Fund Schrödinger Fellowship (to T.L.), and the National Oceanographic and Atmospheric Administration Postdoctoral Program in Climate and Global Change (F.M.G.).

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