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Static SIMS Studies of Reactions on Mimics of Polar Stratospheric Clouds III: Mechanism of Chlorine Nitrate Decomposition and Reaction

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Static secondary ion mass spectrometry (SSIMS) was used to probe the interactions of chlorine nitrate ($ClONO_2$) or of chlorine nitrate plus HCl with condensed water ice films to probe the molecular interactions that may occur on polar stratospheric clouds. The experiments were carried out in an ultrahigh vacuum chamber on ice films at temperatures between 90 and 170 K and at pressures up to 5×10^{-7} mbar. A reference set of SSIMS spectra obtained at <100 K on gold and on ice were used as the basis set from which to probe molecular transformations and surface reactions. At 90−100 K chlorine nitrate adsorbs on gold or ice as a molecular species. Depth profiling experiments through chlorine nitrate multilayers laid down on an ice film indicated a change in the degree of polarization of the Cl−O bond in the chlorine nitrate molecules as proximity to water molecules increased (i.e., as the chlorine nitrate/ice interface was approached). Upon warming, the chlorine nitrate began to desorb from the ice film at 120 K. Despite the polarizing influence of the water molecules, no hydrolysis products were observed under these conditions. In contrast, the $ClONO_2$ reacted readily above 120 K when HCl was present. Formation of nitrate ions, implying the formation of surface-adsorbed nitric acid was indicated by the appearance of an NO_3^- signal in the negative ion SSIMS spectrum. This was accompanied by a simultaneous increase in the partial pressure of chlorine species in the gas phase. It was thus concluded that chlorine nitrate can react directly in the presence of the strong solvated Cl^- nucleophile to form molecular chlorine (which desorbs) and solvated or condensed nitric acid.

1. Introduction

The continuing depletion of ozone from earth's upper atmosphere is being increasingly recognized as a serious problem, particularly in the springtime and at extreme latitudes.[1] Under normal conditions, ozone is constantly consumed and re-formed in a series of gas-phase reactions that occur naturally in the stratosphere. Elevated concentrations of chlorine-containing radicals perturb this steady-state balance, increasing the rate of ozone consumption and thus leading to decreased ozone levels.[2] The especially severe depletion of ozone observed every spring over the Antarctic has been linked to the presence of polar stratospheric clouds, which can exist during the winter and early spring.[3,4] The clouds form when temperatures in the stratosphere are extremely low (185−210 K) and contain solid or supercooled particles made up of water and nitric acid condensed around a sulfuric acid nucleus.[5] Early laboratory simulations soon determined that the excessive ozone depletion is ultimately due to heterogeneous reactions between the highly reactive surfaces of the cloud particles and gaseous chlorine-containing species in the atmosphere.[6]

Of principal importance in determining the chlorine balance of the stratosphere is the substances HCl and chlorine nitrate ($ClONO_2$). These compounds participate in the ozone cycle as reservoir species that limit the amount of active ozone-depleting species. They do not react directly in the gas phase; however, they can react heterogeneously in the presence of an appropriate surface to produce molecular chlorine, which can subsequently be photolyzed to produce active chlorine radicals. The overall surface reaction is

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{1}$$

Laboratory simulations using a variety of gas kinetic techniques have indicated that chlorine nitrate and HCl react rapidly in the presence of polar stratospheric cloud particles to generate chlorine. At atmospheric levels of HCl the reaction is first order in $ClONO_2$, suggesting that the direct mechanism is likely, although macroscopic kinetic studies cannot be determinative of detailed mechanism.[7] Isotopic exchange studies of $ClONO_2$ hydrolysis at around 190 K using $H_2{}^{18}O$ demonstrate clearly that the Cl−O bond is broken and that the NO_3 remaining contains no oxygen from the water.[8] Numerous spectroscopic and theoretical studies have attempted to probe the microscopic mechanism of this reaction.[9−15] No one technique is able to provide a full mechanistic description for a reaction system of this complexity. Much of the spectroscopic groundwork has been laid by the IR studies of Sodeau, Horn et al.[9,13−17] A number of other approaches have also proven useful, e.g., gas-phase ion molecule chemistry[8,18] and laser-induced thermal desorption experiments.[19] Some of the early spectroscopic work suggested a two-stage reaction mechanism via HOCl for the reaction between $ClONO_2$ and HCl.[13] (More recent evidence from our initial SSIMS studies[20] and thorough IR investigations[16,17] suggests a direct one-stage reaction.) Both spectroscopic[16,17] and theoretical studies,[12,21,22] point to the conclusion that the exact chemistries of the chlorine nitrate hydrolysis and its reaction with HCl in the presence of water are extremely sensitive to both temperature and the relative amount of water that is present. Understanding the role and influence of the water molecules,

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which in the stratosphere are introduced when chlorine nitrate condenses on or interacts with the polar stratospheric cloud particles, is obviously crucial to unravelling the chemistry of this system.

As these earlier gas-phase and surface studies have demonstrated, the surface chemistry involved is potentially rather complex, involving a number of different ionic and neutral species in a water matrix. This study is part of a series of investigations in which *static* secondary ion mass spectrometry (SSIMS) has been used to probe the interactions of atmospherically relevant species with ice.[20,23−27] The aim has been to use the *mass spectrometric* power of SSIMS to identify and follow as many of the reaction components as possible. Our goal in this study is to investigate the $ClONO_2$/ice and $ClONO_2$/HCl/ice systems in order to probe the surface reaction mechanisms.

SSIMS involves bombarding the surface under investigation with a high-energy (typically in the region 5−12 keV) *primary* ion beam and analyzing the emitted secondary ions using a time-of-flight mass analyzer. While the technique is apparently destructive, the essence of the *static* mode of operation is to use an extremely low dose of primary ions (never more than 10^{13} ions cm^{-2}, or roughly one for every hundred surface atoms or molecules) such that within the time scale of the experiment very much less than 1% of the top surface layer receives an ion impact. Under these conditions on a random impact basis no spot on the surface should receive more than one primary ion strike. The species generated arise from an area no greater than 10 nm^2 and are remote from the next point of analytical impact. On average, the number of species generated per impact is no more than 1. The ions formed are a small fraction (frequently much less than 10^{-3}) of the total species emitted. The vast majority of the surface will be unaware of the removal of these species or any local effects as a consequence of the sputtering event. Thus, the spectral information arises from a surface that is, for all practical purposes, undamaged. There is now a very large body of evidence from a wide range of chemistries, from model single-crystal adsorbate systems to complex polymer-based materials, which amply demonstrates that in using *static* analysis conditions there is a clear relationship between SSIMS spectra and surface chemistry.[27,28] However, it has to be acknowledged that although the theoretical base is growing (e.g., ref 29), there is as yet no comprehensive theory for secondary ion formation in SSIMS. The application of SSIMS to surface chemistry problems relies on an empirical approach, widely accepted in mass spectrometry, in which observed spectra are compared with spectra assembled from appropriate reference materials. Analysts using SSIMS in applied surface analysis now routinely use libraries of standard SSIMS spectra.[30]

In the present experiments the same approach is used. A number of the reactants and products will be very susceptible to ion−molecule reactions that could be stimulated by the primary ion bombardment process. The resulting spectra will therefore be a convolution of the chemistry of the surface and the ion−molecule reactions of the SSIMS process. This is similar to the situation found in mass spectrometry in general where many spectral features are a consequence of molecular rearrangements or fragmentations that occur during or after ionization. When static SIMS spectra are interpreted, it is important to remember that the secondary ions observed should not necessarily be taken to have been literally present at the surface. In this case calibration spectra of the neat frozen compounds on gold and on water ice have been acquired as a basis set at 100 K before any reaction is likely to occur. These spectra are taken as characteristic of the condensed molecules themselves. Changes in the chemistry at the surface as a consequence of temperature and the presence of other molecules can then be inferred from changes in the SSIMS spectra.

This approach has been successfully used in our previous studies. Water ice itself has a very distinctive spectrum consisting of two series of $(H_2O)_n^+$ and $(H_2O)_nH^+$ ions.[23−25] The relative intensities of these series (as a function of n) are sensitive to the degree to which the ice films have been annealed. They are also very sensitive to the degree of ionization. Thus, when the acid content is increased, there is a significant rise in the $(H_2O)_nH^+$ yield relative to $(H_2O)_n^+$. This is consistent with the sensitivity of SSIMS to the presence and formation of preformed ions in the material being analyzed.

The contrasting behavior of chlorine-containing molecules interacting with ice is very clearly reflected in their SSIMS spectra and illustrates the approach taken to interpretation. A primary question with regard to the interaction of HCl with water ice at the low temperatures encountered in the stratosphere is whether the interaction is mainly dissociative or whether some molecular interaction can be detected. In our earlier study, the only significant new features resulting from the interaction of HCl with ice at 90 K and above were Cl^-, $Cl(H_2O)^-$, and a greatly increased yield (greater than a factor of 3) of H_3O^+ compared to pure water ice.[23] As noted above, it is well-known that when a surface contains species in the ionic state, the yield of that species in the SSIMS spectrum will generally be high. The clear implication is that HCl dissociates immediately on contact with water ice even at these low temperatures. However, it is legitimate to ask what the spectrum of HCl and water ice would look like if the interaction were nondissociative. SSIMS spectra from nondissociated inorganic metal chlorides in the solid state are characterized by series of positive ions $(MCl)_nM^+$ and negative ions $(MCl)_nCl^-$.[30,31] Hydrated chlorides are characterized by such clusters with the addition of varying numbers of H_2O species, viz., $(MCl)_nCl^-\cdot xH_2O$. Thus, an ion cluster is formed by the undissociated molecule plus the corresponding anion or cation to yield a cluster of the appropriate charge. By analogy, it is reasonable to expect that nondissociated HCl would give rise to similar ion clusters in the spectrum. Only an extremely small $(HCl)Cl^-$ was observed from HCl on/in ice at 90 K. This might imply a very small amount of molecular HCl. This reasoning is further supported by the studies reported later on nitric acid. This molecule condensed in a molecular form on gold, and the spectrum was much the same on water ice at 100 K. Similar cluster ions, e.g., $(HNO_3)_nNO_3^-$, were observed. At higher temperatures when dissociation was more extensive, the relative yield of cluster ions containing the undissociated acid molecule declined. We concluded from all these considerations taken together that HCl dissociated immediately on contact with water ice to generate Cl^- and $(H_2O)H^+$.[25] The extent of uptake of HCl into the ice film as a function of temperature and film depth could be sensitively monitored by the relative intensities of the H_3O^+ and H_2O^+ ions. In agreement with data from other techniques,[13] there was no evidence of molecular adsorption and at low temperature the ions were rather immobile, whereas at temperatures above 140 K the whole film became very mobile.

The SSIMS spectra observed from chlorine was in complete contrast. Upon interaction with ice in the region of 95 K, in addition to the water spectrum, the main new peaks were a series Cl_n^- and Cl_n^+ observable for $n = 1-7$. This spectrum was also observed in the absence of water. We concluded that covalent chlorine does not dissociate on contact with water at this low temperature. We further concluded that the $Cl_n^{\pm}$ spectral features are characteristic of situations where chlorine is covalently bonded in surface molecules. This conclusion is supported by our studies of Cl_2O[26] and $ClONO_2$.[32] The SSIMS spectra of both these molecules either neat on gold or neat on ice at very low temperatures before reaction display the $Cl_n^{\pm}$ series. Obviously, the actual presence of $Cl_n^{\pm}$ at the surface cannot be implied. They arise as a consequence of the ion−molecule rearrangements that occur as the species leave the surface. Their appearance is most easily rationalized by suggesting that the sputtering process generates $Cl^{\bullet}$ radicals that combine with other ionic chlorine species in the emission region to form the clusters we observe. The influence of radicals in stimulating molecular rearrangements is well documented in EI and CI mass spectrometry.[33] This process only occurs for covalently bound chlorine. The cluster series is not observed in fully ionic systems such as the HCl system.

Thus, the evidence is that chlorine adsorbs solely in a molecular form on ice at 90−100 K. However, the SSIMS data clearly show that at temperatures above about 130 K chlorine and water react at the ice surface to produce a mixture of hypochlorous acid and solvated HCl. Cl_2O behaves a little differently.[26] Even at 90 K, there is evidence that it disrupts the long-range hydrogen bonding between the water molecules dramatically changing the form of the variation of $(H_2O)_nH^+/(H_2O)_n^+$ as a function of n. At temperatures above 120 K in agreement with earlier IR studies[13] the SSIMS data demonstrate that reaction occurs with water to produce a mixture of water and hypochlorous acid. These studies provide considerable encouragement to exploit the chemical specificity of static SIMS further to investigate the possible reactions of $ClONO_2$ on ice. An initial exploratory study suggested that the reaction between HCl and $ClONO_2$ on ice could proceed via a direct reaction between solvated chlorine ions and $ClONO_2$ to yield gas-phase chlorine and nitric acid condensed in the ice.[20] This contrasted with the two-stage mechanism, which is sometimes suggested to occur via HOCl. This paper reports a detailed SSIMS study of this heterogeneous reaction.

2. Experimental Section

The SIMS instrument was a Kratos time-of-flight model equipped with a 10 kV Ar^+ primary ion source. For the majority of the experiments in this study, the instrument was operated in static mode (static SIMS). In this mode, the primary ion beam is pulsed and the total ion dose is kept within the range $(1-5) \times 10^{12}$ ions/cm^2. As explained in Introduction, under these conditions, the technique is surface-sensitive, with over 95% of the ions detected arising from the first two layers.

The equipment and the experimental setup have been described in greater detail previously[25] and are illustrated here in Figure 1. The general procedure was to simulate polar stratospheric cloud particles by condensing thin films of pure water/ice onto a cooled substrate (ca. 90 K) mounted in the ultrahigh vacuum (UHV) chamber. Reactants (chlorine nitrate, HCl) were introduced subsequently at various temperatures and reactant partial pressures. The resulting surface chemistry was interrogated using SSIMS, while a small quadrupole mass spectrometer was used to monitor the composition of the background gases in the UHV chamber.

The reactants were introduced through leak valves from reservoirs in a small glass vacuum line that was used for sample purification and preparation. Individual Teflon dosing nozzles lead from each leak valve inside the UHV chamber to a position about 5 mm above the cooled polycrystalline gold foil used as the substrate. The gold foil was mounted on a liquid nitrogen cooled sample manipulator. Each reactant was either dosed by opening the leak valve to a given partial pressure for a set time or back-dosed by adjusting the leak valve to give a constant, continuous partial pressure in the chamber. The ice films were thermally annealed to 150 K to induce a transition from the amorphous to a crystalline phase prior to introducing the reactants.[34]

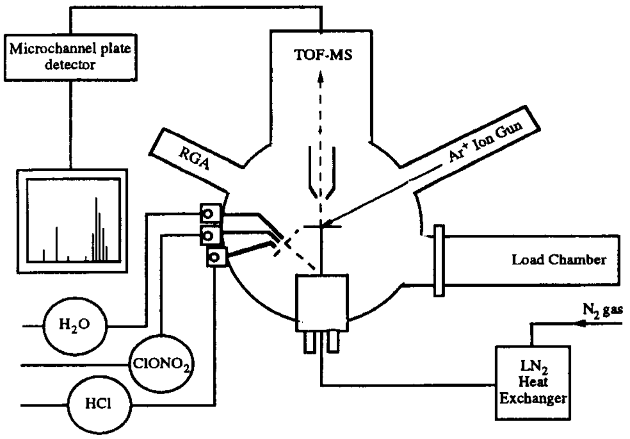

Figure 1. Schematic of the Kratos time-of-flight secondary ion mass spectrometer (ToF-MS), liquid nitrogen cooled sample manipulator, residual gas analyzer (RGA), and gas dosing system.

The minimum temperature readily achieved using our liquid nitrogen cooling arrangement was between 90 and 100 K. The temperature could be regulated up to 180 K or above, at which temperature most of the reactants of interest desorbed under UHV conditions. The maximum safe operating pressure for our experiments was around 10^{-6} mbar. It was therefore not always possible to use background partial pressures sufficiently high to sustain a film at temperatures in the region of 180 K. Much of the work reported was therefore carried out in the lower temperature regime, i.e., $<$170 K.

For certain experiments it was desirable to employ the primary ion beam in the SIMS instrument to deliberately remove material from the film and allow analysis of the newly exposed underlying layers. This *dynamic* SIMS approach was achieved by allowing the primary ion beam to continuously bombard the sample for several minutes. This etching procedure was alternated with low ion dose static SIMS analyses using a pulsed primary ion beam. The approximate number of layers removed during the etching was calculated from the ion dose and from the sputter yield for condensed water that was measured previously.[25]

The water used was HPLC solvent grade (Fisons, U.K.). HCl was purchased in a lecture bottle (Aldrich, UK, purity 99+%) and used as received. Chlorine nitrate was prepared in a three-step synthesis from Cl_2O and N_2O_5 based on the method of Schmeisser.[35] Cl_2O was prepared as described previously[26] by passing Cl_2 gas over dry mercury(II) oxide. N_2O_5 was prepared by reacting NO_2 with ozone and then trapping and purifying the resultant product.[36] After production, $ClONO_2$ was stored in an evacuated glass tube in a solid CO_2/acetone bath and protected from light at all times. Prior to use, the $ClONO_2$ was pumped briefly to remove most of the residual Cl_2. The leak valve and vacuum chamber were passivated by opening the valve to allow some $ClONO_2$ into the chamber prior to the experiments. During this time, and throughout the course of the experiments, the background composition of the gas in the vacuum chamber was monitored using the quadrupole mass spectrometer residual gas analyzer.

To interpret the SSIMS spectra of the $ClONO_2$/ice and

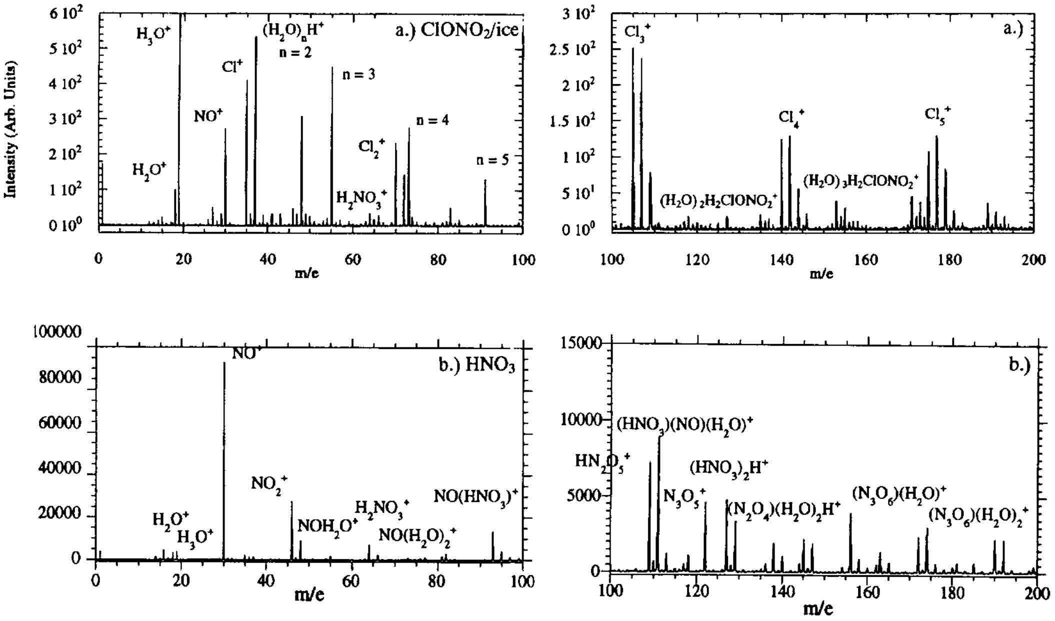

Figure 2. (a) Positive ion SSIMS spectrum of $ClONO_2$ on ice, $T = 90-100$ K. Water-dosed at 90 K for 5 min to 2×10^{-7} mbar. $ClONO_2$-back-dosed continuously to approximately 1×10^{-7} mbar. (b.) Positive ion SSIMS spectrum of HNO_3 on ice, $T = 110$ K. Water-dosed at 90 K for 60 s to 1×10^{-7} mbar. HNO_3-dosed 30−60 s to 1×10^{-7} mbar.

$ClONO_2$/HCl/ice systems under reactive conditions, it was necessary to acquire a set of reference spectra under nonreactive conditions. Standard SSIMS spectra of the reactants and possible intermediate molecules ($ClONO_2$, HNO_3, Cl_2O) condensed at ∼90 K as multilayer films on a clean gold substrate were obtained. Molecular HCl, an important starting material, did not condense at this temperature. It has previously been demonstrated that HCl interacts completely dissociatively upon interaction with solid ice at 90 K and above,[37] and this system has been well characterized by SSIMS in an earlier study.[25] As outlined in Introduction, these reference spectra were used as a basis of comparison to relate the spectral changes to changes that occurred in the surface chemistry when the molecules interacted with ice and other molecules. A further set of spectra in which these molecules were exposed to previously grown ice films at 90−100 K were also acquired. The exposure levels were sufficient to condense multilayers of the molecular solid for species such as Cl_2, HNO_3, and $ClONO_2$ under relatively unreactive (low temperature) conditions. Multilayer condensation was indicated by the absence from the SSIMS spectra of the characteristic peaks that were associated with the gold substrate.

A typical reaction experiment involved first cooling the gold substrate to 90 K. Water was then dosed through the leak valve and Teflon nozzle to a pressure of 2×10^{-7} mbar or less for periods of 5−15 min. This produced a clean multilayer film of condensed amorphous water. For the $ClONO_2$/ice experiments, the chlorine nitrate was dosed to a pressure of 1×10^{-7} mbar at 90 K. At higher temperatures (>150 K) the chlorine nitrate was back-dosed continuously in order to sustain a good film. For the $ClONO_2$/HCl/ice experiments, the ice film was exposed to HCl dosed to a pressure of 1×10^{-7} mbar for 2 min at 90 K prior to introducing the chlorine nitrate. The higher temperature data were obtained by raising the temperature in stages and observing the resulting changes in the SSIMS spectra.

3. Results

3.1. Reference Spectra, 90−100 K. The first task was to acquire the necessary reference spectra and to determine which features are diagnostic of the surface chemistry or of changes in surface chemistry. The characteristic features of chlorine nitrate and of nitric acid, condensed as molecular multilayers, are illustrated in Figures 2 (positive ion SSIMS spectra) and 3 (negative ion SSIMS spectra).

The SSIMS spectra of pure water ice and of ice that has been exposed to HCl have been described in detail previously.[24,25] Peaks from cluster ions with the general formulas of $(H_2O)_n^+$ and $(H_2O)_nH^+$ dominate the positive ion spectrum of pure water ice, while the negative ion spectrum shows little besides O^- and OH^+. As indicated in Introduction, when HCl is introduced even at temperatures as low as 90 K, it dissociates immediately to produce a film of solvated ions. This is reflected in the positive ion SSIMS spectra by a greater than 3-fold increase in the absolute and relative intensities of the protonated $(H_2O)_nH^+$ cluster ion peaks compared to the unprotonated clusters.[25]

At temperatures of 90−100 K we found it possible to condense multilayers of chlorine nitrate both onto a gold substrate and onto a pregrown ice film. During the course of the analyses, the chlorine nitrate leak valve was left open to give a constant back-pressure of approximately 1×10^{-7} Torr of $ClONO_2$. This was done to allow passivation of the system and to ensure multilayer condensation of a pure film by maximizing the chlorine nitrate relative to background water vapor partial pressure. Co-deposition of a certain amount of water was inevitable, especially with the layered $ClONO_2$/ice films. The water vapor partial pressure typically decreased over time. Thus, in the mixed $ClONO_2$/ice systems, the outermost region of the film should have less co-condensed water than the underlying layers closer to the chlorine nitrate/water interface.

A molecular ion of chlorine nitrate did not appear as an intense peak in either the positive or negative ion spectra (very similar to Figures 2a and 3a). Instead, there were peaks from numerous cluster ions. A spectrum dominated by fragment ions is frequently observed in SSIMS, as in other mass spectrometries. Some of these ions will arise from direct fragmentation of surface molecules, while some can arise from preformed ions that may exist at the surface, and some will arise from ion−

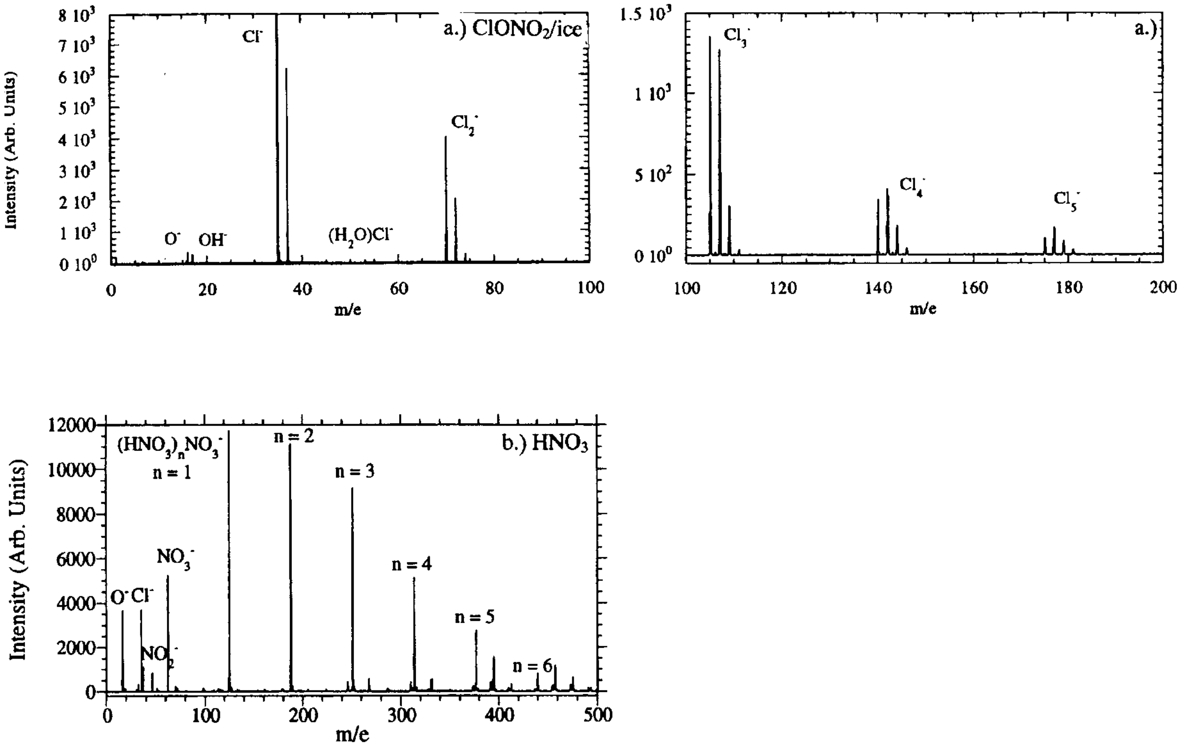

Figure 3. (a) Negative ion SSIMS spectrum of $ClONO_2$ on ice, $T = 90-100$ K. Water-dosed at 90 K for 5 min to 2×10^{-7} mbar. $ClONO_2$-back-dosed continuously to approximately 1×10^{-7} mbar. (b) Negative ion SSIMS spectrum of HNO_3 on ice, $T = 110$ K. Water-dosed at 90 K for 60 s to 2×10^{-7} mbar. HNO_3-dosed 30−60 s to 1×10^{-7} mbar.

molecule reactions occurring in the SSIMS process. The principal nitrogen-containing ion in the spectra of chlorine nitrate is NO^+, with no sign of NO_3^-. This is in clear contrast to HNO_3, which gave a very intense NO_3^- signal either when condensed neat onto gold or when condensed as multilayers on top of an existing ice film (Figure 3b). Evidently, HNO_3, unlike HCl, will condense in a relatively pure state at these temperatures (minimal interaction with water), although the ready formation of the NO_3^- ion reflects the high degree of polarization of the $H-ONO_2$ bond resulting from the fact that HNO_3 is a very strong acid. Thus, the *absence* of the NO_3^- ion in the chlorine nitrate spectrum suggests minimal polarization of the $Cl-ONO_2$ bond, although the $X-NO_3$ structure is thought to be similar in both molecules. Clearly, the ionic state, or degree of polarization, is significant in determining the secondary ions observed.

As outlined in Introduction, a distinctive feature in the chlorine nitrate positive ion spectrum is the presence of small Cl_m^+ clusters, for $1 \le m \le 5$ or higher. The emission of these Cl_x clusters is reminiscent of the spectra of Cl_2 and Cl_2O.[26] It is clear that these cluster ions are rather characteristic of the SSIMS spectrum of a covalent chlorine-containing species present as a *molecular* solid or adsorbate. In contrast Cl_m ions are not observed when *dissociative* adsorption or reaction occurs, for example, from ice films that have been exposed to HCl, where Cl^- is the principal chlorine ion.[24,25]

Other peaks associated with the chlorine nitrate were from NO^+, NO_2^+, $(H_2O)_nNO^+$ ($n \le 3$), and $H_2NO_3^+$, with the NO^+ peak being the largest. Water cluster peaks $(H_2O)_n^+$ and $(H_2O)_nH^+$ were also clearly visible. The presence of water cluster ion peaks, even from the ostensibly pure substance condensed on gold, has been observed previously[26] and is due to the presence of residual water vapor in the chamber. The NO^+, NO_2^+, and $H_2NO_3^+$ peaks have been observed previously from both nitric acid (Figure 2b) and N_2O_5.[38] Their presence here reflects the fact that those species all have a common $X-NO_3$ structure.

The spectra of $ClONO_2$ condensed on top of an existing ice film at 90−100 K (Figures 2a and 3a) were overall very similar to the spectra of $ClONO_2$ condensed neat on gold. Upon close examination, some small but significant differences were apparent. The Cl_2^+ and higher cluster peaks were less prominent when water was present. A sequence of peaks under the general formula $(ClONO_2 + yH)^+{\cdot}nH_2O$ [or $(M + yH)^+{\cdot}nH_2O$ where $M = ClONO_2$], where $y = 2$ or 3 and $n = 0 \rightarrow 5$, are observed between *m/z* 99 and *m/z* 200. In the negative ion spectrum, trace quantities of a related cluster ion (*m/z* 169, 171) with the formula $(ClONO_2{\cdot}4H_2O)^-$ was visible in some spectra (Figure 3a). These cluster ions clearly reflect a significant degree of interaction between $ClONO_2$ and water.

Previous IR studies have indicated that at temperatures below 130 K chlorine nitrate, which is much less polar than HCl, will condense, intact, on a gold substrate.[14] Given this, plus the clear difference between the negative ion spectra of $ClONO_2$ compared to that from HNO_3, it seems reasonable to conclude that the peaks observed in the low-temperature spectra of condensed chlorine nitrate are characteristic of the molecular solid/adsorbate. From the similarities in the low-temperature $ClONO_2$/gold and $ClONO_2$/ice spectra, it appears that chlorine nitrate can condense in multilayers on top of the ice. Furthermore, at least at the exposed surface region, farthest from the chlorine nitrate/ice interface, the chlorine nitrate appeared to be condensing as a molecular solid.

3.2. Interaction of Chlorine Nitrate with Ice. The spectra shown in Figures 2a and 3a were acquired from chlorine nitrate condensed 20−50 or more layers thick on top of the previously deposited ice film. If proximity to water molecules polarizes $ClONO_2$ to some degree, one might expect the phenomenon to become more visible as the extent of mixing between the

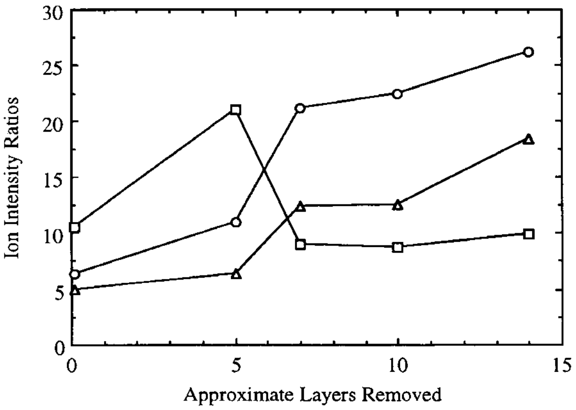

Figure 4. Changes in the positive ion static SIMS spectra of an overlayer of $ClONO_2$ on ice as layers are removed by etching with the primary ion beam between spectra, $T = 90-100$ K: (△) H_3O^+/H_2O^+ ion intensity ratio; (□) $\Sigma[NO^+ + NO_2^+]/\Sigma[H_2O^+ + (H_2O)_2^+]$ ion intensity ratio multiplied by 10 (for scaling purposes); (○) $\Sigma[Cl^+ + Cl_2^+ + Cl_3^+]/\Sigma[H_2O^+ + (H_2O)_2^+]$ ion intensity ratio multiplied by 10 (for scaling purposes).

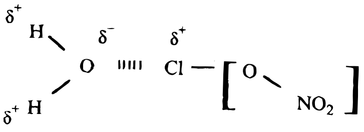

Figure 5. Polarization of the chlorine nitrate molecule by water.

chlorine nitrate and water increases. Given the layered nature of our $ClONO_2$/ice films, with a chlorine-rich outer layer atop regions with progressively more and more water, we were able to correlate changes in composition with distance (depth) from the outer surface. These changes were monitored using a dynamic SIMS approach, as described in the Experimental Section. The actual SIMS spectra of the newly exposed surfaces were acquired in static mode, using a pulsed ion beam.

With this technique, clear changes emerged in the positive ion spectra of the film as the $ClONO_2$-rich outer layers were removed and the ratio of $ClONO_2$ to H_2O increases. These differences are illustrated in Figure 4, which plots changes in certain ion intensity ratios as a function of depth. One ratio plotted is the H_3O^+/H_2O^+ intensity ratio, a quantity that can be associated with the degree of acidity of (i.e., number of protons) in the ice film.[24,25] The ratio starts at about 5, at the outside of the film farthest away from the water interface, and increases with depth. This trend is consistent with an increasingly ionic character toward the more water-rich chlorine nitrate/water interface compared with less strongly polarized $ClONO_2$ molecules toward the outer surface (where less water is present).

If it is suggested that the generation of Cl_m^+ secondary ions may be encouraged by polarization of the $ClONO_2$ molecules toward $Cl^{\delta+}-(NO_3)^{\delta-}$, then this may be reflected in the yield ratio $\Sigma Cl_m^+/\Sigma[(H_2O^+) + (H_2O)_2^+]$ where $m = 1 \rightarrow 3$. The increase in Cl_m^+ signals relative to the signal of (unprotonated) water cluster peaks suggests an increasing polarization of the $ClONO_2$ molecule as it interacts with the water molecules (Figure 5). Correspondingly, the $[NO^+ + NO_2^+]/\Sigma[(H_2O^+) + (H_2O)_2^+]$ ratio drops. Taken together, these observations imply a trend toward a more negatively polarized NO_3 group. This represents a clear change from the chlorine nitrate condensed at the outer surface, where water is relatively scarce. These results are consistent with the recognized sensitivity of the SSIMS technique to changes in chemical environment (matrix effects). In this particular experiment, we have made use of this phenomenon to demonstrate how an increasing proportion of water in the local environment perturbs the Cl−O bond in chlorine nitrate.

We briefly examined the high-temperature behavior of chlorine nitrate and water ice by increasing the temperature and observing the effect on the mixed films that were grown and initially studied at 90−100 K. When the temperature was raised to 120 K, there was an immediate pressure rise within the vacuum chamber, indicating the rapid desorption of some species. This was accompanied by a decrease in the relative intensities of the SSIMS features associated with the $ClONO_2$. For example, the NO^+ peak intensity decreased relative to the intensities of the water cluster peaks. The Cl_m^+ peaks, including the Cl^+ peak ($m = 1$), also decreased markedly relative to the water clusters. This therefore indicated desorption of chlorine nitrate or a related species from the film.

3.3. Chlorine Nitrate and HCl on Ice, 90−170 K. Thus far, under the conditions studied here, there has been little indication of a strong reaction between chlorine nitrate and water. In the stratosphere, both chlorine nitrate and HCl are normally present and are known to react readily in the presence of icy cloud particles.[7] Chlorine nitrate was therefore introduced at 100 K to ice that had been exposed to HCl. SSIMS spectra were monitored as the temperature was raised in stages to approximately 170 K. A constant back-pressure of $ClONO_2$ was maintained throughout in order to help sustain a film.

At 90−100 K, both the positive and negative ion spectra of $ClONO_2$ + HCl on ice were similar to the spectra of $ClONO_2$ alone on ice. The similarities and differences in the sets of results are listed in Table 1. As expected, when the HCl was present, the intensities of the protonated water cluster peaks that appear in the positive ion spectrum were high relative to the intensities of the corresponding unprotonated clusters. However, there were some new features as a consequence of the HCl presence. $(H_2O)HNO_3^+$ and $(H_2O)HNO_3H^+$ clusters appeared, along with minor peaks attributed to $(H_2O)_n(NO)HNO_3^+$ for $1 \leq n \leq 4$. These ion series are observed in the positive ion spectra of nitric acid and water ice.[38]

At 95 K in the negative ion spectra, there were no noteworthy differences from the spectral features observed from a summation of the spectra from the separate systems H_2O/HCl and H_2O/$ClONO_2$. The major peaks were from O^-, OH^-, and Cl_m^- for m up to 5 or more, with smaller peaks from $(H_2O)Cl^-$. Very small peaks appeared from ClO^-, $HOCl^-$, and HCl_2^-. The latter ions may or may not be present in trace quantities in the negative ion spectrum of $ClONO_2$ on ice, although the HCl_2^- ion especially is one that is often associated with the presence of HCl.[24,25]

The HCl-containing film was then warmed as the $ClONO_2$/ice system was warmed previously. Positive spectra of the $ClONO_2$/HCl/ice system were acquired after equilibrating the system at 120, 130, 140, and 170 K for a few minutes. In the presence of HCl, clear changes emerged in both the positive and negative ion SSIMS spectra as the temperature was raised. When the temperature was increased initially, from 100 to 120 K, the NO^+ and Cl_m^+ ($m \geq 1$) peak intensities decreased relative to the intensities of the water cluster peaks. This was accompanied by a pressure rise within the vacuum chamber. The protonated to unprotonated water cluster ratios remained high, indicating that HCl was not being lost. Up to this temperature, the behavior mirrored that of the straight $ClONO_2$/ice system at 110−130 K. The spectral features characteristic of $ClONO_2$ decreased relative to the water clusters, while the background

TABLE 1: Comparison of the Principal Features of the SSIMS Spectra of $ClONO_2$ on Ice with $ClONO_2$ + HCl on Ice at T = 90−100 K[a]

ions	$ClONO_2$ on ice	$ClONO_2$ + HCl on ice
$(H_2O)_n^+$, $(H_2O)_n^+H^+$	Most intense peak in spectrum is H_3O^+; typical water cluster distribution for $n > 1$	Most intense peak in spectrum is H_3O^+; typical water cluster distribution for $n > 1$
H_3O^+/H_2O^+ ratio	13	45
Cl_m^+	present in significant amounts to $m = 5$	present in significant amounts to $m = 5$
NO^+, NO_2^+	present in similar proportions in both systems	present in similar proportions in both systems
HNO_3^+	not visible	minor peak
$H_2NO_3^+$	trace quantity	minor peak
$(H_2O)HNO_3^+$	not visible	trace quantities
$(H_2O)_nHNO_3H^+$	not visible	trace quantities ($n = 1, 2$)
$(H_2O)_n(NO)HNO_3^+$	not visible	rrace quantities ($n = 0,1$)
O^-, OH^-	present with moderate intensity	oresent with moderate intensity
Cl_m^-	most intense peak Cl^-, decreasing intensity present to m = 5	most intense peak Cl^-, decreasing intensity present to m = 5
$(H_2O)Cl^-$	minor peak in both spectra	minor peak in both spectra
ClO^-, $HClO^-$, HCl_2^-	trace quantities	trace quantities

[a] $ClONO_2$/ice: water-dosed at 90 K for 5 min to 2×10^{-7} mbar, not annealed. $ClONO_2$-back-dosed continuously to approximately 1×10^{-7} mbar. $ClONO_2$/HCl/ice: water-dosed at 95 K for 18 min to 3×10^{-8} mbar, not annealed. HCl-dosed 2 min to 1×10^{-7} mbar. $ClONO_2$-back-dosed continuously to approximately 1×10^{-7} mbar.

pressure in the chamber rose, indicating in both cases the desorption of chlorine nitrate or a related species from the film.

In contrast, upon warming the $ClONO_2$/HCl/ice system to 130 K, the NO^+ and NO_2^+ peaks remained visible. Other nitrogen-containing clusters included $(H_2O)_nNO^+$ for $1 \leq n \leq 4$, $(H_2O)NO_2^+$, $H_2NO_3^+$, $(HNO_3)(H_2O)_nH^+$ for n up to 7 or higher, and $(HNO_3)(H_2O)_nNO^+$ for $0 \leq n \leq 5$. The Cl_m^+ cluster intensities became very small, while a small $Cl_3O_2^+$ peak appeared. Instead of gradually decreasing in intensity, these chlorine- and nitrogen-containing features persisted, but the resulting spectrum no longer resembled that of molecular $ClONO_2$. The appearance of some new species at the surface of the film is clearly suggested. Further warming to 170 K produced no new peaks. A decrease in the intensities of the nitrogen-containing peaks relative to those of the water clusters did indicate a loss of the newly formed species from the film.

The negative ion spectra proved to be very informative. It will be recalled that when the film of $ClONO_2$ on ice *in the absence* of HCl was warmed to 130 K, the $ClONO_2$ features disappeared from the negative ion spectrum. Only O^-, OH^-, and Cl^- peaks, plus very small (trace) quantities of Cl_2^-, remained. Most notably, no NO_3^- peak appeared. As discussed earlier under certain conditions, chlorine nitrate can undergo hydrolysis to form a mixture of hypochlorous and nitric acids. However, the absence of the NO_3^- ion in the negative ion SSIMS spectrum rules out the formation of condensed nitric acid at the surface of the film in this experiment. *In the presence* of HCl and ice, $ClONO_2$ did react upon warming. When the system was warmed from 100 to 120 K, the initial change was again disappearance of the Cl_2^- and higher clusters. The Cl^- and $(H_2O)Cl^-$ intensities decreased relative to the O^- and OH^- peaks. Notably, *a small NO_3^- peak appeared for the first time in a $ClONO_2$ system.* Warming further to 140 K caused the Cl^- and $(H_2O)Cl^-$ intensities to decrease further. The NO_3^- peak increased, and new NO^-, NO_2^-, and $H(NO_3)_2^-$ peaks appeared. The low- and high-temperature spectra in fact look completely different, as illustrated in Figure 6. A spectrum taken at 160 K was similar to the 140 K spectrum, again with significant NO_2^-, NO_3^-, and $H(NO_3)_2^-$ peaks. Associated with these major changes in the surface chemistry, there was also a significant rise in residual gas pressure in the UHV chamber. This was identified as being principally due to Cl_2 (m/z 70, 72, 74). These gas-phase observations taken together with the SSIMS data provide clear evidence that chlorine nitrate reacts readily at a solid, icy surface when HCl is present.

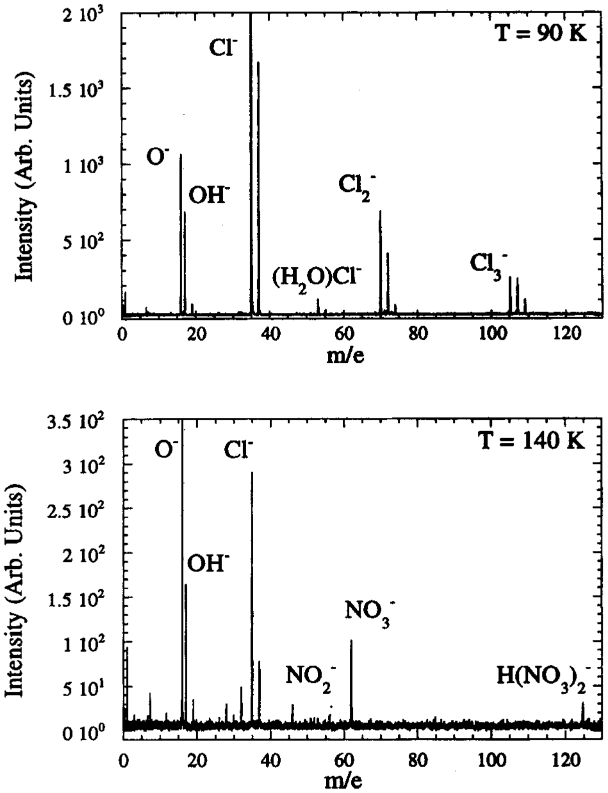

Figure 6. Negative ion SSIMS spectra of $ClONO_2$ on ice that had been exposed to HCl. Water-dosed at 95 K for 18 min to 3×10^{-8} mbar. HCl-dosed 2 min to 1×10^{-7} mbar. $ClONO_2$-back-dosed continuously to approximately 1×10^{-7} mbar. (a) T = 90−100 K. (b) T = 140 K.

4. Discussion

We have acquired static SIMS data from condensed chlorine nitrate and from $ClONO_2$/water and $ClONO_2$/water/HCl systems under a variety of conditions. Our low-temperature spectra of condensed multilayers of neat chlorine nitrate on gold indicate little ionic character in the condensed solid under these conditions. A key piece of evidence for this is the comparison of the spectra of chlorine nitrate and of pure nitric acid condensed under similar conditions. Nitric acid ionizes in the aqueous phase to form solvated H^+ and NO_3^- ions. Although the presence of nascent ions at the surface is not necessary to produce secondary ions in the SSIMS process, these species will form most readily if the $H-NO_3$ bond is already strongly polarized, with relatively high formal charges on the proton and on the NO_3. The strong NO_3^- signal in the negative ion SSIMS spectrum of HNO_3 condensed at 90 K is evidence of the highly polar nature of the $H-NO_3$ bond.

In clear contrast, *no NO_3^- signal appears in the analogous spectrum of chlorine nitrate*. Chlorine nitrate is difficult to purify completely and tends to decompose on available surfaces until passivation occurs. Thus, traces of Cl_2 and Cl_2O can be expected in the system. However, the presence of Cl_m^- and Cl_m^+ peaks ($1 \leq m \leq 5$ or more) and of nitrogen-containing clusters such as NO^+ and NO_2^+ in the low-temperature spectra of chlorine nitrate on ice indicated condensation of a species containing chlorine, nitrogen, and oxygen. Although a strong Cl^- signal was observed, this is typical of a system in which chlorine is present in any form. The higher number chlorine clusters are more diagnostic, since they were absent in the completely ionized HCl/ice systems studied previously.[24,25] The SSIMS evidence therefore points toward the condensation of chlorine nitrate molecules in which the $Cl^+-NO_3^-$ bond is not strongly polarized, i.e., as a molecular solid. At higher temperatures, we observed desorption of chlorine/nitrogen containing species from the film. Under typical UHV conditions, rapid desorption of $ClONO_2$ from a solid film begins around 120−130 K.[14]

The FT-RAIRS experiments of Banham et al.[13] detected hydrolysis in condensed thin films of water exposed to $ClONO_2$ at elevated temperatures. These observations were only possible when a background partial pressure of $ClONO_2$ was maintained at a level sufficient to replenish chlorine nitrate as it desorbed. Similar IR experiments performed at low temperatures did not detect any hydrolysis products. When chlorine nitrate undergoes hydrolysis, the $Cl-ONO_2$ bond breaks to form nitric acid and HOCl.[8] Our SSIMS experiments on $ClONO_2$ interacting with pure ice at 90−100 K indicate that, even at these low temperatures, proximity to water molecules does tend to polarize the Cl−O bond. The degree of polarization increased as the proportion of water in the chlorine nitrate/ice mixture increased, and while there was evidence of what may be regarded as prehydrolysis species $(M + 2H)_n{\cdot}H_2O$, no large-scale hydrolysis *products* were observed. The presence of nitric acid can severely inhibit the hydrolysis reaction. While the reaction itself produces nitric acid, it has to be strongly emphasized that failure to observe hydrolysis here cannot be attributed to the presence of residual nitric acid in the UHV system. At this point in these studies *no nitric acid had been introduced to the system*; furthermore, the absence of NO_3^- or $H(NO_3^-)_n$ clusters in the spectra implies that nitric acid has not been formed, so we are rather confident that under the temperature and water content conditions employed, although polarization of the $Cl-NO_3$ bond was observed, no hydrolysis occurred. These observations support the suggestions arising from recent theoretical studies of the $ClONO_2$ hydrolysis that increasing numbers of water molecules can increase the polarization (or preionization) of the nitrate, which may lead to an increase in the hydrolysis rate.[12,22]

Low-temperature hydrolysis of chlorine nitrate has been reported in a recent laser-induced thermal desorption (LITD) study by Berland, Tolbert, and George,[19] who studied ultrathin films of very pure $ClONO_2$ deposited on ice between 75 and 180 K. They reported detection of hydrolysis reaction products at temperatures as low as 86 K. LITD is a very sensitive technique; the HOCl levels reported were about a monolayer or less at the $ClONO_2$/ice interface. SSIMS also is a highly sensitive technique, which should be capable of detecting hydrolysis *products* at monolayer coverages or less. However, chlorine nitrate condensed at the outer surface of a multilayer film deposited on ice would not be expected to hydrolyze significantly at such low temperatures, when both substances are frozen and therefore very little of the $ClONO_2$ is in direct proximity to the water molecules. Our initial low-temperature $ClONO_2$/ice experiments, on the outer layers of the film, would have been probing this region. The depth profiling experiments did indicate an increasing degree of polarization in the $ClONO_2$ molecules as the ice interface was approached. This clearly indicated that there is a chemical effect due to interactions with the water molecules. This is further supported by the appearance of the $(M + 2H)^+_n{\cdot}H_2O$ species. It should be noted that the ultrathin films used in the LITD experiments were designed to maximize the contact between the chlorine nitrate molecules and the ice. Under similarly favorable conditions, it is possible low-temperature hydrolysis products would also be observed in SSIMS experiments. Whether it is possible to rule out completely the transient heating effects during LITD of this system is a moot point. Both water and chlorine nitrate display significant absorption bands in the region of 1000 cm^{-1} that might contribute.[13] Heating effects are unlikely under our pulsed static SIMS conditions because the ion beam fluence is so low. However, whatever the precise differences in the two experiments, it is clear that both LITD and SSIMS point to a clear and important effect of increasing concentrations of neighboring water molecules on the polarization and reactive behavior of chlorine nitrate.

TABLE 2: Comparison of Ion Intensity Ratios from Positive Ion SSIMS Spectra of $ClONO_2$ on Gold, $ClONO_2$ on Ice, and $ClONO_2$ + HCl on Ice in the Temperature Range 100−170 K[a]

	NO^+/Cl^+	$H_2NO_3^+/Cl^+$	$(H_2O)(HNO_3)H^+/Cl^+$
	$ClONO_2$ on Gold		
$T = 110$ K	0.3	0.1	0.02
	$ClONO_2$ on Ice		
$T = 100$ K	0.4		
	$ClONO_2$ + HCl on Ice		
$T = 100$ K	0.5	0.1	0.1
$T = 130$ K	80	13	5
$T = 140$ K	329	71	31
$T = 170$ K	84	18	8

[a] Water-dosed at 90 K. HCl and $ClONO_2$ dosed at 90−100 K. For $T > 120$ K, $ClONO_2$-back-dosed continuously to a partial pressure of approximately 1×10^{-7} mbar.

The SSIMS data did clearly indicate the formation of a reaction product or products upon warming a film of $ClONO_2$ on ice that had been previously exposed to HCl. Closer examination of the high-temperature $ClONO_2$/HCl/ice data allows us to infer the nature of the newly formed species. Monitoring the intensities of the chlorine or nitrogen-containing cluster ions relative to the water cluster ion intensities, as described earlier, gives a measure of the relative proportion of Cl- or N-containing molecules at the surface. A measure of the changes in the chemical structure of the chlorine nitrate may be obtained by examining the ratios of nitrogen-containing clusters (e.g., NO^+, $H_2NO_3^+$, or $(H_2O)HNO_3H^+$) to a Cl-containing cluster (such as Cl^+). These ratios are shown in Table 2 for $ClONO_2$ on gold, $ClONO_2$ on ice at 100 K, and for $ClONO_2$ + HCl on ice at temperatures from 100 to 170 K. They clearly show the similarities in the three systems at low temperatures, and the major change in chemical composition as the HCl-containing system is warmed to 140 K and then to 170 K.

The presence of the NO^+ and NO_2^+ ions, coupled with the emerging $(HNO_3)(H_2O)_nH^+$ and $(HNO_3)(H_2O)_nNO^+$ clusters in the positive ion spectra, and NO_3^- in the negative ion $ClONO_2$/HCl/ice spectra are particularly informative. These ions were previously and characteristically associated with solid nitric acid (Figure 3b). We can therefore conclude that nitric acid, one of the anticipated final products of the reaction between chlorine nitrate and HCl, is forming and remaining condensed in the ice film.

The loss of the Cl-containing cluster ions in both the positive and negative ion spectra is also interesting. This loss corresponded to the appearance of a significant pressure of chlorine in the *residual background gas* of the UHV system. This observation is consistent with the formation at the surface of molecular chlorine, which immediately desorbs as chlorine gas. No new chlorine-containing SSIMS cluster ions appeared at any stage. Our SSIMS experiments thus indicate that molecular chlorine forms via a direct attack of the $Cl^{\delta+}$ from chlorine nitrate on solvated Cl^- ions and promptly desorbs into the gas phase. This is precisely what is observed in spectroscopic experiments, where the amount of Cl_2 released can be related directly to the amount of Cl^- available at the ice surface.[16] Furthermore, it is in line with the likely implications of kinetic studies under stratospheric type conditions.[7] These results are extremely significant, since they confirm the conclusion from our earlier exploratory experiments[20] that chlorine nitrate hydrolysis is not a necessary first step in the reaction between $ClONO_2$ and HCl but is rather a significant competing reaction channel. When a strong nucleophile (such as Cl^-) is present, chlorine nitrate will interact preferentially with it rather than with water. A similar direct attack by a strong nucleophile has been observed in the gas phase when $ClONO_2$ was observed to react with Cl^- generated from CCl_4 in an ion cyclotron resonance (ICR) mass spectrometer.[9] The mechanism for the reaction between chlorine nitrate and HCl in the presence of a solid, icy surface is therefore as follows:

$$HCl_{(g)} + nH_2O_{(s)} \rightarrow H_3O^+ + Cl^- + (n-1)H_2O_{(s)}$$

$$Cl^+{-}ONO_2^- + H_3O^+ + Cl^- \rightarrow Cl_{2(g)} + HNO_{3(s)} + H_2O_{(s)}$$

As we have seen under certain conditions, chlorine nitrate may hydrolyze even in the absence of a strong nucleophile.[13,14,19] The hydrolysis reaction itself is of interest, since it generates hypochlorous acid, which is potentially reactive, and HNO_3. The HOCl thus produced may be released into the atmosphere as an "active" chlorine species. Other work has also indicated that HOCl on an icy surface can react with HCl to produce molecular chlorine.[13,16] However, given the demonstrated preference for $ClONO_2$ to react directly with a strong nucleophile such as Cl^-, chlorine nitrate hydrolysis is unlikely to play an important role in the overall reaction when HCl is present in abundance.

In the atmosphere, a balance between the two mechanisms is likely to exist. Chlorine nitrate may encounter water more readily than chloride ions. At the prevailing temperatures of 185 K or higher, this should promote hydrolysis and the subsequent release of molecular chlorine in a two-step mechanism involving HOCl. If chlorine nitrate encounters chloride ions directly, the nucelophilic attack mechanism is clearly favored. Which mechanism dominates overall will depend on specific conditions prevailing in the stratosphere.

5. Summary and Conclusions

We now summarize the findings of our SSIMS experiments on $ClONO_2$/ice and $ClONO_2$/HCl/ice systems. At 90−100 K, chlorine nitrate condenses on ice or on gold as a molecular species. There is evidence for some degree of polarization of the $ClONO_2$ molecules and interaction with water, even at this temperature, but there is no indication from our experiments that a *chemical reaction* occurs either on pure ice or on ice that has been exposed to HCl. The conditions, most particularly the proximity of the chlorine nitrate and water molecules, are crucial.

At 120 K, chlorine nitrate condensed on ice begins to desorb. On a pure ice substrate, essentially all the $ClONO_2$ desorbs by 130 K and there were no signs of a significant reaction between chlorine nitrate and water.

Chlorine nitrate reacts rapidly with HCl in the presence of a cold icy surface. Upon contact with ice, the HCl dissociates virtually instantaneously to produce a film of solvated H_3O^+ and Cl^- ions. The Cl^+ from the chlorine nitrate reacts directly with the solvated Cl^- from the HCl to release molecular chlorine, leaving condensed nitric acid behind on the surface. In the presence of a sufficiently strong nucleophile, such as Cl^-, this is the dominant process for the heterogeneous decomposition of chlorine nitrate. This reaction is of great significance to atmospheric ozone chemistry, since it provides a mechanism for the rapid conversion of chlorine nitrate to active chlorine radicals.

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