# Static SIMS Studies of Reactions on Mimics of Polar Stratospheric Clouds II: Low-Temperature, Low-Pressure Interactions of $Cl_2$ and $Cl_2O$ with Solid Ice Films

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The interactions of molecular chlorine, dichlorine monoxide, and hypochlorous acid with solid ice films have been examined. At 90−100 K, chlorine can be made to condense as a molecular solid, forming a discrete layer on top of an existing film of solid $H_2O$. Interaction between the $Cl_2$ and the water molecules is minimal. At temperatures above approximately 130 K, the $Cl_2$ and water react to produce a mixed film of water, hypochlorous acid, and solvated HCl. As with chlorine, the dichlorine monoxide did not react with water at 90 K. However, there was evidence of a hydrogen-bond-like interaction between the $Cl_2O$ and $H_2O$ molecules. Upon warming to 120 K or higher, the two reacted to produce a mixed film of hypochlorous acid and water. The reactions that occurred at the higher temperatures are of interest because of the well-documented influence of polar stratospheric clouds, which consist of solid water or water/nitric acid particles, on the release of active chlorine species into the stratosphere.

## Introduction

The discovery that the clouds that form every winter over the Antarctic play an important role in ozone depletion has prompted numerous studies of the possible chemistry involved. These clouds are made up of tiny particles of condensed water/nitric acid mixtures or of water alone condensed around a water/nitric acid core. In the presence of these tiny cloud particles, the conversion of relatively inert chlorine-containing species into molecular chlorine is greatly enhanced.

The production and release of molecular chlorine is a crucial step in the ozone-depletion cycle, since the $Cl_2$ photolyzes readily in sunlight to provide a steady source of chlorine radicals. Thus, the heterogeneous chemistry of gaseous chlorine-containing species interacting with a solid icy surface is of great interest to atmospheric chemists. In this study, we use static secondary-ion mass spectrometry (SSIMS) to study the interactions of molecular chlorine, of dichlorine monoxide, and of hypochlorous acid with films of condensed water grown under ultrahigh vacuum (UHV) conditions. Our purpose was to ascertain the nature of the interactions of these species with ice, along with the nature of any reaction products or reactive intermediates formed.

Previous studies have used IR spectroscopy and temperature-programmed mass spectrometry (TPMS) to study the interactions of chlorine-containing species with ice films. Reflection−absorption IR spectroscopy (RAIRS) in particular is useful for studying reactions at surfaces. For example, RAIRS has been used to follow the reaction between molecular chlorine and water co-deposited onto a cooled, inert substrate.[1] At 180 K, under UHV conditions, neither water nor molecular chlorine condensed individually. When both were introduced simultaneously, the IR spectrum observed was thus attributed to the condensation of a reaction product. The IR spectrum of the condensed product contained a strong, sharp absorption band, blue-shifted from that due to condensed water. This band is apparently characteristic of water of hydration, leading to speculation that it arose from a $[H_2OCl]^+$ ion.

The same study examined the reactions of dichlorine monoxide ($Cl_2O$) on ice. Although it is not a major constituent of atmospheric chlorine, dichlorine monoxide in the gas phase reacts with water in an equilibrium reaction to produce hypochlorous acid:[2]

$$Cl_2O + H_2O \leftrightarrow 2HOCl \quad K_{eq}(298\ K) = 0.1 \qquad (1)$$

This reaction, and particularly the hypochlorous acid that is formed, is of interest due to the host of reactions that could take place on the watery surfaces of polar stratospheric cloud particles.

The RAIRS spectrum of $Cl_2O$ and $H_2O$ codeposited at 80 K from the gas phase clearly showed stretching modes from pure molecular $Cl_2O$, along with weak bands attributed to solid−solid interactions between the water and the dichlorine monoxide. A spectrum of solid $Cl_2O$ condensed on top of a solid ice film was similar but lacked the weak solid−solid interaction bands. Premixing $Cl_2O$ and water in the gas phase, then condensing the resulting mixture onto the cooled substrate gave a mixed $H_2O-Cl_2O-HOCl$ film, with the HOCl showing a large degree of hydrogen bonding. Heating to 140 K removed all traces of residual $Cl_2O$.

The IR experiments proved very informative and laid an important foundation in the study of these systems. However, no one technique is ideal for providing definitive, unambiguous answers to all the questions one may wish to address. Static secondary-ion mass spectrometry (SSIMS) was adopted as a highly sensitive technique that is capable of providing detailed chemical information about species as they exist in situ, on the surface of the film.[3] In static SIMS, secondary particles (anions, cations, neutrals, and electrons) are ejected from the surface as a result of bombardment by a high-energy primary ion beam. When the primary ion dose is kept low (less than $10^{13}$ ions/cm$^2$), damage to the sample during analysis can be minimized. The sputtered secondary ions are then detected by a mass spectrometer. By use of time-of-flight analysis, very high

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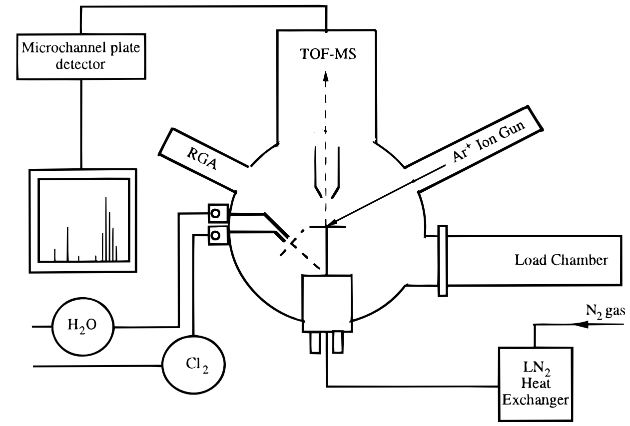

**Figure 1.** Schematic of the secondary-ion mass spectrometer and sample-dosing apparatus: TOF-MS, time-of-flight mass spectrometer, detector for the secondary ions; RGA, quadrupole mass spectrometer used for residual-gas analysis.

transmissions can be obtained for these secondary ions, making SIMS an extremely sensitive technique for detecting trace quantities of ionizable species from the surface.

Little data are available on the characteristic SIMS spectra of condensed systems such as these. Thus, it was necessary to establish a base of standard "reference" spectra for simple systems to aid in the interpretation of the more complex systems. This was done for pure water, for molecular chlorine, and for dichlorine monoxide by condensing each reagent individually onto an inert gold substrate at 90−100 K. Mixed systems of relevance to atmospheric chemistry, such as $Cl_2$/water or $Cl_2O$/water, were then studied for comparison.

In the stratosphere, cloud particles exist at temperatures of 185 to 210 K. We are therefore more interested in how these systems react at higher temperatures. Under UHV conditions, condensed water begins to desorb rapidly by 150 K,[4] and the reactants tended to desorb at even lower temperatures.[5] Thus, for the work at higher temperatures, it was sometimes deemed appropriate to establish a constant backpressure of water, the reactant, or both (to a total pressure of $10^{-5}$ mbar or less) in order to maintain a film of reasonable thickness. Doing so produced conditions that were more representative of the stratosphere, where the total pressures are in the range 1−100 mbar (depending on the exact altitude). This means that the surfaces of stratospheric cloud particles exist in a state of dynamic flux, with material constantly desorbing and recondensing.[4] By raising the temperature until material began to desorb rapidly, then establishing a sustaining backpressure of the relevant species, we were able to simulate these conditions in our vacuum chamber.

## Experimental Section

The experiments were performed using a Kratos time-of-flight secondary-ion mass spectrometer (TOF−SIMS) equipped with a special gas-dosing and -handling system, a temperature-controlled sample manipulator, and a VG micromass quadrupole mass spectrometer for residual gas analysis (Figure 1). The TOF-SIMS uses 10 kV $Ar^+$ ions as the primary source, with typical ion doses during data acquisition being on the order of $2 \times 10^{12}$ ions/cm$^2$. Details of the system have been described elsewhere.[6]

The chlorine (99.5% purity) was used as purchased from Aldrich. The $Cl_2O$ was synthesized by passing a stream of $Cl_2$ in nitrogen (zero grade, 99.995%) through a glass column packed with dry, yellow mercuric oxide (Aldrich, 99+%) dispersed on a bed of glass beads.[7] The product was trapped under liquid nitrogen, then purified by pumping briefly under dry ice/acetone to remove residual $Cl_2$.

Water, $Cl_2$, and $Cl_2O$ were introduced into the vacuum chamber from separate reservoirs in the glass dosing line using a set of leak valves. Hypochlorous acid (HOCl) was synthesized at room temperature in one of the reservoirs by mixing gaseous $Cl_2O$ and $H_2O$. The resulting $Cl_2-H_2O-HOCl$ mixture was then introduced through a single leak valve. Inside the vacuum chamber, a set of 3-mm diameter Teflon tubes were used to direct the reagents. The sample stub could be rotated out of the analysis position to one directly in front of the nozzles, causing the relatively large amounts of the material to be selectively deposited onto the gold substrate (dosing). Alternatively, when smaller amounts were required, or to help maintain a film during analyses at higher temperatures (140 K or higher), material could be backdosed by opening the leak valves while leaving the sample stub in the analysis position.

Under the dosing conditions normally employed, we expect to form an ice film consisting of several hundred to a thousand layers. Except where otherwise noted, the water films were then thermally annealed to 150 K, then cooled back to the temperature of the experiment before introducing the second component. This should cause the ice film, which is almost certainly amorphous as dosed, to crystallize.

## Results and Discussion

**Molecular Chlorine at $T = 90$ K.** Spectra were obtained at 90 K for both neat $Cl_2$ condensed onto a gold substrate and for $Cl_2$ condensed on ice. The spectra of pure $Cl_2$ on gold were very similar to the $Cl_2$/ice spectra, which are shown in Figure 2. In both cases the positive-ion SIMS spectra consisted of chlorine-cluster ion peaks ($Cl_m^+$, $1 \leq m \leq 10$ or higher) plus $(H_2O)_nH^+$ and $(H_2O)_n^+$ cluster peaks. The last two families are typical of systems in which condensed water is present, and in the spectrum of "neat" $Cl_2$ on gold, they indicate the presence of trace quantities of residual water.

The negative-ion SIMS spectrum of condensed $Cl_2$ on gold similarly consisted of a series of $Cl_m^-$-cluster ion peaks ($1 \leq m \leq 10$ or higher). The $O^-$ and $OH^-$ peaks arise from condensed water and are very much smaller in the spectrum of neat $Cl_2$ on gold than in the $Cl_2$/ice spectrum. The negative-ion $Cl_m$ clusters give much more intense signals than the corresponding positive-ion clusters, which is reasonable, since chlorine is highly electronegative. In both the positive- and negative-ion spectra, the $m = 1$ peak was the most intense, with the intensities decreasing uniformly as $m$ increased.

It is important to make the comparison between the $Cl_2$/ice and neat $Cl_2$ spectra. The $Cl_2$/ice spectrum was a simple superimposition of the corresponding neat $Cl_2$ and water spectra. No new peaks were observed. The $(H_2O)Cl^-$ ion was present in both cases in the "neat" spectrum, presumably forming from the trace quantities of residual water that condensed along with the $Cl_2$. In general, there were no significant, systematic shifts in the relative peak intensities. Changes of this sort would be expected if a reaction were occurring, allowing us to conclude that $Cl_2$ does not chemically interact with ice at 90−100 K.

**Dichlorine Monoxide at $T = 90$ K.** The experiment was repeated for $Cl_2O$, again at temperatures of 90−100 K. The $Cl_2O$ spectra were more complex than the $Cl_2$ spectra, although the major peaks were similar. The characteristic patterns for mixtures of the $^{35}Cl$ and $^{37}Cl$ isotopes simplified interpretation of the spectra. Figure 3 shows typical spectra of neat $Cl_2O$ condensed on gold, which in general gave clearer signals than

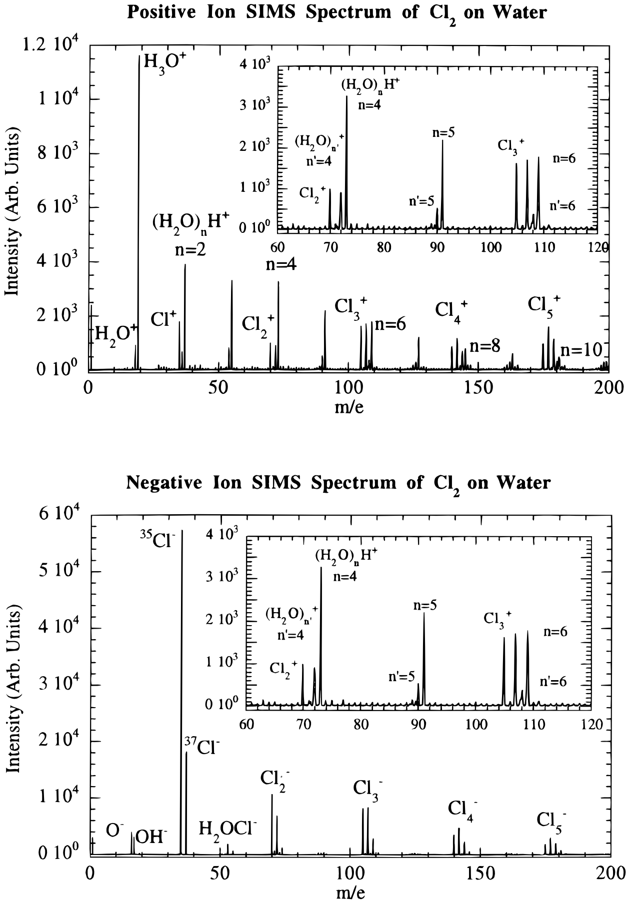

**Figure 2.** Positive- and negative-ion SIMS spectra of chlorine condensed on ice. Water was dosed to $2 \times 10^{-7}$ mbar for 30 s at 95 K, and the sample was unannealed. Chlorine was dosed to $4 \times 10^{-8}$ mbar for 30 s at 95 K. Spectra recorded at 95 K.

did the $Cl_2O$/ice films. Trace quantities of water were codeposited along with the $Cl_2O$. The water peaks are clearly evident in the positive-ion spectrum, where the most prominent peaks are the $(H_2O)_nH^+$-cluster ions. The unprotonated $(H_2O)_n^+$ clusters are less prominent. As with the $Cl_2$, the spectra of $Cl_2O$ on ice were similar to the spectra of neat $Cl_2O$ (minimal water present).

Numerous minor peaks appeared in the positive- and negative-ion spectra. These are itemized in Tables 1 and 2, which together give a comprehensive list of peaks that appeared in the various systems studied. To facilitate comparisons between spectra, the intensities in the negative-ion spectra are tabulated as a percentage of the total over all peaks. In the positive-ion table, the water-cluster peaks for $n > 2$ have been omitted from the total to avoid obscuring the important chlorine-containing species.

For $Cl_2O$ (Figure 3) and $Cl_2O$ on ice at 90 K (Tables 1 and 2), it is worth noting the presence of the molecular ion peak in both the positive- and negative-ion spectra. In fact both $Cl_2O^+$ ($m/e = 86$) and the protonated molecular ion $Cl_2OH^+$ ($m/e = 87$) appeared in the positive-ion spectrum, with the analogous $Cl_2O^-$ and $Cl_2OH^-$ ions appearing in the negative-ion spectrum. In both cases they appeared as relatively minor peaks and were most readily observed when the $Cl_2O$ overlayer was very pure. However, that the parent ions appeared in both the positive- and negative-ion spectra suggests that the $Cl_2O$ molecules remain intact and condense on top of, or cocondense with, the water molecules at 90−100 K.

Although new peaks that might indicate the formation of reaction products did not appear in either case, the positive-ion spectra show an interesting and unique feature that bears thinking about. We have observed in general that low-temperature positive-ion spectra, even those of the "neat" compounds condensed on gold, contain two sets of water-cluster peaks, namely, the $(H_2O)_n^+$ and $(H_2O)_nH^+$ families. In the SIMS spectrum of pure condensed water, the dominant peak in each is the $n = 1$ peak. The cluster intensities then decrease as a function of $n$, with the exception of $n = 4$ where a local maximum may appear. This enhanced intensity for water clusters with $n = 4$ has been observed previously[8−10] and can be attributed to the exceptional stability of the $(H_2O)_4H^+$ ion. The existence of this and other exceptionally stable clusters (with "magic numbers" at $n = 4$, 21, and 28) is widely acknowledged, and the phenomenon has been well studied.[11−14]

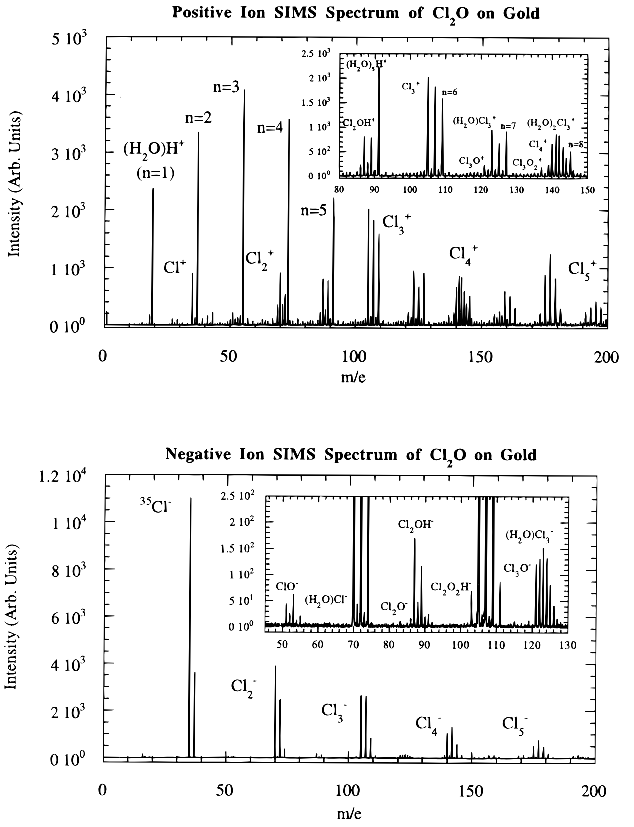

**Figure 3.** Positive- and negative-ion SIMS spectra of dichlorine monoxide condensed onto a clean gold substrate. $Cl_2O$ was backdosed to $5 \times 10^{-8}$ mbar at 100 K. Spectra were recorded at 100 K.

In our experiments, the introduction of HCl,[6] molecular chlorine, or other adsorbates in general[15] did not perturb the water-cluster distribution. The local maximum at $n = 4$ was not uniformly evident. Its appearance may depend on the exact surface density or distribution of the water molecules, since it was most pronounced in the pure water spectra. However, when $Cl_2O$ was present, the distribution was markedly different. The maximum overall intensity was shifted to the $n = 3$ cluster, rather than occurring at $n = 1$ as observed in all other instances. The difference is illustrated in Figure 4, which plots the relative peak intensities of the $(H_2O)_nH^+$ ions as a function of cluster number ($n$) at 90−100 K for pure water, for $Cl_2O$ alone and on ice, and for related systems studied in our lab. In each case the most intense water-cluster peak intensity was normalized to unity. The maximum at $n = 3$ in the $Cl_2O$ spectra is clearly visible and is in marked contrast to the distributions observed in the other systems.

This difference is clearly significant and may arise from the

**TABLE 1: Integrated Peak Intensities from Positive-Ion SIMS Spectra**[a]

| *m*/*e*, ion | HCl/ice 90 K | $Cl_2$/ice 90 K | $Cl_2O$/ice 100 K | $Cl_2O/H_2O$ 140 K | $HOCl/H_2O$ 130 K | $Cl_2/H_2O$ 130 K |
|---|---|---|---|---|---|---|
| 18, $H_2O^+$ | 3.8 | 3.8 | 0.7 | 5.2 | 3.4 | 4.0 |
| 19, $H_3O^+$ | 79.8 | 45.9 | 15.7 | 72.2 | 81.5 | 79.2 |
| 35, $Cl^+$ |  | 7.3 | 6.6 |  | 0.1 |  |
| 36, $(H_2O)_2^+$ | 0.6 | 2.9 | 0.4 | 1.3 | 0.5 | 0.5 |
| 37, $(H_2O)_2H^+$ | 15.2 | 17.3 | 26.1 | 18.0 | 13.8 | 16.3 |
| 51, $ClO^+$ | 0.2 | 0.2 | 2.8 | 0.6 | 0.1 |  |
| 52, $HOCl^+$ |  | 0.2 | 0.7 |  | trace |  |
| 53, $H_2OCl^+$ | 0.2 | 0.4 | 1.2 | 1.2 | 0.2 |  |
| 67, $ClO_2^+$ |  |  | 2.8 |  | trace |  |
| 69, $H_2OClO^+$ | 0.1 |  | 2.6 | 0.8 | trace |  |
| 70, $Cl_2^+$ |  | 4.5 | 5.3 |  |  |  |
| 71, $HCl_2^+$ |  | 0.4 | 2.6 | 0.1 | 0.4 |  |
| 85, $H_2OCl_2O^+$ |  |  | 0.5 |  |  |  |
| 86, $Cl_2O^+$ |  |  | 2.2 |  |  |  |
| 87, $HCl_2O^+$ |  |  | 3.5 |  |  |  |
| 88, $H_2OCl_2^+$ |  |  | 2.6 |  |  |  |
| 89, $H_2OHCl_2^+$ | 0.1 | 0.6 | 4.0 | 0.4 |  |  |
| 102, $Cl_2O_2^+$ |  |  | 1.6 |  |  |  |
| 105, $Cl_3^+$ |  | 7.2 | 10.9 |  |  |  |
| 140, $Cl_4^+$ |  | 4.2 | 3.2 |  |  |  |
| 175, $Cl_5^+$ |  | 5.1 | 4.0 |  |  |  |
| 19/18, $H_3O^+/H_2O^+$ | 21.0 | 12.1 | 22.4 | 13.9 | 24.0 | 19.8 |

[a] All intensities are normalized, expressed as a percentage of the total counts from all peaks in a given spectrum, to facilitate comparisons among the various systems: for HCl/ice, 90 K,[6] water dosed to $6.6 \times 10^{-7}$ mbar for 50 s, annealed 10 min at 150 K, HCl backdosed to $6.2 \times 10^{-8}$ mbar for 35 s; for $Cl_2$/ice, 90 K, as per Figure 2; for $Cl_2O$/ice, 100 K, water dosed to $1 \times 10^{-7}$ mbar for 120 s, annealed 10 min at 150 K, $Cl_2O$ dosed to $1.5 \times 10^{-7}$ mbar for 135 s; for $Cl_2O/H_2O$, 140 K, water dosed to $2.3 \times 10^{-7}$ mbar for 120 s, annealed 10 min to 150 K, $Cl_2O$ backdosed to $1 \times 10^{-7}$ mbar (the $Cl_2O$ reacts, producing a film of hypochlorous acid (see text)); for $HOCl/H_2O$, 130 K, gaseous $Cl_2O$ and $H_2O$ premixed at room temperature, dosed to $1 \times 10^{-7}$ mbar (total) for 60 s at 90 K, heated slowly to 130 K; for $Cl_2/H_2O$, 140 K, water dosed to $3.5 \times 10^{-7}$ mbar for 60 s at 90 K, annealed 10 min to 150 K, $Cl_2$ dosed to $3.0 \times 10^{-7}$ mbar for 60 s at 80 K, heated slowly to 130 K.

**TABLE 2: Integrated Peak Intensities from Negative-Ion SIMS Spectra**[a]

| *m*/*e*, ion | HCl/ice 90 K | $Cl_2$/ice 90 K | $Cl_2O$/ice 100 K | $Cl_2O/H_2O$ 140 K | $HOCl/H_2O$ 130 K | $Cl_2/H_2O$ 130 K |
|---|---|---|---|---|---|---|
| 16, $O^-$ | 20.6 | 15.1 | 4.2 | 13.5 | 15.2 | 18.3 |
| 17, $OH^-$ | 8.6 | 9.4 | 0.4 | 13.1 | 9.4 | 12.4 |
| 35, $Cl^-$ | 69.6 | 71.1 | 78.3 | 65.2 | 71.6 | 67.0 |
| 51, $ClO^-$ | 0.1 | 0.1 | 0.2 | 0.3 | 0.1 | 0.1 |
| 52, $ClOH^-$ | 0.1 | 0.1 |  | 0.3 | 0.1 | 0.1 |
| 53, $H_2OCl^-$ | 0.6 | 1.9 | 0.1 | 5.3 | 1.9 | 1.5 |
| 70, $Cl_2^-$ | 0.2 | 1.0 | 6.1 | 0.5 | 1.0 | 0.2 |
| 71, $HCl_2^-$ | 0.2 | 0.7 | 0.1 | 1.1 | 0.3 | 0.3 |
| 86, $Cl_2O^-$ |  |  | 0.2 |  |  |  |
| 87, $HCl_2O^-$ |  |  | 0.4 |  |  |  |
| 88, $H_2OCl_2^-$ | trace | 0.1 | 0.1 | 0.2 | trace |  |
| 89, $H_2OHCl_2^-$ | trace | 0.1 | 0.2 | 0.5 | trace | 0.1 |
| 105, $Cl_3^-$ |  | 0.3 | 4.3 |  | 0.3 |  |
| 121, $Cl_3O^-$ |  |  | 1.0 |  |  |  |
| 122, $Cl_3OH^-$ |  |  | 0.2 |  |  |  |
| 137, $Cl_3O_2^-$ |  |  | 0.6 |  |  |  |
| 139, $H_2OCl_3O^-$ |  |  | 0.8 |  |  |  |
| 140, $Cl_4^-$ |  | 0.1 | 1.5 |  | 0.1 |  |
| 175, $Cl_5^-$ |  | trace | 1.1 |  |  |  |
| 191, $Cl_5O^-$ |  |  | 0.3 |  |  |  |
| 71/70, $HCl_2^{-/Cl}{}_2^-$ | 1.0 | 0.70 | 0.02 | 2.1 | 0.30 | 1.5 |

[a] All intensities are expressed as a percentage of the total counts from all peaks in a given spectrum: for HCl/ice, 90 K, water dosed to $5 \times 10^{-7}$ mbar for 30 s, unannealed, HCl backdosed continuously to $1.5 \times 10^{-7}$ mbar; for $Cl_2$/ice, 90 K, as per Figure 2; for $Cl_2O$/ice, 100 K, as per Table 1; for $Cl_2O/H_2O$, 140 K, as per Table 1; for $HOCl/H_2O$, 130 K, as per Table 1; for $Cl_2/H_2O$, 140 K, water dosed to $4.0 \times 10^{-7}$ mbar for 60 s at 83 K, annealed 10 min at 150 K, $Cl_2$ dosed to $3.0 \times 10^{-7}$ mbar for 60 s at 90 K, system heated slowly to 140 K, $Cl_2$ continuously backdosed to $9.3 \times 10^{-8}$ mbar at 140 K.

way dichlorine monoxide and water molecules interact at this temperature. In a film of pure water ice, the molecules interact by hydrogen bonding. Each $\delta^+$ hydrogen in one water molecule is capable of interacting with the $\delta^-$ oxygen of an adjacent molecule to form an extensive, long-range hydrogen-bonded network. One would expect the extent of hydrogen bonding to influence the SIMS spectrum, for instance, by affecting the observed cluster distribution. Systematic changes have in fact been observed in the distributions from water and from $C_1$ to $C_8$ alcohols.[9]

Consider the effect of introducing $Cl_2O$ to a film of pure water ice. The $Cl_2O$ molecule can be thought of as a substituted analogue of water, since the relative electronegativities are such that the oxygen atom is polarized $\delta^-$ while the chlorines are $\delta^+$. This means that the $Cl_2O$ molecules can interact as the water molecules themselves do (Figure 5), inserting themselves

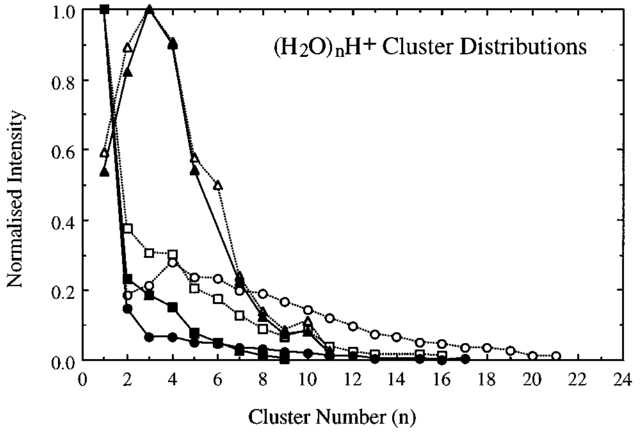

**Figure 4.** Comparison of $(H_2O)_nH^+$-cluster intensities as a function of cluster number $n$ for various systems at $T \approx 90$ K: (○) pure ice; (●) HCl on ice;[6] (□) $Cl_2$ on ice; (△) $Cl_2O$ on gold; (▲) $Cl_2O$ on ice; (■) $ClONO_2$ on ice.[15] In each case, the maximum $(H_2O)_nH^+$ intensity has been normalized to unity.

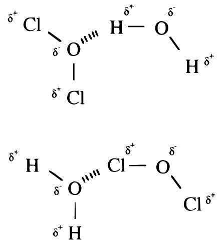

**Figure 5.** Schematic showing the hydrogen bonding or hydrogen-like bonding that is possible between water molecules and dichlorine monoxide.

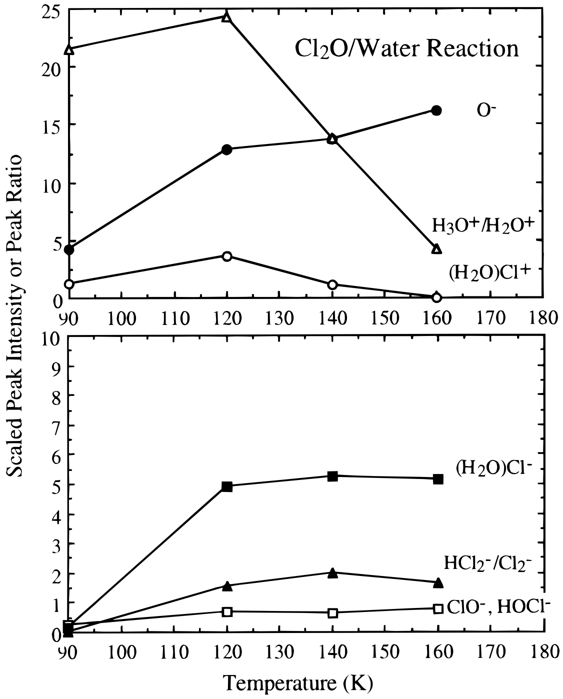

**Figure 6.** Highlights of the changes that occur in the $Cl_2O$/ice system as the temperature is raised from 90 to 160 K: (△) $H_3O^+/H_2O^+$ ratio; (●) $O^-$ normalized intensity; (○) $(H_2O)Cl^+$ normalized intensity; (■) $(H_2O)Cl^-$ normalized intensity; (▲) $HCl_2^-/Cl_2^-$ ratio; (□) $ClO^-$, $HOCl^-$ normalized intensities. All normalized intensities were scaled as a percentage of the total counts from all peaks in a given spectrum. $Cl_2O$ was dosed to approximately $1 \times 10^{-6}$ mbar for 300 s at 90 K.

and interrupting the long-range network of tetrahedrally coordinated pure water. This could explain the observed perturbation of the water-cluster ion distribution in low-temperature systems containing $Cl_2O$, as well as the presence of the $H_3O^+$ analogues $H_2ClO^+$ and $HCl_2O^+$. The other species studied, such as HCl, $Cl_2$, $ClONO_2$, etc., do not have the same effect presumably because they do not "mimic" water molecules in the same way. Among the molecules studied in our lab,[6,15] $Cl_2O$ is unique in interacting this way with ice at 90−100 K.

**$Cl_2O$ and Water at Higher Temperatures**. Temperatures in the stratosphere are typically much greater than 90−100 K, and it is at these higher temperatures that we might expect reactions to occur, either between coadsorbed species or between an adsorbate and the ice film itself. Naturally, the spectra obtained from mixed systems, or in systems where a reaction has occurred, become more complex. These spectra are best interpreted by starting at a low temperature, then monitoring the changes observed as the temperature is increased.

By comparison of the $Cl_2O$/water spectra at 90 and at 140 K (Tables 1 and 2), it is immediately clear that raising the temperature caused the features associated with the $Cl_2O$ to disappear. Most obvious were the loss of the $Cl_m^-$ peaks for $m > 2$ in the negative-ion spectrum, the loss of all $Cl_m^+$ peaks in the positive-ion spectrum, and the shift of the $(H_2O)_nH^+$-cluster ion distribution back to "normal" (maximum intensity for $n = 1$). As with the other mixed systems, there was no local maximum for $n = 4$. The relative intensities of the water peaks increased in both the positive- and negative-ion spectra, indicating an increased proportion of water at the surface.

The changes of the sort described above would result from the desorption of $Cl_2O$, which occurs at 120 K.[1] Certain other changes occurred at this stage, which seem to indicate that the $Cl_2O$ does not merely desorb from the film. Figure 6 highlights the important changes. For instance, as the temperature was raised, there was a decrease in the $H_3O^+/H_2O^+$ ratio in the positive-ion spectrum, an increase in the relative importance of the $O^-$ and $(H_2O)Cl^-$ ions in the negative-ion spectrum, and a dramatic increase in the $HCl_2^-/Cl_2^-$ ratio. At temperatures of 130 K and higher, $Cl_2O$ was backdosed in order to maintain the film. By 160 K, it was necessary to backdose the water as well. The changes seen in the film suggest the simultaneous occurrence of a reaction between $Cl_2O$ and water, with products that remain condensed at temperatures of 140 K or higher.

Water and $Cl_2O$ are known to react in the gas phase to produce an equilibrium mixture of $Cl_2O$, HOCl, and water. It is therefore interesting to compare the high-temperature spectra of $Cl_2O$ adsorbed on a pregrown ice film with spectra of $Cl_2O$ that has been premixed with water, then condensed onto the gold substrate. Table 3 shows data from $Cl_2O$ and water that were premixed in roughly equal proportions at room temperature, then condensed at 90−100 K. The initial spectra taken at this temperature show some of the features associated with low-temperature $Cl_2O$ on ice. These include the presence of $Cl_m$ clusters for $m > 2$ in both the positive- and negative-ion spectra, the presence of the $(H_2O)Cl^+$ ion in the positive-ion spectrum, and the low $HCl_2^-/Cl_2^-$ ratio (0.082) in the negative-ion spectrum.

Warming the film to 130 K caused the expected loss of the $Cl_2O$ features and an increase in the $H_3O^+/H_2O^+$ ratio, along with the increase in the $HCl_2^-/Cl_2^-$ ratio, and $O^-$ and $(H_2O)Cl^-$ intensities observed upon warming straight $Cl_2O$ on ice. Again, these changes are consistent with the loss of $Cl_2O$ and the formation of a reaction product or products, which remain condensed. At this temperature, introducing a backpressure of the $Cl_2O/H_2O/HOCl$ equilibrium mixture should result in no

**TABLE 3: Highlight of Changes in the Spectra from a $Cl_2O/H_2O/HOCl$ Mixture Formed at Room Temperature by Premixing Gaseous $Cl_2O$ and $H_2O$ in the Gas-Dosing/Preparation Line**[a]

Positive Ions

| | $m/e = 18$ $H_2O^+$ | $m/e = 19$ $H_3O^+$ | $m/e = 53$ $(H_2O)Cl^+$ | $m/e = Cl_m^+$ $m \leq 4$ | 19/18 $H_3O^+/H_2O^+$ |
|---|---|---|---|---|---|
| 100 K | 4.5 | 67.4 | 0.5 | 5.6 | 14.9 |
| 130 K | 3.4 | 81.5 | 0.2 | 0.3 | 24.0 |
| backdosing, 130 K | 3.2 | 81.5 | 0.1 | 25.5 | |

Negative Ions

| | $m/e = 16$ $O^-$ | $m/e = 35$ $Cl^-$ | $m/e = 53$ $(H_2O)Cl^-$ | $Cl_m^-$ $m \leq 4$ | 71/70 $HCl_2^-/Cl_2^-$ |
|---|---|---|---|---|---|
| 100 K | 5.0 | 73.2 | 1.6 | 88.1 | 0.08 |
| 130 K | 15.2 | 71.6 | 1.9 | 73.0 | 0.30 |
| backdosing, 130 K | 22.0 | 60.9 | 2.3 | 61.2 | 2.2 |

[a] All intensities are expressed as a percentage of the total counts from all peaks in a given spectrum. Mixture was dosed as per $HOCl/H_2O$ in Table 1, slowly heated to 130 K. Backdosing was to a total pressure of $5 \times 10^{-7}$ mbar.

further condensation of $Cl_2O$. Opening the leak valve did produce further changes, which must therefore be attributed to the condensation of mixed hypochlorous acid (HOCl) and water. The changes appeared primarily in the negative-ion spectrum, where the $O^-$ and $(H_2O)Cl^-$ increased in both absolute and relative intensity, while the $HCl_2^-/Cl_2^-$ ratio jumped from 0.28 to 2.15. These are the traits that appeared when pure $Cl_2O$ condensed on ice was warmed to 140 K. The definite similarities between the two systems suggest that upon warming, the condensed $Cl_2O$ and water react to produce hypochlorous acid (HOCl) at the ice surface.

**$Cl_2$ and Water at Higher Temperatures**. The conversion of $Cl_2O$ to hypochlorous acid at the surface upon warming the film is not especially surprising. Of greater interest is a possible reaction between condensed molecular chlorine and ice as the temperature is raised. Tables 1 and 2 highlight the differences between $Cl_2$/water spectra at 90 and at 130 K. Loss of the $Cl_m^{\pm}$ peaks, coupled with a rise in the background partial pressure of $Cl_2$ (monitored on the quadrupole mass spectrometer used for residual-gas analysis), indicated desorption of at least some $Cl_2$. However, as in the case of $Cl_2O$, other changes appeared that seem to indicate that a reaction occurs as well. These changes are illustrated by a series of positive- and negative-ion spectra, recorded at temperatures between 100 and 165 K. Certain key quantities were plotted as a function of temperature, with the $Cl_2$ backdosed as necessary to maintain a constant backpressure of approximate;y $2 \times 10^{-7}$ mbar (Figure 7). As indicated by the graphs, the $H_3O^+/H_2O^+$ ratio increased with temperature, with the biggest change coming between 110 and 130 K. The $O^-$ relative intensity showed an abrupt increase at temperatures above 130 K. The relative intensities of the $ClO^-$, $HOCl^-$, and $(H_2O)Cl^-$ ions all increased steadily with temperature, as did the $HCl_2^-/Cl_2^-$ ratio.

Certain similarities exist between these graphs and the graphs from the $Cl_2O$/water system (Figure 6), suggesting that similar reactions involving HOCl may be occurring in both systems. However, there are significant differences, including a decrease in the $H_3O^+/H_2O^+$ ratio from $Cl_2O$/water above 120 K (Figure 6), a decrease that was not observed when $Cl_2O$ was backdosed at 130 K (Table 3). For $Cl_2$/water, with a constant $Cl_2$ backpressure of approximately $2 \times 10^{-7}$ mbar, the ratio remains high. A high $H_3O^+/H_2O^+$ ratio has previously been associated with a high concentration of acidic protons within the film.[6] There is also a slight falloff of the $HCl_2^-/Cl_2^-$ ratio for the $Cl_2O$/water at 160 K, as opposed to a steady rise in the case of $Cl_2$/water. These changes may signify the presence of HOCl plus water in the $Cl_2O$/water case, and both HOCl and HCl plus water in the case of $Cl_2$/water, with net reactions that proceed as follows:

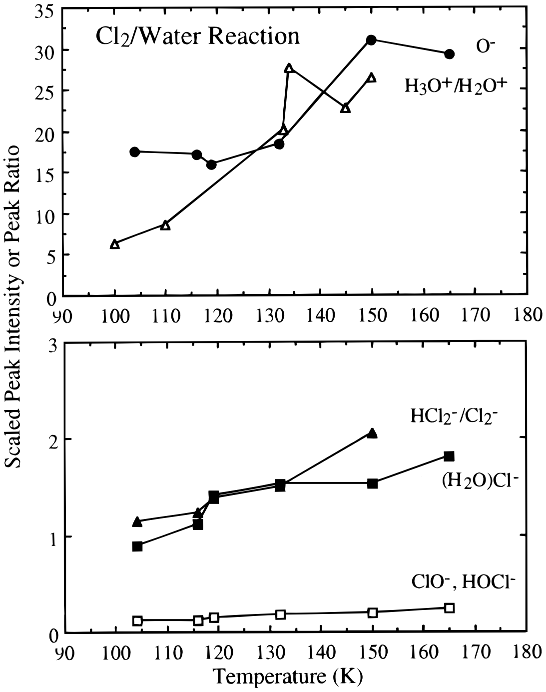

**Figure 7.** Highlights of the changes that occur in the $Cl_2$/ice system as the temperature is raised from 105 to 165 K: (△) $H_3O^+/H_2O^+$ ratio; (●) $O^-$ normalized intensity; (■) $(H_2O)Cl^-$ normalized intensity; (▲) $HCl_2^-/Cl_2^-$ ratio; (□) $ClO^-$, $HOCl^-$ normalized intensities. All normalized intensities were scaled as a percentage of the total counts from all peaks in a given spectrum. $Cl_2$ background partial pressure was held approximately constant at $2 \times 10^{-7}$ mbar.

$$Cl_2O + nH_2O \rightarrow 2HOCl + (n-1)H_2O \qquad (2)$$

$$Cl_2 + 2H_2O \rightarrow HOCl + H_3O^+ + Cl^- \qquad (3)$$

Reaction 2 is consistent with the known gas- or liquid-phase chemistry of $Cl_2O$ and water. It is also consistent with the hydrogen bondlike interactions between $Cl_2O$ and water (Figure 5) that were proposed earlier. The RAIRS experiments with $Cl_2$ and water at 180 K, which were alluded to previously,[1] gave evidence of the formation and deposition of a reaction product at that temperature. Our experiments, with $Cl_2$ and $H_2O$ both slowly warming from the condensed phase, indicate that a reaction may begin at temperatures as low as 130 K. In the stratosphere, the partial pressure of gaseous $Cl_2$ is typically somewhat lower than the pressures on the order of $10^{-7}$ mbar used in these experiments. However, there have been questions concerning the possible fates of molecular chlorine that may be formed during heterogeneous reactions on solid PSC's. Our experiments indicate that, in addition to desorbing as the molecular species, $Cl_2$ can react with water to form a condensed film rich in ionic, and potentially reactive, species.

## Summary and Conclusions

The interactions of molecular chlorine, dichlorine monoxide, and hypochlorous acid with water ice have been examined under various conditions. At 90−100 K, $Cl_2$ can be made to condense as a molecular solid on top of a previously condensed ice film. Interaction between the two on the molecular level is minimal. As the temperature is slowly raised, the $Cl_2$ and water react to produce a mixture of water, hypochlorous acid, and solvated HCl. The reaction begins by about 130 K and, thus, is well underway at the higher temperatures of the stratosphere.

There is evidence that dichlorine monoxide interacts with ice even at 90 K by forming hydrogen bondlike interactions with the $H_2O$ molecules. This interrupts the long-range tetrahedrally coordinated structure of pure hydrogen-bonded water molecules and is manifested by a marked and significant change in the distribution of water-cluster peaks in the positive-ion SIMS spectrum. The change was unique to dichlorine monoxide, a fact that was attributed to the similarities between the $H_2O$ and $Cl_2O$ molecules. Each has an $X_2O$ structure, with the oxygen atom carrying a $\delta^-$ charge balanced by a corresponding $\delta^+$ charge on the X atoms (X = H or Cl). At temperatures of 120 K or higher, the $Cl_2O$ and water react to produce a mixture of hypochlorous acid and water.

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