Acid−Base Chemistry on Crystalline Ice: HCl + NH_3

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The chemical interaction of (i) HCl, (ii) NH_3, and (iii) HCl + NH_3 with crystalline ice has been examined as a function of temperature ($T = 80-150$ K) utilizing FTIR spectroscopy. The infrared spectra reveal the formation of ionic hydrates for HCl and molecular hydrates for NH_3. The acid−base reaction leads to the formation of the ammonium ion, NH_4^+. While it is produced to a limited extent between 80 and 140 K, NH_4^+ is a dominant species above 140 K. All species appear as lower amorphous hydrates for $T = 80-140$ K. Dramatic changes in the spectra occur above 140 K as higher crystalline hydrates are formed. This temperature coincides with the amorphous to crystalline phase transformation of ice. This change appears to be due to a greater number of water molecules on the surface that are available for hydration and crystallization.

Introduction

It is now well accepted that heterogeneous chemical reactions occur on ice-like particles in the polar stratosphere and that the resulting reactive species participate in the formation of the ozone hole over Antarctica every spring.[1−3] One of the most common reactions referred to in the literature is the formation of molecular chlorine by[4−10]

$$HCl(ad) + ClONO_2(ad) \rightarrow Cl_2(g) + HNO_3(ad)$$

This reaction represents a "double punch" for ozone loss in that it (1) produces the photoreactive species $Cl_2(g)$ and it (2) ties up the NO_x species $ClONO_2$ in the form of nitric acid which would remain on/in the ice. Some of the questions that one might ask concerning these types of reactions are: Do the reactions occur in the ice or on the ice? If on the ice, how should the ice surface be described? Is there a dynamic surface layer that enhances the chemical reactivity? Is it quasi liquid-like?[11] Is it dynamic due to the fast evaporation and condensation of water on the surface?[12] Or is it dynamic due to greater surface mobility? If so, should that mobility be described as translational, rotational, or orientational? Additionally, what is the nature of the chemical mechanism? Does it involve ions or neutrals?[13−21]

In an effort to help develop a better understanding of these heterogeneous reactions, our research group has been examining chemical reactions in ice and on ice surfaces. In the laboratory we simulate the surface of these atmospheric ice particles, known as polar stratospheric clouds or PSCs, using thin films of pure water ice. The interaction of reactive species with the ice surface is monitored using infrared transmission spectroscopy.

Using spray deposition of water vapor we are able to create thin films of two forms of ice: amorphous and crystalline ice. Amorphous ice is formed at temperatures between 80 and 140 K, while crystalline ice is formed above 140 K.[22−24] Additionally, amorphous ice can be converted nonreversibly into the thermodynamically more stable crystalline ice by heating to temperatures above 140 K. While this phase transition temperature is not well defined, but depends on the preparation and history of the ice, our laboratory has consistently obtained data indicating a transition temperature of about 140 K. Furthermore, like others,[25−27] we have discovered that these two forms of ice can exhibit different reactivity. The difference is generally attributed to the greater hydrogen bonding ability of the amorphous ice due to a greater number of available OH groups on the surface.[25,26] In an effort to avoid observing these differences, we have recently focused our attention to chemical interactions on crystalline ice.

In this report we present results for the interaction of (i) HCl on crystalline ice, (ii) NH_3 on crystalline ice, and (iii) the HCl + NH_3 reaction on crystalline ice. The infrared spectra reveal the formation of ionic hydrates for HCl, and molecular hydrates for NH_3. The acid−base reaction leads to the formation of the ammonium ion, NH_4^+. While it is produced to a limited extent between 80 and 140 K, NH_4^+ is a dominant species above 140 K. All species appear as lower amorphous hydrates for $T = 80-140$ K. Dramatic changes in the spectra occur above 140 K as higher crystalline hydrates are formed. (Note: 140 K coincides with the amorphous to crystalline phase transformation of ice.) We believe this change is due to a greater number of water molecules on the surface that are available for hydrating the ionic species. This would suggest that an important driving force for heterogeneous chemistry on ice particles in the atmosphere is the ability of water to be involved in stabilizing the ionic species through hydration, as suggested recently by theoretical work.[28]

Experimental Section

Experiments were performed using a setup very similar to a matrix isolation apparatus.[29,30] Inside a commercial vacuum cryostat an infrared transparent window (ZnSe, 25 × 2 mm) was attached to a copper block that was cooled by liquid nitrogen and warmed by a resistive heater. The temperature, measured with a silicon diode attached to the copper block, was controlled to better than 0.2 K using a Lakeshore temperature controller. The cryostat was evacuated with a vacuum line that included a liquid nitrogen trap, diffusion pump, and mechanical pump. Pressure in the vacuum line was measured with a commercial, heated capacitance manometer (range = 1 to 10^{-4}

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Torr) or hot ion gauge (range = 10^{-4} to 10^{-7} Torr). Tests indicate that the cryostat can be pumped down to 10^{-5} Torr with the vacuum line. The addition of liquid nitrogen creates internal cryopumping, and the pressure drops to 10^{-7} Torr, as measured with a cold ion gauge attached to the cryostat.

The cryostat sat inside the sample compartment of a commercial FTIR spectrometer and the ZnSe window was mounted such that transmission spectroscopy could be utilized. The outer windows of the cryostat were KBr. A commercial gas generator continuously purged the FTIR with clean, dry, CO_2-less air. The gas purge included the volume between the sides of the FTIR compartment and the outer KBr windows of the cryostat.

Gases (H_2O, HCl, and NH_3) were introduced from the vacuum line to the cryostat using a variable leak valve. The gases were directed at the ZnSe window and an effusive beam exposed one side of the window. Since the pressure in the cryostat does not appear to change during an experiment, the gas "over spray" either condenses on the cold copper block or is cryopumped away. Effective surface coverages were determined in the following manner. A particular pressure of water vapor was introduced and stabilized in the vacuum line. The variable leak valve was adjusted for a constant flow rate. After a period of time the valve was closed and the resulting ice film's thickness was determined using the IR absorbance at 820 cm^{-1} along with a "Beer's Law-like" conversion factor (1 μm = 0.163 ABS at 820 cm^{-1}) from the literature.[31,32] This process was repeated for various gas pressures. Knowing the ice film thickness, the density of ice, and the sticking or uptake coefficient of $\gamma = 1$, the gas pressure transferred through the leak valve was converted to an effective surface coverage.

For HCl and NH_3 we have assumed $\gamma \approx 0.1-1$ on ice for $T = 80-150$ K. We varied the pressure transferred from the vacuum line into the cryostat through the leak valve over the range 1−5 mTorr. This leads to a surface coverage of $1-50 \times 10^{15}$ molecules/cm^2. The large range is due to our uncertainty in γ. The lower value corresponds to our detection limit.

Regarding the ice phase, we can create thin films of amorphous or crystalline ice by spray deposition of pure water vapor. Amorphous ice is a thermodynamically metastable form of ice and is formed at $T < 140$ K. Above 140 K the amorphous phase is quickly converted, nonreversibly, into the crystalline form. Likewise, spray deposition of water vapor above $T = 140$ K forms crystalline ice. In the studies presented in this report we deposited water vapor at $T = 150$ K. *All of the results therefore concern the crystalline ice surface.*

Experiments were performed in the following manner. After a thin film (1 μm thick) of ice was created, the temperature was adjusted to the temperature of interest, and the ice was allowed to stabilize for 20 min to 2 h. A background spectrum was collected and HCl or NH_3 vapors were sprayed onto the ice. A new IR spectrum was then collected which represents a "difference spectrum", i.e., (spectrum of ice with reactant) − (spectrum of ice). In the case of the HCl + NH_3 reaction, a background spectrum was taken just before each reactive species was added to the ice film. In this way all of the spectra presented in this report represent difference spectra. All infrared spectra were collected with 4 cm^{-1} resolution and 240 scans each.

Results

Interaction of HCl on Crystalline Ice. For $T = 80-140$ K the interaction of HCl on ice was performed as follows. Crystalline ice was formed at 150 K, cooled to 80 K and allowed to stabilize for 20 min to 2 h. A background spectrum was collected, then HCl was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. The resulting infrared spectrum is shown in Figure 1a. This spectrum has been observed previously and is attributed to the amorphous monohydrate, $HCl{\cdot}H_2O$.[18,19,33] This species is ionic and is probably better represented by the notation $H_3O^+{\cdot}Cl^-$, as suggested by others.[20,21] The molecular notation appears to have caused some confusion in the literature in terms of whether the HCl is ionized on the ice.[34] The infrared analysis of the spectrum clearly attributes the spectral features to an H_3O^+ ionic species. Namely, the ν_4 antisymmetric bending vibration occurs at 1700 cm^{-1}, the ν_2 symmetric bending vibration occurs at 1100 cm^{-1}, a torsional vibration occurs at 700 cm^{-1} (not shown), and a combination vibration occurs at 2100 cm^{-1}.[33] This species is stable in time for $T = 80-140$ K. A chemical expression to represent the formation of this ionic species is

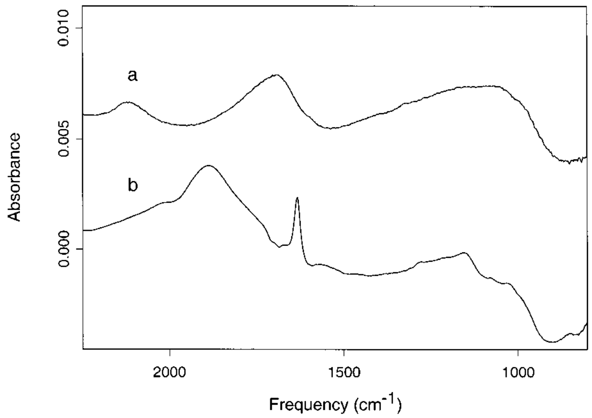

Figure 1. (a) Infrared spectrum of the ionic amorphous monohydrate, $H_3O^+{\cdot}Cl^-$, formed from the interaction of HCl on crystalline ice for $T = 80-140$ K. (b) Infrared spectrum of the ionic crystalline hexahydrate, $H_3O^+(H_2O)_5{\cdot}Cl^-$, resulting from the interaction of HCl on crystalline ice above 140 K. (The background spectrum is crystalline ice.)

$$HCl + H_2O \rightarrow H_3O^+{\cdot}Cl^- \text{ (for } T = 80-140 \text{ K)} \qquad (1)$$

For $T > 140$ K the interaction of HCl was examined in two ways: (1) the thin ice film with HCl deposited between 80 and 140 K (from above) was heated above 140 K, or (2) HCl was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) onto crystalline ice at 150 K. In either case, the resulting spectrum is shown in Figure 1b. This spectrum is attributed to the ionic crystalline hexahydrate, $HCl{\cdot}(H_2O)_6$, which has been observed previously.[31,35,36] The important spectral features due to the hydrated hydronium ion, H_3O^+, are as follows: the ν_4 antisymmetric bending vibration occurs at 1900 cm^{-1}, the ν_2 symmetric bending vibration occurs at 1150 cm^{-1}, and a very sharp peak occurs at 1635 cm^{-1} that has been attributed to a bending vibration of the proton-ordered waters of hydration.[36] As suggested by others,[20] a better notation for this ionic species is $H_3O^+ (H_2O)_5{\cdot}Cl^-$. An expression for its formation is

$$HCl + H_2O \rightarrow H_3O^+ (H_2O)_n{\cdot}Cl^- \text{ (for } T > 140 \text{ K)} \qquad (2)$$

where $n = 5$. It is interesting to note that recent theoretical studies of this reaction have indicated that six waters are needed for HCl ionization to occur in water clusters.[37]

Thus, for our experimental conditions, HCl interaction on crystalline ice films forms the lower amorphous hydrate of H_3O^+ for $T = 80-140$ K, while the higher crystalline hydrate is produced for $T > 140$ K. For the reaction HCl + NH_3, discussed below, we refer to these ice films as acidic-crystalline ice.

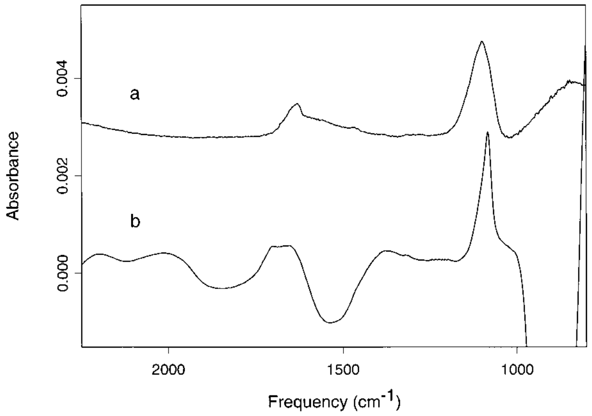

Figure 2. (a) Infrared spectrum of the molecular amorphous monohydrate, $NH_3 \cdot H_2O$, (at 1100 and 1630 cm^{-1}) produced from the interaction of ammonia on crystalline ice for $T = 80-140$ K. (b) Infrared spectrum of molecular polyhydrate, $NH_3(H_2O)_n$, (probably crystalline) resulting from the interaction of ammonia on crystalline ice above 140 K. This spectrum has been reduced by a factor of 2 for comparison purposes with (a). The "negative" peaks are described in the text. (The background spectrum is crystalline ice.)

Interaction of NH_3 on Crystalline Ice. The interaction of ammonia on crystalline ice was studied in a manner similar to that presented above for HCl. Crystalline ice was formed at 150 K, cooled to 80 K and allowed to stabilize for 20 min to 2 h. A background spectrum was collected, then NH_3 was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. The resulting spectrum is shown in Figure 2a. This spectrum is assigned to the molecular monohydrate of ammonia, $NH_3 \cdot H_2O$.[38] This species was also observed by Devlin's group in a study of the interaction of ammonia with ice nanocrystals.[39] The most distinguishing spectral features for the ammonia are the ν_2 symmetric bending vibration at 1100 cm^{-1} and the ν_4 antisymmetric vibration at 1630 cm^{-1}.[38] An expression for the formation of this molecular complex is

$$NH_3 + H_2O \rightarrow NH_3 \cdot H_2O \text{ (for } T = 80-140 \text{ K)} \qquad (3)$$

Ice with $NH_3 \cdot H_2O$ is referred to as basic-crystalline ice below.

After warming this film to $T > 140$K, another spectrum was collected and is shown in Figure 2b. (Note: the same background was used as above, namely, the crystalline ice at 80 K. Also, the spectrum has been reduced by a factor of 2 for comparison purposes.) The peak at 1100 cm^{-1} has grown in intensity, sharpened, and experienced a red-shift. We attribute this new spectrum to a higher hydrate of ammonia. It is also possible that the ammonia hydrate has crystallized. The "dips" or negative peaks are due to (i) loss of water molecules that are used for hydrating the ammonia and (ii) spectral shifts of the ice due to the temperature change. An expression for the formation of this ammonia species is

$$NH_3 + H_2O \rightarrow NH_3(H_2O)_n \text{ (for } T > 140 \text{ K)} \qquad (4)$$

This spectrum has not been reported previously, and we are unable at this time to determine the value of *n*. Additionally, using the very low exposures in this study, we were unable to deposit the ammonia directly on the ice at $T > 140$ K due to the volatility of the ammonia gas.[39]

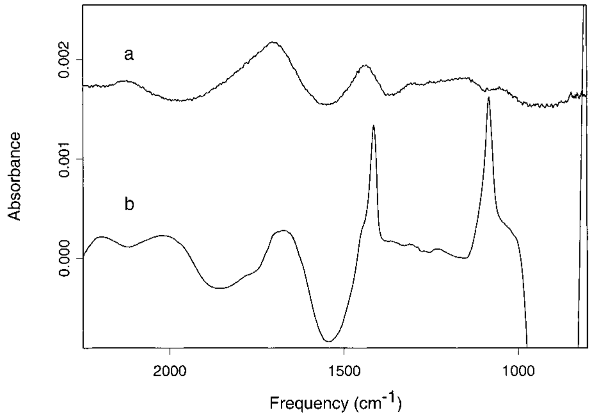

Figure 3. (a) Infrared spectrum resulting from the interaction of HCl on basic-crystalline ice (i.e., ammonia hydrate) for $T = 80-140$ K, which produces a limited amount of the ammonium ion, tentatively designated $NH_4^+ \cdot Cl^-$, (at 1450 cm^{-1}). The other features are due to $H_3O^+ \cdot Cl^-$ (compare with Figure 1a). (b) Infrared spectrum following the interaction of HCl on basic-crystalline ice above 140 K, which produces the polyhydrated ammonium ion, $NH_4^+(H_2O)_n \cdot Cl^-$, (at 1400 cm^{-1}) and the polyhydrated ammonia species, $NH_3(H_2O)_n$, (at 1075 cm^{-1}). Both species are probably crystalline. This spectrum has been reduced by a factor of 2 for comparison purposes with (a). The "negative" peaks are explained in the text. (The background spectrum is crystalline ice with ammonia hydrate on the surface.)

Interaction of HCl on Basic-Crystalline Ice. Once the interactions of HCl and NH_3 were studied independently with crystalline ice, we examined the HCl + NH_3 reaction on ice. This was accomplished in a couple of ways. Either HCl was added to basic-crystalline ice (i.e., the ammonia hydrate on ice), or ammonia was added to acidic-crystalline ice (i.e., the HCl hydrates on ice), presented below. For the acid added to basic-ice, the following procedure was utilized for $T = 80-140$ K. Crystalline ice was formed at 150 K, cooled to 80 K, and allowed to stabilize for 20 min to 2 h, a background spectrum was collected, then NH_3 was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. (See Figure 2a.) Another background spectrum was collected, then HCl was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. The resulting spectrum is presented in Figure 3a. It is dominated by features attributed to $H_3O^+ \cdot Cl^-$. (Compare Figures 3a and 1a.) However, there is a new feature at 1450 cm^{-1} that is attributed to the ammonium ion, NH_4^+, along with a very small "dip" at 1100 cm^{-1} that is due to the loss of ammonia. This ion has not been observed on ice before. The spectral assignment is based on comparison to infrared spectra of the ammonium ion in other environments. For example, the ν_4 vibration of NH_4^+ has been observed by Ewing's group in $(NH_4)_2SO_4$ aerosols (ca. 1420−1450 cm^{-1})[40] and by Sodeau's group in NH_4NO_3 thin films (ca. 1462−1492 cm^{-1}).[41] The NH_4^+ is probably in an amorphous phase. Consistent with the notation used above for HCl, we tentatively express this reaction as

$$HCl + NH_3 \rightarrow NH_4^+ \cdot Cl^- \text{ (for } T = 80-140 \text{ K)} \qquad (5)$$

The interaction of HCl with basic-ice (i.e., the ammonia hydrate on ice) above 140 K was examined in two ways. (1) The film created according to the procedure above was simply heated. (2) Crystalline ice was formed at 150 K, cooled to 80 K, and allowed to stabilize for 20 min to 2 h, a background spectrum was collected, then NH_3 was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. (See Figure 2a.) Another background spectrum was collected, the film was warmed to $T > 140$ K, then HCl was spray deposited (ca. $1-50 \times 10^{15}$ molecules/cm^2) and an infrared spectrum was collected. In either case, the resulting spectra are essentially identical. A typical spectrum is presented in Figure 3b. (This spectrum has been reduced by a factor of 2 for comparison purposes.) Comparison with Figure 2b indicates the formation of hydrated ammonia. Additionally, a new peak appears at 1400 cm^{-1}. This peak exhibits very similar characteristics to that for hydrated ammonia, presented above. We attribute this new feature to the hydrated ammonium ion.[42,43] (It is also possible that the NH_4^+ hydrate has simply crystallized.) Its formation can be expressed as

$$HCl + NH_3 \rightarrow NH_4^+(H_2O)_n \cdot Cl^- \text{ (for } T > 140 \text{ K)} \quad (6)$$

As discussed above regarding Figure 2, the "dips" or negative peaks are due to (i) loss of water molecules that are used for hydrating the ammonium ion and (ii) spectral shifts of the ice due to the temperature change. Notice, the only ionic species appears to be the ammonium ion. There is no evidence of the hydronium ion for these conditions. H_3O^+ peaks appear only after excess acid is added.

Interaction of NH_3 on Acidic-Crystalline Ice. The interaction of ammonia on acidic-crystalline ice (i.e., HCl hydrates on ice) was examined for the two types of acidic conditions, namely, ice with $H_3O^+ \cdot Cl^-$ and ice with $H_3O^+(H_2O)_5 \cdot Cl^-$ on the surface. In the first case, crystalline ice was formed at 150 K, cooled to 80 K, and allowed to stabilize for 20 min to 2 h, a background spectrum was collected, then HCl was spray deposited (ca. 1−50 × 10^{15} molecules/cm^2) and an infrared spectrum was collected. (See Figure 1a.) Another background spectrum was collected, ammonia was spray deposited and an infrared spectrum was collected. The resulting spectrum is shown in Figure 4a. Comparison with Figure 2a indicates the formation of $NH_3 \cdot H_2O$, along with a new peak at 1450 cm^{-1}. This new peak is identical to that discussed above for the ammonium ion. Its formation is given by eq 5 above. When this ice film is warmed to $T > 140$ K, the spectrum changes in a fashion identical to that presented above for HCl on basic-ice. Compare Figure 4c to 3b. (Figure 4c has been reduced by a factor of 2 for comparison purposes.) Again, we attribute these new peaks at 1400 cm^{-1} to the hydrated ammonium ion, and at 1100 cm^{-1} to hydrated ammonia. (There is no evidence, under these conditions, that the hydrated hydronium ion is formed, as indicated by the absence of peaks at 1900 and 1635 cm^{-1}. Only for excess HCl is there a presence of H_3O^+.) The formation of these hydrated species is given by eqs 6 and 4, respectively.

For ammonia interaction with the other form of acidic-ice, namely ice with $H_3O^+(H_2O)_5 \cdot Cl^-$ on the surface, the experimental procedure was as follows. Crystalline ice was formed at 150 K and allowed to stabilize for 20 min to 2 h, a background spectrum was collected, then HCl was spray deposited (ca. 1−50 × 10^{15} molecules/cm^2) and an infrared spectrum was collected. (See Figure 1b.) The acidic-ice film was then cooled to 80 K and allowed to stabilize for 20 min to 2 h. Another background spectrum was collected, then ammonia was spray deposited (ca. 1−50 × 10^{15} molecules/cm^2) and an infrared spectrum was collected. This spectrum is shown in Figure 4b. It is very similar to Figure 4a, indicating the formation of $NH_3 \cdot H_2O$ and the ammonium ion, $NH_4^+ \cdot Cl^-$. Notice, however, the relative size of the ammonium ion peak at 1450 cm^{-1}. It appears that when the hydronium ion has a larger hydration shell it is less reactive, in terms of protonating the ammonia. When this acid-ice film is warmed to $T > 140$ K, the higher hydrates of ammonia and the ammonium ion are again produced, as shown in Figure 4d. Notice the negative peaks in Figure 4d at 1900 and 1635 cm^{-1} due to the loss of $H_3O^+(H_2O)_5 \cdot Cl^-$. (Compare to Figure 1b.)

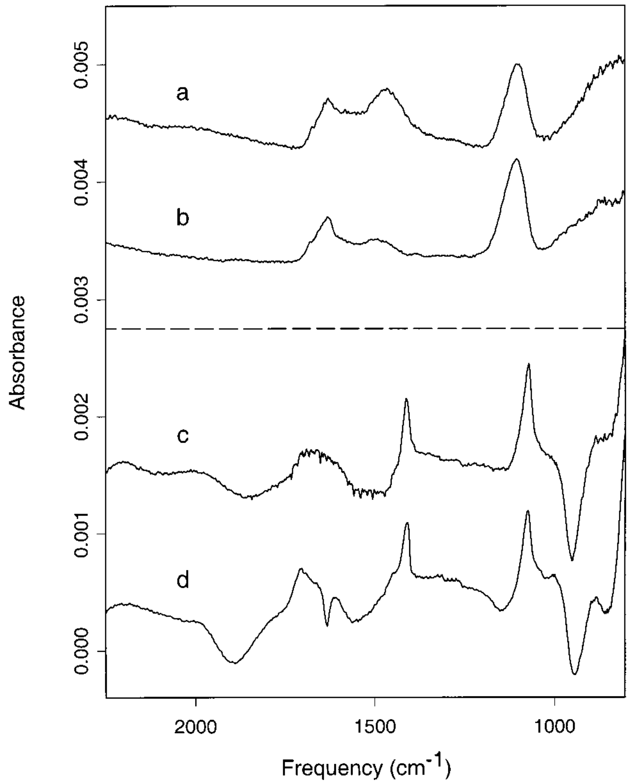

Figure 4. (a) Infrared spectrum resulting from the interaction of NH_3 on acidic-crystalline ice (i.e., ice with $H_3O^+ \cdot Cl^-$ on the surface) for $T = 80-140$ K, which produces a limited amount of the ammonium ion, tentatively designated $NH_4^+ \cdot Cl^-$, (at 1450 cm^{-1}). The other features are due to the molecular amorphous monohydrate, $NH_3 \cdot H_2O$, (compare with Figure 2a). (b) Same as (a) but with the $H_3O^+(H_2O)_5 \cdot Cl^-$ on the ice surface. Notice the smaller NH_4^+ peak. (c) Same as (a) but for $T > 140$ K. The polyhydrated ammonium ion, $NH_4^+(H_2O)_n \cdot Cl^-$, (at 1410 cm^{-1}) and the polyhydrated ammonia species, $NH_3(H_2O)_n$, (at 1075 cm^{-1}) are formed, as in Figure 3b. Both species are probably crystalline. (d) Same as (b) but for $T > 140$ K. Notice the "negative" peaks due to loss of $H_3O^+(H_2O)_5 \cdot Cl^-$ (compare with Figure 1b). Figures (c) and (d) have been reduced by a factor of 2 for comparison purposes. (The background spectra are crystalline ice with HCl hydrates on the surface.)

Conclusion

Using Fourier transform infrared spectroscopy, the interaction of HCl, NH_3, and HCl + NH_3 on crystalline ice has been examined as a function of temperature. The spectroscopic data indicate that for $T = 80-140$ K the HCl reacts on the ice surface producing the amorphous ionic species, $H_3O^+ \cdot Cl^-$. Above 140 K the HCl forms the crystalline hydrated ionic species, $H_3O^+(H_2O)_5 \cdot Cl^-$. These results show clearly that the HCl is ionized on the ice surface, as others have previously observed.[18,19,31,33,35,36] The interaction of ammonia with crystalline ice produces the molecular amorphous hydrate, $NH_3 \cdot H_2O$, for $T = 80-140$ K, and a polyhydrate (probably crystalline), $NH_3(H_2O)_n$, for $T > 140$ K.

For the HCl + NH_3 reaction on crystalline ice, we have observed the formation of a limited amount of the ammonium ion (tentatively designated amorphous $NH_4^+ \cdot Cl^-$) for $T = 80-140$ K. However, above 140 K the reaction appears to go to completion and all of the HCl is consumed in forming the ionic crystalline polyhydrate, $NH_4^+(H_2O)_n \cdot Cl^-$. This acid−base reaction on ice has not been reported in the literature before.

We believe these results reveal something important about the nature of the crystalline ice surface. In particular, the amount of "free" water molecules that are available on the surface is limited for $T = 80-140$ K. The strong acid HCl reacts on the surface but appears to only form the ionic amorphous monohydrate, $H_3O^+{\cdot}Cl^-$. The weak base NH_3 interacts with the ice to form the molecular amorphous monohydrate, $NH_3{\cdot}H_2O$. The reaction of $HCl + NH_3$ occurs to a limited extent to form the ammonium ion because there are few water molecules available to hydrate the ion.

Above 140 K, the crystalline ice surface experiences a type of "premelting" and more water molecules become available for chemistry. Thus, HCl now reacts to produce the most stable hydrate, $H_3O^+(H_2O)_5{\cdot}Cl^-$. Ammonia also forms a higher hydrate. And, the reaction $HCl + NH_3$ appears to go to completion because there are enough water molecules available to completely hydrate the ammonium ion (and the counterion, Cl^-).

We have observed similar results for the interaction of nitric acid on crystalline ice.[44] For $T = 80-140$ K only the amorphous monohydrate, $HNO_3{\cdot}H_2O$, is formed, which is predominantly molecular. Above 140 K the amorphous trihydrate is formed, $HNO_3(H_2O)_3$ or $H_3O^+(H_2O)_2{\cdot}NO_3^-$, which is predominantly ionic.

While these studies were performed at temperatures colder than those found in the stratosphere, we suggest that they provide some insight into the nature of heterogeneous chemistry on ice. In particular, it appears that an important driving force for chemical reactivity is the ability of water to be involved in stabilizing the ionic species through hydration, as also suggested recently by experimental[45] and theoretical work.[46] Simple acid–base chemistry readily occurs above 140 K with the formation of ionic species. Thus, at higher temperatures we would suggest that similar ionic mechanisms are involved in heterogeneous ice chemistry, as others are also recommending.[20,21,28,45]

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