**Atmospheric
Chemistry
and Physics**

FTIR spectroscopic studies of the simultaneous condensation of HCl and H₂O at 190 K – Atmospheric applications

I. Xueref[1,2] **and F. Dominé**[1]

[1]Laboratoire de Glaciologie et de Géophysique de l'Environnement, CNRS, 54 rue Molière, B.P.96, 38402 Saint Martin d'Hères CEDEX, France
[2]Now at: Department of Earth and Planetary Sciences & Division of Engineering and Applied Sciences, Harvard University, 20 Oxford Street, Cambridge MA 02138, USA

Abstract. Type II polar stratospheric cloud particles are made up of ice that forms by water vapor condensation in the presence of numerous trace gases, including HCl. These gaseous species can co-condense with water molecules and perturb ice structure and reactivity. In order to investigate the effect of co-condensing dopants on the structure of ice, we have designed an experimental system where ice films can be stabilized at 190 K, a temperature relevant to the polar stratosphere. We have co-condensed different HCl : H₂O gaseous mixtures, with ratios 5:1, 1:10, 1:50 and 1:200 and studied the solids formed by infrared spectroscopy. The IR spectra obtained show that: (1) HCl is likely undergoing ionic dissociation when it is incorporated by co-condensation into the ice at 190 K; (2) this dissociation is done by several water molecules per HCl molecule; and (3) significant differences between our spectra and those of crystalline solids were always detected, and indicated that in all cases the structure of our solids retained some disorganized character. Considering the major impact of HCl on ice structure observed here, and the well known impact of the structure of solids on their reactivity, we conclude that the actual reactivity of stratospheric ice particles, that catalyze reactions involved in ozone depletion, may be different from what has been measured in laboratory experiments that used pure ice.

1 Introduction

Ice plays an important role in physical and chemical atmospheric processes such as stratospheric ozone depletion (Solomon, 1990), rain acidity (Hov et al., 1987; Galloway and Likens, 1981), ice cores composition (Legrand and Mayewski, 1997) and snow chemistry (Dominé and Shepson, 2002). For example, ice particles that form type II Polar Stratospheric Clouds (PSCs) catalyze reactions be-

tween chlorinated species that are inert in the gas phase, and this catalysis is a key step in stratospheric ozone depletion (Molina et al., 1993). Based on thermodynamics (Hobbs, 1974) and on observations of ice crystals replica (Goodman et al., 1989) these ice particles are thought to be made of I_h crystalline ice. When it forms, ice can incorporate trace gases by simultaneous condensation of those gases and of water vapor, a process called co-condensation (Dominé and Thibert, 1996). It is then legitimate to wonder whether the incorporation of dopants in atmospheric ice could result in a modification of its structure and reactivity.

Indeed, recent laboratory studies at temperatures relevant to the polar stratosphere have come to the conclusion that the physical properties of ice are affected by its dopant concentration. Livingston et al. (2000), using very high HCl concentrations, have measured diffusion coefficients of HCl in ice of the order of 5×10^{-11} cm²/s at 190 K. This is several orders of magnitude higher than what could be reasonably envisaged for a solid so far from its melting point, and is much higher than other measured values (Dominé and Xueref, 2001; Thibert and Dominé, 1997; Wolff et al., 1989). Dominé and Xueref (2001) have demonstrated that the high values measured by Livingston et al. (2000) were caused by the high HCl concentrations, that led to ice amorphization. The resulting disordered solid then allowed much faster diffusion of impurities.

For a solid, a change in structure can lead to a change in reactivity. For example, Ferry et al. (1996, 1997) have shown that H₂O simply physisorbs on a perfect crystalline surface of MgO cleaved in vacuum, while it chemically dissociates when adsorbed at a surface having structural defects. It is therefore important to investigate the potential impact of dopants on ice structure and reactivity. An interesting dopant is HCl. First of all, it is soluble in ice (Thibert and Dominé, 1997). Second, it can form numerous solid HCl : H₂O mixtures. Several crystalline hydrates can form (Delzeit et al., 1993; Gilbert and Sheppard, 1973; Vuillard,

---

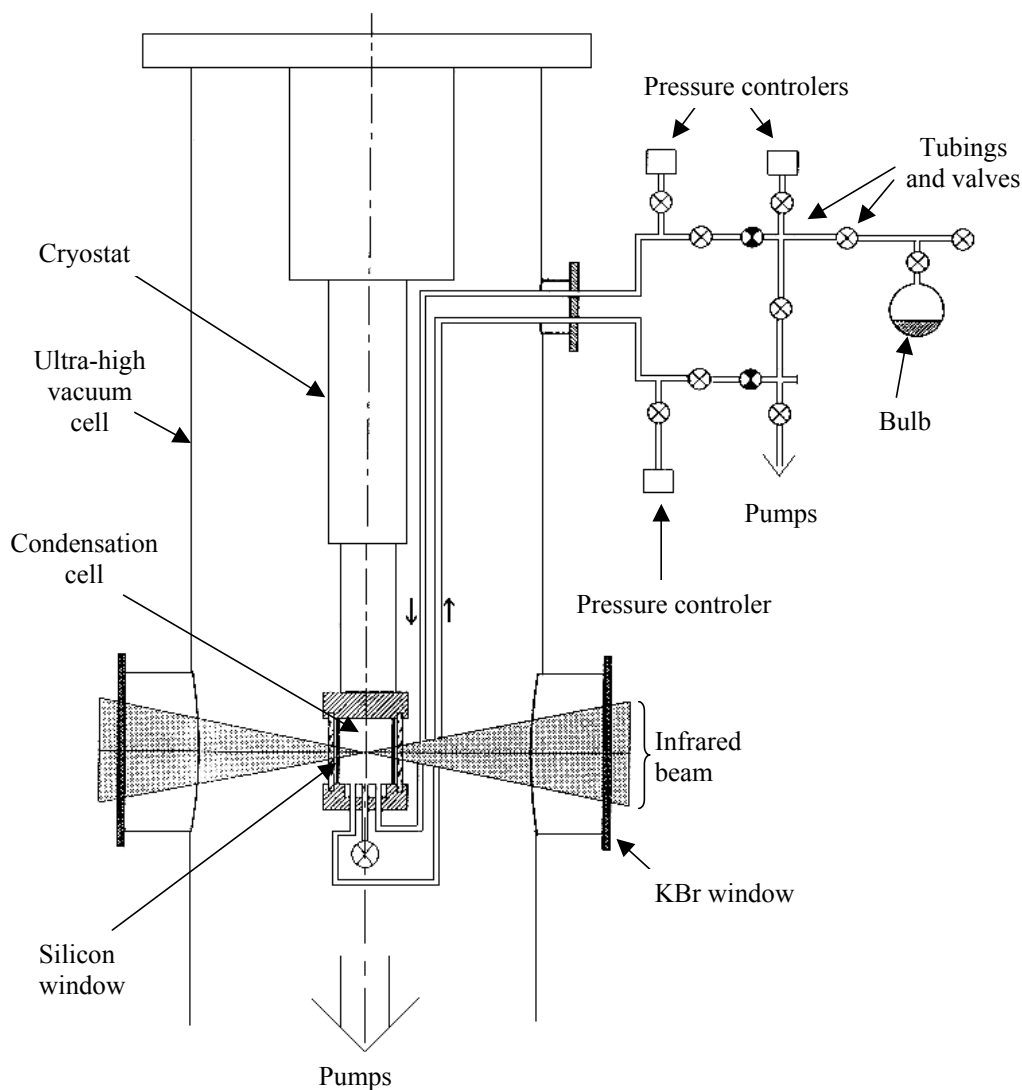*Correspondence to:* I. Xueref (irx@io.harvard.edu)

Fig. 1. Experimental set-up.

1955) and at temperatures lower than 110 K, non-crystalline mixtures are readily formed by co-condensing H_2O and HCl vapors. Third, HCl is of great atmospheric interest, and its implication in stratospheric ozone destruction (Solomon, 1990) is probably sufficient to warrant detailed studies of its interactions with ice.

Numerous laboratory studies of HCl-ice interactions have been performed in recent years, and most of those interested in the structure of the solids resulting from $HCl-H_2O$ co-condensation have used FTIR spectroscopy as an investigation tool. Ice has a high vapor pressure at temperatures relevant to the stratosphere and troposphere (Haynes et al., 1992; Marti and Mauersberger, 1993), and it readily sublimates at $T > 180$ K in laboratory experiments that use high vacuum apparatus. For this reason, almost all FTIR studies to date have been performed at $T < 180$ K.

Among those studies, some have consisted in exposing pure ice films to gaseous HCl (Ritzhaupt and Devlin, 1991;

Delzeit et al., 1993; Koehler et al., 1993; Banham et al., 1995; Demirdjian et al., 2002; Toubin et al., 2002). In this case, HCl and H_2O generally form a homogeneous solid on the ice surface. This solid extends to the whole ice volume for very high pressures, such as 10 Torr (Delzeit et al., 1997). It can be crystalline when $T > 168$ K or non-crystalline ($T < 150$ K). The heating of the non-crystalline phase can induce its crystallization, but not systematically (Banham et al., 1995; Delzeit et al., 1997).

Several studies have shown that HCl is totally dissociated into ions when incorporated into ice forming above 110 K (Horn et al., 1992; Delzeit et al., 1993), leading to ice acidification, whereas it stays under its molecular shape below 80 K. The minimum temperature for the formation of ice by condensation of water vapor in the troposphere and in the stratosphere is about 188 K, the temperature of formation of type II PSC ice particles. Thus when incorporated in ice forming near that temperature, HCl is expected to be

ionically dissociated (Gertner and Hynes, 1996), but this remains to be proven experimentally.

The co-condensation process has not been studied at temperatures of stratospheric interest. Several authors (Horn et al., 1995; Delzeit et al., 1993; Ritzhaupt and Devlin, 1991; Gilbert and Sheppard, 1972; Ferriso and Hornig, 1955, 1953; Ault and Pimentel, 1973) have focused on the co-condensation of HCl and H_2O below 168 K, followed by a heating of the sample. The solids formed were non-crystalline and had the same composition as the condensing gaseous mixtures. At these low temperatures, the nucleation of HCl hydrates formed by co-condensation is thus apparently difficult. However, Gilbert and Sheppard (1973) observed that heating the solids formed at low temperature above 150 K initiates their crystallization. Horn et al. (1995) also observed the beginning of crystallization, at 160 K.

Furthermore, it is known that the quantity of HCl incorporated by co-condensation into ice follows a kinetics law, and at 190 K, this amount is about four times bigger than the thermodynamic solubility of HCl in ice (Dominé and Thibert, 1996). Considering this fact, it is relevant to ask which phases HCl and H_2O will form together. $HCl-H_2O$ phase diagrams (Thibert and Dominé, 1997) show five solid phases at 190 K: four hydrates (mono-, di-, tri- and hexa-hydrates) and a solid solution of HCl in ice. But since HCl is incorporated in excess in the co-condensation process, H_2O and HCl are not in thermodynamic equilibrium and therefore they could form: 1) a supersaturared homogeneous solid solution of HCl in ice, 2) an heterogeneous solid made of one or several hydrates and of a solid solution of HCl in ice, and/or 3) the HCl in excess could diffuse to the surface and then escape into the surrounding air, thus leading to a solid solution in thermodynamic equilibrium. In a previous study (Dominé and Xueref, 2001), we have reported preliminary results showing that the co-condensation of a gaseous mixture HCl : H_2O 1:50 at 190 K formed a non-crystalline $HCl-H_2O$ solid. As far as we Know, Dominé and Xueref (2001) is the only study that showed results on the co-condensation of gaseous HCl and water vapor above 168 K and especially at 190 K. These results are complemented here by a study showing the co-condensation of gaseous HCl : H_2O ratios of 5:1, 1:10 and 1:200 at 190 K, with the following aims: 1) to determine the chemical state under which HCl is incorporated into the ice formed by co-condensation; 2) to identify the solid phases formed; and 3) to understand the impact of the incorporated HCl on the ice structure.

2 Methods

2.1 Experimental set-up

In order to avoid ice sublimation, we have based our set-up (Fig. 1) on a stainless steel condensation cell of reduced volume ($\sim$12 cm^3). It is made of a stainless steel body and of 2 copper plates, which support 2 silicon windows that are connected to the closed cycle helium cryostat. This configuration ensures that the windows will be slightly colder than the cell body and that vapor condensation will take place preferentially on the windows. The temperature of the cell window is monitored by a silicon diode. The condensation cell is surrounded by an ultra-high vacuum cell to insulate it from ambient air. With this set-up, we were able to stabilize ice films for several hours at 190 K (Xueref, 1999).

The doped ice films were made in the condensation cell by admitting HCl and H_2O vapors into the cell, and condensation on the Si windows was observed by FTIR spectroscopy, using a Nicolet 800 spectrometer with a 2 cm^{-1} resolution. Vapors are brought in by stainless steel tubes connected to a glass bulb containing an HCl solution. The concentration of the solution is chosen so that the ratio of the HCl and H_2O vapor pressures above the solution corresponds to that desired for the condensation mixture, using the data of Fritz and Fulget (1956). The condensation cell and the tubing are evacuated by a turbo-molecular pump. Before the condensation process, the mean vacuum is $\sim$10^{-5} Torr or better. The total pressure is controlled before and after the condensation cell, using high precision MKS Baratrons gauges (1 Torr and 0.1 Torr full scale). Another turbomolecular pump is used to evacuate the surrounding high vacuum cell down to $\sim$10^{-8} Torr. This cell is equipped with two KBr windows aligned with the inner cell Si windows.

HCl adsorbs onto stainless steel (Thibert and Dominé, 1997) and conditioning of the stainless steel tubing was required to ensure that the gas composition in the condensation cell was the same as in the bulb. Two methods were used, that both gave satisfactory results. In the first one, the gas mixture was left flowing through the tubings and the condensation cell heated to $\sim$318 K for about 3 h. The flow was then stopped, the cell cooled down, and gases were re-admitted through the conditioned tubes. In the second method, the cell, cooled to 190 K, and the tubings were conditioned for 3 h with a flow of N_2 containing $\sim$10 ppm of HCl. In principle, neither method is perfect. In the first one, the conditioning of the cell is at a temperature higher than that used in the experiments. In the second one, water is absent, and dry HCl adsorbs less on stainless steel than does wet HCl. In practice, however, and even though we did not measure the gas phase composition inside our cell, we observed that the spectral bands positions did not change during condensation, that lasted for up to several hours. From this observation, we deduced that conditioning was adequate, and that no HCl uptake by the tubing surfaces was taking place during our experiments.

2.2 Spectral references

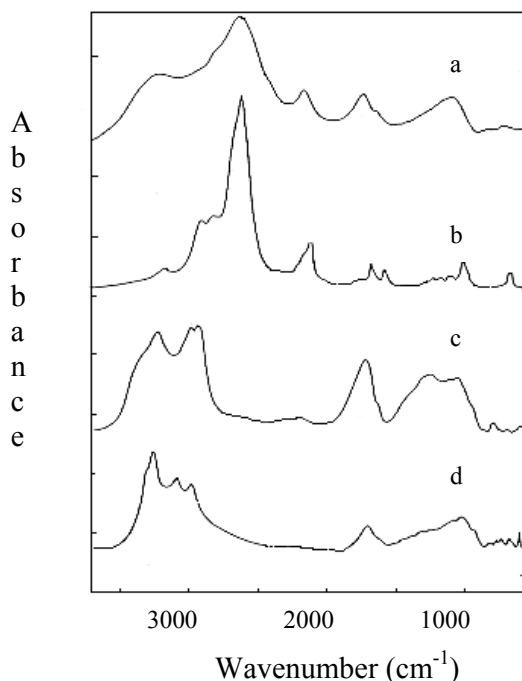The analysis of our spectra will be made by comparison with those of crystalline and non-crystalline solids made up of

Fig. 2. IR spectra of HCl−H$_2$O solids (after Delzeit et al., 1993), recorded on a sample made by condensing a HCl : H$_2$O 1:1 gaseous mixture at 15 K **(a)**, heated at 155 K **(b)**, then at 195 K **(c)** and finally at 215 K **(d)**. Spectra assignments: (a) non-crystalline solid of composition HCl.H$_2$O; (b) monohydrate of HCl; (c) dihydrate of HCl; (d) trihydrate of HCl. Note that Delzeit et al. assigned (d) to the tetrahydrate of HCl, but that hydrate does not exist (see text).

HCl and H$_2$O, that have been reported in the literature. The available spectra are briefly reviewed below.

2.2.1 Spectra of HCl hydrates

The spectra of HCl hydrates have been recorded by several authors and have been given different assignments (Delzeit et al., 1993; Ritzhaupt and Devlin, 1991; Gilbert and Sheppard, 1973; Ferriso and Hornig, 1955, 1953; Ault and Pimentel, 1973). We show here the spectral assignments of some of these solids given by Delzeit et al. (1993) on Fig. 2 and by Ritzhaupt and Devlin (1991) on Fig. 3. The assignments given by the authors to the mono-, di- and hexa-hydrates seem to us reliable. However, as already mentioned by Banham et al. (1995), and as visible on available phase diagrams (e.g. Vuillard, 1955; Thibert and Dominé, 1997), the tetrahydrate discussed by Delzeit et al. (1993) does not exist, and the solid in question is certainly the trihydrate.

2.2.2 Spectra of non-crystalline solids of composition HCl.nH$_2$O

Delzeit et al. (1993) and Ritzhaupt et al. (1991) have published the spectra of non-crystalline HCl−H$_2$O solids of HCl : H$_2$O compositions 1:1, 1:2, 1:4, and 1–6. (Fig. 4).

Table 1. Structure and detailed formula of the hydrates of HCl

Hydrate	Structure	Formula
Monohydrate[1]	Rhomboedric	$H_3O^+.Cl^-$
Dihydrate[2]	Monoclinic	$H_5O_2^+.Cl^-$
Trihydrate[3]	Monoclinic	$H_5O_2^+ + Cl^-.H_2O$
Hexahydrate[4]	Orthorhombic	$H_7O_3^+Cl^-.H_2O$

[1] Yoon and Carpenter (1959);
[2] Lundgren and Olovsson (1967a);
[3] Lundgren and Olovsson (1967b);
[4] Taesler and Lundgren (1978).

Note that those authors called those solids "amorphous hydrates", but we will not use that terminology: in this study, we choose to define "hydrates" as fully crystallized solids. Therefore, for a compound with a disorganized feature, we will prefer the term "non-crystalline solid".

2.2.3 Vibrating entities and origin of the bands of ice and HCl.nH$_2$O solids spectra

The vibrational spectra of ice have been extensively studied (Hardin and Harvey, 1973; Bertie and Whalley, 1964). The bands centered around 3200 cm^{-1} and 1600 cm^{-1} are mainly due to the stretching and to the bending of H$_2$O molecules, respectively. The bands around 800 cm^{-1} and 2200 cm^{-1} are assigned to libration modes of these molecules.

Spectra of crystalline and non-crystalline HCl.nH$_2$O solids are also Known. These solids have complex structures and compositions. They are mainly made up of H$_2$O and hydrated hydronium ions H$_{2x+1}$O$_x^+$, and can also contain H$_{2x+1}$O$_x^+$.Cl$^-$ or HCl.H$_2$O complexes at low temperature. The hydrates of HCl are fully made of hydrated hydronium ions, with various numbers of water molecules, and of H$_2$O molecules. Their exact composition is given in Table 1. The non-crystalline solids are characterized by structural disorder, and therefore their spectra show a broadening of the absorption bands, compared to the spectra of hydrates. These disorganized solids can contain entities similar to those of the crystalline solids but also HCl.H$_2$O complexes if they are made at temperatures lower than 110 K (Horn et al., 1992). Despite the structural and compositional complexity of HCl.nH$_2$O crystalline and non-crystalline solids, band assignments could be made in the following absorption regions (Delzeit et al., 1993; Ritzhaupt and Devlin, 1991; Horn et al., 1992):

- the bands with wavenumbers $k < 2200$ cm^{-1} are due to: (1) the fundamental modes of the H$_3$O$^+$ ion and of the H$_2$O molecule, with torsion and libration modes of H$_2$O and H$_3$O$^+$ around 700 cm^{-1}, the symmetric bending mode ν_2 of H$_3$O$^+$ around 1100 cm^{-1} and the asymmetric bending mode of H$_3$O$^+$ around 1700 cm^{-1}; and

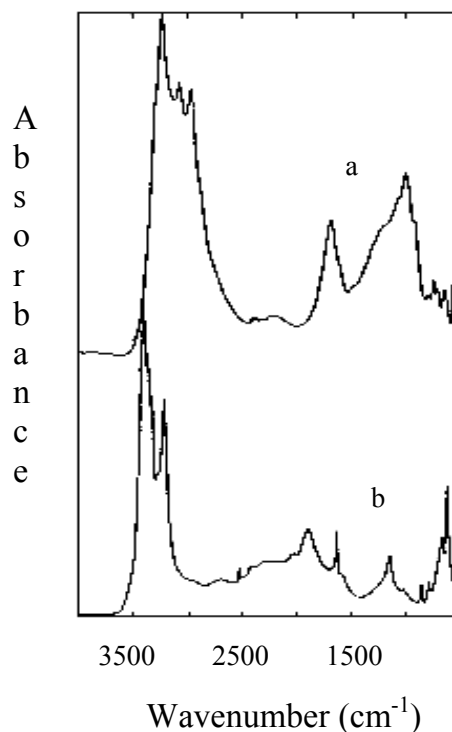**Fig. 3.** IR spectra of hydrates of HCl (after Ritzhaupt and Devlin, 1991) recorded on samples made by condensing HCl : H_2O 1:4 **(a)** and 1:6 **(b)** gaseous mixtures at 80 K, then heated at 175 K (a) and 180 K (b). Spectra assignments: (a) Trihydrate of HCl; (b) Hexahydrate of HCl. Again, Ritzhaupt and Devlin initially assigned (a) to the tetrahydrate of HCl).

Fig. 4. Spectra of HCl$-$H$_2$O non-crystalline solids (after Delzeit et al., 1993 and Ritzhaupt and Devlin, 1991) formed by the condensation, at the temperature mentioned below, of gaseous mixtures of composition: **(a)** $(1 + x)$HCl.H$_2$O $(x > 0)$, at 15 K; **(b)** HCl.H$_2$O at 85 K; **(c)** HCl.2H$_2$O at 85 K; **(d)** HCl.4H$_2$O at 80 K; **(e)** HCl.6H$_2$O at 80 K.

(2) a combination of different modes of H_3O^+ around $2100 \, cm^{-1}$

– the bands with $k > 2800 \, cm^{-1}$ are due to the stretching modes of the OH groups of the $H_{2x+1}O_x^+$ ions and of H_2O

– the band around $2500 \, cm^{-1}$ that can be observed on the spectra of the non-crystalline solids HCl : H_2O 1+x:1, 1:1 and 1:2 formed below 85 K, is attributed to: (1) a stretching mode of the H_3O^+ ion when it is associated to the Cl^- ion (ionic complex $H_3O^+.Cl^-$); and/or (2) the molecular complex HCl.H_2O.

3 Results

Infrared spectra of our samples are shown on Figs. 5 to 8. The weak intensity doublet around $2350 \, cm^{-1}$ is due to ambient carbon dioxide present on the path of the IR beam. This doublet could not be avoided due to the unpredictability of ambient air composition. The sharp bands between $2750 \, cm^{-1}$
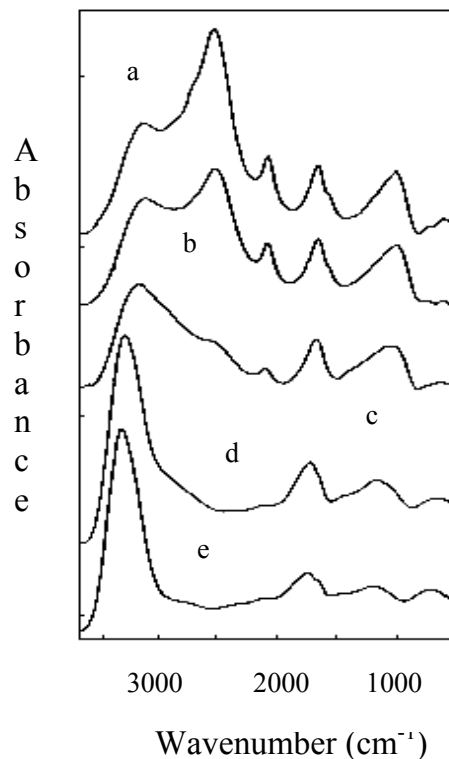
and $3050 \, cm^{-1}$ and in the range $1600 \, cm^{-1}$ to $3700 \, cm^{-1}$ are caused by gaseous HCl and water vapor, respectively.

3.1 Condensation of a HCl : H_2O 5:1 gaseous mixture at 190 K

The evolution of the IR spectrum during the growth of a solid formed by the condensation of a HCl : H_2O 5:1 mixture at 190 K is shown on Fig. 5. While band positions remain constant, their shapes evolve during the first 10 min of condensation, and then remains stable until the end of the experiment (35 min). We define a transitory regime that corresponds to the first 10 min of the experiment, followed by a stationary one characterized as follows.

– In the transitory regime, the sample spectrum is similar to that of the non-crystalline solid of composition HCl.2H$_2$O (Fig. 4c): the absorption bands show similar shapes and frequencies, for all wavenumbers above $900 \, cm^{-1}$ (below that frequency, our signal to noise ratio is degraded by some IR diffusion and we will therefore not make any comparison in that low frequency region). However, we did not measure the composition of the solid formed, and its composition may not be exactly
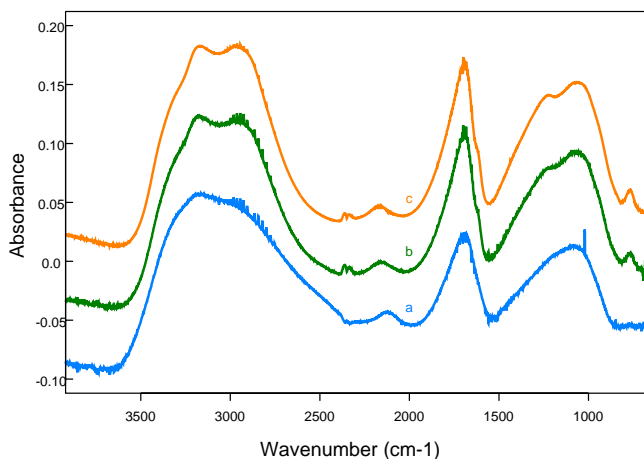
Fig. 5. Temporal development of the infrared spectrum of a sample made by condensing a gaseous mixture HCl : H_2O 5:1 at 190 K. Spectra **(a)**, **(b)** and **(c)** correspond respectively to 5, 10 and 35 min after the beginning of the deposition process.

HCl : H_2O 1:2. Our spectrum shows a shoulder at 2930 cm^{-1}, while the spectrum of the $HCl.2H_2O$ non-crystalline solid shows a shoulder around 2580 cm^{-1}. Besides the possibility that the composition of both solids may be slightly different, these small differences may be due to:

– the shoulder at 2930 cm^{-1} in our spectrum is in the OH stretching mode region. It can be due to a greater distribution of the H-bonding strengths in this solid than in that discussed by Delzeit et al. (1993) and which was formed by the condensation of gases at 85 K (Fig. 4). Whenever they exist between two neighboring water molecules or between one water molecule and a neighboring H_3O^+ ion, these H-bonds induce a shift of the OH groups stretching frequency toward lower k values. Their strength is therefore more important, meaning for example, that two neighboring oxygen atoms are closer, or that intermolecular coupling is stronger.

– the shoulder around 2580 cm^{-1} is present on the spectrum of the non-crystalline solid of composition $HCl.2H_2O$ (formed at 85 K) and not on our spectrum (film formed at 190 K). Our interpretation of this is that at 190 K, HCl is totally ionized, while at 85 K, HCl remains molecular or is solvated by only one molecule, presumably because of limited solid state mobility of molecules at 85 K. At 190 K, on the contrary, molecular HCl cannot exist anymore in the solid state (Honig and Hook, 1960; Hornig and Osberg, 1955), and faster molecular motion allows solvation by more than one H_2O molecule. This suggestion of complete ionization of HCl at 190 K is consistent with previous stud-

ies (Delzeit et al., 1993; Gertner and Hynes, 1996; Horn et al., 1992; Packer and Clary, 1995).

– In the permanent regime (Fig. 5c), the absorption bands of our spectrum and those of the dihydrate of HCl (Fig. 2c) are similar in frequencies, and to a lesser extent in shapes. We observe 2 main bands in the OH stretching mode region, with a shoulder near 3300 cm^{-1}, a sharp band at 1700 cm^{-1} with a shoulder at 1600 cm^{-1}, and 2 main unresolved bands in the OH asymetric bending mode region around 1060 cm^{-1} and 1200 cm^{-1}. In our spectrum, however, bands are less sharp than in the dihydrate spectrum, implying that crystallization is incomplete. The hydrated hydronium ions thus have a wider range of environments in our sample than in the HCl dihydrate.

An interesting observation is that a 5:1 mixture forms a 1:2 solid. Molecular HCl cannot be stabilized in the solid phase at 190 K, and it needs to be solvated. The richest possible HCl concentration is therefore 1:1, but HCl is very volatile (Honig and Hook, 1960; Hornig and Osberg, 1955), and at 190 K, tremendous pressures are probably needed to stabilize a solid of 1:1 composition (Thibert and Dominé, 1997). We observe that under the conditions used, only a solid of 1:2 composition can be stabilized. Modeling studies (Gertner and Hynes, 1996; Packer and Clary, 1995) have also shown that the incorporation of HCl in ice at 190 K is much easier when several water molecules participate in its solvation.

In conclusion, these results show that the condensation of a gaseous mixture HCl : H_2O 5:1 at 190 K leads to the rapid formation of a solid whose IR spectrum is close to that of a non-crystalline solid of composition $HCl.2H_2O$ formed at 85 K, although our sample appears to have a wider H-bond strength distribution. The sample re-organizes itself in about 10 min and partial crystallization to a solid resembling the dihydrate takes place.

3.2 Condensation of HCl : H_2O 1:n gaseous mixtures at 190 K with n=10, 50 and 200

Results obtained by condensing gaseous mixtures with HCl : H_2O ratios 1:10, 1:50 and 1:200 are shown in Fig. 6. As in the case of the 5:1 gas mixture, spectral shapes evolved during condensation to stabilize after 12, 11 and 15 min, for the 1:10, 1:50 and 1:200 ratios, respectively, but these evolution sequences did not show any feature that would deserve detailed discussion, especially considering that the evolution of the 1:50 mixture has already been reported by Dominé and Xueref (2001). Figure 6 shows the spectra of the stabilized solids. The 3 spectra of the 1:10, 1:50 and 1:200 mixtures are fairly similar, with the OH stretching band becoming narrower as the HCl fraction decreases. Comparisons between these stabilized spectra and those of hydrates (Figs. 2 and 3) and non-crystalline solids (Figs. 4 and 6) indicate that the

solids formed in our experiments are non-crystalline. The solid formed by the 1:10 gaseous mixture appears to have a composition in the 1:2 to 1:4 range, while those formed by the 1:50 and 1:200 gaseous mixtures both appear to be in the composition range 1:4 to 1:6 (Fig. 6).

The species forming these solids can be qualitatively determined by the analysis of the band positions. Note that in the HCl : H_2O 1:200 case, a defect in the parallelism of both faces of the Si window resulted in undulations in the spectrum. A mathematical correction was applied (Xueref, 1999), but residual undulations remain, and these should not be interpreted as bands. They are particularly visible around 1300 cm^{-1}, and around 2100 cm^{-1} and 2600 cm^{-1}.

- As for the HCl : H_2O 5:1 condensation study, no spectra showed any absorption peak around 2500 cm^{-1}, meaning there is neither any HCl.H_2O nor H_3O^+.Cl$^-$ complex in the samples. HCl is thus ionized and Cl$^-$ is solvated by several water molecules.

- The positions of the bands between 1000 and 2200 cm^{-1} correspond relatively well to the frequencies of the internal bending modes of H_3O^+ ($\nu2\sim1100$ cm^{-1} and $\nu4\sim1700$,cm^{-1}) as well as to the frequency of the combination band of H_3O^+ modes around 2100 cm^{-1}.

- Above 2600 cm^{-1} (region of the OH groups stretching modes for H_2O and H_3O^+), our sample spectra are characterized by a broad band centered around 3350 cm^{-1}. The oxygen atoms of the water molecules or hydronium ions therefore undergo H-bondings of different strengths, meaning several types of environments are possible. Indeed, a distribution of H-bond strengths is likely, since the intensities of the interactions between $H_2O/H_{2x+1}O_x^+$, H_2O/Cl^-, and H_2O/H_2O are certainly not of the same strengths. The band width also increase with the HCl concentration, as expected from a higher distribution of H-bond energies in the samples more concentrated in HCl.

In conclusion, the condensation of HCl : H_2O 1:n with $n=10$, 50 and 200 at 190 K leads to the formation of non-crystalline solids of compositions in the ranges 1:2 and 1:4, 1:4 and 1:6, and 1:4 and 1:6, respectively. HCl is fully ionized by several water molecules that interact with hydronium and chlorine ions, leading to a solid made of $H_{2x+1}O_x^+$ and Cl$^-$ ions, and water molecules. Different H-bonding strengths are observed between these species and/or the water molecules.

3.3 Comparison of the samples spectra with ice Ih and amorphous ice spectra

Figure 7 compares the spectra of ice I_h and amorphous ice (Trotta, 1996) with those of our stabilized samples. Figure 8 details ansd superposes the OH stretch region. Two observations can be stressed. First, for the 3 more dilute compo-
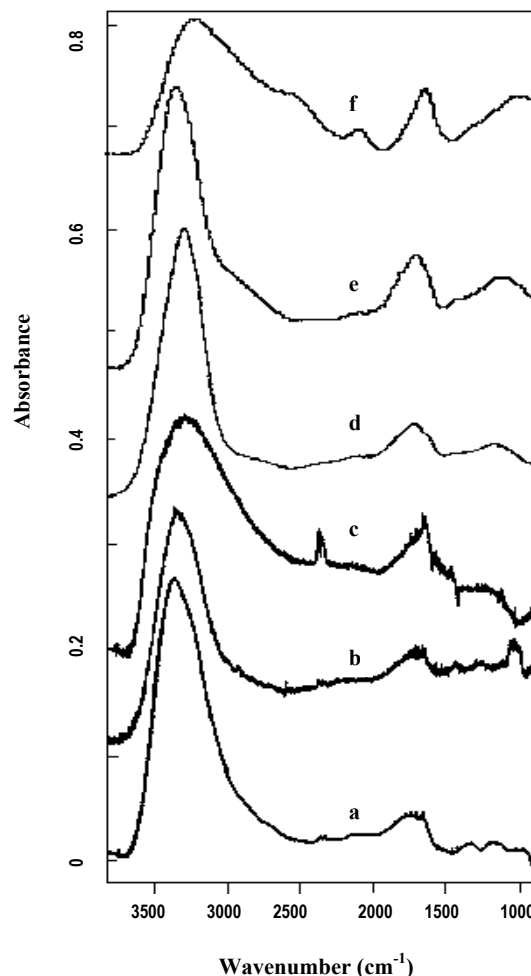

Fig. 6. Comparison of the spectra of our samples made by condensing HCl : H_2O gaseous mixtures of ratios 1:200 **(a)**, 1:50 **(b)** and 1:10 **(c)** at 190 K, with those of non-crystalline solids of composition HCl : H_2O 1:6 **(d)**, 1:4 **(e)** and 1:2 **(f)** from Delzeit et al. (1993) and Ritzhaupt and Devlin (1991).

sitions, the band shapes and frequencies in the OH stretch region resemble more those of amorphous ice than those of crystalline ice, which is consistent with the interpretation that our samples are non-crystalline solids. HCl provokes an amorphization of ice, and the magnitude of this effect increases with the HCl concentration. Second, the OH stretch band is more intense between 2800 cm^{-1} and $\sim$3190 cm^{-1} than for ice, and this intensity increases with the HCl concentration. This suggests that this spectral region is associated to OH-group stretch in the hydrated hydronium ions and in the $H_{2x+1}O_x^+$.Cl$^-$ complexes contained in the samples, and whose concentrations increase with that of HCl. These observations highlight the strong perturbation produced by HCl on ice structure and the mechanism of incorporation of HCl into ice by ionic solvation with several water molecules per HCl molecule.
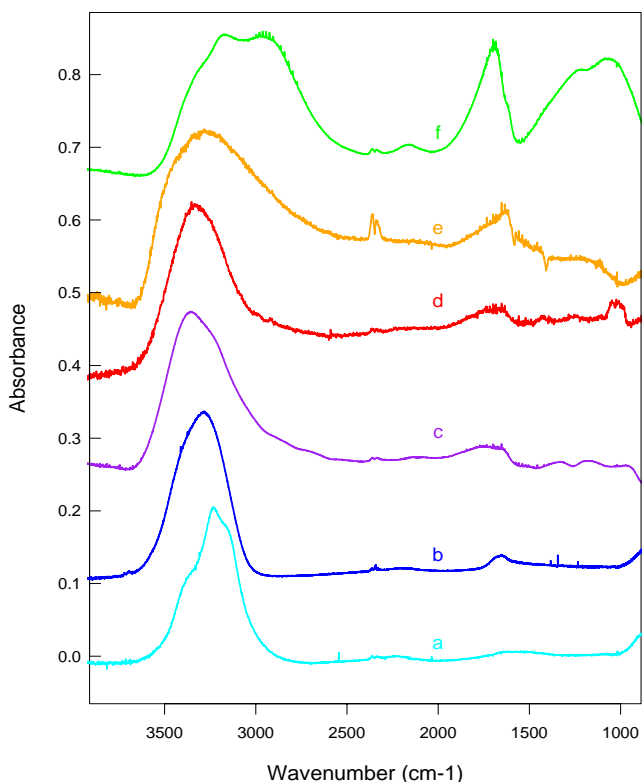
Fig. 7. Comparison of the spectra of our samples with those of crystalline **(a)** and amorphous ice **(b)** from Trotta (1996). Our samples were made at 190 K by deposition of HCl : H₂O gaseous mixtures of ratios 1:200 **(c)**, 1:50 **(d)**, 1:10 **(e)** and 5:1 **(f)**.

In the case of the more concentrated 5:1 mixture, the solid formed appears more crystalline than the other samples, as its spectrum fairly closely resembles that of the dihydrate (cf. Fig. 2, spectrum c). This point is discussed below.

4 Discussion

As pointed out in the introduction, this study had three main goals: define the chemical state in which HCl is incorporated into ice during co-condensation with H₂O at 190 K; determine the phases that HCl and H₂O form together; and understand the effect of HCl on ice structure. These points are discussed below and the conclusions are used for atmospheric applications in the next section.

4.1 HCl chemical state

According to our interpretation, our results show for the first time that HCl is dissociated ionically into HCl : H₂O mixtures co-condensed at 190 K. This was expected, after the works of Horn et al. (1992) who observed this ionization process by exposing ice to DCl at 110 K, and of Delzeit et al. (1993) who heated an HCl : H₂O solid formed at 85 K to 150 K and observed the transformation of the HCl.H₂O
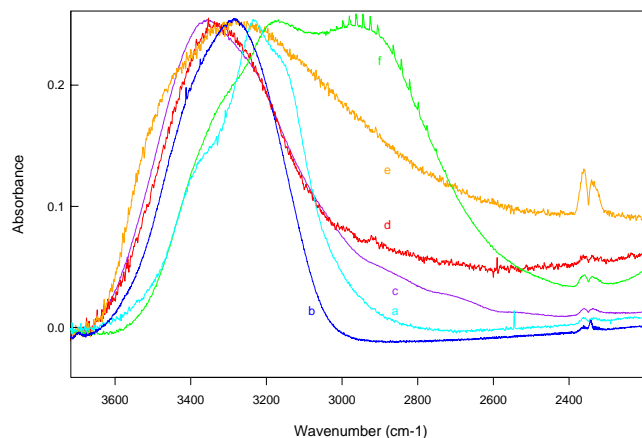

Fig. 8. Comparison of IR absorption bands in the OH stretching mode region. **(a)** Crystalline ice; **(b)** amorphous ice, from Trotta (1996); **(c)** gaseous HCl : H₂O mixture of composition 1:200 condensed at 190 K; **(d)** ibid, mixture 1:50; **(e)** mixture 1:10; **(f)** mixture 5:1.

molecular complex into the $H_3O^+.Cl^-$ ionic complex. However, the novelty of this study is that we investigated by IR spectroscopy solids formed at 190 K, i.e. at a temperature significantly higher than in previous studies. Furthermore, the absence of the ionic complex $H_3O^+.Cl^-$, indicated by the absence of the characteristic band, implies that the hydronium ions produced by the ionization of HCl are likely hydrated into $H_{2x+1}O_x^+$. This is also supported by the fact that hydrated hydronium ions are present in HCl hydrates (Table 1). Those solids and our samples are likely made of similar vibrating species with similar absorption bands.

4.2 Phase

Our results show that in all cases, the co-condensation of HCl and H₂O at 190 K forms a non-crystalline phase. HCl is stabilized in the solid by several waters of hydration. Crystallization is almost complete in the 5:1 mixture, that forms a 1:2 solid, possibly because there are fewer waters of hydration, and molecular mobility is less hindered. In the other mixtures, with less HCl, there are more waters of hydration, and this may result in interactions that produce larger, less mobile clusters, thus preventing molecular rearrangement and crystallization. HCl was thus in all cases incorporated in an homogeneous non-crystalline or incompletely crystallized phase.

4.3 Structure

While the condensation of pure water vapor at 190 K involves the formation of crystalline ice I_h, the condensation of gaseous mixtures HCl : H₂O 1:n, $n \geq 10$, forms non-crystalline solids: the network of the crystalline ice is thus deformed by the incorporation of HCl, and this effect increases with the HCl concentration. It is remarkable that

the condensation of a mixture with a HCl : H$_2$O ratio as low as 1:200 manifests itself by structural deformations of the ice as important as those observed here. This implies that the interactions between HCl and H$_2$O are both intense and multiple, one single HCl molecule being likely to interact strongly with several water molecules simultaneously. This again confirms our explanation of an incorporation of HCl by ionic solvation by several water molecules.

There are some differences in the structure of the different samples. On the one hand, we have seen that the non-crystalline solid formed by condensing a gaseous mixture HCl : H$_2$O 5:1 reorganizes itself in about 10 min into a compound close to the dihydrate of HCl. On the other hand, in the 3 more dilute cases, the non-crystalline samples do not reorganize themselves, neither into a single crystalline structure, nor into a mixture of crystalline structures, that could be ice and a hydrate. The difference between the more concentrated and the more dilute mixtures deserve discussion. The dihydrate of HCl is uniquely made of H$_5$O$_2^+$ ions and Cl$^-$ ions: it does not contain water molecules. Since the solid formed at the beginning of the condensation is close to the non-crystalline compound of composition HCl.2H$_2$O, one can therefore suppose that it is also mainly made of the ionic species H$_{2x+1}$O$_x^+$ and Cl$^-$. The motions (diffusion or/and rotations) necessary to reorganize the solid into a crystalline structure are thus small compared to those required in the case of the more concentrated mixtures. In order to form distinct crystallites of ice and hydrates of HCl, the ions of these solids would have to travel through the water molecules that are surrounding them. Another likely process of reorganization would be the degassing of the molecules and ions contained in the solids toward the surrounding air. But here also, the molecules would have to diffuse through the solid. The differences of structural organization between the solid formed by condensing a HCl : H$_2$O 5:1 gaseous mixture and the solids formed by condensing the mixtures HCl : H$_2$O 1:n with $n \geq 10$ are likely to come from a limitation of the solid phase motions of the H$_{2x+1}$O$_x^+$ and Cl$^-$ ions.

5 Atmospheric applications

This work provides the first direct experimental evidence that at 190 K, the chemical state of HCl in polar stratospheric heterogeneous reactions is likely to be ionic, under the form of choride and hydrated hydronium ions. These results are important for future experimental and modeling studies on stratospheric heterogeneous chemistry.

Furthermore, ice that forms type II PSCs condenses in the presence of HCl. Our results show that this dopant will be incorporated and is likely to modify ice structure. The HCl : H$_2$O mixing ratio in the winter polar stratosphere is about 1/2500 (Chu et al., 1993; Marti and Mauersberger, 1993), i.e. 12.5 times less than the smallest mixing ratio we have studied (1/200). However, for this latter ratio, the ob-served impact of HCl on ice structure is large enough to produce very important spectral modifications. It thus appears reasonable to suggest that in the polar stratosphere, the co-condensation of HCl with H$_2$O will also perturb ice structure. At this point, it appears premature to speculate on the magnitude of this effect, and in particular it is not certain that it will be large enough to affect ice crystallinity. However, it seems very likely that a large number of defects will be created.

HCl is not the single trace gas present when PSCs' particles are forming. HNO$_3$ is also in the surrounding phase (P$_{HNO_3} \sim 4 \times 10^{-8}$ Torr; Molina et al., 1993). This gas can thus also be incorporated into PSC ice. Like HCl, HNO$_3$ is a strong acid that can interact strongly with water molecules. Its incorporation into ice could therefore contribute to a perturbation of the ice network and modify its properties.

Furthermore, type Ia PSCs particles are thought to be made of nitric acid trihydrate (Voigt et al., 2000). If dopants are incorporated into this crystalline solid during their condensation, its structure and reactivity may also be perturbed.

The influence of surface morphology of materials on their reactivity has already been highlighted by several authors, e.g. Ferry et al. (1996, 1997), Langel and Parrinello (1994, 1995), Scamehorn et al. (1994), Madix (1996), Van der Vegt (1992), Tersoff (1994), Pimpinelli and Villain (1998), Nayakama et al. (1999). The catalytic properties of ice in the presence of dopants that perturb its structure may then be different from those of pure crystalline Ih ice. The parameters (sticking coefficients, surface coverage, reaction probability) involved into the quantification of the stratospheric heterogeneous reactions at the type II PSCs' particles surfaces have been until now measured in laboratory on pure I_h ice (e.g. Hanson and Ravishankara, 1992; Rieley et al., 1995; De More et al., 1994; Fluckiger et al., 2000; Aguzzi and Rossi, 2002; Hynes et al., 2002). Their actual values are therefore not necessarily representative of ice with a structural disorder. Our study suggests that these parameters should be measured again on ice doped with trace gases like HCl and HNO3 in order to get values that can be applied with greater confidence to the stratosphere.

References

Aguzzi, A. and Rossi, M. J.: Heterogeneous Hydrolysis and Reaction of $BrONO_2$ and Br_2O on Pure Ice and Ice Doped with HBr, J. Phys. Chem. A, 106, 5891–5901, 2002.

Ault, B. S. and Pimentel, G. C.: Infrared spectrum of the water-hydrochloric acid complex in solid nitrogen, J. Phys. Chem., 77, 1, 57–61, 1973.

Banham, S. F., Horn, A. B., Koch, T. G., and Sodeau, J. R.: Ionisation and solvation of stratospherically relevant molecules on ice films, Faraday Discuss., 100, 321–332, 1995.

Bertie, J. E. and Whalley, E.: Infrared spectra of ices Ih and Ic in the range $4000\,cm^{-1}$ to $350\,cm^{-1}$, J. Chem. Phys., 40, 6, 1637–1645, 1964.

Chu, L. T., Leu, M.-T., and Keyser, L. F.: Uptake of HCl in water ice and nitric acid films, J. Phys. Chem., 97, 7779–7785, 1993.

Delzeit, L., Powell, K., Uras, N., and Devlin, J. P.: Ice surface reactions with acids and bases, J. Phys. Chem., B 101, 2327–2332, 1997.

Delzeit, L., Rowland, B., and Devlin, J. P.: Infrared spectra of HCl complexed/ionized in amorphous hydrates and at ice surfaces in the 15-90 K range, J. Phys. Chem., 97, 10 312–10 318, 1993.

De More, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, R. F., Howard, C. J., Ravishankara, A. R., Kolb, C. E., and Molina, M. J.: Chemical Kinetics and photochemical data for use in stratospheric modeling, JPL Publication, 97, 4, 1994.

Demirdjian, B., Ferry, D., Suzanne, J., Toubin, C., Picaud, S., Hoang, P. N. M., and Girardet, C.: Structure and dynamics of ice Ih films upon HCl adsorption between 190 and 270 K. I. Neutron diffraction and quasielastic neutron scattering experiments, J. Chem. Phys., 116, 12, 5143–5149, 2002.

Dominé, F. and Shepson, P. B.: Air-Snow Interactions and Atmospheric Chemistry, Science, 297, 5586, 1506–1510, 2002.

Dominé, F. and Thibert, E.: Mechanism of incorporation of trace gases in ice growth from the gas phase, Geophys. Res. Lett., 23, 3627–3630, 1996.

Dominé, F. and Xueref, I.: Evaluation of Depth Profiling Using Laser Resonant Desorption as a Method to Measure Diffusion Coefficients in Ice, Anal. Chem., 73, 17, 4348–4353, 2001.

Ferriso, C. C. and Hornig, D. F.: Infrared spectra of oxonium halides and the structure of the oxonium ion, J. Chem. Phys., 23, 8, 1464–1468, 1955.

Ferry, D., Glebov, A., Senz, V., Suzanne, J., Toennies, J. P., and Weiss, H.: Observation of the second ordered phase of water on the MgO (100) surface: low energy electron diffraction and helium atom scattering studies, J. Chem. Phys., 105, 4, 1697–1701, 1996.

Ferry, D., Glebov, A., Senz, V., Suzanne, J., Toennies, J. P., and Weiss, H.: The properties of a two-dimensional water layer on MgO (001), Surface Science, 377–379, 634–638, 1997.

Fluckiger, B., Chaix, L., and Rossi, M.: Properties of the HCl/ice, HBr/ice, and H_2O/ ice interface at stratospheric temperatures (200 K) and its importance for atmospheric heterogeneous reactions, J. Phys. Chem. A, 104, 11 739–11 750, 2000.

Fritz, J. J. and Fulget, C. R.: Vapor pressure of aqueous hydrogen chloride solutions, 0° to 50°C, Indust. Eng. Chem., 1, 10–12, 1956.

Galloway, J. N. and Likens, G. E.: Acid precipitation: the importance of nitric acid, Atmosph. Environ., 15, 1081–1085, 1981.

Gertner, B. J. and Hynes, J. T.: Molecular dynamics simulation of hydrochloric acid ionization at the surface of stratospheric ice, Science, 271, 1563–1566, 1996.

Gilbert, A. S. and Sheppard, N.: Infrared spectra of the hydrates of hydrogen chloride and hydrogen bromide. Absorption bands of the $H_5O_2^+$ species, J. Chem. Soc. Faraday Trans. II, 69, 1628–1642, 1973.

Goodman, J., Toon, O. B., Pueschel, R. F., Snetsinger, K. G., and Verma, S.: Antarctic stratospheric ice crystals, J. Geophys. Res., 94, 16 449–16 457, 1989.

Hanson, D. R. and Ravishankara, A. R.: Investigation of the reactive and non reactive processes involving $ClONO_2$ and HCl on water and nitric acid doped ice, J. Phys. Chem., 96, 2682–2691, 1992.

Hardin, A. H. and Harvey, K. B.: Temperature dependences of the ice I hydrogen bond spectral shifts – I. The vitreous to cubic ince phase transformation, Spectrochemical Acta, 29 A, 1139, 1973.

Haynes, D. R., Tro, N. J., and George, S. M.: Condensation and evaporation of H_2O on ice surfaces, J. Phys. Chem., 96, 8502–8509, 1992.

Hobbs, P. V.: Physics and Chemistry of ice, edited by: Whalley, E., Jones, S. J., and Gold, L. W., Royal Society of Canada, Ottawa, 1974.

Honig, R. E. and Hook, H. O.: Vapor pressure data for some common gases, RCA Review, 21, 360–368, 1960.

Horn, A. B., Chesters, M. A., McCoustra, M. R. S., and Sodeau, J. R.: Adsorption of stratospherically important molecules on thin D_2O ice films using reflection absorption infrared spectroscopy, J. Chem. Soc. Faraday Trans., 88, 7, 1077–1078, 1992.

Hornig, D. F. and Osberg, W. E.: Infrared spectrum and the structure of the low-temperature phases of crystalline HCl, HBr and HI, J. Chem. Phys., 23, 4, 662–670, 1955.

Hov, Ø., Allegrini, I., Beilke, S., Cox, R. A., Eliassen, A., Elshout, A. J., Gravenhorst, G., Penkett, S. A., and Stern, R.: Evaluation of atmospheric processes leading to acid deposition in Europe, Comission of the European Communities Report EUR 11441, Bruxelles, Belgium, 1987.

Hynes, R. G, Fernandez, M. F., and Cox, R. A.: The uptake of HNO_3 on water ice and the co-adsorption of HNO_3 and HCl in the temperature range 210–235 K, J. Geophys. Res., 107, 4797, 2002.

Koehler, B. G., McNeill, L. S., Middlebrook, A. M., and Tolbert, M. A.: Fourier transform infrared studies of the interaction of HCl with model polar stratospheric cloud films, J. Geophys. Res., 98, D6, 10 563–10 571, 1993.

Langel, W. and Parrinello, M.: Hydrolysis at stepped MgO surfaces, Phys. Rev. Lett., 73, 504, 1994.

Langel, W. and Parrinello, M.: *Ab initio* molecular dynamics of H_2O absorbed on solid MgO, Chem. Phys., 103, 3240, 1995.

Legrand, M. and Mayewski, P.: Glaciochemistry of polar ice cores: a review, Rev. Geophys., 35, 219–243, 1997.

Livingston, F. E., Smith, J. A., and George, S. M.: Depth-proiling and diffusion measurements in ice films using infrared laser resonant desorption, Anal. Chem., 72, 5590–5599, 2000.

Lundgren, J.-O. and Olovsson, I.: Hydrogen bond studies. XV. The crystal structure of hydrogen chloride dihydrate, Acta Cryst., 23, 966–971, 1967a.

Lundgren, J.-O. and Olovsson, I.: Hydrogen bond studies. XVI. The crystal structure of hydrogen chloride trihydrate, Acta Cryst., 23, 971–976, 1967b.

Madix, R. J.: Atom-resolved Investigation of Surface Reactions:

Ammonia and Oxygen on Cu(110) at 300 and 400 K, Faraday Discussion, 105, 139, 1996.

Marti, J. and Mauersberger, K.: A survey and new meaurements of ice vapor pressure at temperatures between 170 and 250 K, Geophys. Res. Lett., 20, 5, 363–366, 1993.

Molina, M. J., Zhang, R., Woolbridge, P. J., Mc Mahon, J. R., Kim, J. E., Chang, H. Y., and Deyer, K.: Physical chemistry of the H_2SO_4/HNO_3/H_2O system: implications for polar stratospheric clouds, Science, 251, 1418–1423, 1993.

Molina, L. T. and Molina, M. J.: Production of Cl2O2 from the self-reaction of the ClO radical, J. Phys. Chem., 91, 433–436, 1987.

Nayakama, K., Aldao, C. M., and Weaver, J. H.: Vacancy-assisted halogen reactions on Si (100)–(201), Phys. Rev. Lett., 82, 568, 1999.

Packer, M. J. and Clary, D. C.: Interaction of HCl with water clusters: (H_2O)nHCl, $n = 1 - 3$, J.Phys. Chem., 99, 14323–1433, 1995.

Pimpinelli, A. and Villain, J.: Physics of crystal growth, Cambridge University Press, Cambridge, UK, 1998.

Rieley, H., Aslin, H. D., and Haq, S.: Sticking of HCl and HBr on a type II polar stratospheric cloud mimic, J. Chem. Soc. Faraday Trans., 91, 15, 2349–2351, 1995.

Ritzhaupt, G. and Devlin, J. P.: Infrared spectra of nitric and hydrochloric acid-hydrate thin films, J. Phys. Chem., 95, 90–95, 1991.

Scamehorn, C. A., Hess, A. C., and Mc Carty, M. I.: Water chemistry on surface defect sites: Chemidissociation versus physisorptionon MgO(001), J. Chem. Phys., 101, 1547, 1994.

Solomon, S.: Progress towards a quantitative understanding of Antarctic ozone depletion, Nature, 347, 347–354, 1990.

Taesler, I. and Lundgren, J.-O.: Hydrogen bond studies. CXXIX. An X-ray determination of the crystal structure of hydrogen chloride hexahydrate, $H_9O_4^+Cl^-$.$2H_2O$, Acta Cryst. B, 34, 2424–2428, 1978.

Tersoff, J., Van Der Gon, D. and Tromp, R. M.: Critical island size for layer by layer growth, Phys. Rev. Lett., 72, 266, 1994.

Thibert, E. and Dominé, F.: Thermodynamics and Kinetics of the solid solution of HCl in ice, J. Phys. Chem. B, 101, 3554–3565, 1997.

Toubin, C., Picaud, S., Hoang, P. N. M., Girardet, C., Demirdjian, B., Ferry, D., and Suzanne, J.: Structure and dynamics of ice I_h films upon HCl adsorption between 190 and 270 K. II. Molecular dynamics simulations, J. Chem. Phys., 116, 12, 5150–5157, 2002.

Trotta, F.: Determination of the optical constants of ices in far and mid infrared. Application to grains of interstellar middle and circumstellar envelops (phD dissertation), Université Joseph Fourier ed., Grenoble, France, in French, 1996.

Van Der Vegt, H. A., van Pinxteren, H. M., Lohmeier, M., and Vlieg, E.: Surface induced layer by layer growth of Ag on Ag (111), Phys. Rev. Lett., 68, 3335, 1992.

Voigt, Ch., Schreiner, J., Kohlmann, A., Zink, P., Mauersberger, K., Larsen, N., Deshler, T., Kröger, C., Rosen, J., Adriani, A., Cairo, F., Di Donfrancesco, G., Viterbini, M., Ovarlez, J., Ovarlez, H., David, Ch., and Dörnbrack, A.: Nitric Acid Trihydrate (NAT) in Polar Stratospheric Clouds, Science, 290, 1756–1758, 2000.

Vuillard, G.: On the hexahydrate of HCl, C.R. Acad. Sci., 241, 1308-1311, in French, 1955.

Wolff, E. W., Mulvaney, R., and Oates, K.: Diffusion and location of hydrochloric acid in ice, Implications for polar stratospheric clouds and ozone depletion, Geophys. Res. Let., 16, 6, 487–490, 1989.

Xueref, I.: Study of the incorporation of HCl and HBr in ice by IR and EXAFS spectroscopies. Atmospheric applications (phD dissertation), Université Joseph Fourier ed., Grenoble, France, in French, 1999.

Yoon, Y. K. and Carpenter, G. B.: The crystal structure of hydrogen choride monohydrate, Acta Cryst., 12, 17–20, 1959.