

Laboratory studies about the interaction of ammonia with ice crystals at temperatures between 0 and -20°C

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Received: 12 October 2006 / Accepted: 27 February 2007 /
Published online: 27 March 2007
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Abstract In laboratory experiments the interactions of ammonia with ice crystals were studied within the temperature range between 0 and -20°C . In a first series of experiments dendritic ice crystals were grown from water vapor in presence of ammonia gas in various concentrations between 4 and 400 ppbv. In a second series of experiments pure ice crystals were exposed to a humidified ammonia–air mixture inside a horizontal flow tube. The influence of temperature, ammonia gas concentration (0.6, 1.5, and 10 ppmv), exposure time, and the presence of impurities such as sulfate on the ammonia uptake by the ice surface was investigated by determining the ammonium content in the melt water of the ice crystals by ion chromatography. During the growth of ice crystals significant amounts of ammonia (around 200 $\mu\text{g/l}$) were taken up even at small gas concentrations. In contrast, even at high gas concentrations the uptake of ammonia by non-growing ice crystals was lower by approximately one order of magnitude. The presence of sulfate on the ice surface affected an enhanced uptake of ammonia by a factor of 5–10. A model is presented which describes the uptake of ammonia by ice considering the chemical processes occurring in the ice surface layer and simultaneous diffusion of ammonia into bulk ice. Even the increased uptake of ammonia by growing ice is rather small compared to the uptake by water droplets; thus, the major process for scavenging of ammonia from the atmosphere via the ice phase might not be the direct uptake by ice crystals but the riming involving super-cooled droplets containing ammonia.

Keywords Ammonia · Ice crystals · Gas scavenging

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1 Introduction

Ammonia (NH_3) as the only inorganic base of major abundance in the atmosphere is one of the most important trace gases for liquid phase and aerosol chemistry. Ammonia is mainly emitted from livestock waste, application of fertilizer, and biomass burning (e.g., Schlesinger and Hartley 1992), i.e. sources of ammonia are basically on the continents. Thus, ammonia concentrations decrease over the oceans. In clean areas, ammonia concentrations lay around 1 ppbv while in polluted areas concentrations between 3 and 25 ppbv are reached (Seinfeld 1986; Erisman et al. 1988; Nowak et al. 2006). Ammonia is characterized by good water solubility and, therefore, plays an essential role in the acid-base-interactions of cloud and rain water (Warneck 2000). Ammonia is taken up very efficiently by water drops (Hannemann et al. 1995, 1996) and can be incorporated – but less efficiently – into ice crystals during their growth (Santachiara et al. 1998). However, laboratory investigations showed that the uptake of trace gases such as SO_2 , HNO_3 , and HCl by ice crystals is significantly lower than the uptake by water drops (Mitra et al. 1990; Diehl et al. 1995, 1998). Thus, riming, i.e. the growth of ice particles by deposition of super-cooled liquid drops might be the major process to incorporate these trace gases into ice particles ultimately leading to their removal from the atmosphere. Therefore, the question arises whether this conclusion applies for ammonia also. The earlier laboratory experiments showed that SO_2 could be incorporated more efficiently during the growth of ice crystals while HNO_3 and HCl were taken up more efficiently on non-growing ice particles. If the latter is the case for ammonia also a higher uptake as measured by Santachiara et al. (1998) could be expected for non-growing ice crystals. In the present investigations the interactions of ammonia with ice is studied by means of single ice crystals to simulate atmospheric conditions in contrast to the earlier work of Santachiara et al. (1998) who worked with ice layers. Two atmospheric processes were simulated in laboratory experiments: (1) uptake during growth of ice crystals, and (2) uptake on non-growing ice crystals. The latter was performed for different conditions, with pure ice crystals and with ice crystals containing sulfate in their surface layer. Hannemann et al. (1996) showed that the uptake of ammonia in water is significantly enhanced in the presence of SO_2 in the environment. To parameterize the experimental data a model is presented which describes the uptake of ammonia by ice due to the chemical processes taking place in the ice surface layer as well as the diffusion of ammonia into bulk ice.

2 Experimental methods

2.1 Uptake during growth of ice crystals

In a first series of experiments, the uptake of ammonia was studied during the growth of dendritic ice crystals. The design of the experimental setup simulated in-cloud scavenging (Mitra et al. 1990; Diehl et al. 1995) and was constructed inside a walk-in cold chamber as shown in Fig. 1. Distilled and deionised water in a glass reservoir was heated and kept at a constant temperature to ensure a steady evaporation. The glass reservoir had dimensions of $20 \times 30 \times 15$ cm and contained 1 l water which had a temperature of approximately 8°C . Above the glass reservoir a grill of aluminium strips (each 2 cm broad) was mounted where the ice crystals grew by the diffusion of water vapor. The air temperature in this region was kept around -15°C and the super-saturation was approximately 15% producing ice crystals with a dendritic structure (Pruppacher and Klett 1997). NH_3 gas was present in the gas

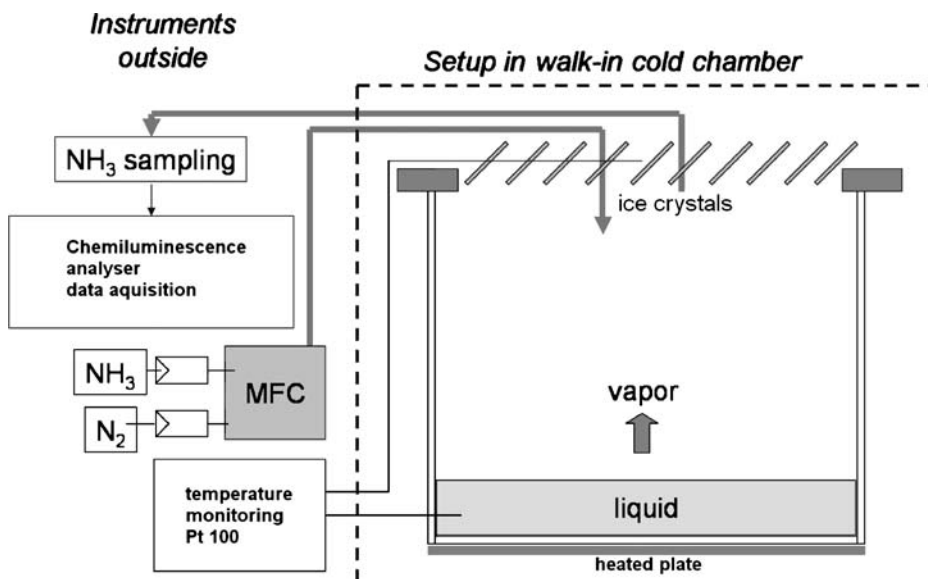


Fig. 1 Experimental setup of ammonia uptake during growth of ice crystals

phase with concentrations between 4 and 400 ppbv. Lower gas concentrations up to 100 ppbv were created by mixing NH₃ and nitrogen and maintaining a stable mixture by means of mass flow controllers. Higher gas concentrations were obtained by evaporating an NH₃*H₂O solution instead of pure water. During the entire growth time of 12 h the NH₃ concentration was monitored by a chemiluminescence analyzer (Environment SA NH30M) with a precision of ± 1 ppbv. The concentrations were measured at different locations to ensure that there was no concentration gradient throughout the crystal growth area. The background NH₃ gas concentration in the cold chamber was less than 1 ppbv. To quantify the NH₃ gas uptake, the melt water of the sampled ice crystals was analyzed for its NH₄⁺ content by ion chromatography (DIONEX DX-300).

2.2 Uptake by non-growing ice crystals

In a second series of experiments, the uptake of ammonia by non-growing dendritic ice crystals was investigated. The design of the experimental setup simulated below-cloud scavenging, i.e. the uptake by free falling ice crystals in the atmosphere. Ice crystals were grown as described in Section 2.1 but from pure water vapor and exposed to ammonia in various concentrations in a small horizontal flow tube installed inside the walk-in cold chamber (see Fig. 2). Compressed air from a gas cylinder was made to pass through two columns packed with ice in order to reach ice saturation; afterwards, NH₃ was added to the air stream. The saturated NH₃-air mixture entered the horizontal flow tube which was made from Teflon and had 30 cm in length and 10 cm in diameter. Inside the flow tube the ice crystals were placed on a Teflon net with some space between individual crystals. Just behind the entrance to the flow tube the NH₃-air mixture passed through a honeycomb to reach nearly laminar conditions. The flow velocity inside the tube was in the range of the terminal velocity of ice crystals in the atmosphere, i.e. approximately 20 cm/s (Pruppacher and Klett 1997). During the experiments the NH₃ gas concentrations were measured at two

(measured as sulfate by ion chromatography) was 0.4 and 1.3 mg/l, respectively, which is in the range of the sulfur content in sampled atmospheric ice crystals (Cadle et al. 1985; Dasch 1987). It was expected that the presence of sulfate ions at the ice crystal surface enhances the dissociation of NH₃ into NH₄⁺ ions so that desorption of NH₃ is hindered.

3 Parameterization of experimental data

In the following, a model is presented which describes the uptake of ammonia by non-growing ice crystals. For pure ice crystals without any impurities in their surface layer diffusion of ammonia into bulk ice is assumed. Ogasawara et al. (2000) found that adsorption of NH₃ on ice surfaces is present as hydrogen bond adsorption of the form HOH–NH₃. The hydrogen bonded NH₃ inside a monolayer forms NH₄⁺ which diffuses into the bulk. Therefore, it is assumed that the adsorbed NH₃ is converted into NH₄⁺ and diffuses from ice surface into the bulk as long as the NH₃ partial pressure in the flow tube is kept constant so that an equilibrium state between gas phase and surface coverage is maintained. The diffusion into the bulk does not influence the equilibrium state because diffusion proceeds slowly in comparison to the mass transport of NH₃ molecules from the gas phase to the ice surface. As a further simplification for the mathematical description diffusion from the surface with constant coverage into a semi-infinite solid is assumed. According to Dominé et al. (1994) the solution of the one-dimensional partial differential equation of diffusion (Fick’s law) with boundary conditions $C(x,t)=C_0$ at $t<0$ and $C(x,t)=0$ for $x>0$ at $t=0$ is given by

$$C(x, t) = C_0 \cdot \left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{Dt}}\right) \right] \tag{1}$$

where C_0 the initial constant surface coverage of formed NH₄⁺, expressed as the NH₄⁺ concentration in 1 l melt water, D the diffusion coefficient of NH₄⁺ in ice, x the depth of diffused ions, and t the exposure time. The error function erf(x) is defined as follows:

$$\Phi_0(x; 0, 1) = \operatorname{erf}(x) = \frac{1}{\sqrt{2\pi}} \int_0^x e^{-\frac{\zeta^2}{2}} d\zeta \tag{2}$$

with ζ an arbitrary integration variable. Referred to the present problem, the amount of diffused NH₄⁺ from the ice crystal surface into the bulk during exposure of the ice crystal to NH₃ gas for a particular exposure time period t^i is given by

$$C_{\text{NH}_4^+}^{\text{abs}}(t^i) = \int_{x=0}^{x_{\text{exp}}} C_{\text{NH}_4^+}(x, t^i) dx \tag{3}$$

with

$$C_{\text{NH}_4^+}(x, t^i) = C_0 \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt^i}}\right) \right] \tag{4}$$

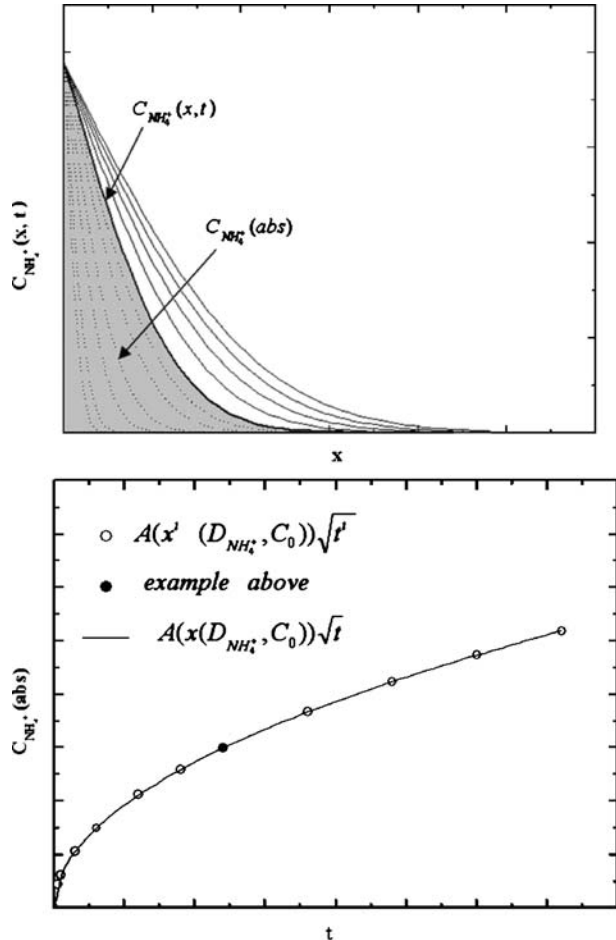
The evaluation of the integral in Eq. 3 with different exposure times t^i ($i=1, 2, \dots, n$) leads to

$$C_{\text{NH}_4^+}^{\text{abs}}(t) = A(x(D, C_0))\sqrt{t} = \sqrt{A^2(x(D, C_0))t} \tag{5}$$

where A is a constant. Equation 5 describes the experimental data, i.e. the amount of NH_4^+ in ice crystals as a function of exposure time t and the constant A . As A depends on the diffusion coefficient D and the initial constant surface coverage of NH_4^+ , C_0 , it is not necessary to know these parameters explicitly. In the upper panel of Fig. 3 one example of $C_{\text{NH}_4^+}(x, t^i)$ is plotted against depth x from the surface (where $x=0$) with different exposure times t^i ($i=1, 2, \dots, 11$) (Eq. 4). It was calculated with $C_0=390 \mu\text{g/l}$, similar to experimental data from measurements with pure ice exposed at -7°C with 1.5 ppmv NH_3 , and with an assumed diffusion coefficient $D = 1 \times 10^{-6} \text{ mm}^2/\text{s}$ based on values for HNO_3 and HCl (Diehl et al. 1995). The lower panel gives $C_{\text{NH}_4^+}^{\text{abs}}(t)$ as function of exposure time t , i.e. the numerical integration of all $C_{\text{NH}_4^+}(x, t^i)$ (Eq. 3). According to Eq. 5, $C_{\text{NH}_4^+}^{\text{abs}}$ is described by the constant A and the exposure time t .

The constants A for the different experimental conditions (gas concentration, temperature) were determined by a non-linear least square fit of the experimental data which was carried out with the Levenberg-Marquardt minimization method (Press et al. 1992).

Fig. 3 Upper panel: $C_{\text{NH}_4^+}(x, t^i)$ plotted versus depth x with 11 different exposure times t^i ($i=1, 2, \dots, 11$) with arbitrary $D = 1 \times 10^{-6} \text{ mm}^2/\text{s}$ and $C_0=390 \mu\text{g/l}$. Lower panel: $C_{\text{NH}_4^+}^{\text{abs}}(t)$ as function of exposure time t , i.e. the numerical integration of all $C_{\text{NH}_4^+}(x, t^i)$ in the upper panel



The value of χ^2 is a measure of the quality of the selected model function to describe the experimental data and is given by

$$\chi^2 = \frac{1}{(n_{\text{eff}} - p)} \sum_{i=1}^N w_i [y_i - f(x_i, p_1, p_2, \dots)]^2 \tag{6}$$

where the experimental data correspond to the dependent variables y_i , $f(x_i, p_1, p_2, \dots)$ is the selected function with the independent variables x_i and the fitting parameters (p_1, p_2, \dots, p_k) , and w_i are the weight factors which include the errors of the experimental data.

$$f = (n_{\text{eff}} - p) \tag{7}$$

is the number of degrees of freedom with n_{eff} being the number of available experimental data, p is the number of parameters of the fitting function. In Eq. 5, there is only one parameter A , i.e. $p_1=A$ and $p=1$ in Eq. 6.

For the uptake of ammonia by ice crystals containing sulfate on their surface it is considered that the dissociation of NH_3 into NH_4^+ ions in the ice surface layer is enhanced by the presence of the sulfate ions, therefore, less ammonia desorbs from the ice surface and more NH_4^+ ions diffuse into the bulk. To describe this situation, the following model function with three parameters A , B , and C_{sat} was created where the constant A is the same as in Eq. 5, B a time constant, and C_{sat} the saturation concentration at the ice surface, i.e. $p_1=A$, $p_2=C_{\text{sat}}$, $p_3=B$, and $p=3$ in Eq. 6. The independent variable is the exposure time t .

$$C_{\text{NH}_4^+}^{\text{abs}} = C_{\text{sat}} \left[1 - \exp\left(-\frac{t}{B}\right) \right] + A\sqrt{t} \tag{8}$$

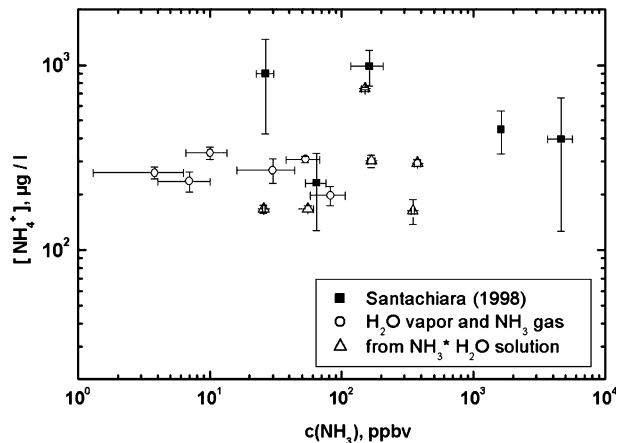
where A is the parameter of the slow diffusion process as in Eq. 5 and B is the time constant of the chemical reaction.

4 Results and discussion

4.1 Uptake during growth of ice crystals

Figure 4 shows the NH_4^+ content in ice crystals grown at different NH_3 gas concentrations in comparison to Santachiara et al. (1998). The error bars in Fig. 4 comprise of the

Fig. 4 Uptake of NH_3 in $\mu\text{g/l}$ during the growth of ice crystals for different gas concentrations in ppbv at $T=-15^\circ\text{C}$ and a super-saturation of 15% in comparison to Santachiara et al. (1998) data



following grouping of data: for the gas concentration, measurements were taken every 100 s and averaged and for the NH_4^+ content in ice five analyses of the same sample were averaged for each data point. The present data lie in the lower range of or slightly below the Santachiara et al. (1998) values. This maybe caused by the different experimental techniques. One observes a nearly constant NH_4^+ uptake of approximately 200–300 $\mu\text{g/l}$ in the ice crystals with increasing NH_3 gas concentrations. This is rather low in comparison to the uptake of other trace gases such as HNO_3 , HCl , and SO_2 in ice crystals during growth (Mitra et al. 1990; Diehl et al. 1995). For these gases the concentrations in ice crystals were around one order of magnitude larger and reach saturation at significant higher gas concentrations. Thus, it can be assumed that in case of ammonia saturation is reached already at small NH_3 gas concentrations which are relevant for the atmosphere. These results indicate that the gas uptake during the growth of ice crystals depends on the type of trace gas.

Early studies of Workman and Reynolds (1956), Lodge et al. (1956), and Gross (1965) found that NH_4^+ is readily accepted by the ice crystal lattice which is in opposition to the present results. However, the important previous step which determines the amount of ions built into the ice lattice is the adsorption of the gas on the ice surface. According to Ogasawara et al. (2000) adsorbed NH_3 is present on ice surfaces as hydrogen bond adsorption of the form $\text{HOH}-\text{NH}_3$. The number of free OH at the ice surface is 2×10^{14} molecules per cm^2 (Superfine et al. 1993). From the surface tension measurements of Donaldson et al. (1999) one monolayer NH_3 corresponds to a surface coverage of $(1.2 \pm 0.2) \times 10^{14}$ molecules per cm^2 . Thus, considering that the growing ice surface is slightly warmer than the environment, one can assume that the adsorbed NH_3 within the first monolayer will create NH_4^+ ions (Ogasawara et al. 2000) which are able to be built into the ice lattice while excessive NH_3 desorbs rather quickly from the ice surface. Kärcher and Basko (2004) showed that the uptake of trace gas depends on the adsorption and desorption rates as compared to the growth rate of ice crystals. The rates of adsorption and desorption of NH_3 are not available so far, however, these rates compared to the growth rate of an ice crystal offer a possible explanation as to why rather such a low uptake of NH_3 during the growth of ice crystals was observed.

Fig. 5 Uptake of NH_3 in $\mu\text{g/l}$ by pure non-growing ice crystals as function of exposure time in min for different gas concentrations at $T = -7^\circ\text{C}$. Symbols: experimental data, solid lines: parameterization of the experimental data due to Eq. 5 with (1) $A^2 = (9.5 \pm 3.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, (2) $A^2 = (11.1 \pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, (3) $A^2 = (116 \pm 21) \mu\text{g}^2/\text{l}^2 \text{ min}$

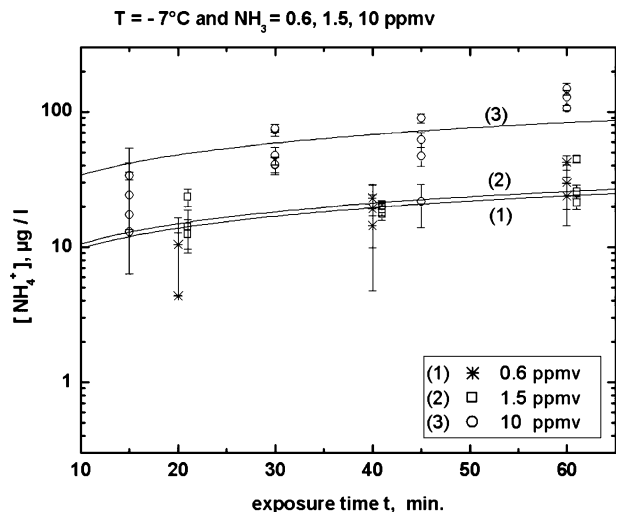
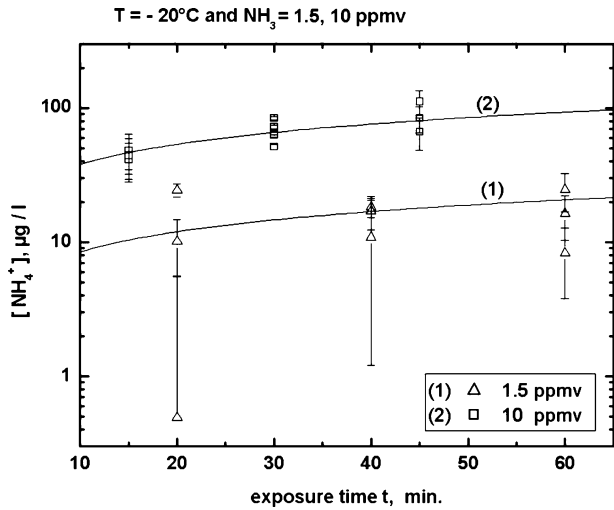


Fig. 6 Uptake of NH_3 in $\mu\text{g/l}$ by pure non-growing ice crystals as function of exposure time in min for different gas concentrations at $T = -20^\circ\text{C}$. Symbols: experimental data, solid lines: parameterization of the experimental data due to Eq. 5 with (1) $A^2 = (7.2 \pm 2.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, (2) $A^2 = (144.8 \pm 1.4) \mu\text{g}^2/\text{l}^2 \text{ min}$



4.2 Uptake by non-growing ice crystals

Figures 5 and 6 show the NH_4^+ amount taken up by non-growing pure ice crystals as functions of exposure time at two temperatures, -7 and -20°C , for different NH_3 gas concentrations (10 ppmv, 1.5 ppmv, and, for -7°C only, 0.6 ppmv). The symbols represent experimental values; the solid lines give the parameterization according to Eq. 5. The values of the constants A^2 are as follows: at -7°C , Fig. 5: for line (1) $A^2 = (9.5 \pm 3.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, for line (2) $A^2 = (11.1 \pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, (3) $A^2 = (116 \pm 21) \mu\text{g}^2/\text{l}^2 \text{ min}$; at -20°C ; Fig. 6: for line (1) $A^2 = (7.2 \pm 2.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, for line (2) $A^2 = (144.8 \pm 1.4) \mu\text{g}^2/\text{l}^2 \text{ min}$. The error bars in Figs. 5, 6, 7, 8 comprise of the following grouping of data: for the NH_4^+ content in ice, five analyses of the same sample were averaged for each data point. In spite of the

Fig. 7 Uptake of NH_3 in $\mu\text{g/l}$ by non-growing ice crystals with sulfate impurities at the surface as function of exposure time in min for surface concentrations of 0.4 and 1.3 $\mu\text{g/l}$. NH_3 gas concentration 1.5 ppmv, temperature -7°C . Symbols: experimental data, solid lines: parameterization of the experimental data due to Eqs. 5 and 8 with (1) $A^2 = (11.1 \pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B = (8.2 \pm 1.7) \text{ min}$, $C_{\text{sat}} = (108 \pm 6) \mu\text{g/l}$, (2) $A^2 = (11.1 \pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B = (6.6 \pm 1.1) \text{ min}$, $C_{\text{sat}} = (193 \pm 12) \mu\text{g/l}$

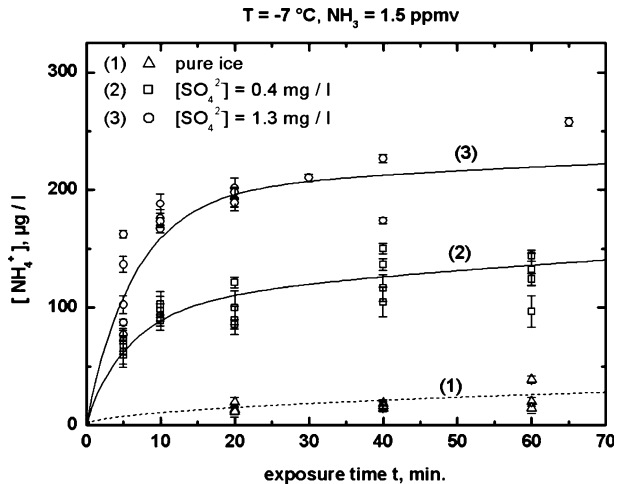
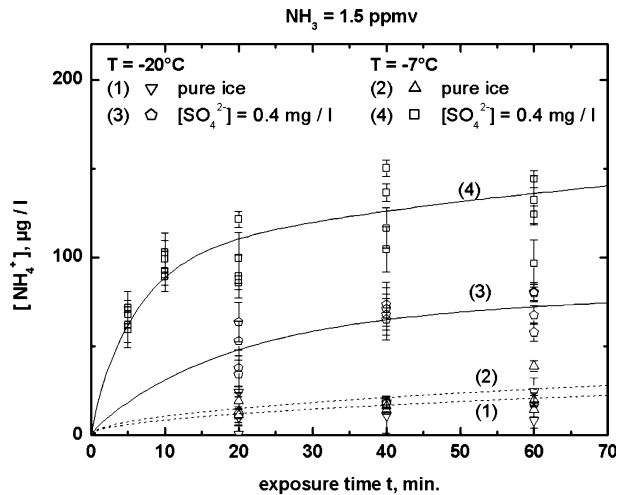


Fig. 8 Uptake of NH_3 in $\mu\text{g/l}$ by non-growing ice crystals with sulfate impurities at the surface as function of exposure time in min for a surface concentration of $0.3 \mu\text{g/l}$ and two temperatures, -7 and -20°C . NH_3 gas concentration 1.5 ppmv . Symbols: experimental data, solid lines: parameterization of the experimental data due to Eqs. 5 and 8 with (1) $A^2=(7.2\pm 2.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, (2) $A^2=(11.1\pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, (3) $A^2=(7.2\pm 2.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(18\pm 9) \text{ min}$, $C_{\text{sat}}=(53\pm 6) \mu\text{g/l}$, (4) $A^2=(11.1\pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(8.2\pm 1.7) \text{ min}$, $C_{\text{sat}}=(108\pm 6) \mu\text{g/l}$



relatively high gas concentrations, even at 10 ppmv , and the long exposure times only little NH_4^+ was taken up by the ice crystals. At lower gas concentrations approximately one order of magnitude less was taken up as during the growth of ice crystals. The measurements at these lower gas concentrations (0.6 and 1.5 ppmv) touch the detection limit of the analytical methods (i.e. $20 \mu\text{g/l}$ in the melt water of ice); this resulted in large error bars. The very good agreement between the experimental values and the parameterized curves indicate that diffusion from ice surface into the bulk is the main uptake mechanism of ammonia.

No significant differences between the uptake at -7 and -20°C at the same gas concentrations were observed which is in contrast to measurements with SO_2 , HNO_3 , and HCl (Mitra et al. 1990; Diehl et al. 1995). These showed a higher gas uptake at warmer temperatures, explained by the presence of a quasi-liquid layer at the ice surface (Pruppacher and Klett 1997). Uras et al. (2000) found in molecular modeling studies a considerable similarity in bonding of adsorbed NH_3 to liquid and solid H_2O surfaces which emphasizes the importance of the dangling OH bonds at the ice surface. This indicates that the quasi-liquid layer is not that important for the uptake of NH_3 by ice crystals without impurities.

The picture changes when the ice crystals contain impurities like sulfate. Under these conditions the uptake of ammonia was significantly enhanced especially for short exposure times as can be seen from Figs. 7 and 8. Figure 7 shows the NH_4^+ uptake at a NH_3 gas concentration of 1.5 ppmv for two different surface coverages with sulfate, corresponding to a sulfate concentration in the melt water of the ice crystals of 0.4 mg/l (2) and 1.3 mg/l (3), at a temperature of -7°C . For comparison also the curve from Fig. 5 for pure ice crystals is shown (1). The symbols represent experimental values; the solid lines (2) and (3) give the parameterizations according to Eq. 8. The values of the constants A^2 and B are as follows: for line (1) as before; for line (2) $A^2=(11.1\pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(8.2\pm 1.7) \text{ min}$, $C_{\text{sat}}=(108\pm 6) \mu\text{g/l}$; for line (3) $A^2=(11.1\pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(6.6\pm 1.1) \text{ min}$, $C_{\text{sat}}=(193\pm 12) \mu\text{g/l}$. The higher the sulfate concentration the more enhanced is the NH_4^+ uptake. As in the atmosphere always other species besides NH_3 are present the coupled uptake is the more realistic case. The very good agreement between the experimental values and the parameterized curves indicate that the ammonia uptake by ice crystals with a sulfate cover is determined by a superposition of two processes, i.e. dissociation in the surface layer and diffusion from ice surface into the bulk. Figure 8 shows the same as Fig. 7 but for two temperatures, -7 and -20°C , for pure ice

crystals (lines 1 and 2) and for a sulfate concentration of 0.4 mg/l (lines 3 and 4). The values of the constants A^2 and B are as follows: for lines (1) and (2) as before; for line (3) $A^2=(7.2\pm 2.6) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(18\pm 9) \text{ min}$, $C_{\text{sat}}=(53\pm 6) \mu\text{g/l}$; for line (4) $A^2=(11.1\pm 2) \mu\text{g}^2/\text{l}^2 \text{ min}$, $B=(8.2\pm 1.7) \text{ min}$, $C_{\text{sat}}=(108\pm 6) \mu\text{g/l}$. Here the influence of temperature on the NH_4^+ uptake is obvious: at -7°C where the thickness of the quasi-liquid layer is enhanced (Pruppacher and Klett 1997) significantly more NH_4^+ was taken up as at -20°C . In comparison to the uptake by pure ice crystals, the uptake proceeded more rapidly until saturation was reached. The saturation concentration was directly influenced by the amount of anions at the ice surface.

5 Summary and conclusions

In the present laboratory experiments the uptake of ammonia by single ice crystals was studied in a temperature range of the lower troposphere, i.e. between 0 and -20°C . In a first series of experiments dendritic ice crystals were grown from water vapor in presence of ammonia gas in various concentrations corresponding to in-cloud scavenging. In agreement with earlier experiments (Santachiara et al. 1998) significant amounts of ammonia (around 200 $\mu\text{g/l}$) were taken up during the growth of ice crystals even at low, atmospherically relevant NH_3 gas concentrations between 1 and 10 ppbv. In a second series of experiments non-growing pure ice crystals were exposed to an ammonia–air mixture inside a horizontal flow tube corresponding to below-cloud scavenging. The influence of temperature, ammonia gas concentration (0.6, 1.5, and 10 ppmv), exposure time, and the presence of impurities such as sulfate on the ammonium production at the ice surface was examined. In opposition to the uptake during growth, even at high gas concentrations the uptake of ammonia on non-growing ice crystals was approximately one order of magnitude lower. This uptake process is ruled mainly by the diffusion of NH_4^+ ions formed after the adsorption of the NH_3 at the ice surface. The experimental data were parameterized by a model assuming diffusion into a semi-infinite solid. Ice crystals containing sulfate at their surface showed an enhanced ammonia uptake by a factor of 5–10. For the parameterization of these data a model comprising a superposition of the diffusion into the bulk and a chemical reaction at the ice surface was suggested. All parameterizations show a good agreement with the experimental results although they are based on assumptions which could not take into account the entire complex processes at the ice surface.

According to earlier laboratory experiments SO_2 is incorporated more efficiently during the growth of ice crystals while HNO_3 and HCl are taken up more efficiently on non-growing ice particles (Mitra et al. 1990; Diehl et al. 1995, 1998). The present experiments indicate that ammonia behaves similar to SO_2 , thus, it might be removed from the atmosphere more efficiently by in-cloud scavenging. Compared to the uptake by water droplets (Hannemann et al. 1995, 1996) both, the uptake of ammonia during growth and by non-growing ice crystals in presence of sulfate is rather small; thus, it can be concluded that not the direct uptake by ice crystals but rather riming might be the major process for the scavenging of ammonia from the atmosphere via the ice phase.

Acknowledgements These studies were supported by the Deutsche Forschungsgemeinschaft DFG under grants MI 483/4-1 and 4-2 and the SFB 641: The tropospheric ice phase. It represents a part of a PhD thesis prepared at the University of Mainz, Germany. Additional support was provided by the Max-Planck Institute of Chemistry in Mainz, Germany. The authors thank Elke Fries and Wolfgang Jaeschke from the Institute of Atmosphere and Environment, University of Frankfurt, for fruitful discussions.

References

- Cadle, S.H., Dasch, J.M., Mulawa, P.A.: Atmospheric concentrations and the deposition velocity to snow of nitric acid, sulfur dioxide and various particulate species. *Atmos. Environ.* **19**, 1819–1827 (1985)
- Dasch, J.M.: On the difference between SO_4^{2-} and NO_3^- in wintertime precipitation. *Atmos. Environ.* **21**, 137–141 (1987)
- Diehl, K., Mitra, S.K., Pruppacher, H.R.: A laboratory study of the uptake of HNO_3 and HCl vapor by snow crystals and ice spheres at temperatures between 0 and -40°C . *Atmos. Environ.* **29**, 975–981 (1995)
- Diehl, K., Mitra, S.K., Pruppacher, H.R.: A laboratory study on the uptake of HCl, HNO_3 and SO_2 gas by ice crystals and the effect of these gases on the evaporation rate of the crystals. *Atmos. Res.* **47–48**, 235–244 (1998)
- Dominé, F., Thibert, E., Landeghem, F., Silvente, E., Wagnon, P.: Diffusion and solubility of HCl in ice: preliminary results. *Geophys. Res. Lett.* **21**, 601–604 (1994)
- Donaldson, D.J.: Adsorption of atmospheric gases at the air – water interface. I. NH_3 . *J. Phys. Chem.* **103**, 62–70 (1999)
- Erismann, J.-W., Vermetten, A.W.M., Asman, W.A.H., Waijers-Ijpelaar, A., Slanina, J.: Vertical distribution of gases and aerosols: the behavior of ammonia and related compounds in the lower atmosphere. *Atmos. Environ.* **22**, 1153–1160 (1988)
- Gross, G.W.: The Workman–Reynolds effect and ionic transfer processes at the ice solution interface. *J. Geophys. Res.* **70**, 2291–2300 (1965)
- Hannemann, A., Mitra, S.K., Pruppacher, H.R.: On the scavenging of gaseous nitrogen compounds by large and small rain drops: part I: a wind tunnel and theoretical study of the uptake and desorption of NH_3 in the presence of CO_2 . *J. Atmos. Chem.* **21**, 293–307 (1995)
- Hannemann, A., Mitra, S.K., Pruppacher, H.R.: On the scavenging of gaseous nitrogen compounds by large and small rain drops: part II: a wind tunnel and theoretical study of the simultaneous uptake of NH_3 , SO_2 , and CO_2 in water drops. *J. Atmos. Chem.* **24**, 271–284 (1996)
- Kärcher, B., and Basko, M. M.: Trapping of trace gases in growing ice crystals. *J. Geophys. Res.* **109**, D22204, doi:10.1029/2004JD005254 (2004)
- Lodge, J.P., Baker, M.L., Pierrard, J.M.: Observation on ion separation in dilute solution by freezing. *J. Chem. Phys.* **24**, 716–719 (1956)
- Mitra, S.K., Barth, S., Pruppacher, H.R.: A laboratory study on the scavenging of SO_2 by snow crystals. *Atmos. Environ.* **24A**, 2307–2312 (1990)
- Nowak, J.B., Huey, L.G., Russell, A.G., Tian, D., Neuman, J.A., Orsini, D., Sjostedt, S.J., Sullivan, A.P., Tanner, D.J., Weber, R.J., Nenes, A., Edgerton, E., Fehsenfeld, F.C.: Analysis of urban gas-phase ammonia measurements from the 2002 Atlanta aerosol nucleation and real-time characterization experiment. *J. Geophys. Res.*, **111**, D17308, doi:10.1029/2006JD007113 (2006)
- Ogasawara, H., Horimoto, N., Kawai, M.: Ammonia adsorption by hydrogen bond on ice and its salvation. *J. Chem. Phys.* **112**, 8229–8232 (2000)
- Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P.: *Numerical Recipes in C*. Cambridge University Press, Cambridge, pp 681 (1992)
- Pruppacher, H.R., Klett, J.D.: *Microphysics of Clouds and Precipitation*. 2nd edn. Kluwer, Dordrecht (1997)
- Santachiara, G., Prodi, F., Udisti, R., Prodi, A.: Scavenging of SO_2 and NH_3 during growth of ice. *Atmos. Res.* **47–48**, 209–217 (1998)
- Schlesinger, W.H., Hartley, A.E.: A global budget for atmospheric NH_3 . *Biogeochemistry* **15**, 191–211 (1992)
- Seinfeld, J.H.: *Atmospheric Chemistry and Physics of Air Pollution*. Wiley, New York (1986)
- Superfine, Q., Du, R., Freysz, E., Shen, Y.R.: Ammonia adsorption by hydrogen bond on ice and its salvation. *Phys. Rev. Lett.* **70**, 2313–2316 (1993)
- Uras, N., Buch, V., Delvin, P.J.: Hydrogen bond surface chemistry: interaction of NH_3 with an ice particle. *J. Phys. Chem.* **104**, 203–209 (2000)
- Warneck, P.: *Chemistry of the Natural Atmosphere*, 2nd edn. Academic, New York (2000)
- Workman, E.J., Reynolds, S.E.: Electric phenomena occurring during freezing of dilute aqueous solution and their possible relationship to thunderstorm electricity. *Phys. Rev.* **78**, 254–259 (1956)