Formation of nitric acid/water ice particles in cirrus clouds

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[1] Nitric acid (HNO$_3$) in cirrus ice crystals has been measured in the last decade during airborne field campaigns at latitudes 53$^\circ$S–68$^\circ$N. The HNO$_3$ content in ice crystals, expressed in terms of HNO$_3$/H$_2$O molar ratio, and the fraction of HNO$_3$ in ice derived from those measurements exhibit a clear upward trend with decreasing temperature. The observations are explained by a novel model describing dissolution of HNO$_3$ in liquid aerosol particles serving as freezing nuclei and subsequent trapping of HNO$_3$ during ice crystal growth. The efficiency of trapping increases with decreasing temperature. Efficient trapping occurs via diffusional burial of the ambient HNO$_3$ below about 203 K, because of long residence times of HNO$_3$ molecules at the ice surface. This opens the possibility for HNO$_3$-induced modifications of processes affecting ice crystal growth. At warmer temperatures, molecular processes in the ice surface layer cause an increasingly rapid escape of adsorbed HNO$_3$ into the gas phase and render trapping less efficient despite faster ice growth rates.


1. Introduction

[2] The study of nitric acid (HNO$_3$) uptake in cirrus cloud particles is an important focus in airborne field campaigns (SUCCESS [Weinheimer et al., 1998], POLSTAR [Schlager et al., 1999], SOLVE [Kondo et al., 2003], INCA [Ziereis et al., 2004], CRYSTAL/FACE [Popp et al., 2004], EUPLEX [Voigt et al., 2006]), spanning tropical to polar latitudes. These measurements cover anvil clouds associated with subtropical deep convection, midlatitude stratiform cirrus and wave clouds, and Arctic cirrus. The studies revealed significant reductions of gas phase HNO$_3$ in the presence of ice at low temperatures and high HNO$_3$ partial pressures, but a consistent and physically plausible theoretical explanation is lacking.

[3] We argue that the frequently applied concept of an instantaneous adsorption equilibrium is not adequate to describe the formation of mixed HNO$_3$/H$_2$O particles in cirrus clouds. Ice crystals are hardly found in equilibrium with H$_2$O in the gas phase, and consequently, the HNO$_3$ content in individual crystals results from an integration of HNO$_3$ uptake and evaporation over their entire life cycles. Hence, the amount of HNO$_3$ taken up by cirrus particles cannot simply be correlated to instantaneous variables like cloud surface area density, but is determined by variability in ice supersaturation and ice crystal fall speeds, and the spatial distribution of HNO$_3$.

[4] To this end, we developed a model of trace gas uptake in growing ice crystals (trapping) which combines surface kinetic and gas diffusion processes of, e.g., HNO$_3$ along with condensing H$_2$O vapor [Kärcher and Basko, 2004]. A recent laboratory study of enhanced HNO$_3$ uptake in ice films growing in a flow tube generally supports this trapping concept [Ullerstam and Abbatt, 2005], but it remains unclear whether such results are applicable to real atmospheric conditions. On the other hand, individual cirrus measurements are difficult to compare with cloud model results because of the nonlocal character of the uptake process. Here we use an approach that integrates many measurements covering a very wide range of cirrus cloud properties.

[5] We demonstrate that two limiting cases of trapping — namely (partial) retention of HNO$_3$ molecules contained in freezing aerosol particles followed by (i) pure dilution by subsequent deposition of H$_2$O on ice or (ii) further uptake of all available ambient HNO$_3$ during ice crystal growth — bound the body of observed molar HNO$_3$/H$_2$O ratios in cirrus. An approximate expression for the efficiency of trapping derived on the basis of the field measurements is capable of describing the observed temperature trends of average molar ratios and ice phase fractions of HNO$_3$ and allows us to delineate important atmospheric implications.

2. Trapping Model

[6] The molar HNO$_3$/H$_2$O ratio per cirrus ice particle is given by

$$\mu = \frac{\omega N_w + \Delta N_w}{N_w + \Delta N_w},$$

where $N_w$ and $N_w$ are equilibrium numbers of HNO$_3$ and H$_2$O molecules in the aerosol particles when freezing commences, and $\Delta N_n$ and $\Delta N_w$ are the numbers of molecules taken up during subsequent ice crystal growth. We assume the homogeneously freezing aerosol to be composed of supercooled ternary (H$_2$O/HNO$_3$/H$_2$SO$_4$) solution (STS) particles. The parameter $\omega$ accounts for three mechanisms that may alter $N_w$: The aerosol composition may not be at equilibrium because of diffusion-limited uptake rates of HNO$_3$; only a fraction of the HNO$_3$ molecules may be locked in the ice particles after freezing (retention effect); and the aerosol particles may not be pure STS particles but could contain, e.g., ammonium or solid inclusions.

[7] Next we define the molar HNO$_3$/H$_2$O ratio per freezing particle:

$$\mu_n = \frac{N_n}{N_w} = \frac{m_n}{m_w} \frac{W_n}{W_w}.$$ 

$\omega$
The last expression follows from \( N_i = \rho V W / m_j \) \((j = n, w)\), with the molecular masses \( m_j \) and the volume \( V \); mass density \( \rho \); and equilibrium species mass fractions \( W_j \) of the aerosol particles. The steady-state molar \( \text{HNO}_3/\text{H}_2\text{O} \) ratio in ice particles is defined by

\[
\mu_\infty = \frac{\Delta N_{w}}{\Delta N_{w} + D_m p_n \epsilon / D_a e_{n} \beta_{w}}.
\]

The last expression in (3) follows from the ratio of diffusion vapor fluxes \( dN/dt \) as given by the trapping model [Kärcher and Basko, 2004, equation (11)]. Here, \( D_i \) are gas diffusion coefficients, \( p_n \) is the ambient \( \text{HNO}_3 \) partial pressure, \( e_{n} [\text{mb}] = 0.01 \exp(28.868 - 6132.9/T[K]) \) is the ice saturation vapor pressure [Marti and Mauersberger, 1993], \( s_{j} \) is the ice supersaturation the cirrus particles experience during their lifetime and which determines the average ice water content of a developed cloud, \( \beta < 1 \) are size-dependent flux corrections accounting for gas kinetic effects at high Knudsen numbers, and \( 0 \leq \epsilon \leq \beta_{w} \) is the trapping efficiency for \( \text{HNO}_3 \) defined in section 3.

With these definitions (1) takes the convenient form

\[
\mu = \mu_\infty + \frac{1}{\mu_\infty} - \frac{N}{1 + N'}, \quad N' = \frac{\Delta N_{w}}{N_{w}},
\]

with \( \Delta N_{w} = \rho(V - V_{i})m_{w} \) and the ice particle mass density \( \rho \); and volume \( V_{i} \geq V \). The ice crystal volume neglects the contributions of \( \text{HNO}_3 \) and \( \text{H}_2\text{SO}_4 \) as they are small compared to \( \text{H}_2\text{O} \). Because crystals sediment and likely fall through regions with different \( p_n \), we do not consider the conservation of total \( \text{HNO}_3 \) in (4). Right after freezing, \( N' \approx 0 \) and we obtain the initial value \( \mu = \mu_\infty \). We note two asymptotic cases for large ice particles, \( N' \gg 1 \): (i) \( \mu \rightarrow \mu_\infty \) for \( \epsilon > 0 \) and (ii) \( \mu \rightarrow \mu_\infty / N' \) for \( \epsilon = 0 \). Case (i) includes trapping of \( \text{HNO}_3 \) at maximum efficiency (\( \epsilon = \beta_{w} \)) and case (ii) assumes no \( \text{HNO}_3 \) uptake in the growing ice particles, i.e., simple dilution by uptake of \( \text{H}_2\text{O} \).

We note that trapping does not necessarily imply that buried \( \text{HNO}_3 \) is distributed over the entire ice particle volume. Instead, trapped molecules could stay within a small volume concentrated near the surface in case they are partially excluded from the crystal lattice during growth. Atmospheric \( \text{HNO}_3 \) concentrations are often too low to establish a monolayer coverage on the crystal surfaces. With the help of the ice water content, IWC, we introduce the partitioning factor \( \phi \) as the ratio of the concentration of \( \text{HNO}_3 \) in ice, \( \mu \text{IWC}/m_{w} \), to the total (gas plus ice phase) \( \text{HNO}_3 \) concentration. The total amount does not contain an aerosol contribution; although cloud-resolving simulations suggest that uptake of \( \text{HNO}_3 \) in STS particles can be substantial at high ice supersaturations prior to and shortly after homogeneous freezing, however, once enough ice crystals form and grow to average sizes, \( \text{HNO}_3 \) is redistributed between aerosol and ice particles and uptake in ice takes over [Kärcher, 2005]. Below we will connect IWC to \( s_{j} \) via IWC = \( m_{n} n_{j} s_{j} \), with \( n_{j} = e_{j}/(kT) \) (\( k \) is Boltzmann’s constant), resulting in

\[
\phi = \left(1 + \frac{p_{n}}{\mu e_{n} s_{j}}\right)^{-1} m_{w} \beta_{w} \left(1 + \frac{D_{m} \beta_{w}}{D_{a} e_{n}}\right)^{-1}.
\]

We fix the ambient pressure \( p \) to 200 mb and use \( \omega = 0.4 \). The model results are not sensitive to \( p \) and the assumed total aerosol \( \text{H}_2\text{SO}_4 \) content \( q_{w} = 0.1 \text{ ppbv} \) and freezing particle radius \( r = 0.5 \text{ µm} \) (\( V = 4\pi r^{3}/3 \)). At equilibrium, STS particles of this size freeze homogeneously at approximate ice supersaturations \( \sigma_{s} = 1.35 - T[K]/259 \) [Koop et al., 2000], which set the \( \text{H}_2\text{O} \) vapor mixing ratios \( q_{w} = (1 + s_{w})e/p \) used to determine \( W_{j} \) and \( p \) in the STS particles along with \( q_{w} \) and \( p_{n} \) [Kärcher and Solomon, 1999, section 2.2]. The values \( \mu_{a} \) strongly depend on increasing \( T \). To evaluate \( \beta_{w} \), we use the mass accommodation coefficients \( \alpha_{n} = 0.3 \) for \( \text{HNO}_3 \) and 0.5 for \( \text{H}_2\text{O} \) [Kärcher, 2005].

The volume of an ice crystal is \( V_{i} = 3\sqrt{3}D_{w}^{2}L/8 \), \( L = D_{w}A \) being the length of a hexagonal column, \( D \) its base circumscribed diameter, and \( A \) its aspect ratio. In the \( T \)-range 195–240 K, we suggest fits to a climatology of lidar and radar data [Wang and Sassen, 2002, Table 1] of average \( D \) and IWC for developed cirrus (\( N' > 0 \)) of the form \( D[\text{µm}] = 1.2T[K]-221.6 \), with \( A = 0.8 \) in this \( D \)-range, and IWC [\text{mg/m}^{3}] = \exp(T[K]/15-13.33). These fits compare well to the original data within their error bounds; they improve the data below \( \sim 210 \) K, because most optically thin clouds remain undetected by the remote sensing leading to a sample bias in the retrievals. The mean \( D \) and IWC values are broadly consistent with \textit{in-situ} measurements. The IWC defines \( s_{j} = \text{IWC}/(m_{w}n_{j}) \); \( s_{j} \) increases from 0.06 (240 K) to 0.86 (195 K), which is reasonable as supersaturation relaxation times also increase [e.g., Kärcher, 2005].

In what follows, we assume an average \( p_{n} \) together with the average \( T \)-dependencies of \( s_{j} \) and \( V_{i} \) to calculate the asymptotic cases of (4). We use an analytic expression for \( \epsilon(T) \) in order to constrain the full solution (4) with the field measurements. This approach cannot track the histories of individual crystals, but provides a basic understanding of the main trends seen in the field data.

### 3. Results and Discussion

Figure 1 (bottom) depicts \( \mu(T, p_{n}) \) from (4) (curves) along with \textit{T}-averaged \textit{in-situ} data (symbols) taken during the airborne measurements mentioned in section 1. We have used a constant value \( p_{n} = 2 \times 10^{-8} \text{ mb} \) close to the average over all campaigns to calculate the asymptotic \( \mu \)-values at maximum trapping, \( \mu = \mu_{\infty} \) with \( \epsilon = \beta_{w} \) (upper dashed curve), and those without trapping, \( \mu = \mu_{\infty}/N' \) (lower dashed curve). Taken together, the \( \text{HNO}_3/\text{H}_2\text{O} \) ratios in ice and the corresponding fractions of \( \text{HNO}_3 \) in ice displayed in the top panel show a clear upward trend with decreasing \( T \).

We should be cautious not to overinterpret the data in Figure 1. All instruments (except the one employed during CRYSTAL/FACE) detect total reactive nitrogen and assume a fraction of it (20–80%) to be \( \text{HNO}_3 \) in the gas phase. The anisokinetic airborne sampling of particles leads to pressure- and size-dependent corrections to the actual ice phase \( \text{HNO}_3 \) concentrations which are associated with some uncertainty. The accuracy of IWC measurements used to derive \( \mu \) depends in part on the presence of very large and very small ice crystals. Flight patterns are also relevant. Measurements taken in forming or dissolving clouds would lead to higher-than-average \( \mu \)-values. Above
Figure 1. Molar HNO₃/H₂O ratio μ and partitioning fraction φ of HNO₃ in cirrus ice as a function of temperature T. Except for POLSTAR and SUCCESS, the symbols represent 5 K-averages (mean values) of in-situ data taken during the airborne campaigns noted in the legend. (bottom) The solid curve is a fit to the μ-data using (4) and (6), and the dashed curves depict approximate lower (μᵣ/N with ω = 0.4) and upper (μᵣ, with ε = βᵣ) limits of trapping. (top) The φ-curves are computed from the corresponding μ-curves using (5). The variability of individual data points is significantly higher than measurement standard deviations which are typically comparable to the data point values. The curved arrow marks the average NAT existence temperature.

235 K, cirrus ice may form by homogeneous freezing of water droplets nucleated above water saturation. In supercooled water droplets, HNO₃ is highly soluble, possibly leading to a higher HNO₃ content in ice after droplet freezing as compared to freezing of STS particles. This potential bias toward high μ is not captured by our uptake model. 

That being said, we very successfully bound the average behavior of the large body of field data (dashed curves) using the typical assumptions entering (4). Individual data points (averaged over 10 s, not shown but discussed in the original references) exhibit a large range of variability of uptake by about a factor of 10 above and below the mean μ-values shown in Figure 1. This scatter in μ is mainly caused by variations in pᵣ, factors determining IWC, and meteorological conditions prevailing during the measurements. Similar arguments hold for the ice partitioning coefficient φ.

Reasons why we are not able to capture the full range of individual data variability in μ are easily explained. Individual data points can lie above the upper limit curve μᵣ/N (ω = 0.4) and below the average value pᵣ used here. Also, ice particles can trap more than pᵣ if they grow and fall long enough. Individual measurements can also lie below the lower limit curve μᵣ/N (ω/V). Fewer HNO₃ molecules may be retained upon freezing and HNO₃ uptake may be limited by gas diffusion, which would reduce ω. A non-STS aerosol composition may enhance uptake, e.g., due to the presence of ammonium; on the other hand, solid inclusions such as dust reduce the liquid particle volume V and may initiate freezing below sₓ, leading to less uptake. Another choice of V would also affect the lower limit. Fortunately, the overall trend of the mean μ-data is not strongly affected by the lower limit result (see below).

The HNO₃ fractions in ice are more difficult to compare with our model results than the molar ratios. While the pᵣ-dependence of μ should be controlled by the abundance of HNO₃ present during ice growth, φ inferred from observations are computed based on local pᵣ-values. As ice crystals sediment, they might move into regions with different pᵣ than were present during their main growth phase. Presumably, this leads to many cases where measured partitioning factors do not represent true cloud averages and a comparison with model results loses relevance.

To establish a parameterization, we note the trapping efficiency from Kärcher and Basko [2004], combining their equations (11) and (17), along with our empirical fit for μ(T) based on the field data:

\[ ε = \frac{β_r}{1 + (1 - β_r)T} \]

The parameter μ equals the ratio of the effective speed vₑ with which adsorbed HNO₃ molecules leave the ice particle surface (and are not buried in the bulk ice) relative to the diffusional ice particle growth rate vᵣ. The assumed functional form of μ is meaningful because vᵣ likely vₑ exhibit an Arrhenius-type T-dependence. An expression for vₑ follows from μ with \[ μ_r = m_D2β_rCh_s/\rho_r \] (with the radius r), an ice crystal volume-equivalent sphere and the capacitance factor C. A ventilation correction can be ignored in this growth law as it is close to unity in our case.

The desired mean molar ratio (bottom solid curve in Figure 1) is obtained by inserting (6) into (4) and fitting μ(T). From 195 to 240 K, \( r_1 \) increases from 0.3 to 2 μm/min and \( ε \) decreases from 0.56 to 0.016. This ε-range corresponds to uptake coefficients \( γ = \xi/\gamma = 0.083 - 2.6 \times 10^{-4} \) [Kärcher and Basko, 2004, equation (13)]. The mean ice partitioning factors (top panel) are obtained from (5). At first glance, one might expect φ to rise with T because of increasing average IWC. However, as T rises, μ decreases at a faster pace than IWC increases. The combined effect results in the negative correlation between φ and T (solid curve), consistent with the main trend seen in the field measurements.

Although the aerosol decay term μᵣ/(1 + N) is not always smaller than the trapping term μᵣ/N(1 + N) in the full solution (4), especially at low T where ice crystals remain relatively small, we have checked that μ ≈ μᵣ is a good approximation in the given range of T. Hence, for practical applications, it is sufficient to use (3) and (6) together with (5), eliminating the need to deal with assumed aerosol composition and retention factor that enter (4) via (2).

For pᵣ > 10⁻⁷ mb [Popp et al., 2004], surface saturation effects may limit the amount of HNO₃ buried upon adsorption (by introducing a negative correlation of μ with pᵣ) and hence weaken the linear pᵣ-dependence of μᵣ. However, such high pᵣ-values occur rarely and contribute only little to the entire data set. Nevertheless, the dependence of uptake on pᵣ should be studied in future extensions of the present work.
[21] In the trapping model, $\xi$ determines the parameter combination $\beta_{p,\lambda} = (1 - \beta_0)\xi$ [Kärcher and Basko, 2004, section 2.5] which separates two distinct trapping regimes. Our $\xi(T)$ from (6) leads to $\beta_{p,\lambda} < 1$ below 203 K, defining a regime where HNO$_3$ molecules stay relatively long at the surface and diffusional burial controls the uptake. Above 203 K, $\beta_{p,\lambda} > 1$; molecular processes that occur in the ice surface layer cause increasingly rapid escape of HNO$_3$ back into the gas phase (relative to the mean ice growth rate), rendering trapping less efficient.

[24] The fact that HNO$_3$ molecules stay relatively long at ice surfaces below 203 K is very interesting, as it paves the way for HNO$_3$-induced modifications of the H$_2$O deposition and ice growth kinetics below the nitric acid trihydrate (NAT) existence temperature $T_{\text{NAT}}$. For our average conditions $p_w = (1 + s)\rho_t$ and $p_n = \rho_m$, we find $T_{\text{NAT}} = 202.6$ K; local $T_{\text{NAT}}$ values may differ by $\pm(1 - 2)$ K. Long residence times of HNO$_3$ in this regime might favor a transition to stable NAT clusters at the ice surface which subsequently interfere with active growth sites for H$_2$O molecules.

[25] Among all data taken in developed clouds shown in Figure 1, only the CRYSTAL/FACE data points in the 202.5 K- and 197.5 K-bins could possibly be influenced by the presence of NAT. (Measurements below $T_{\text{NAT}} + 2$ K are not included in the SOLVE data set [Kondo et al., 2003].) While NAT-induced modifications of ice crystal growth at low $T$ are apparent in concomitant observations of ice supersaturation [Gao et al., 2004], such an effect is not visible in terms of $\mu$ and cannot be ascribed with certainty to the $\phi$-data point at 197.5 K.

4. Summary and Conclusions

[26] Our discussion revealed the complexity of factors controlling observed molar HNO$_3$/H$_2$O ratios in cirrus ice and HNO$_3$ ice partitioning coefficients, but also showed that the available field measurements of uptake of HNO$_3$ in cirrus clouds can be integrated with the physical theory of trapping in growing ice crystals. Fitting an analytical expression for the trapping efficiency to the field data allowed us to constrain the model without the need to know the details of the molecular processes that occur at the ice particle surfaces. A key finding is that as the temperature decreases, trapping increases in importance.

[27] We offered a number of reasons causing the scatter of data points around our model results, among which are the large variability of controlling factors (e.g., ice water content, HNO$_3$ abundance) and the comparison of local measurements with model results based on a nonlocal process. At this stage of intercomparison between theory and observations, we see no practical way of significantly improving the data analysis. Despite the difficulty of tracking air parcel and ice crystal trajectories, we suggest targeted cloud sampling in future airborne campaigns. Together with cloud-resolving models employing Lagrangian ice particle tracking, this will allow more detailed comparisons to be performed.

[28] An increased residence time of HNO$_3$ molecules at the ice crystal surfaces at temperatures below the NAT existence temperature, as suggested by our analysis, is a necessary prerequisite for efficient impurity pinning of surface growth steps, as proposed by Gao et al. [2004] to explain observations of enhanced relative humidity in cold subtropical anvil cirrus. This issue deserves more attention in the future.

[29] Our results are not directly comparable to the laboratory study of Ullerstam and Abbatt [2005], because these experiments used ice films possibly distinct from cirrus ice crystals, among other factors. It would be helpful to understand in which circumstances results of such important laboratory measurements can be applied to real atmospheric situations. An alternative is to carry out uptake experiments in cloud chambers with freely suspended ice particles such as reported by Diehl et al. [1995], but at temperatures below 235 K.

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