Supersaturations, microphysics and nitric acid partitioning in a cold cirrus cloud observed during CR-AVE 2006: an observation–modelling intercomparison study

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Abstract
Supersaturations, microphysics and nitric acid partitioning in a very cold subvisible tropical cirrus cloud observed on 2 February 2006, during the field campaign CR-AVE, are studied by comparing a simulated set of possible cloud development scenarios with the in situ observations. The scenario that best matches the observations is a cirrus cloud forming by heterogeneous freezing of a small number of ice nuclei with subsequent unimpeded mass accommodation of water on ice. Variation of the freezing process, the accommodation coefficient or the amount of available water leads to simulated clouds that differ microphysically from the observed cloud in important respects. In particular, the simulations suggest that heterogeneous ice nucleation or another freezing mechanism producing only a low number of ice crystals could be an important process for cold cirrus cloud formation, possibly explaining the frequent observations of high supersaturations inside the cirrus cloud in this temperature regime.

Keywords: cirrus clouds, supersaturations, nitric acid

1. Introduction
Cirrus clouds play an important, but uncertain role in the Earth’s climate system since their microphysical and radiative properties are still not well characterized (Solomon et al 2007). Ice cloud microphysics affects the water vapour condensation rate and fall speed of the ice crystals, (e.g. Khvorostyanov et al 2006), that influences the vertical redistribution of water and
nitric acid, (e.g. Popp et al 2006, Krämer et al 2008a), in the upper troposphere.

The microphysical properties of cirrus are determined to a large degree by the initial freezing mechanism: homogeneous nucleation of ice in ubiquitous supercooled liquid phase aerosol particles may produce a large number of small crystals when nucleating ice at a relative humidity with respect to ice (RH_{ice})\textsuperscript{9} between 140 and 180\% (freezing thresholds) in the temperature range 240–180 K (Koop et al 2000). Conversely, ice particles may arise heterogeneously by nucleation of very rare ice nuclei (IN), consisting of an insoluble core which may be coated with a liquid layer, freeze at lower critical supersaturations and produce lower ice crystal concentrations (Kärcher and Lohmann 2003). The number concentration, chemical composition, and freezing thresholds of the various types of IN in the upper troposphere are a subject of current research.

The water partitioning inside and outside of cirrus clouds is closely linked to their pathway of formation: for homogeneously formed cirrus, that are believed to be the most common ice clouds (Hoyle et al 2005), the maximum clear sky RH_{ice} is expected to correspond to the freezing threshold. Inside of a cirrus cloud formed via this pathway, the supersaturation should decrease to saturation on a timescale of minutes due to water vapour consumption of the large number of prevailing ice crystals.

However, upper tropospheric observations of RH_{ice} of up to 200\% inside and outside of cold cirrus clouds have been frequently reported in recent years, (e.g. by Gao et al 2004, Jensen et al 2005, Krämer et al 2008b, Peter et al 2008). Such cloud free supersaturations may have significant impact on climate, since higher critical supersaturation for ice cloud formation than hitherto assumed would lead to a decrease in high cloud cover in climate model simulations (Gettelman and Kinnison 2007). High supersaturations inside of clouds could be indicative of unknown microphysical and radiative properties with consequences for climate and the vertical redistribution of water and nitric acid. Peter et al (2006, and references therein) summarized this ‘supersaturation puzzle’ and raised the question whether it is caused by a lack of understanding of conventional ice cloud microphysics.

Here, we used the detailed kinetic box-model model for aerosol and ice dynamics (MAID), described in the accompanying paper of Bunz et al (2008). This model employs conventional ice microphysics, together with field observations of an exceptionally cold tropical cirrus (180–185 K) during the field experiment Costa Rica-Aura Validation Experiment (CR-AVE) in 2006 (Jensen et al 2007, Popp et al 2007), to examine the partitioning of H\textsubscript{2}O, the cloud microphysics and the HNO\textsubscript{3} uptake on ice in cold cirrus. Various sensitivity runs were performed with MAID to evaluate if one of the multiple sets of observationally based initial parameters could lead to the formation of the observed cirrus. Our aim is to help resolve the ‘supersaturation puzzle’ by examining whether the observed high supersaturations inside of cirrus can be explained by conventional microphysics.

2. A subvisible tropical cirrus cloud: observations and model approach

2.1. Cirrus observations

Comprehensive in situ observations were made from instruments mounted on the NASA WB-57F (table 1) during CR-AVE in 2006. The measurements used in this paper were total water H\textsubscript{2}O\textsubscript{total} (ALIAS), gas phase water H\textsubscript{2}O\textsubscript{gas} (HWV, ICOS and JLH), ice crystal number density N_{ice} and mean size R_{ice} (CAPS), aerosol number N_{aer} and size R_{aer} (N-MASS and FCAS-II), total and gas phase nitric acid HNO\textsubscript{3}\textsubscript{total}, HNO\textsubscript{3}\textsubscript{gas} (CIMS). The flights were launched from San Jose, Costa Rica from 14 January to 11 February. The flight of 2 February was chosen for the analysis discussed herein. Figure 1 (top panel) shows the flight track for this day.
A cold, subvisible cirrus cloud with low ice crystal number densities ($N_{\text{ice}} = 0.001–0.07 \text{ cm}^{-3}$) was detected by the CAPS over a one hour period on the southward leg of the flight. The mean ice crystal sizes $R_{\text{ice}}$ range between about 1 and 20 $\mu\text{m}$ in radius. Shattering of ice crystals on the inlet of the instrument can lead to an overestimate of the ice crystal concentration (Heymsfield et al 2007, Field et al 2006), however, this only occurs in clouds where the ice crystal population contains particles larger than approximately 50 $\mu\text{m}$. Nevertheless, the observed ice crystal number densities are regarded as an upper limit. High RH$_{\text{ice}}$ values of up to 250% were detected by the HWV and ICOS instruments inside of the very cold, subvisible tropical cirrus (derived optical depths for this cloud were less than 0.001). The HWV and Harvard ICOS data (not shown here) agree in the TTL to 0.5 ppmv or better throughout the mission. However, the JLH instrument reported much lower values of around 100%. An uptake of 20–80% of the total available HNO$_3$ in the ice crystals was derived from the CIMS measurements.

### 2.2. Temperature histories along cirrus trajectories

Isentropic backward-trajectories based on ECMWF wind fields (figure 1, top panel) were calculated starting along the flight leg inside of the cirrus every 3 min. The synoptic scale trajectory temperature is adjusted to match the temperature measured along the flight track. The offset between trajectory and measured temperature, typically around $-4 \text{ K}$, is applied along the entire trajectory. In addition, mesoscale temperature fluctuations with a peak to peak amplitude of 1.2 K were superimposed on the trajectory temperature histories. These fluctuations are calculated using functional relations provided by Gay (2006), who, based on hundreds of temperature profile measurements using a microwave temperature profiler (MTP), evaluated the magnitude of the mesoscale component with respect to the atmospheric temperature fluctuations and their dependence on altitude, latitude and season.

Figure 1 (bottom panel) shows the temperature history and the first appearance of ice crystals for the first (HET) and second (HOM) simulated cirrus scenarios discussed in section 3. The cold cirrus evolved at temperatures between 184 and 188 K approximately 1.5 days before it was probed by the WB-57. During cloud evolution, the temperature decreased to about 180 K and then increased again shortly before the WB-57 sampling, probably close to the end of the lifetime of the cloud near the evaporation threshold. In the time period 18:30–18:35 UTC the aircraft flew at a slightly higher pressure altitude. The temperature is higher along the entire trajectory and correspondingly no cloud is detected on-board the WB-57. This feature corresponds to those trajectories deviating from the general route of the trajectory bundle shown in the top panel of figure 1.

### 2.3. Model approach

The detailed microphysical and kinetic simulations were performed with MAID, that was developed especially to balance exactly all trace gas components between the gas phase, aerosol particles and ice. The simulations were run along all twenty trajectories ending at the flight leg inside of the cirrus. A short summary of the modules implemented in MAID is given in section 3 and in the caption of figure 3. For a detailed description of MAID see Bunz et al (2008). Different possible scenarios of cirrus formation and evolution are simulated along all trajectories. The scenarios, all initialized based on the in situ observations are described in section 3 and figure 3.

The model results at the end of the trajectories are compared with the in situ observations to identify the scenario best matching the measurements. In section 3 we discuss in detail the temporal evolution of different cirrus scenarios along a representative selected trajectory. In section 4 the model results at the end of all trajectories are compared with the in situ observations and the scenario showing the best agreement with the measurements is discussed.

### 3. Scenarios of cirrus evolution

Four out of numerous scenarios of formation and development of the very cold subvisible tropical cirrus, simulated with
MAID along one selected trajectory (dashed line in figure 1, bottom panel) will be discussed here. The temperature along the trajectory ranges between 181 and 192 K and is shown in figure 2. Results of the simulations are presented in figures 3 and 4 and discussed below.

The scenario HET. In this scenario the primary freezing mechanism is heterogeneous freezing. A second, homogeneous ice nucleation event may occur if the homogeneous freezing threshold is exceeded after the initial heterogeneous ice formation.

The number density of the aerosol particles is \( N_{\text{pisc}} = 158 \ \text{cm}^{-3} \) (derived from the N-MASS, FCAS-II measurements), the initial water amount is 2.3 ppmv H\(_2\)O (derived from JLH measurements) and water fully accommodates on ice (accommodation coefficient of water on ice \( \alpha = 1.0 \)). The properties of the heterogeneous ice nuclei (IN) are unknown here, thus we assume the following: the freezing thresholds lie about 15\% below the homogeneous freezing thresholds provided by Koop et al (2000) and are derived from freezing experiments of soot particles coated with sulfuric acid performed at the large AIDA chamber (Möhler et al 2005b). The IN number density is set to 0.1 \text{cm}^{-3} (Blake and Kato 1995). To check the reliability of these assumptions, we performed model simulations by varying the IN freezing thresholds and number density. A discussion of these sensitivity simulations will be given at the end of this section.

In accordance with the IN number, only a few ice crystals nucleate when the heterogeneous freezing threshold is reached (vertical red line in panels (a) and (b) of figure 3). The in situ observations of \( N_{\text{ice}} \) and \( R_{\text{ice}} \) (green diamonds) at the end of the model simulation agree reasonably well with the model results. Sedimentation is not considered in the simulations. We calculated with a terminal velocity of the 10 \( \mu \text{m} \) ice crystals of 1.7 \text{ cm s}^{-1} and an average synoptical uplift of the air mass of 1.4 \text{ cm s}^{-1} (derived from the trajectories shown in figure 1), that the ice crystals fall approximately only 325 m during the 30 h time period. Thus, sedimentation is small in this case.

\( RH_{\text{ice}} \) (panel (e)) further increases after the first ice crystals appear (dashed vertical line) because the available ice surface area is too small to efficiently deplete the gas phase water vapour. After about 3 h, \( RH_{\text{ice}} \) starts to decrease slowly down to around ice saturation while varying in response to the temperature fluctuations. In very good agreement, the \( RH_{\text{ice}} \) observed by the JLH instrument is slightly below saturation (the simulated \( RH_{\text{ice}} \) is—here and in the following scenarios—compared with the observations of the instrument used for the initialization of MAID).

The scenario is reiterated multiple times, driven with slightly differing periods of temperature fluctuations to show the probability of pure heterogeneous freezing occurring without a second homogeneous freezing event. In about 90\% of the simulations no additional homogeneous freezing event occurs. Then, the peak to peak amplitude of the temperature fluctuations is increased until homogeneous freezing starts. We found that an amplitude of 2.4 K is needed to initiate homogeneous ice nucleation. Analysis of MTP temperature measurements yields actual temperature fluctuations of only 1–2 K. Thus, it seems very likely that homogeneous freezing did not occur in the observed ice cloud.

The scenario HOM is identical to HET except that the initial freezing mechanism is purely homogeneous freezing (blue lines in figure 3). Due to the higher homogeneous freezing thresholds, the cirrus forms later with the nucleation of a larger concentration of ice crystals that deplete the gas phase water more efficiently than in the HET scenario (red lines). Thus, \( RH_{\text{ice}} \) (panel (f) in figure 3) relaxes to near ice saturation shortly after ice formation. The agreement between the modelled and observed \( RH_{\text{ice}} \) is as good as for the heterogeneous scenario, but the microphysical measurements do not match the simulations, \( N_{\text{ice}} \) observed by CAPS are much smaller than the simulated. If ice crystal shattering would have enhanced the measured \( N_{\text{ice}} \) (see section 2), the true ice particle number would have been smaller than the observed and thus the overestimation of the simulated ice crystal number even larger.

The scenario HET + more water varies from the HET scenario by the amount of water, which is now 4.3 ppmv H\(_2\)O according to the water measurements of HWV (burgundy lines in figure 3). Due to the higher homogeneous freezing thresholds, the cirrus forms later with less water (red). Since a large amount of water is still available in the gas phase after this freezing event, a second, homogeneous ice nucleation process occurs and produces a cloud with similar properties as in the HOM (blue) scenario. \( RH_{\text{ice}} \) keeps rising as long as the ice crystal number is as low as in the heterogeneous case but, after the second freezing event has occurred and thus more ice crystals are present, immediately turns to the behaviour of the homogeneous scenario. Here, the \( RH_{\text{ice}} \) observation of around 240\% is far above the simulated value (panel (g) in figure 3).

The scenario HET + lower \( H_{\text{2O}} \) accommodation again corresponds to the HET case but the accommodation coefficient of water on ice \( \alpha \) is set to 0.005 according to recent laboratory studies (Magee et al 2006), see orange lines in figure 3. Heterogeneous ice nucleation occurs at the same time as in the HET (red) scenario; however, because of the reduced water uptake of the ice crystals and thus larger amount of gas phase water, this nucleation is quickly followed by
Figure 3. Different scenarios of the evolution of microphysical parameters $N_{\text{ice}}, R_{\text{ice}}$ (panels (a), (b)), nitric acid partitioning $\text{HNO}_3_{\text{ice}}$, $\text{HNO}_3_{\text{ptcl}}$ (panels (c), (d)) and supersaturations $\text{RH}_{\text{ice}}$ (panels (e)-(h)) modelled with MAID along the selected trajectory shown in figure 1. 

**Green diamonds**: observations of $N_{\text{ice}}, R_{\text{ice}}$: CAPS, $\text{HNO}_3_{\text{ice}}$: CIMS, $\text{RH}_{\text{ice}}$: JLH, HWV (see table 1); **dashed vertical lines**: cirrus cloud formation.

**HET** (red lines): IN number density $= 10^{-2} \text{ cm}^{-3}$ (Blake and Kato 1995), $\text{H}_2\text{O} = 2.3 \text{ ppmv}$ (ALIAS, JLH), accommodation of water on ice $\alpha = 1.0$, aerosol particle lognormal number size distribution parameters $N_{\text{ptcl}} = 158 \text{ cm}^{-3}$, $R_{\text{ptcl}} = 0.012 \mu\text{m}$, $\sigma_{\text{ptcl}}$: 1.2, amplitude of mesoscale temperature fluctuations $= 1.2 \text{ K}$. **HOM** (blue lines): same as red, but solely homogeneous freezing. **HET + more water** (burgundy lines): same as red, but 4.3 ppmv $\text{H}_2\text{O}$ (ALIAS, HWV). **HET + lower $\text{H}_2\text{O}$ accom.** (orange lines): same as red, but $\alpha = 0.005$ (Magee et al 2006).

MAID is operated with heterogeneous freezing after Kärcher and Lohmann (2003) with freezing thresholds of soot particles coated with sulfuric acid after Möhler et al (2005b), homogeneous freezing after Koop et al (2000), nitric acid uptake on ice after Kärcher and Voigt (2006), for more information on MAID see Bunz et al (2008).
Figure 4. Scenario HET: sensitivity of RH\textsubscript{ice}, \(N\textsubscript{ice}\) and HNO\textsubscript{3}\textsubscript{ice} to IN freezing thresholds (left) and number (right). Red lines correspond to HET in figure 3, dashed vertical lines indicate cirrus cloud formation, green diamonds show observations of \(N\textsubscript{ice}\) (CAPS) and HNO\textsubscript{3}\textsubscript{ice} (CIMS; instruments see table 1).

Nitric acid partitioning. In the course of a cirrus cloud evolution, nitric acid is partitioned between the gas phase, the interstitial aerosol particles and the ice crystals. In the MAID simulations, the amount of HNO\textsubscript{3} in the liquid interstitial particles (figure 3, panel (c)) ranges between 0.01 and 20\% of the total available HNO\textsubscript{3} and is determined by RH\textsubscript{ice}, i.e. the higher the amount of water in the gas phase, the larger the liquid interstitial particles, thus containing more HNO\textsubscript{3} (Krämer \textit{et al 2006}). Consequently, HNO\textsubscript{3} remains on the interstitial particles in the scenario HET (red lines) maintaining higher RH\textsubscript{ice} and escaping rapidly—due to shrinking of the interstitial particles—in those scenarios, where RH\textsubscript{ice} decreases rapidly after homogeneous ice formation (blue: HOM, burgundy: HET + more water). In the scenario HET + lower H\textsubscript{2}O accommodation (orange lines), there are very few interstitial particles, because almost all aerosol particles form ice crystals. Thus, the fraction of the HNO\textsubscript{3} residing in the interstitial particles is negligible.

The amount of nitric acid trapped by the ice crystals is simulated according to Kärcher and Voigt (2006). It widely ranges from 15 to 100\% for the different scenarios (figure 3, panel (d)). We found that this large variability is determined by the integral ice particle size \(\overline{N\textsubscript{ice}}R\textsubscript{ice}\), which is lowest in the scenario HET (red). This case shows the lowest uptake of HNO\textsubscript{3} on ice and, as for RH\textsubscript{ice} and the microphysical properties, the best agreement with the \textit{in situ} observations (green star: CIMS observation). The larger \(\overline{N\textsubscript{ice}}R\textsubscript{ice}\) in the scenarios HOM (blue) and HET + more water (burgundy) leads to a much higher HNO\textsubscript{3} uptake on ice. In the scenario HET + lower H\textsubscript{2}O accommodation (orange), HNO\textsubscript{3,ice} varies a lot, driven by the fluctuations in RH\textsubscript{ice}. A similar, temperature driven variation in RH\textsubscript{ice} is seen in the scenario HET (red), but without reflecting this in HNO\textsubscript{3,ice}. The fluctuations of HNO\textsubscript{3,ice} in the HET + lower H\textsubscript{2}O accommodation (orange) scenario is because the same amount of water condenses on much smaller ice crystals. The consecutive phases of uptake/release of
HNO$_3$ ice accompanying the deposition/sublimation of water on ice appear much more pronounced in the HET + $\text{H}_2\text{O}$ accommodation (orange) than in the HET scenario (red). The scenario HET: sensitivity to IN freezing thresholds and numbers. In summary, the HET scenario, incorporating pure heterogeneous nucleation, JLH water vapour and full accommodation of water on ice, matches the observations best. HET was initialized with assumptions on the IN freezing thresholds and number (IN freezing thresholds: slightly below homogeneous freezing line, from AIDA chamber coated soot experiments; IN number: 0.1 cm$^{-3}$). Here, we finally investigate the influence of changing IN properties on the ice cloud microphysics and water vapour as well as HNO$_3$ partitioning.

In figure 4 the red line is the scenario HET as shown in figure 3. The blue scenario (left panel) is the same model run, but the freezing thresholds are reduced to slightly above 100%, simulating very efficient mineral dust IN. As for the coated soot particles, the freezing thresholds are derived from measurements at the AIDA chamber (Möhler et al. 2006). Less ice crystals appear in the beginning of the mineral dust scenario (middle left panel). Since the water depletion is now less efficient than in the HET scenario, a subsequent homogeneous ice nucleation event occurs, forming an ice cloud with properties similar to the HOM scenario (figure 3, panels (a) and (f)).

In the right panel of figure 4, the sensitivity of the HET scenario to the IN number is shown. To this end, two additional scenarios are performed, one with reduced (0.001 cm$^{-3}$, blue) and one with enhanced (0.1 cm$^{-3}$, violet) IN numbers. In the case of fewer IN, an ice cloud very similar to the mineral dust case appears (blue line in middle right panel), where the initial low ice crystal number causes a subsequent homogeneous ice nucleation event to occur generating an ice cloud with properties very similar to the cloud in the HOM case. In the case of more initial IN (violet line), the water consumption of the appearing ice crystals is effective enough to prevent a subsequent homogeneous freezing event. Nevertheless, the number of ice crystals is high enough to give the ice cloud the characteristics of a homogeneously formed cloud, i.e. RH$_{\text{ice}}$ is effectively reduced to saturation in a short time period (figure 4, upper right panel). The $N_{\text{ice}}$ observation (green triangle in figure 4, middle right panel) lies between the HET case and the case of more initial IN. But, the measured HNO$_3$ uptake in ice (figure 4, bottom right panel) is much better reproduced by the HET case, where fewer ice crystals consume the available HNO$_3$.

From the additional sensitivity studies with varying IN properties it seems that the assumptions for IN number and freezing thresholds made here represent the actual IN properties fairly well, though we cannot conclude from the AIDA freezing thresholds of coated soot to the chemical composition of the IN present at the point of WB-57 observations. Altogether, it is interesting to see that lowering or enhancing the IN freezing thresholds or numbers always turns the ice cloud to the characteristics of a homogeneously formed cloud which was not observed here.

4. Overall comparison and discussion

The overall comparison of the MAID simulations with the in situ observations at the end of all twenty trajectories is presented in a scatterplot (figure 5). The results of the HET and the HOM scenarios described above are plotted in figure 5, where each star represents the endpoint of one trajectory.

The HET scenario (red stars in panels (a)–(d) of figure 5, red lines in figure 3) is found to provide the best description of the in situ cirrus observations during the CR-AVE flight on 2 February 2006, not only for the selected trajectory shown in figure 3 but for all simulations along the twenty trajectories shown in figure 1 (top panel). This is illustrated in figure 5, where the red stars are found to group closest around the 1:1 line (dashed) for all parameters. The microphysics, $N_{\text{ice}}$ and size $R_{\text{ice}}$, of the observed cold (180–190 K) ice cloud are the key parameters for this conclusion: with MAID only purely heterogeneous freezing could produce an ice cloud with such a low number of ice crystals of the observed size (red stars in figure 5, panels (a) and (b)). Variation of the freezing process, the accommodation coefficient or the amount of available water lead to a microphysically different cloud (blue stars in figure 5, panels (a) and (b)) with more, but smaller ice crystals.

This finding is comparable to the recent study of Khvorostyanov et al. (2006), simulating a thin tropopause cirrus observed during the field experiment CRYSTAL-FACE (Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiment) with two models, using different approaches than MAID to simulate the formation of cirrus clouds. Khvorostyanov et al. (2006) stated that the simulated cloud microphysical properties are similar to observations when operating the models with heterogeneous immersion freezing as ice nucleating mechanism. But, in contrast to the study presented here, they also state that simulations using homogeneous nucleation theory are also able to produce comparable microphysical properties. Jensen et al. (2007) analysed another CR-AVE flight (1 February 2006). They used simple growth-sedimentation calculations as well as full cloud simulations to investigate the formation of large (100 μm length) crystals. In agreement with the findings here, Jensen et al. (2007) concluded that the growth of the large crystals would not have been possible if homogeneous freezing of aqueous aerosols and subsequent ice crystal growth had rapidly depleted vapour in excess of saturation.

The relative humidity RH$_{\text{ice}}$ (figure 5, panel (c)) mostly fluctuates around ice saturation at the end of all trajectories and scenarios in accordance with the observations of the JLH instrument (red and blue stars). Analysis of the four cirrus scenarios considered here (section 3) reveals that this is because the cloud existed for 1.5 days and none of the scenarios could maintain a very high supersaturation over such a long period. Very high supersaturations are only found in the simulations of the younger ice cloud formed heterogeneously. The burgundy stars in figure 5 (panel (c)) represent the HET + more water scenario, which is initialized and compared with the water observations of the HWV instrument. With the conventional microphysics implemented in MAID, these observations could not be reproduced.
Figure 5. Overall comparison of MAID results for the HET and HOM scenarios (figure 3) with in situ observations (OBS.) at the end of all 20 trajectories. Panels (a) and (b): microphysics $N_{ice}$, $R_{ice}$ (blue stars: HOM versus CAPS, red stars: HET versus CAPS), panel (c): supersaturations RH$_{ice}$ (blue stars: HOM versus JLH, red stars: HET versus JLH, burgundy stars: HET versus HWV), panel (d): nitric acid on ice HNO$_3$,$_{ice}$ (blue stars: HOM versus CIMS, red stars: HET versus CIMS); 1:1 is the dashed line.

During the CR-AVE flight analysed by Jensen et al. (2007), also very high supersaturations of 230–240% relative humidity were reported by both HWV and ICOS. Jensen et al. (2007) investigated the growth of the ice crystals for different aspect ratios to examine the likelihood of the observed supersaturations. However, no clear conclusion could be drawn from this analysis, both higher/lower water amounts could be reproduced when using lower/higher ice crystal aspect ratios.

5. Conclusions and outlook

We have addressed the question raised in the ‘supersaturation puzzle’ (Peter et al. 2006), i.e. if observations of high supersaturations inside of cirrus can be explained by conventional microphysics, by comparing observations in a cold ice cloud with a set of sensitivity simulations carried out with the box-model MAID employing conventional ice microphysics.

Our simulations indicate that the observed cloud already lived for 1.5 days and that the relative humidity is reduced to around saturation, which is in accordance with the observations of the JLH instrument. The high supersaturations reported by both the HWV and ICOS instruments could not be reproduced with MAID. What is clear from these simulations is that the significant water vapour measurement differences that still exist must be resolved to provide the necessary constraints to cloud microphysical models for climate forecast models. But, our simulations also suggest that significant supersaturation of up to $\sim$150% existed inside the cold cirrus in the early stage of the clouds lifetime. These high supersaturations were caused by the low number of ice crystals formed by heterogeneous ice nucleation, here the most probable freezing mechanism.

But how likely is heterogeneous ice formation as a major freezing process in the uppermost UT? And what kind of heterogeneously freezing aerosol particles may exist persistently in that region? One possibility are soot particles, maybe coated with sulfuric acid that were measured by Schwarz et al. (2006) in the uppermost UT at mid-latitudes or aerosol particles with a fraction of organic material as observed by Murphy et al. (2007) up to 17 km between 0° and 40° North. For the CR-AVE flight analysed here, we showed that heterogeneous freezing of coated soot particles may explain the observed cirrus microphysics and subsequent in-cloud supersaturation. Laboratory experiments at the AIDA chamber (Möhler et al. 2005b, 2005a) confirm that both of these aerosol types at least decrease the supersaturation thresholds for ice formation.

However, supercooled liquid aerosol particles, which can freeze homogeneously are believed to represent a major part of the UT aerosol population. Furthermore, it seems likely
that temperature fluctuations sufficiently large to reach the homogeneous freezing thresholds occur frequently under UT conditions. Thus, it seems that the ‘supersaturation puzzle’ turns into a ‘freezing puzzle’ with new questions (i) what kind of heterogeneously freezing aerosols are present in the uppermost UT or (ii) do mechanisms yet unknown exist that can suppress or slow down the homogeneous formation of ice crystals at temperatures below 200 K?

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