Condensed-phase nitric acid in a tropical subvisible cirrus cloud

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In situ observations in a tropical subvisible cirrus cloud during the Costa Rica Aura Validation Experiment on 2 February 2006 show the presence of condensed-phase nitric acid. The cloud was observed near the tropopause at altitudes of 16.3–17.7 km in an extremely cold (183–191 K) and dry (<5 ppm H2O) air mass. Relative humidities with respect to ice ranged from 150–250% throughout most of the cloud. Optical particle measurements indicate the presence of ice crystals as large as 90 μm in diameter. Condensed HNO3/H2O molar ratios observed in the cloud particles were 1–2 orders of magnitude greater than ratios observed previously in cirrus clouds at similar HNO3 partial pressures. Nitric acid trihydrate saturation ratios were 10 or greater during much of the cloud encounter, indicating that HNO3 may be present in the cloud particles as a stable condensate and not simply physically adsorbed on or trapped in the particles. Citation: Popp, P. J., et al. (2007), Condensed-phase nitric acid in a tropical subvisible cirrus cloud, Geophys. Res. Lett., 34, L24812, doi:10.1029/2007GL031832.

1. Introduction

Subvisible cirrus clouds that form near the tropical tropopause represent an uncertain though potentially significant component in Earth’s radiation budget [McFarquhar et al., 2000]. Subvisible cirrus also represent the last opportunity for the removal of water vapor from air entering the stratosphere in the tropics [Jensen et al., 1996]. Owing to the high altitudes and remote locations of subvisible cirrus in the tropics, however, comprehensive in situ observations of these clouds have been limited [Peter et al., 2003]. While cirrus ice particles are known to be effective scavengers of nitric acid (HNO3) under a range of conditions [Voigt et al., 2007], previous measurements in subvisible cirrus over the western Indian Ocean revealed no evidence of HNO3 condensed with the ice particles [Luo et al., 2003].

We report here observations of condensed-phase HNO3 in a tropical subvisible cirrus cloud at high relative humidities with respect to ice (150–250% throughout most of the cloud). These measurements were conducted onboard the NASA WB-57F high-altitude research aircraft as part of the Costa Rica Aura Validation Experiment (CR-AVE). The data are used here to assess the uptake of HNO3 in subvisible cirrus particles and explore the role of nitric acid trihydrate (NAT) formation in the uptake process.

2. Observations

Condensed-phase HNO3 was detected in situ with the NOAA chemical ionization mass spectrometer (CIMS) located in the third pallet position of the WB-57F aircraft. The NOAA CIMS methodology for sampling condensed-phase HNO3 in cirrus clouds has been described in detail elsewhere [Popp et al., 2004]. Briefly, the instrument measures HNO3 with two independent channels of detection connected to separate forward- and downward-facing inlets. The forward-facing inlet samples both gas- and particle-phase HNO3. Particles larger than ∼1 μm in diameter are inertially stripped from the airstream sampled by the downward-facing inlet, effectively yielding a measure of gas-phase HNO3. The difference in the signal between the two channels and knowledge of the particle sampling efficiency of the forward-facing inlet allows a determination of the amount of HNO3 in the condensed phase.

Condensed-phase HNO3 was observed coincident with a subvisible cirrus cloud on the southbound leg of a WB-57F science flight over the eastern Pacific Ocean on 2 February 2006. The cloud was observed over a geographic extent of approximately 800 km, at latitudes between 7°N and the equator. This flight originated and terminated at Juan Santamaría International Airport in San Jose, Costa Rica (10°N, 84°W). The cloud described here was observed visually by the WB-57F flight crew, but only when viewed horizontally with a long optical path. A real-time display of ice particle number density in the WB-57F cockpit, measured with an optical particle counter, was used to determine a range of flight altitudes to perform porpoising maneuvers through the cloud (Figure 1d). Time series data of HNO3 mixing ratios observed from the forward and downward CIMS channels are shown in Figure 1a. The presence of condensed-phase HNO3 is indicated by a significant difference in the HNO3 mixing ratio observed in the forward and downward CIMS channels (pink highlighted region in Figure 1). The presence of cirrus ice particles is indicated...
The subvisible cirrus cloud was observed at flight altitudes of approximately 16.3–17.7 km. Microwave temperature profiles indicate that the cirrus layer was observed at or slightly higher than the lapse-rate tropopause (Figure 1d). The cold-point tropopause during the cloud encounter occurred approximately 500 m higher than the lapse-rate tropopause, but still within the cloud. Ambient temperatures in this region ranged from 183–191 K (Figure 1a). These low temperatures and ambient water vapor values of 2.3–5.2 ppm correspond to relative humidities with respect to ice of 150–250% throughout most of the cloud (Figure 1e). Measurements in subvisible cirrus during at least one other CR-AVE flight revealed similarly high relative humidities [Jensen et al., 2007]. Gas-phase HNO$_3$ mixing ratios observed near the tropical tropopause were less than 100 ppt. Despite these low values, the low ambient temperatures caused nitric acid trihydrate (NAT) saturation ratios to be 10 or greater during much of the cloud encounter [Hanson and Mauersberger, 1988].

Condensed-phase HNO$_3$ values, calculated by accounting for the particle sampling efficiency of the CIMS instrument [Popp et al., 2004], exceeded 30 ppt during the cloud encounter (Figures 1b and 1c). Ice water content shows a strong temporal correlation with condensed-phase HNO$_3$ in the cloud (Figure 1c), consistent with previous measurements in convectively formed subtropical cirrus clouds [Popp et al., 2004]. Measurements in the convective cirrus also showed a strong correlation between condensed-phase HNO$_3$ and ice particle SAD. Ice particle SADs are derived by integrating particle size distribution and number density measurements from the Cloud, Aerosol, and Precipitation Spectrometer (CAPS) assuming quasi-spherical particles in this size range [Baumgardner et al., 2001]. Ice particle SADs in the cloud were typically less than 50 $\text{m}^2\text{cm}^{-3}$ (Figure 1d), which is in strong contrast to SADs of up to $6 \cdot 10^5 \text{m}^2\text{cm}^{-3}$ observed in the convectively-formed cirrus [Popp et al., 2004]. We note that the SAD values observed at the beginning of the cloud encounter...
(<66600 UT, Figure 1d) are lower than expected, given the enhanced values of IWC and condensed-phase HNO$_3$ observed during the same time period (Figure 1c).

Ice particle size distributions reported by the CAPS instrument show the presence of large ice crystals (30–90 μm diameter) in the cloud, as well as a smaller particle mode at 10–20 μm (Figure 2). The size distributions also indicate that the ice particle surface area and volume density, and therefore ice water content, are dominated by the large-particle mode. An ice particle growth model [Jensen et al., 2007] indicates that growth times for the largest particles shown in Figure 2 (90 μm) are ~3–4 hours under conditions observed in the subvisible cirrus cloud. Smaller particles (30 μm) have growth times less than one hour.

3. Discussion

We assume that the sampled particles are composed primarily of ice, with a small molar fraction of HNO$_3$ contained in the bulk of the particle [Kärcher and Voigt, 2006]. The data reported here suggest the observed condensed-phase HNO$_3$ does not exist as a separate population of NAT particles or STS aerosol. First, condensed-phase HNO$_3$ exhibits a strong temporal correlation with ice water content in the cloud and was only observed in the presence of cirrus particles, as indicated by enhancements in both ice water content and ice particle surface area density (Figure 1). Second, a population of STS aerosols cannot grow to sizes large enough to produce the differential response shown by the CIMS instrument in Figure 1a. Particles smaller than approximately 1 μm in diameter are neither enhanced in the forward-facing CIMS inlet nor inertially stripped from the airstream sampled by the downward-facing inlet. Finally, maximum values of ice water content observed in the cloud (~2.5 ppm, Figure 1c) can be accounted for by the large (30–90 μm) ice particle mode observed by the CAPS instrument (Figure 2).

Results from the Aerosol Inorganics Model (AIM) [Carslaw et al., 1995] indicate that, under ambient conditions typical for the observed cloud (with ice formation inhibited in the model run to simulate ice supersaturation), gas-phase HNO$_3$ will be depleted at temperatures less than approximately 191 K should NAT form (Figure 3). The model also indicates that the background sulfate aerosol can take up a substantial fraction of the available HNO$_3$ at temperatures less than approximately 188 K, resulting in the production of a supercooled ternary solution (STS) of water, sulfuric acid and HNO$_3$. At temperatures less than 186 K, essentially all of the ambient HNO$_3$ can be partitioned into the STS phase. We note, however, that the AIM describes HNO$_3$ partitioning under equilibrium conditions and does not account for the uptake of HNO$_3$ by cirrus ice crystals. The observations reported here indicate that HNO$_3$ partitions into the ice phase when present, sometimes completely, despite the fact that NAT or STS aerosols are also thermodynamically stable. These results are consistent with numerical simulations of a polar cirrus cloud that indicate HNO$_3$ will be driven from the liquid aerosol and incorporated in cirrus particles as soon as ice forms [Kärcher, 2005].

Microphysical modeling studies together with in situ observations provide evidence that HNO$_3$ can be trapped and subsequently buried in growing ice particles under
conditions typical of the tropical tropopause [Kärcher and Voigt, 2006; Voigt et al., 2006; Voigt et al., 2007]. The trapping process is fundamentally controlled by the HNO$_3$ residence time on the ice surface and the particle growth rate [Kärcher and Basko, 2004]. As a result, the efficiency of the trapping process increases with decreasing temperature and increasing relative humidity. The HNO$_3$ content in cirrus particles can be expressed as the condensed HNO$_3$/H$_2$O molar ratio [Voigt et al., 2006]. The observed HNO$_3$/H$_2$O ratios in the subvisible cirrus reported here are 1–2 orders of magnitude greater than ratios previously observed in cirrus clouds at similar HNO$_3$ partial pressures (Figure 4). It’s reasonable to speculate that these high ratios result from the low temperatures (183–191 K) and the associated high RH values (150–250%) in the cloud. Under such conditions, trapping theory predicts that the maximum condensed HNO$_3$/H$_2$O ratio in a cirrus particle is approximately one quarter of the ambient gas-phase HNO$_3$/H$_2$O ratio [Kärcher and Voigt, 2006]. This limitation of less than unity is due to the effective gas phase diffusion coefficients of HNO$_3$ and H$_2$O. Since the mean condensed HNO$_3$/H$_2$O ratio reported here ($1.4 \times 10^{-5}$, Figure 4) is $\approx 0.25$ times the ambient HNO$_3$/H$_2$O ratio at higher altitudes ($\sim 18$ km) where these particles nucleate (Figure 1, 71100 UT), these results indicate very efficient trapping of HNO$_3$ in the observed cloud. These observations are consistent with laboratory measurements that reveal enhanced and long-term HNO$_3$ uptake on growing ice films at RH values greater than 100% (compared to static ice films), indicative of the trapping of HNO$_3$ in the film [Ullerstam and Abbatt, 2005]. It is also worth noting that the HNO$_3$ dissolved in ice at equilibrium, extrapolated from laboratory measurements at higher temperatures and HNO$_3$ partial pressures [Thibert and Domine, 1998], is approximately an order of magnitude too low to produce the condensed HNO$_3$/H$_2$O molar ratios in the cloud reported here (Figure 4). We conclude, therefore, that the condensed HNO$_3$ we observe is truly trapped in the particle and not simply dissolved in the ice.

[12] Water vapor was measured with multiple instruments onboard the WB-57F during CR-AVE. Recently, the accuracy of water vapor measurements at low mixing ratios has been under careful scrutiny because significant differences have been reported between various instruments during previous measurement campaigns. The water vapor data shown in Figure 1 are provided by the Harvard Water Vapor (HWV) instrument using a Lyman-α fluorescence detection scheme [Weinstock et al., 1994]. The reported accuracy of the HWV instrument was ±15% at water vapor mixing ratios less than 10 ppm during the flight on 2 February 2006. While there was no significant difference between the HWV and Integrated Cavity Output Spectroscopy (ICOS) instruments [Sayres, 2006] during this flight (data not shown), the ICOS measurements were $\sim 0.5$ ppm lower than the HWV measurements on at least one other CR-AVE flight [Jensen et al., 2007]. The reported accuracy for the ICOS instrument is ±5%, with a potential bias of 0.25 ppm. Thus, a difference of 0.5 ppm does not represent a significant discrepancy between the two instruments. At the low water vapor mixing ratios observed in the subvisible cirrus cloud, a difference in water vapor of 0.5 ppm represents a decrease of approximately 25% in the calculated RH. We conclude, therefore, that water vapor is highly supersaturated throughout most of the cloud (RH of at least 125–225%) regardless of the water vapor measurement chosen for this analysis.

[13] Finally, we note that the cloud described here was highly supersaturated with respect to NAT. Measurements in contrail cirrus at temperatures less than $T_{NAT}$ have fueled speculation that HNO$_3$ serves to increase the relative humidity with respect to ice in low-temperature cirrus clouds via the formation of NAT-like hydrates on the particle surface [Gao et al., 2003]. With the simultaneous observation of condensed-phase HNO$_3$ and high relative humidities in the cloud reported here, it seems reasonable to speculate that HNO$_3$ uptake by subvisible cirrus particles might play an important role in the water vapor budget near the tropopause [Gao et al., 2003]. It is also worth noting...
that NAT formation on the particle surface is likely to increase the HNO$_3$ residence time on the particle (i.e. decrease the rate of escape from the surface) and further enhance the HNO$_3$ trapping process [Kärcher and Voigt, 2006].

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