Analysis of the physical state of one Arctic polar stratospheric cloud based on observations

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Abstract. During the Arctic Airborne Stratospheric Expedition, simultaneous measurements of aerosol size distribution and NO_y ($HNO_3 + NO + NO_2 + 2 \cdot N_2O_5$) were made along ER-2 flight paths. The flow characteristics of the NO_y instrument allow us to derive the condensed NO_y amount (assumed to be HNO_3) present during polar stratospheric cloud (PSC) events. Analysis of the January 24th flight indicates that this condensed HNO_3 amount does not agree well with the aerosol volume if the observed PSCs are composed of solid nitric acid trihydrate (NAT), as is generally assumed. However, the composition agrees well with that predicted for liquid $H_2SO_4/HNO_3/H_2O$ solution droplets using a new Aerosol Physical Chemistry Model (APCM). The agreement corresponds in detail to variations in temperature and humidity. The weight percentages of H_2SO_4, HNO_3, and H_2O derived from the measurements all correspond to those predicted for ternary, liquid solutions.

Introduction

Most papers discussing polar stratospheric clouds (PSCs) have assumed, on the basis of thermodynamic stability, that the particles are composed of solid nitric acid ices and water ice [see, for example, *Turco et al.*, 1989]. However, there is increasing uncertainty about the phase and composition of the HNO_3-containing, Type I PSCs. Knowledge of the particle composition is important to understand current ozone levels and predict future ozone depletion. Key factors, such as when PSCs form, the surface area of the clouds that form, and the reactivity of the particle surfaces, are influenced by the composition of the particles. This paper will examine *in situ* measurements of Type I PSCs to determine whether they are more consistent with solid particles or liquid particles.

The most stable form of HNO_3 under stratospheric conditions is solid nitric acid trihydrate (NAT) [*Hanson and Mauersberger*, 1988] and the temperature of PSC formation is roughly consistent with NAT [*Fahey et al.*, 1989; *Hofmann and Deshler*, 1991]. However, comparisons of PSC formation and temperature in the Arctic usually show that PSCs do not form until NAT supersaturations of about 10 are reached [*Dye et al.*, 1990; *Arnold*, 1992; *Kawa et al.*, 1992]. This discrepancy has led to several alternative theories for PSC composition,

including nitric acid dihydrate (NAD) [*Worsnop et al.*, 1993] and liquid $HNO_3/H_2SO_4/H_2O$ (ternary) solutions [*Arnold*, 1992; *Tabazadeh et al.*, 1994a; *Tabazadeh et al.*, 1994b], and inhibitive nucleation barriers [*Peter et al.*, 1992]. Existing techniques for measuring PSCs have, at best, limited ability to identify the composition of the particles.

PSC formation is dependent upon the physical state of the ambient sulphate aerosol. At normal stratospheric temperatures, this aerosol consists of a supercooled liquid solution of H_2SO_4 and H_2O [*Turco et al.*, 1982]. At cold enough temperatures, the particles absorb significant amounts of HNO_3, forming a ternary solution [*Zhang et al.*, 1993; *Tabazadeh et al.*, 1994b]. However, the solutions also become more supercooled and may freeze; the temperature at which crystallization occurs is still uncertain. Only once background aerosol particles have crystallized should HNO_3 be able condense as a solid compound.

This paper will analyze measurements of PSCs made by *in situ* ER-2 instruments to determine the HNO_3 composition of the particles. We have chosen to examine January 24th, 1989, when the coldest Arctic temperatures measured by the ER-2 were observed. Furthermore, the measurements made with the Forward Scattering Spectrometer Probe (FSSP) on this flight have been analyzed in previous papers [*Dye et al.*, 1990; *Dye et al.*, 1992; *Poole et al.*, 1990; *Kawa et al.*, 1992].

A key step in our analysis is the use of NO_y measurements to infer the amount of condensed HNO_3. The NO_y instrument on the ER-2 measures the total mixing ratio of reactive nitrogen species (accuracy: ±10%) [*Fahey et al.*, 1989]. However, the instrument inlet enhances the concentration of particles relative to gases, leading to an enhancement of condensed phase NO_y [*Fahey et al.*, 1989]. Given data from other ER-2 instruments, as discussed later, this enhancement allows the mixing ratio of condensed NO_y, assumed to be HNO_3, to be estimated. Comparison of the condensed HNO_3 and the FSSP volume allows the particle composition to be estimated. The FSSP instrument measures particles in the 0.21-12 µm radius range, using the intensity of scattered light produced by the particles to optically count and size them (uncertainty in calculated volume: ±30%) [*Dye et al.*, 1990].

The measured values are compared to calculations made assuming the particles are either made of NAT [*Hanson and Mauersberger*, 1988] or are composed of an equilibrium, ternary solution of $HNO_3/H_2SO_4/H_2O$. The calculations in either case use the actual ER-2 measurements of temperature, pressure [*Chan et al.*, 1990] and H_2O mixing ratio [*Kelly et al.*, 1990]. HNO_3 mixing ratios were estimated to be 90% of NO_y^* (see below). For the liquid solution calculations, a new Aerosol Physical Chemistry Model (APCM) was employed [*Tabazadeh et al.*, 1994a; *Jacobson et al.*, 1994]. The APCM is an equilibrium model which calculates the composition of

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stratospheric aerosols as a function of temperature, relative humidity, total [HNO_3], and total [H_2SO_4]. To constrain the APCM, the ambient sulphate mass was derived from FSSP and condensation nuclei counter (CNC) measurements made prior to the PSC event (assuming equilibrium H_2SO_4/H_2O composition) on January 24th and kept constant in all calculations; the results are not highly sensitive to the sulphate mass. Other new models for the ternary solution exist; that of *Beyer et al.* [1994] yields comparable compositions.

Flight characteristics

During the Arctic Airborne Stratospheric Expedition (AASE) the ER-2 aircraft made flights north from Norway which penetrated into the polar vortex. On January 24th, a maximum latitude of ~80°N was reached at 43000 seconds UT, at which point the airplane dove about 4 km. From 39900-43000 UT, the airplane was in the vortex, as defined by low [N_2O] [*Loewenstein et al.*, 1990]. Upon reattaining cruising altitude (~20 km) at 45500 UT the ER-2 was no longer in the vortex.

During the northernmost part of this flight, temperatures were below the NAT equilibrium temperature (T_{eq}) (Figure 1) and enhanced particle volumes and [NO_y] values were observed, except for 43000-45500 UT (the dive). For numerous brief periods the temperature was below the ice frost point. For the flight conditions, the ice crystallization temperature of *Jensen et al.* [1991] is ~0.5 K below the ice frost point, indicating that aerosol freezing may be able to occur. Conditions are also favorable for aerosol freezing by NAT crystallization [*Molina et al.*, 1993], since temperatures are below the liquid HNO_3/H_2O solution T_{eq} (Figure 1), at which point HNO_3 uptake is significant because the its vapor pressure drops below the ambient HNO_3 partial pressure. Back trajectories (M.R. Schoeberl, personal communication, 1994) indicate that this air mass had experienced temperatures up to 1 K colder in the previous few hours, further increasing the probability of the sampled particles being solid in the time periods 39000-43500 UT and 45000-46000 UT.
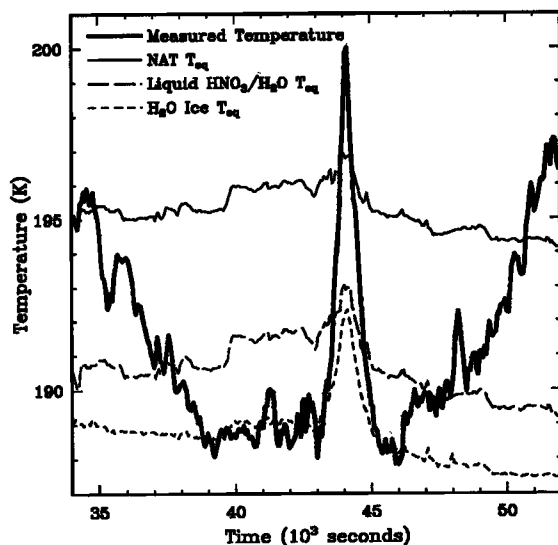
Deriving condensed HNO_3

Fahey et al. [1989] measure NO_y, [NO_y]$_m$, as:

$$[NO_y]_m = \int E(r) \cdot [HNO_3]_c(r) dr + [HNO_3]_g + [NO_x] \quad (1)$$

where $E(r)$ is the enhancement of aerosol HNO_3, [HNO_3]$_c(r)$ is condensed HNO_3 in particles with radius r, [HNO_3]$_g$ is gas-phase HNO_3, and NO_x consists of NO, NO_2, N_2O_5, all of which are assumed to be gas-phase only.

A linear relationship between [N_2O] and [NO_y]$_m$ [*Fahey et al.*, 1990] (in the absence of nitrate particles) allows an [NO_y] surrogate, [NO_y^*] to be derived from ER-2 N_2O measurements [*Loewenstein et al.*, 1990] (uncertainty: ±10%). Using [NO_y^*], equation (1) becomes:

$$[NO_y]_m = \int (E(r)-1) \cdot [HNO_3]_c(r) dr + [NO_y^*] \quad (2)$$

Unfortunately, the N_2O-NO_y^* relationship no longer holds at $N_2O < 140$ ppbv. Values this low were observed from 41800-42800 UT on January 24th; [NO_y]$_m$ decreased simultaneously. Alhough [NO_y]* has been adjusted, this period is shaded on all figures to indicate that the analysis is highly uncertain.

Particulate nitrate is enhanced because the instrument inlet is anisokinetic, resulting in a size-dependent enhancement, $E(r)$, which can be calculated from equations in *Fahey et al.* [1989] (uncertainty: ±30%) and ER-2 measurements, namely FSSP particle radius, ambient air density, and aircraft air speed [*Chan et al.*, 1990]. The maximum value for $E(r)$ is ~10. An average enhancement factor, E_{av}, can be calculated using the observed particle concentrations:

$$E_{av} = \sum E(r) V(r) / \sum V(r) \quad (3)$$

where $E(r)$ is the size-dependent enhancement, $V(r)$ is the FSSP volume, and the summation is over the FSSP size bins.

Combining equations (2) and (3) yields this expression for condensed HNO_3:

$$[HNO_3]_{c,meas} = ([NO_y]_m - [NO_y^*]) / (E_{av} - 1) \quad (4)$$

Figure 1. Observed temperature (thick solid line), compared to T_{eq} for NAT (thin solid line), T_{eq} for HNO_3/H_2O liquid (long dashed line), and T_{eq} for ice (short dashed line).
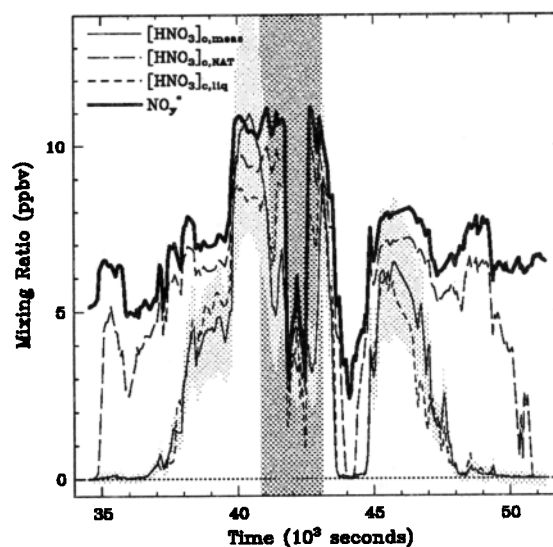

Figure 2. Condensed HNO_3 from measurements (thin solid line, light shading shows uncertainty) compared to that predicted for NAT (long dashed line) and a ternary liquid solution (thin dashed line). NO_y^* is also presented (thick solid line). In the darkly shaded region, all values are uncertain.

This quantity has been calculated from 60 second averages of the ER-2 measurements and is presented in Figure 2. Also shown are $[NO_y^*]$, $[HNO_3]_{c,NAT}$, the amount of condensed HNO_3 necessary for NAT to be in equilibrium, and $[HNO_3]_{c,liq}$, the amount of condensed HNO_3 in a ternary liquid solution as calculated by the APCM [*Tabazadeh et al.*, 1994a]. $[HNO_3]_{c,meas}$ is less than $[HNO_3]_{c,NAT}$ for much of the flight, implying a large NAT supersaturation, in particular for 35000-38000 UT and 47000-51000 UT. Similarly in the dive, the NAT model overpredicts the vertical extent of the cloud. $[HNO_3]_{c,liq}$ matches the measured value much better, both in magnitude and in the onset temperature of HNO_3 condensation, at all four transition points.

Particle Composition

The number of HNO_3 moles per condensed cm^3 (the molar density) can readily be determined by dividing the amount of condensed HNO_3 by the aerosol volume measured by the FSSP. The molar density is a more sensitive indicator of particle composition than $[HNO_3]_{c,meas}$, in particular at cold temperatures where most of the HNO_3 condenses regardless of particle composition. Furthermore, the molar density is a constant value for any crystalline solid, including NAT, since the composition is fixed. Temperature-dependent variations are more consistent with variable-composition liquid solutions. The measured molar density (Figure 3) is consistently a factor of two smaller than that for NAT and the measured values have clear temperature variations. The measured values do agree with the APCM's liquid solution predictions.

The HNO_3 and H_2SO_4 weight percents, the typical measure of liquid composition, can also be estimated from the measurements. The concentration of condensed HNO_3 was determined as above. The condensed H_2SO_4 mass can be estimated by assuming a distribution for the sulphate aerosol particles which, at warmer temperatures where the particles should be liquid H_2SO_4/H_2O solutions, agrees with that measured by the FSSP and extends to sizes below 0.21 μm to match the CNC number.
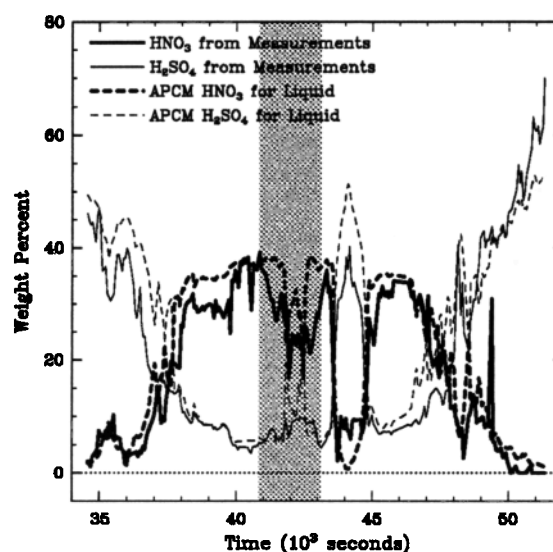
Figure 4. Liquid compositions derived from the measurements (solid lines) compared to those calculated by the APCM (dashed lines). HNO_3 is represented by thick lines; H_2SO_4 by thin. In the darkly shaded region, all values are uncertain.

The remaining particle mass is assumed to be liquid water. The results (Figure 4) show that both the HNO_3 and H_2SO_4 values agree well with the APCM calculations.

Conclusions

Our analysis shows that the FSSP and NO_y measurements of January 24th are not consistent with the presence of solid NAT particles, although temperatures were often cold enough for solid particles to be expected. The measurements show little, if any, HNO_3 condensation until the temperature is several degrees colder than the NAT condensation temperature, leading NAT models to overpredict the horizontal and vertical extent of the PSC. Furthermore, the inferred aerosol HNO_3 molar density is smaller than that of NAT and shows significant temperature-related variations. The temperature variability is inconsistent with any crystalline solid, including NAD. The data are consistent with PSC particles consisting of a ternary $HNO_3/H_2SO_4/H_2O$ liquid solution. A new model of aerosol composition, the APCM, is able to predict the observed composition, its temperature variations, and the horizontal and vertical extent of the observed PSC.

It is difficult to explain the apparent absence of solid particles at temperatures as cold as 188 K on this date. These data suggest that stratospheric quasi-binary HNO_3/H_2O solutions may remain liquid, in contrast to their laboratory behavior [*Molina et al.*, 1993]. Also ice crystallization, predicted by *Jensen et al.* [1991], was not apparent, which may be resolved by a slight temperature bias or small errors in the theory. We conclude that stratospheric $HNO_3/H_2SO_4/H_2O$ aerosols are extraordinarily resistant to freezing. Similar conclusions have been reached by *Tabazadeh et al.* [1994b], *Peter and Crutzen* [1993], and *Carslaw et al.* [1993].

The agreement between the aerosol composition deduced from the measurements and that calculated with the model of *Tabazadeh et al.* [1994a] is excellent considering the uncertainty in the field measurements and resulting accuracy of the derived values. An important assumption in the data analysis is that the total amount of NO_y present is $[NO_y^*]$ as calculated
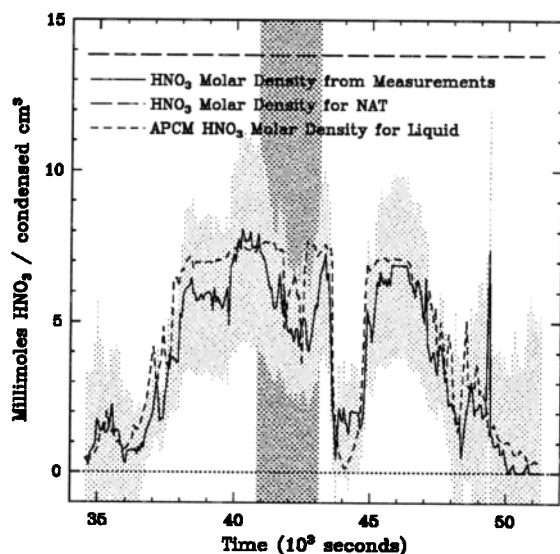

Figure 3. Molar density of HNO_3 (units: millimoles per condensed cm^3) from measurements (solid line, light shading shows uncertainty) compared to that predicted for NAT (long dashed line) and a ternary liquid solution (thin dashed line). In the darkly shaded region, all values are uncertain.

from [N_2O]. However, "reverse" calculations to determine the NO_y mixing ratio consistent with NAT particles show that no such match is possible in the PSC event, showing that although the use of [NO_y]* is a source of uncertainty it does not affect our conclusions.

Although the measurements from this date indicate that the observed particles were liquid, this does not imply that all polar stratospheric clouds are made up of liquid particles. Colder temperatures experienced by air parcels at other times and locations may allow particles to freeze, particularly in the Antarctic. Future work will extend this analysis to other available Arctic and Antarctic measurements. However, the presence of liquid PSCs may have important implications for the modelling of heterogeneous chemistry and ozone depletion, both because of the more limited spatial extent of liquid PSCs compared to NAT PSCs, as indicated by this data, and because of the differing reactivities of NAT surfaces and liquid solutions.

References

Arnold, F., Stratospheric Aerosol Increases and Ozone Destruction: Implications from Mass Spectrometer Measurements, *Ber. Bunsenges. Phys. Chem.*, *96*, 334-350, 1992.

Beyer, K.D., S.W. Seago, H.Y. Chang, and M.J. Molina, Composition and freezing of aqueous H_2SO_4/HNO_3 solutions under polar stratospheric conditions, *Geophys. Res. Lett.*, *21*, 871-874, 1994.

Carslaw, K.C., P. Brimblecombe, and S.L. Clegg, Calculated partitioning of hydrogen chloride and nitric acid into aqueous stratospheric acid aerosols (abstract), *Eos Trans. AGU 74*, 149, 1993.

Chan, K.R., S.W. Bowen, T.P. Bui, S.G. Scott, and J. Dean-Day, Temperature and Wind Measurements and Model Atmospheres of the 1989 Airborne Arctic Stratospheric Expedition, *Geophys. Res. Lett.*, *17*, 341-344, 1990.

Dye, J.E., *et al.*, Observed Particle Evolution in the Polar Stratospheric Cloud of January 24, 1989, *Geophys. Res. Lett.*, *17*, 413-416, 1990.

Dye, J.E., *et al.*, Particle Size Distributions in Arctic Polar Stratospheric Clouds, Growth and Freezing of Sulfuric Acid Droplets, and Implications for Cloud Formation, *J. Geophys. Res.*, *97*, 8015-8034, 1992.

Fahey, D.W., *et al.*, In Situ Measurements of Total Reactive Nitrogen, Total Water, and Aerosol in a Polar Stratospheric Cloud in the Antarctic, *J. Geophys. Res.*, *94*, 11299-11315, 1989.

Fahey, D.W., *et al.*, A diagnostic for denitrification in the winter polar stratospheres, *Nature*, *345*, 698-702, 1990.

Hanson, D., and K. Mauersberger, Laboratory Studies of the Nitric Acid Trihydrate: Implications for the South Polar Stratosphere, *Geophys. Res. Lett.*, *15*, 855-858, 1988.

Hofmann, D.J., and T. Deshler, Stratospheric Cloud Observations During Formation of the Antarctic Ozone Hole in 1989, *J. Geophys. Res.*, *96*, 2897-2912, 1991.

Jacobson, M.Z., R.P. Turco, and A. Tabazadeh, Simulating equilibrium within aerosols and non-equilibrium between gases and aerosols, *J. Geophys. Res.*, in press 1994.

Jensen, E.J., O.B. Toon, and P. Hamill, Homogeneous Freezing Nucleation of Stratospheric Solution Droplets, *Geophys. Res. Lett.*, *18*, 1857-1860, 1991.

Kawa, S.R., *et al.*, The Arctic Polar Stratospheric Cloud Aerosol: Aircraft Measurements of Reactive Nitrogen, Total Water, and Particles, *J. Geophys. Res.*, *97*, 7925-7938, 1992.

Kelly, K.K., *et al.*, A Comparison of ER-2 Measurements of Stratospheric Water Vapor Between the 1987 Antarctic and 1989 Arctic Airborne Missions, *Geophys. Res. Lett.*, *17*, 465-468, 1990.

Loewenstein, M., J.R. Podolske, K.R. Chan, and S.E. Strahan, N_2O as a Dynamical Tracer in the Arctic Vortex, *Geophys. Res. Lett.*, *17*, 477-480, 1990.

Middlebrook, A.M., *et al.*, FTIR Studies of Thin H_2SO_4/H_2O Films: Formation, Water Uptake, and Solid-Liquid Phase Changes, *J. Geophys. Res.*, 1994.

Molina, M.J., *et al.*, Physical Chemistry of the $H_2SO_4/HNO_3/H_2O$ System: Implications for Polar Stratospheric Clouds, *Science*, *261*, 1418-1423, 1993.

Peter, Th., and P.J. Crutzen, The role of stratospheric cloud particles in polar ozone depletion: An overview, *J. Aerosol Sci.*, *24*, S119-S120, 1993.

Peter, Th., R. Müller, K. Drdla, K. Petzoldt, and E. Reimer, A Micro-Physical Box Model for EASOE: Preliminary Results for the January/February 1990 PSC Event over Kiruna, *Ber. Bunsenges. Phys. Chem.*, *96*, 362-367, 1992.

Poole, L.R., *et al.*, The Polar Stratospheric Cloud Event of January 24, 1989: Part 1. Microphysics, *Geophys. Res. Lett.*, *17*, 537-540, 1990.

Tabazadeh, A., R.P. Turco, K. Drdla, and M.Z. Jacobson, A study of Type I polar stratospheric cloud formation, *Geophys. Res. Lett.*, *21*, 1619-1622, 1994b.

Tabazadeh, A., R.P. Turco, and M.Z. Jacobson, A model for studying the composition and chemical effects of stratospheric aerosols, *J. Geophys. Res.*, *99*, 12897-12914, 1994a.

Turco, R.P., O.B. Toon, and P. Hamill, Heterogeneous Physicochemistry of the Polar Ozone Hole, *J. Geophys. Res.*, *94*, 16493-16510, 1989.

Turco, R.P., R.C. Whitten, and O.B. Toon, Stratospheric Aerosols: Observation and Theory, *Rev. Geophy. Space Physics*, *20*, 233-279, 1982.

Worsnop, D.R., L.E. Fox, M.S. Zahniser, and S.C. Wofsy, Vapor Pressures of Solid Hydrates of Nitric Acid: Implications for Polar Stratospheric Clouds, *Science*, *259*, 71-74, 1993.

Zhang, R., P.J. Wooldridge, and M.J. Molina, Vapor Pressure Measurements for the $H_2SO_4/HNO_3/H_2O$ and $H_2SO_4/HCl/H_2O$ Systems: Incorporation of Stratospheric Acids into Background Sulfate Aerosols, *J. Phys. Chem.*, *97*, 8541-8548, 1993.

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