

Infrared Transmittance Spectra of Polar Stratospheric Clouds

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Abstract

Polar stratospheric clouds (PSCs) are responsible for polar ozone depletion. Infrared transmittance spectra of PSCs recorded by the Fourier transform spectrometer (FTS) on the Atmospheric Chemistry Experiment (ACE) satellite were used to determine the composition and properties of PSCs. These unique broad band infrared spectra identify PSCs as nitric acid trihydrate (NAT), supercooled ternary solutions (STS) of nitric and sulfuric acid, and ice, as expected. Quantitative modeling of these PSC spectra shows that supercooled nitric acid (SNA) is also common, i.e., “STS” with no observable sulfuric acid in their infrared spectra. ACE-FTS observations therefore classify PSCs into 4 basic spectral types, NAT, STS, SNA and ice, as well as their mixtures. As an example, this classification scheme was applied to the Antarctic for July to September 2019. The composition and particularly the phase of PSCs are critical to the understanding and detailed chemical modeling of polar stratospheric ozone depletion.

Key Words

Atmospheric Chemistry Experiment

Infrared solar absorption spectroscopy

Polar stratospheric clouds

Satellite remote sensing

Introduction

In 1974, Molina and Rowland [1] described the destruction of stratospheric ozone by chlorine atoms produced by the ultraviolet (UV) photolysis of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2). Stratospheric ozone protects life on the Earth by absorbing damaging UV radiation in the 200-300 nm region. CFCs manufactured for numerous applications including air conditioning and blowing agents are inert in the troposphere. Ultimately the production of CFCs, halons (bromine-containing chemicals) and other ozone depleting substances was controlled by the Montreal Protocol on Substances that Deplete the Ozone Layer [2, 3].

Fortunately, the destruction of stratospheric ozone by chlorine atoms is mitigated by the storage of chlorine in “reservoir” molecules such as hydrochloric acid (HCl) and chlorine nitrate (ClONO_2) that do not react with ozone [4]. In 1985, however, Farman et al. [5] made the startling observation that more than one-third of the total column density of ozone disappeared over Halley Bay, Antarctica in the springtime. An explanation for this Antarctic “ozone hole” was made the following year when it was suggested [6] that the heterogeneous reaction of HCl with ClONO_2 on polar stratospheric clouds (PSCs) would produce Cl_2 and HNO_3 . The Cl_2 is photodissociated in the springtime to make reactive Cl atoms and the HNO_3 is left behind as a condensed PSC phase. The conversion of chlorine-containing reservoir molecules into reactive chlorine catalyzed by PSCs is not confined to Antarctica but also occurs to a lesser extent in the Arctic.

The chemical composition and phase of PSCs are crucial in the detailed understanding of polar chemistry. The heterogeneous reaction rate constants included in various chemical transport models used to simulate polar ozone chemistry, e.g., [7], need to be based on laboratory measurements that are representative for specific types of PSCs, e.g., [8]. The abundances of different types of PSCs needed for comparisons with the chemical models are derived from satellite observations that classify and characterize these PSCs [9].

The accepted basic types of PSCs are solid nitric acid trihydrate (NAT, Type Ia), supercooled ternary solutions of nitric acid and sulfuric acid in water (STS, Type Ib), and ice (Type II) or mixtures of these three types [9]. As the temperature in the stratosphere drops in the polar winter, water and nitric acid vapors dissolve in liquid sulfate aerosols (H_2SO_4 solutions) in the Junge layer [10] increasing their size [11]. At about 195 K, nitric acid trihydrate (NAT) starts to crystallize and PSCs are in the form of NAT and STS [12]. As the temperature drops lower, at about 188 K ice starts to form. Note that temperatures below 195 K for NAT and 188 K for ice are typically required for nucleation [9]. Mixtures of PSC types are common, both internal (together in a particle) and external (particles mixed together) are possible [9]. The evidence for this picture is based on extensive laboratory measurements, ground-based and satellite lidar observations, visible light scattering, infrared emission spectroscopy, thermodynamic modeling, *in situ* mass spectrometry, to name some of the methods that have been used to study PSCs [8-9, 11-13]. Largely missing from this list of techniques is the direct measurement of characteristic infrared transmittance spectra of PSCs in the stratosphere from orbit as provided by the Atmospheric Chemistry Experiment, ACE [14].

PSCs have been classified for many years based on lidar measurements of the backscatter ratio and depolarization ratio of the returned signal [15]. Solid particles such as NAT and ice are not spherical and have depolarized return signals. The size of the backscatter ratio further distinguishes the PSCs, and additional PSC types have been defined such as “Type Ia-enhanced” which are mainly smaller NAT particles and “MIX” which are typically mixtures of NAT and ice [15]. Pitts et al. [16,17] divide NAT PSCs into 3 types (Mix1, Mix2, Mix2-enhanced). Another NAT subcategory called “enhanced NAT mixtures” [9] has been defined from lidar observations corresponding to higher NAT number densities and particles less than 3 μm in radius.

Extensive thermal emission spectra of PSCs have also been recorded by MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) [18-22] and CRISTA (Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere) [23] satellite instruments. The most characteristic feature in these emission spectra is band at 820 cm^{-1} assigned as a nitrate vibration present in NAT [19,20,23]. The PSC classification method for MIPAS emission spectra is based on radiance differences for NAT, STS and ice in the 790-1450 cm^{-1} region with validation by lidar [19-22]. The Bayesian MIPAS classifier uses the PSC categories STSmix, NAT, ICE, NAT_STS, and unknown [21-22].

The thermodynamic calculations of Carslaw et al. [11,24] offer considerable insight into the formation and composition of PSCs. In particular, the growth of PSCs by HNO_3 vapor dissolving in H_2SO_4 /water droplets starting at 195 K to form STS is predicted; by 190 K the supercooled liquid has a composition of about 40% HNO_3 and 1% H_2SO_4 (by weight). In other words, supercooled PSCs composed almost entirely of nitric acid and water were predicted. Kim et al. [25] observed such PSCs and called them “NAW (nitric acid water, or SBS, supercooled binary solution)” with the ILAS-II (Improved Limb Atmospheric Spectrometer) satellite instrument. ILAS-II measured low resolution transmittance spectra of PSCs by solar occultation in 3-12 μm (3300-830 cm^{-1}) region in the 2003 Antarctic winter.

We present four broad band (752-4233 cm^{-1}) transmittance spectra of NAT, STS, SNA and ice. Each spectrum is simulated using to appropriate optical constants and characteristic spectral features are identified. The four canonical spectra are quite different and form the basis of a classification scheme.

Methods

The Atmospheric Chemistry Experiment (ACE) satellite was launched by NASA on 12 August 2003 [14] for a nominal two-year mission. Now in its 19th year, the satellite continues to operate well with only a minor degradation in performance. The ACE orbit is nearly circular with an altitude of 650 km at launch and is inclined at 73.9° to the equator. The primary instrument on the ACE satellite is a high resolution (0.02 cm^{-1}) Fourier transform spectrometer (FTS) operating in the 750-4400 cm^{-1} (2.2-13.3 μm) spectral region [14]. The ACE-FTS uses the Sun as a light source and measures atmospheric transmittance spectra during sunrise and sunset in the limb geometry (solar occultation). The spectra are processed on the ground [26] to provide concentration profiles as a function of altitude for 44 gaseous molecules [27]. The absorption features due to these molecules can be removed from the spectra to create “residual” spectra that contain broad features

due to cloud and aerosol particles [28]. The geographic sampling of ACE is depicted by Fig. 6 in reference [14], and the vertical resolution on the Earth's limb as determined by the field of view is typically 3 km.

Residual spectra are created by dividing the observed spectrum by a calculated spectrum. The calculated spectrum contains the gas-phase contributions based primarily on spectroscopic data from the HITRAN2016 database [29]. The molecular concentrations are from ACE-FTS processing version 4.1/4.2 results [26]. The residual spectra contain features from anything not included in the calculated spectrum such as contributions from condensed phases such as PSCs.

Unfortunately, residual spectra are contaminated, for example, by features from several HNO_3 bands that are missing from the HITRAN2016 line list as well as non-Voigt effects in the lineshape calculation. These systematic features can be excluded from the analysis, or they can be removed by division using a nearby reference spectrum. This leaves the PSC of interest as the primary contributor to the calibrated residual spectrum. The spectra presented in this paper were typically corrected using reference spectra without PSCs recorded at the same latitude within a few hours. For the ice spectrum, the reference spectrum was from a different year but at the same latitude and season. The residual spectra were reduced to 4 cm^{-1} spectral resolution by averaging the high resolution wavenumber points in order to improve the signal-to-noise ratio and smooth the spectra.

The Beer-Lambert equation for transmittance τ was used to simulate the observed PSC spectra:

$$\tau = A \exp(-\sigma_{\text{ext}} N \ell) = A \exp(-\alpha \ell), \quad (1)$$

in which ℓ (cm) is the path length, α (cm^{-1}) is the extinction coefficient, N is the particle concentration (particles/ cm^3), σ_{ext} ($\text{cm}^2/\text{particle}$) is the extinction cross section. The T-matrix scattering code [30] was used to calculate the particle extinction coefficient α , and A is a fitted baseline parameter. The T-matrix method works for a randomly oriented distribution of axially symmetric particles (spheroids) with an axial ratio R ($R = 1$ for a sphere, $R > 1$ for an oblate ellipsoid and $R < 1$ for a prolate ellipsoid). The fitting results do not depend on whether an oblate or prolate model is chosen so $R > 1$ was used for solid particles.

The extinction cross section σ_{ext} includes both absorption and scattering, and depends on wavenumber, particle size distribution and optical constants of the material at a particular temperature. The temperatures were fixed to the values from ACE-FTS version 4.1/4.2 retrievals. A lognormal particle size distribution was used (equation (2)) as defined by the particle density N , median radius r_m and width S (S is the distribution standard deviation σ in $\ln(r)$ space, $\sigma = \ln(S)$) [31].

$$n(r) = \frac{N}{\sqrt{2\pi}} \frac{1}{\ln(S)} \frac{1}{r} \exp \left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2(S)} \right] \quad (2)$$

For the limb geometry of ACE, the particle density and cloud path length cannot be determined independently and the particle column density $N\ell$ (particles/ cm^2) along the line of sight is retrieved.

The classification of PSCs into 4 types (NAT, STS, SNA and ice) is based on inspection and fitting, discussed in more detail below. Pure PSCs are those that have spectra that are very similar to the 4 canonical spectral types defined by Figs. 1-4. NAT and SNA spectra were fitted as described for Figs. 1 and 2, STS were SNA spectra with the sulfate band at 1118 cm^{-1} and ice PSCs were identified by inspection in comparison with Fig. 4.

Results and Discussion

Simulation of characteristic ACE residual spectra can provide information on composition, particle size and particle shape. For example, Fig. 1 is a spectrum of a nitric acid trihydrate PSC.

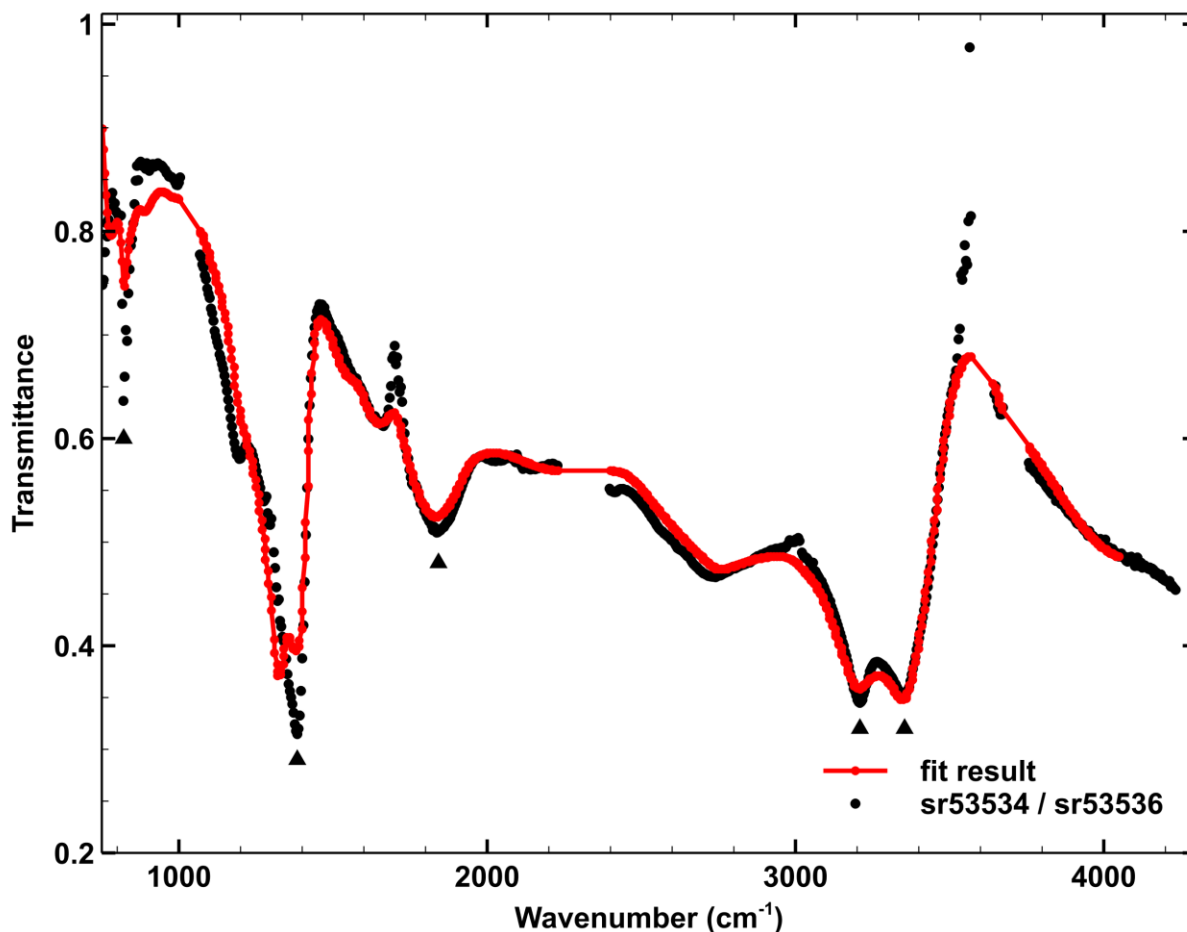


Fig. 1. Nitric acid trihydrate. Type Ia NAT PSC spectrum observed in Antarctica at a tangent altitude of 19.5 km from occultation sr53534 (sr stands for sunrise and 53534 is the orbit number since launch) on 22 July 2013 at 63.65°S latitude and 17.71°W longitude. The spectrum has been divided by the reference spectrum sr53536 to remove artifacts from incomplete removal of gaseous molecules. Triangles mark features discussed in the text.

Fig. 1 is a typical NAT spectrum along with a simulation using the optical constants of Toon *et al.* [32] for β -NAT at 196 K and the T-matrix light scattering code of Mishchenko and Travis [30].

The particles are assumed to have a lognormal distribution with a median radius r_m . The retrieved parameters are $r_m = 0.87 \pm 0.01 \mu\text{m}$, $R = 3.1 \pm 0.1$, $N\ell = 3.8 \pm 0.1 \times 10^7 \text{ particles/cm}^2$, $A = 0.928 \pm 0.003$ and $S = 1$ (fixed). The retrieved temperature from v.4.1/4.2 processing was 192.5 K, but this value played no role in the simulation. NAT has a sharp nitrate band due to the ν_2 out-of-plane bending mode [33] at 821 cm^{-1} , broader features at 1384 cm^{-1} (nitrate ν_3 antisymmetric N-O stretching mode [33]) and 1842 cm^{-1} , and a characteristic OH stretching doublet at 3209 and 3354 cm^{-1} . The peak maxima are relatively broad and the wavenumber accuracy in locating the peak positions is typically $3\text{-}5 \text{ cm}^{-1}$. The observed (black) and calculated (red) spectra in Fig. 1 show some relatively minor deviations perhaps due to the optical constants used and the assumption of $S=1$ for the lognormal particle distribution.

We have recently begun a detailed analysis of 17 years of ACE-FTS residual spectra from about 100,000 orbits. For PSCs, the usual three types (NAT, STS and ice) were readily identified along with their mixtures. A fourth type of PSC was often present: supercooled nitric acid (SNA) solution in water. Fig. 2 shows a typical spectrum of supercooled nitric acid in the Antarctic polar vortex.

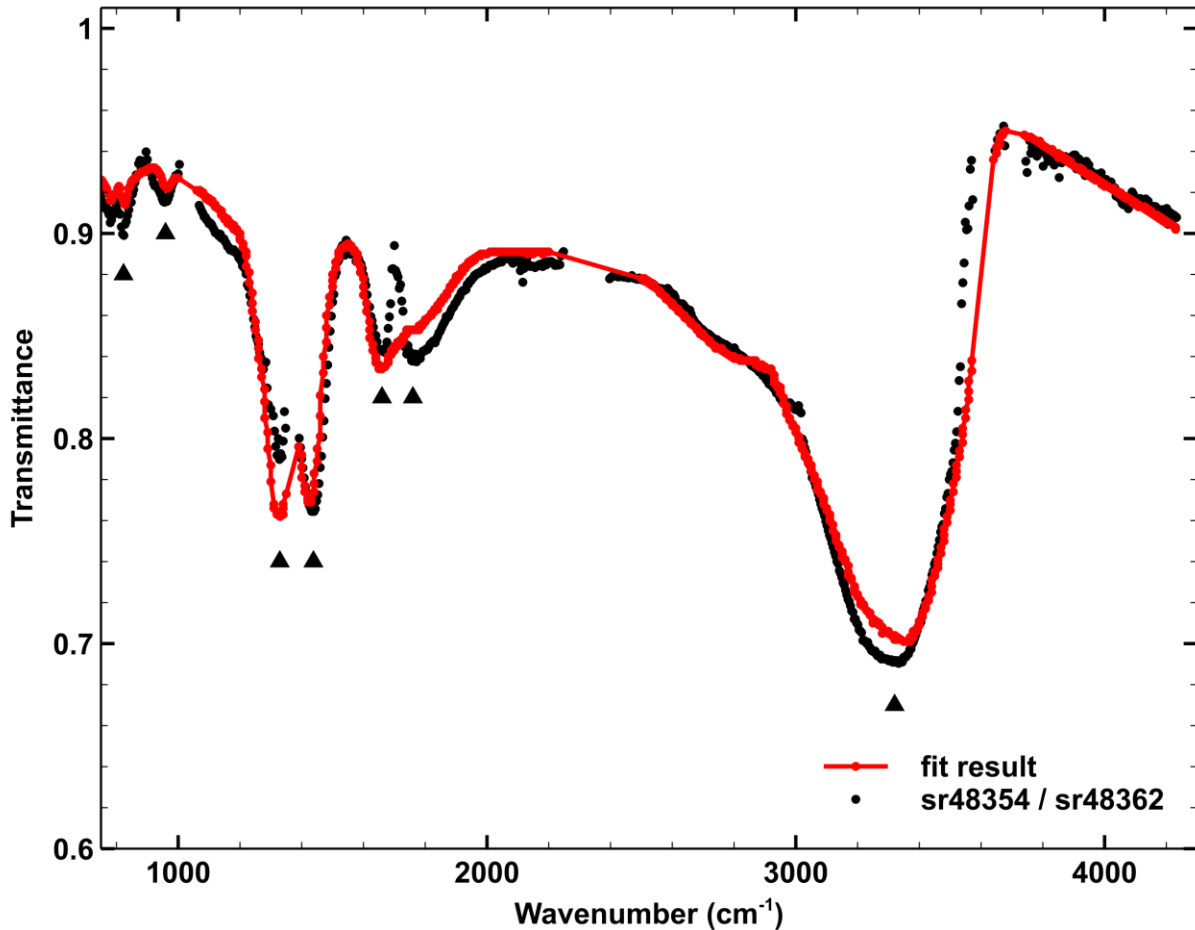


Fig. 2. Supercooled nitric acid. Spectrum observed in Antarctica at a tangent altitude of 22.0 km from occultation sr48358 on 5 August 2012 at 67.16°S latitude and 47.69°W longitude. The

spectrum has been divided by the reference spectrum sr48362. Triangles mark features discussed in the text.

The spectrum of supercooled nitric acid in Fig. 2 was simulated using the optical constants of Norman *et al.* [34] for spherical particles. The retrieved parameters are $r_m = 0.393 \pm 0.005 \mu\text{m}$, $R = 1$ (fixed), $47.5 \pm 0.3\%$ by weight HNO_3 , $N\ell = 1.65 \pm 0.07 \times 10^8 \text{ particles/cm}^2$, $A = 1$ (fixed) and $S = 1$ (fixed). The retrieved temperature from v.4.1/4.2 processing was 190.8 K, but the optical constants used had a temperature of 220 K. Supercooled nitric acid has an NO_3^- band at 823 cm^{-1} (ν_2 out-of-plane bending mode [33]), an HNO_3 band at 959 cm^{-1} (ν_5 , NO_2 deformation [35]) a characteristic doublet at 1329 cm^{-1} and 1438 cm^{-1} (probably ν_3 E' antisymmetric stretching mode of NO_3^- with degeneracy lifted [35]), a broader feature at 1660 cm^{-1} (probably antisymmetric NO_2 stretching mode of HNO_3 [35]) extending to 1760 cm^{-1} , and a very broad characteristic OH stretching feature (H_2O and HNO_3) at 3320 cm^{-1} . Notice that concentrated supercooled $\text{HNO}_3/\text{H}_2\text{O}$ solutions contain both NO_3^- and HNO_3 bands. As for Fig. 1, the observed (black) and calculated (red) spectra in Fig. 2 show some relatively minor deviations likely due to the optical constants used and the assumption of $S=1$ for the lognormal particle distribution.

The spectra of solid NAT and supercooled nitric acid are quite distinct and are simulated by optical constants determined by laboratory measurements [36]. In particular, solid NAT has a doublet near 3300 cm^{-1} , while the liquid has a single broad feature; in contrast NAT has a strong band near 1350 cm^{-1} compared to a clear doublet near 1400 cm^{-1} for the liquid. Notice also that both the solid and liquid have a nitrate feature near 820 cm^{-1} , with NAT slightly sharper and stronger, and supercooled nitric acid shifted slightly to higher wavenumbers.

SNA PSCs are a distinct spectral category because they have no discernable H_2SO_4 (1% by weight detection limit) and are therefore effectively binary (not ternary) solutions. This low H_2SO_4 abundance was predicted by Carslaw *et al.* [11,24] and also observed by Kim *et al.* [25]. Our detection limit was estimated using the Wagner *et al.* [37] optical constants of H_2SO_4 (10% by weight) at 230 K and the SNA spectrum in Fig. 2. The H_2SO_4 extinction was calculated using the same parameters used for the simulation in Fig. 2 and it was found that 1% H_2SO_4 produced a detectable feature at 1118 cm^{-1} in the SNA spectrum.

Residual ACE-FTS spectra can be used to classify PSC spectra into 4 basic types, supercooled nitric acid (SNA), NAT, STS and ice. The spectra of supercooled sulfuric and nitric acid solutions resemble supercooled nitric acid but with an additional sulfate band at 1118 cm^{-1} (Fig. 3). The 1118 cm^{-1} feature corresponds to the strong antisymmetric ν_3 bending mode of the sulfate ion [33].

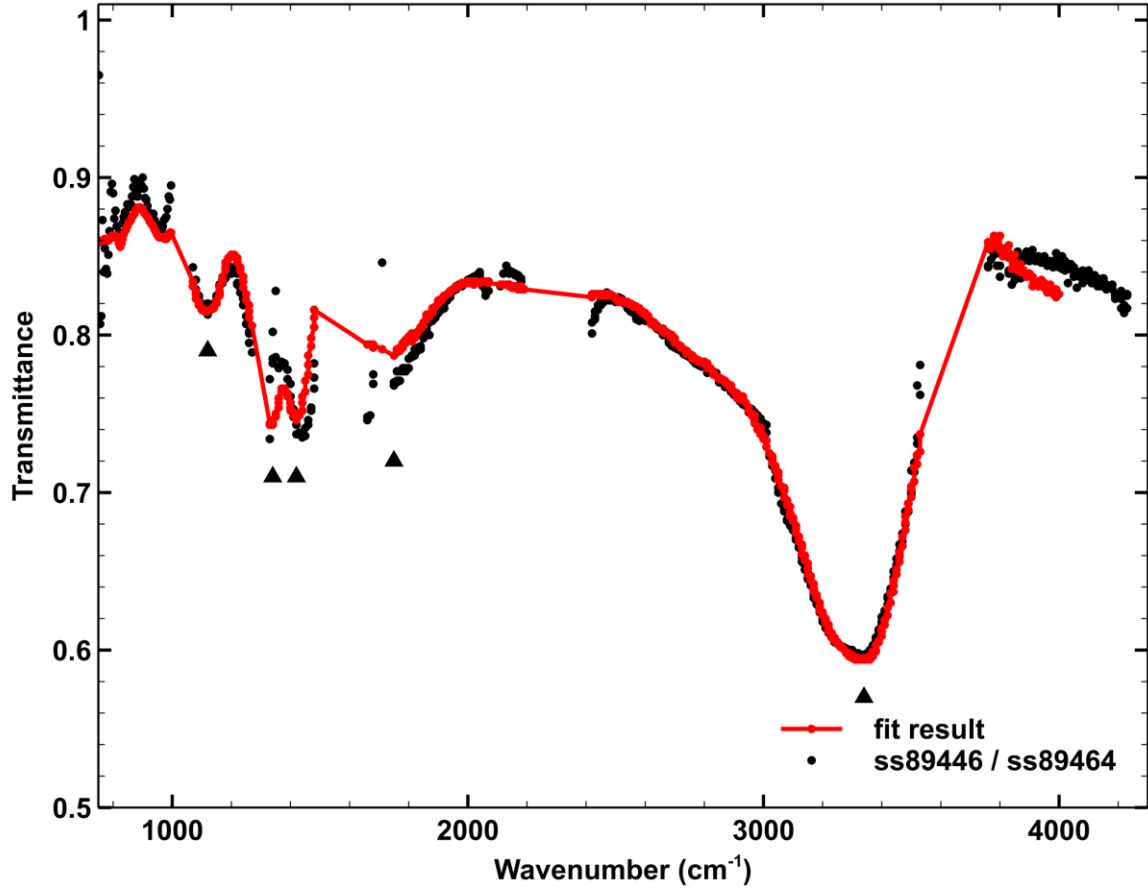


Fig. 3. STS. Type Ib PSC spectrum observed in the Arctic at a tangent height of 14.3 km from occultation ss89446 on 20 March 2020 at 74.69°N latitude and 98.96°W longitude, calibrated with ss89464. Triangles mark features discussed in the text.

Fig. 3 shows an STS spectrum recorded in the Arctic, and a simulation using the optical constants of Lund Myhre *et al.* [38] for nitric acid, sulfuric acid and water mixtures. Typical STS spectra have relatively low concentrations of sulfuric acid, which is a problem for spectral simulation because the available optical constants do not match the atmospheric conditions. Some of the discrepancies between observation and model in Fig. 3 are probably due to the optical constants. The spectrum in Fig. 3 has an unusually high concentration of sulfuric acid because of the Raikoke volcanic eruption [39]. More typical STS PSCs have similar spectra as Fig. 3, but with a weaker 1118 cm^{-1} sulfate band.

The retrieved concentrations of nitric acid and sulfuric acid for Fig. 3 are $14 \pm 4\%$ and $25 \pm 3\%$, respectively. The optical constants are for a temperature of 243 K, although the retrieved v.4.1/4.2 atmospheric temperature is 195 K at the tangent altitude. Note that the temperature is actually decreasing with altitude and if the PSC was not at the tangent point, then the PSC temperature would be a few kelvin lower. The parameter values for the simulation are $r_m = 0.417 \pm 0.007 \mu\text{m}$, $N\ell = 1.18 \pm 0.07 \times 10^8 \text{ particles/cm}^2$ and $A(>1810 \text{ cm}^{-1}) = 0.940 \pm 0.003$, $A(<1810 \text{ cm}^{-1}) = 0.945 \pm 0.002$, with R and S fixed to 1. STS (Fig. 3) has characteristic nitric acid bands at 1420 cm^{-1}

(actually part of a doublet as shown in the simulation) and 1720 cm^{-1} , a sulfate band at 1120 cm^{-1} and a strong broad OH stretching band at 3300 cm^{-1} .

The spectra of ice are also quite distinct with two large positive features at 1000 cm^{-1} and 3550 cm^{-1} (Fig. 4) [28].

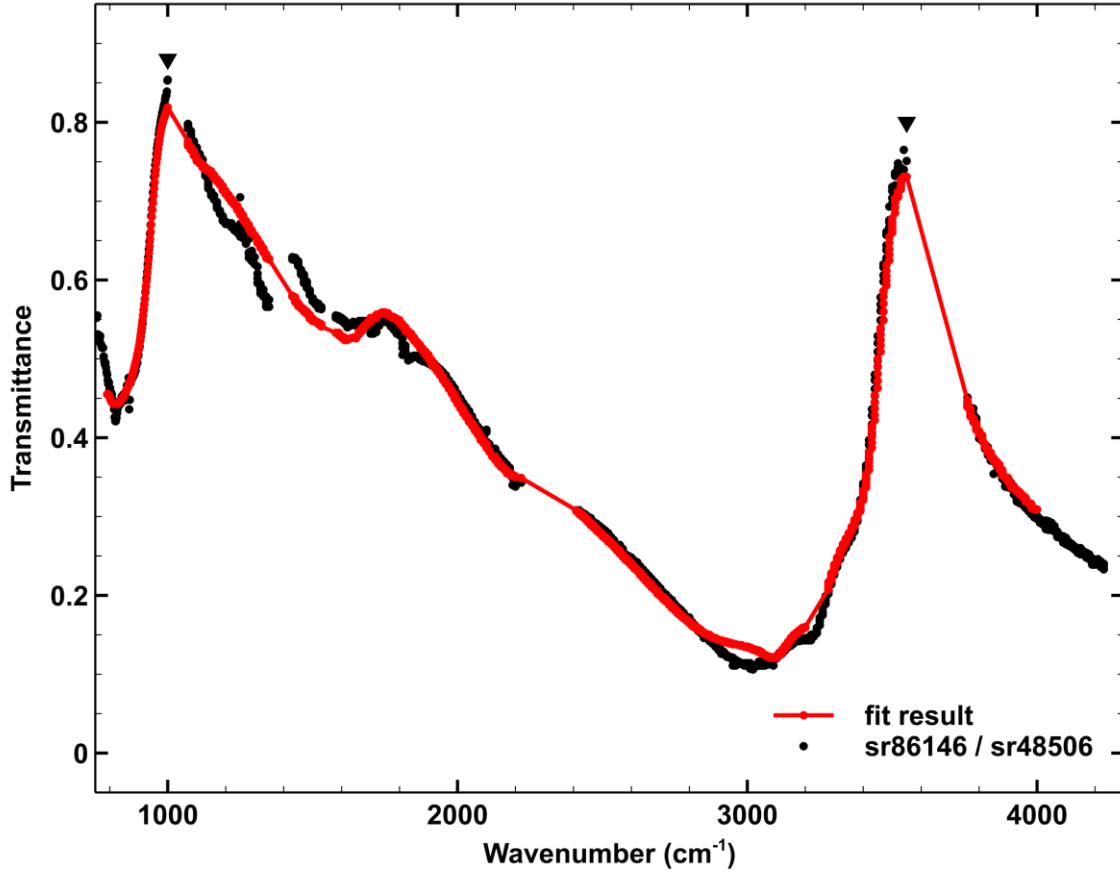


Fig. 4. Ice. Type II spectrum observed in Antarctica at a tangent height of 14.8 km from occultation sr86146 on 9 August 2019 at 67.47°S latitude and 75.09°W longitude, calibrated with sr48506. Triangles mark features discussed in the text.

Fig. 4 is a spectrum of PSC ice in Antarctica. The optical constants of Clapp *et al.* [40] were used to simulate the spectrum (orange in Fig. 4) with a temperature of 197 K from the ACE-FTS retrievals. It turns out that the ice cloud was sufficiently opaque that there was a jump in the FTS pointing from 21.6 km to 14.9 km and the PSC was probably located near 20 km where the temperature was about 188 K. The parameter values for the simulation were $r_m = 2.6 \pm 0.1\text{ }\mu\text{m}$, $N\ell = 3.5 \pm 0.4 \times 10^6\text{ particles/cm}^2$, $A = 0.93 \pm 0.03$ and $R = 4.3 \pm 0.3$, with S fixed to 1. PSC ice has two characteristic upward features at 1000 cm^{-1} and 3550 cm^{-1} and a slope between them. The transmission spectra can be explained as particle scattering, the downward slope to higher wavenumbers, with 3 characteristic ice absorption features at about 830 cm^{-1} (libration), 1680 cm^{-1} (weak bending mode) and 3090 cm^{-1} (OH stretching). PSC ice also has spectra similar to cirrus clouds [28], which have a shallower slope between the two upward features and have a larger

particle size (e.g., r_m of 7 μm). PSC ice is difficult to simulate accurately probably because the myriad of ice shapes are not well modeled by an oblate spheroid with the width of the particle size distribution set to zero.

The distinction between solid PSCs (NAT and ice) and liquid PSCs (SNA and STS) is critical to understanding and modeling polar chemistry. For liquid PSCs the reagents can dissolve in the particle, while surface chemistry predominates for solid PSCs. Kirner *et al.* [41] used a chemistry-climate model to show that liquid PSCs are responsible for 90% of Antarctic ozone depletion.

Fig. 5 shows PSC speciation of the 2019 Antarctic winter-spring season (11 July to 6 September) based on ACE-FTS residual spectra. The ACE orbit samples the Antarctic polar vortex between 57°S and 82°S latitude in Fig. 5 for this time period (see Fig. 6 in ref. [14] for a diagram of ACE sampling). Solar occultation constrains the sampling so that every day there are up to 15 measurements on a longitude circle at a slowly changing latitude. Fig. 5 sorts the observed PSCs into 4 categories (NAT, STS, SNA and ice) and marks the presence of each type as function of latitude and date. ACE-FTS measurements are made at twilight for either sunrises (first part of the individual panels in Fig. 5) or for sunsets (last part of the individual panels in Fig. 5). Only “pure” spectra are included in Fig. 5, and the overall PSC statistics are: 174 NAT, 182 STS, 154 SNA and 45 ice, with 426 additional PSCs classed as mixtures. Pure PSCs are those that have spectra that are very similar to the 4 canonical spectral types defined by Figs. 1-4. NAT and SNA spectra were fitted as described for Figs. 1 and 2, STS were SNA spectra with the sulfate band at 1118 cm^{-1} and ice PSCs were identified by inspection in comparison with Fig. 4.

While STS and NAT are the dominant PSC types, SNA and ice are also important contributors. At first glance Fig. 5 seems to show that SNA and NAT PSCs form first and then as the season progresses STS and ice become more prominent. This is a deceptive observation because of ACE sampling: as ACE measurements progress the temperatures become cooler, and the sampling shifts further south. For example, for the ice plot in Fig. 5, the retrieved ACE air temperature changes from about 200 K at beginning to about 180 K at the end of the plot. In the Antarctic for 10 June 2011, Spang *et al.* [22] find NAT furthest from the pole, then STS and then ice closest to the pole, in general agreement with ACE observations. Our conclusions on the relative importance of the contributors are based on “pure” PSCs, including mixtures might alter the picture. We plan to develop an automatic classification scheme and apply it to the entire ACE dataset.

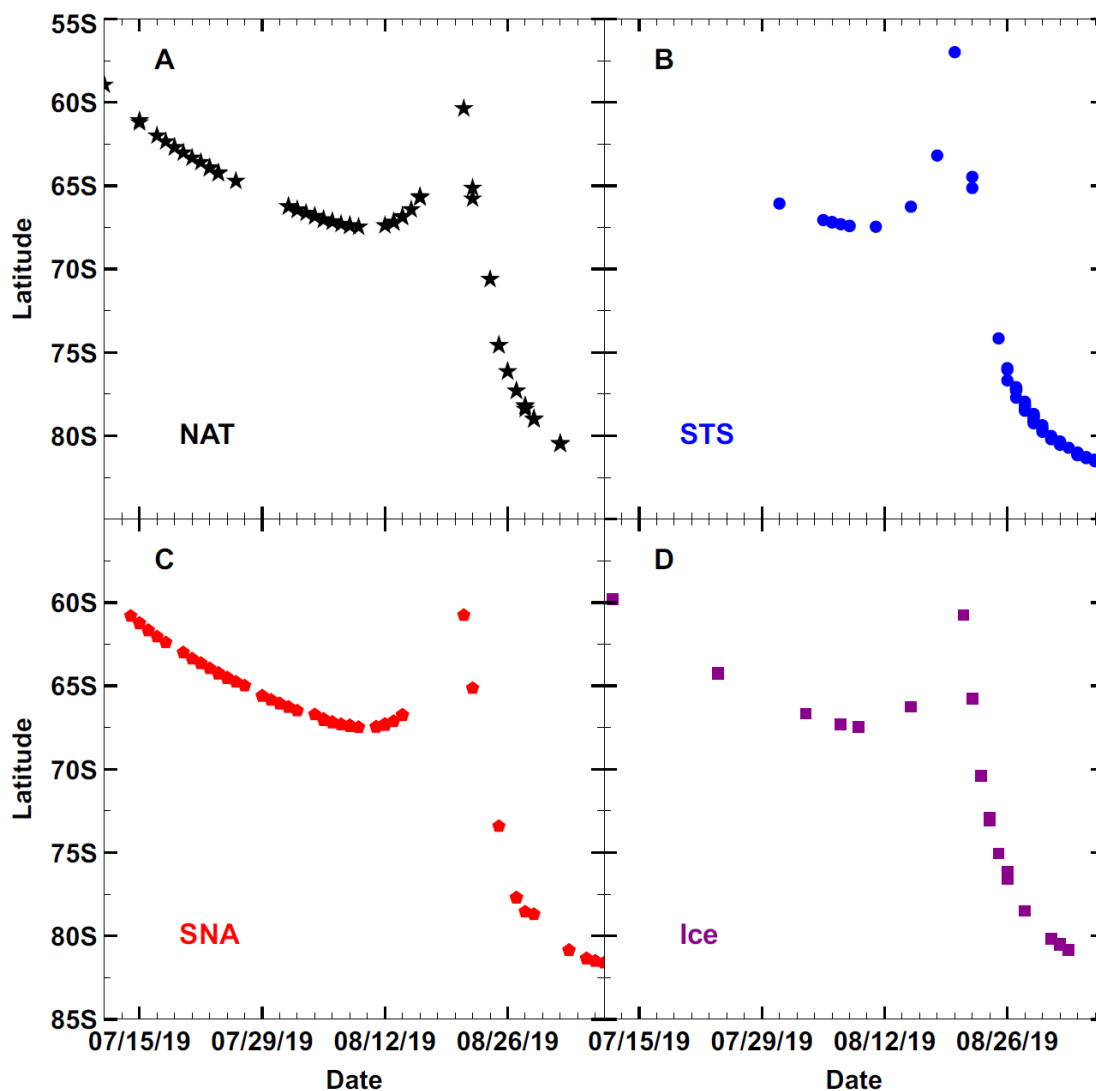


Fig. 5. PSC classification. PSC types for Antarctic for 11 July to 6 September 2019 as function of latitude and time. (A) Nitric acid trihydrate, NAT. (B) Supercooled ternary solutions, STS. (C) Supercooled nitric acid, SNA. (D) Ice.

Conclusions

Infrared transmittance spectra of PSCs composed of nitric acid and water, with no detectable H_2SO_4 (1% detection limit), are observed with the ACE-FTS and are called supercooled nitric acid (SNA). ACE-FTS observations clearly show that PSCs can be classified into four basic spectral types, NAT, STS, SNA and ice, along with their mixtures. For each type, a characteristic spectrum is provided and key distinguishing features are identified. STS PSCs are divided into a “high H_2SO_4 ” type (STS) and a “low H_2SO_4 ” type (SNA) that has no observable H_2SO_4 (<1%) based on the absence of a characteristic sulfate band at 1118 cm^{-1} in the infrared spectrum. Spectral simulations provide PSC properties such as particle size and composition, although there are minor discrepancies between simulations and observations. The optical constants derived from

experiment, particularly for STS, are not satisfactory and need to be improved. We have classified PSCs for part of the 2019 Antarctic winter-spring and find general agreement with MIPAS observations. Our work is a first step in creating an automated classifier for all ACE spectra of clouds and aerosols.

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