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# Atlas of ACE spectra of clouds and aerosols

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#### ABSTRACT

Clouds and aerosols play a vital role in the Earth's climate. Detecting polar mesospheric clouds, polar stratospheric clouds and aerosols is useful for monitoring climate change and atmospheric chemistry. ACE (Atmospheric Chemistry Experiment) satellite data are used to provide an infrared spectral atlas of polar mesospheric clouds, three types of polar stratospheric clouds (nitric acid trihydrate, sulfuric/nitric acid ternary solutions, and ice), cirrus clouds, stratospheric smoke from fires and sulfate aerosols. Most of the example spectra have been modeled using the appropriate optical constants and the calculated extinction of sunlight by the particles.

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#### 1. Introduction

The ACE satellite (also known as SCISAT) was launched into low Earth orbit in August 2003 for a nominal 2-year mission [1]. The primary instrument on ACE is a high resolution (0.02 cm<sup>-1</sup>) infrared Fourier transform spectrometer (ACE-FTS), operating in the 750–4400 cm<sup>-1</sup> range. The FTS measures sequences of atmospheric transmission spectra during sunrise and sunset in the limb geometry (solar occultation technique). These spectra are analyzed on the ground [2] to provide altitude volume mixing ratio (VMR) profiles for atmospheric gasses [3] with a typical vertical resolution of 3 km. The original primary mission goal was to study ozone in the stratosphere and upper troposphere, but because of the longevity ACE has measured trends in atmospheric composition for 44 gases [3]; changes in greenhouse gas concentrations are the primary cause of climate change.

Although the ACE mission has focused mainly on trace gases, the atmospheric spectra also contain observations of condensed phases such as clouds and aerosols. Liquid and solid particles have broad spectral features compared to gases and appear mainly as part of the "baseline" once gas phase components are removed. This was recognized early in the mission and for example, ACE provided the first broad-band spectra of polar mesospheric clouds

\* Corresponding author. E-mail address: jsorense@odu.edu (J.J. Sorensen). (PMCs) [4]. These spectra confirmed that PMCs are small nonspherical ice particles [4,5]. The increasing occurrence of PMCs is an indicator of climate change. Early observations of cirrus clouds were carried out by Eremenko et al. [6].

In addition to the infrared spectra from the ACE-FTS, aerosols and clouds are also being monitored by two filtered solar imagers at 0.525 and 1.02  $\mu$ m [1]. These imagers provide altitude profiles of aerosol and cloud extinction.

Infrared spectra of smoke particles injected into the stratosphere by pyrocumlonimbus (pyroCb) events have been published [7]. These smoke particles from extreme wildfires alter the chemistry of the stratosphere and can deplete ozone [8].

Recently, ACE spectra of sulfate aerosols have been analyzed in considerable detail focusing on the eruption of the Raikoke volcano [9]. Stratospheric sulfate aerosols generally cool the surface of the Earth and warm the stratosphere [10].

Recently, we have started to analyze the entire ACE record from 2004 to the present for spectral signatures of clouds and aerosols. Overall ACE has now observed about eight different types of cloud and aerosol spectra (not counting mixtures), broadly characterized as PMCs, stratospheric smoke, sulfate aerosols, cirrus clouds, polar stratospheric clouds (PSCs) and volcanic ash. The raw ACE spectra have been corrected to remove gas phase features and constitute a remarkable set of actual broad band spectral examples. In almost all cases we have been able to simulate the spectra to determine composition and particle size. This paper therefore presents an "at-las" of ACE spectra of clouds and aerosols.

# 2. Methods: residual ACE-FTS spectra

Residual spectra are generated by dividing the measurement by a calculated spectrum, where the calculated spectrum consists of all known gas-phase contributions to the spectrum. This calculation employs the latest cross sections for large molecules and a line list containing spectroscopic constants based primarily on HITRAN (high resolution transmission molecular absorption database) 2016 [11]. Volume mixing ratio profiles are taken from ACE-FTS processing version 4.1/4.2 results [2] for the given occultation. The calculated spectrum also includes collision induced absorption contributions to the spectrum from N<sub>2</sub> [12] and O<sub>2</sub> [13], as well far wing contributions from the  $\nu_3$  band of CO<sub>2</sub> [14].

Features in the residual spectrum will consist of anything contributing to the measurement that was not included in the calculated spectrum, such as aerosols [7,9], including ubiquitous background sulfate aerosols. Unfortunately, residual spectra are polluted by features from a number of HNO<sub>3</sub> bands that are missing from the HITRAN 2016 line list, plus systematic residuals that arise from ignoring non-Voigt effects such as speed-dependence or line-mixing in the calculated spectrum. These systematic features can be ignored, excluding the affected wavenumber regions from the analysis if they excessively impact the analysis, or they can be removed through calibration by an occultation under background conditions. Choosing a calibration measurement featuring similar conditions (location, time of year, tangent height, HNO<sub>3</sub> levels) removes most of the systematic features from the residual spectrum, including the contribution from background sulfate aerosols. This leaves the aerosol(s) of interest as the primary contributor(s) to the calibrated residual spectrum, which simplifies the analysis.

#### 3. Methods: spectral simulations

The simulated transmission spectra were calculated using the Beer-Lambert equation

$$\tau = Aexp(-\sigma_{ext}N\ell) = Aexp(-\alpha\ell) \tag{1}$$

in which  $\ell$  (cm) is the path length,  $\alpha$  (cm<sup>-1</sup>) is the extinction coefficient, *N* is the particle concentration (particles/cm<sup>3</sup>),  $\sigma_{ext}$  (cm<sup>2</sup>/particle) is the extinction cross section. The absorption coefficient was calculated with either T-matrix [15] or Mie scattering [16] codes and *A* is a baseline parameter fitted to improve the agreement with ACE spectra. The T-matrix method solves Maxwell's equations for light scattering by 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 Mie scattering code from Oxford University was used for spherical sulfate aerosols [16].

The extinction cross section  $\sigma_{\text{ext}}$  includes both absorption and scattering, and depends on wavenumber, particle size distribution and optical constants of the material at a particular temperature. In most cases, the temperatures were fixed to the values from ACE-FTS version 4.1/4.2 retrievals that are based mainly on the relative intensity of CO<sub>2</sub> lines [2]. A lognormal particle size distribution was used (Eq. (2)) as defined by the particle density *N*, median radius *r*<sub>m</sub> and width *S* (S is the distribution standard deviation  $\sigma$  in ln(r) space,  $\sigma = \ln(S)$ ) [16].

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

Note that in some cases (e.g., PMCs) the distribution used had zero width (S = 1) and a single  $r_m$  value.

The input to the T-matrix and Mie scattering codes are suitable optical constants at a temperature as close as possible to the observed ACE temperature. Typically the path length was fixed to 200 km and the particle concentration *N* was determined from the fit of the observed spectrum with the calculated spectrum. Only the particle column density  $N\ell$  (molecules/cm<sup>2</sup>) along the atmospheric limb path to the Sun can be determined from ACE infrared spectra. The particle size distribution parameter *S* for a lognormal distribution cannot be determined from ACE infrared spectra so was fixed to various values as noted below. The output from the scattering codes is the extinction coefficient  $\alpha$  as a function of wavenumber.

# 4. Stratospheric smoke particles

Extreme wildfires can inject smoke particles as well as numerous molecules released by combustion into the stratosphere [7]. The most severe wildfires occurred in the Australian "Black Summer" in December 2019 and January 2020. As a result of climate change, these pyroCb events are becoming more frequent [17]. The ACE-FTS recorded infrared spectra (e.g., Fig. 1) of stratospheric smoke from the Australian fires [8] as well and from other pyroCbs [7].

The smoke spectra from different fires are surprisingly similar and show spectral features assignable to C = O carbonyl stretching (1740 cm<sup>-1</sup>), CH stretching (2962 cm<sup>-1</sup>) and OH stretching (3225 cm<sup>-1</sup>) modes, suggestive of a surface carboxylic acid group [18]. In addition, surface H<sub>2</sub>O is present based on the librational mode at 800 cm<sup>-1</sup> and OH stretching mode as shoulder at 3420 cm<sup>-1</sup> (the bending mode is weak and not observed) [19]. These features are marked with tick marks in Fig. 1. Presumably the hydrated soot particles are being oxidized by the OH free radical.

#### 5. Polar mesospheric clouds (PMCs)

Polar mesospheric clouds, called noctilucent clouds by groundbased observers, are found near 83 km altitude at high latitudes around the summer solstice (June in the Northern Hemisphere and December in the southern Hemisphere) when temperatures are the lowest [20]. PMCs seem to be occurring more frequently and may be indicators of climate change [21]. Increasing concentrations of CO<sub>2</sub> causes the mesosphere to cool and increasing CH<sub>4</sub> introduces more H<sub>2</sub>O into the mesosphere. PMCs are small ice particles, and the ACE-FTS has recorded their spectra from 750 to 4200 cm<sup>-1</sup> (Fig. 2).

The PMC infrared spectrum (Fig. 2) shows an OH stretching feature at 3238 cm<sup>-1</sup> that can be used to retrieve the temperature of the ice particles [5,22]. The weak bending mode at about 1600 cm<sup>-1</sup> is very weak and the librational mode at 850 cm<sup>-1</sup> is seen at the lower edge of the spectrum. The spectrum was simulated using the ice optical constants of Clapp et al. [23] with the particle size  $(r_{\rm m})$  fixed to 40 nm [5] and the distribution width, S, set to 1 (i.e., zero width). The retrieved temperature of the ice was 132.3(7.8) K, the axial ratio, R, was 2.0(1.2) and the column density was 8.6(2.0)x10<sup>9</sup> particles/cm<sup>2</sup> with one standard deviation in parenthesis. The ice temperature retrieval is based on the location of the peak position near 3238 cm<sup>-1</sup> and is substantially lower than the air temperature of 157.7 K at the tangent point. There was a baseline offset between the InSb and MCT detectors [1] so two baseline parameters were fitted: for wavenumbers greater than 1810 cm<sup>-1</sup>, A = 0.998(1) and for less than 1810 cm<sup>-1</sup>A = 1.002(1).

# 6. Cirrus clouds

Cirrus clouds occur in the upper troposphere where temperatures are low enough to produce ice particles [24]. Cirrus clouds occur at all latitudes and are particularly prominent in the tropics.



Fig. 1. Stratospheric smoke spectrum observed at a tangent height of 17.6 km from occultation ss88712 (ss is sunset and 88,712 is the orbit number) on 30 January 2020 at 47.50°S latitude and 163.16°E longitude.



Fig. 2. PMC spectrum observed at a tangent height of 81.6 km from occultation ss85825 on 18 July 2019 at 67.99°N latitude and 48.95°E longitude. There is an artifact at 1810 cm<sup>-1</sup> where the MCT and InSb detector regions meet.

Cirrus clouds play a significant role in global heat balance. They reflect a significant portion of the incident solar flux back into space which results in net cooling of the Earth's surface [25] and also absorb infrared radiation emitted from the surface.

The cirrus cloud transmission spectrum (Fig. 3) shows two prominent peaks at 961 cm<sup>-1</sup> and 3506 cm<sup>-1</sup>. The simulations in Fig. 3 were carried out with the ice optical constants of Clapp et al. [23]. For this simulation, the temperature was fixed to 198.84 K from the v.4.1/4.2 retrieval, and the retrieved parameters were  $r_{\rm m} = 7.09 \ \mu\text{m}$ , R = 2.20, S = 1.23, A = 0.648 and the column density  $N\ell = 2.88 \times 10^5$  particles/cm<sup>2</sup> (all with unrealistically small error bars, not reported). The simulation is not perfect mainly because the model is too simple to represent the myriad of different shapes that cirrus ice particles have [24].

# 7. Sulfate aerosols

ACE occasionally observes enhanced stratospheric  $SO_2$  from large volcanic eruptions [26]. The corresponding enhancement in aerosol extinction from these eruptions is seen with the ACE imagers [26]. Analysis of the residual ACE-FTS spectra confirms that these stratospheric aerosols are due to sulfuric acid droplets [9]. Sulfate aerosols are important for both climate and chemistry [10]. They scatter sunlight to space, generally cooling the Earth's surface [27] and absorbing infrared radiation, heating the stratosphere. Their properties and composition have been studied, for example, by light scattering and mass spectroscopy [28] as well as infrared remote sensing [29]. They provide a medium for chemical reactions that, for example, destroy stratospheric ozone [30]. The explosive eruption of the Raikoke volcano in Russia's Kuril Islands in June 2019 provided many spectra of sulfate aerosols (e.g., Fig. 4). ACE is also able to observe much weaker background sulfate aerosols, which resemble scaled down versions of Fig. 4.

For the simulation shown in Fig. 4, the sulfuric acid optical constants of Lund Myhre et al. [31] were used, with some extra data points determined by interpolation and extrapolation [9]. In this simulation, the temperature was fixed to 213 K from the v.4.1/4.2 retrievals and S was set to 1.3. The fitted median radius  $r_{\rm m}$  was 0.23(2) µm, the composition was 75.1(4)% by weight sulfuric acid, the column density was 1.6(3)x10<sup>8</sup> particles/cm<sup>2</sup> and A = 1.0005.

The spectrum (Fig. 4) shows three characteristic bands with increasing intensity at 908, 1060 and 1194 cm<sup>-1</sup>, a broader band at 1740 cm<sup>-1</sup> and a very broad OH stretching band at 2900 cm<sup>-1</sup> that



Fig. 3. Cirrus cloud spectrum observed at a tangent height of 15.5 km from the tropical occultation sr79241 (sr stands for sunrise) on 28 April 2018 at 1.22°S latitude and 99.55°E longitude.



# Sulfate Aerosols, sr86498

Fig. 4. Sulfate aerosol spectrum from the Raikoke eruption observed at a tangent height of 22.9 km from the occultation sr86498 on 2 September 2019 at 26.69°N latitude and 47.97°W longitude.

extends beyond  $3500 \text{ cm}^{-1}$  [31]. These features have been marked with tick marks in Fig. 4.

# 8. Volcanic ash

In addition to  $SO_2$  and sulfate aerosols, volcanic eruptions emit copious amounts of volcanic ash [32,33]. Volcanic ash poses a significant hazard to aviation and to human health. The ACE satellite, however, rarely detects volcanic ash because it settles out of the atmosphere relatively quickly compared to sulfate aerosols. ACE imagers and ACE-FTS measured the ash (Fig. 5) from the Puyehue-Cordón Caulle volcano (latitude 40.6°S, longitude 72.1°W) in Chile that erupted 4 June 2011.

The simulation in Fig. 5 is based on considerable trial and error using the T-matrix code [15] with the optical constants of Reed et al. [32]. Ultimately, a bimodal lognormal distribution was used with  $r_m = 0.08 \ \mu m$  for the fine mode and  $r_m = 0.5 \ \mu m$  for the coarse mode with S = 2 and R = 1.2. The spectrum (Fig. 5) shows a single strong absorption band at 1070 cm<sup>-1</sup> due to the characteristic Si-O stretching vibration of volcanic ash. The long extinction tail to higher wavenumbers is caused by scattering.

#### 9. Polar stratospheric clouds

Polar stratospheric clouds are responsible for polar ozone depletion. In 1974, Molina and Rowland [34] discovered that chlorofluorocarbons (CFCs) are photodissociated in the stratosphere to release Cl atoms that can destroy ozone. Stratospheric ozone absorbs ultraviolet radiation that causes skin cancer and damages ecosystems. The stratospheric chlorine released from CFCs mostly ends up in reservoir compounds such as HCl and ClONO<sub>2</sub> that do not destroy ozone [35]. However, condensed phase PSCs catalyze the reaction of HCl with ClONO<sub>2</sub> to form Cl<sub>2</sub> which is dissociated by sunlight to make destructive Cl atoms. PSCs are therefore responsible for the Antarctic ozone hole and Arctic ozone declines that occur in the springtime.

PSCs begin to form when the stratospheric temperature drops to about 195 K: nitric acid forms solid nitric acid trihydrate (NAT,  $HNO_3 \cdot 3H_2O$ ), and a supercooled ternary solution (STS) of nitric acid and sulfuric acid in water also forms [36]. At about 188 K, water vapor freezes to form ice. These three types of PSCs are called Type Ia (NAT), Type Ib (STS) and Type II (ice) in the older literature, although the modern terminology categorizes to PSCs by their



Fig. 5. Volcanic ash spectrum of the Puyehue-Cordón Caulle volcano observed at a tangent height of 13.8 km from the occultation ss42121 on 9 June 2011 at 45.73°S latitude and 46.00°E longitude.



Fig. 6. NAT PSC spectrum observed in Antarctica at a tangent height of 23.7 km from occultation sr86203 on 13 August 2019 at 67.17°S latitude and 29.76°W longitude.



Fig. 7. STS PSC spectrum observed in the Arctic at a tangent height of 14.0 km from occultation ss89431 on 19 March 2020 at 75.83°N latitude and 94.72°W longitude.

composition (i.e., NAT, STS and ice). This simple picture is misleading because PSCs are often mixtures of different types and phases. Nevertheless, relatively pure examples of each type are present in the stratosphere, and we provide characteristic infrared spectra.

#### 10. Polar stratospheric clouds: Nitric acid trihydrate

Fig. 6 shows a typical NAT spectrum recorded in the Antarctic polar vortex, and a simulation using the optical constants of Toon et al. [37] for  $\beta$ -NAT at 196 K. The retrieved values for the simulation were  $r_{\rm m} = 0.94(3) \ \mu\text{m}$ , R = 2.0(2),  $N\ell = 4.7(4) \text{x} 10^6$  particles/cm<sup>2</sup> and A = 0.960(2). NAT has a characteristic nitrate

bands at 821 cm<sup>-1</sup>, at 1350 cm<sup>-1</sup>, a weaker feature at 1830 cm<sup>-1</sup> and a characteristic OH stretching doublet at 3204 and 3346 cm<sup>-1</sup>.

# 11. Polar stratospheric clouds: Supercooled ternary solutions

Fig. 7 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. STS retrievals are difficult because the available optical constants do not match the atmospheric conditions. Typical STSs have low concentrations of sulfuric acid and their optical constants at low temperatures are often not available.



Fig. 8. Ice PSC spectrum observed in Antarctica at a tangent height of 21.5 km from occultation ss32454 on 22 August 2009 at 71.96°S latitude and 65.57°W longitude.

For the STS PSC in Fig. 7, the retrieved concentrations of nitric acid and sulfuric acid are 13(5)% and 26(4)%, respectively. The sulfuric acid concentration is somewhat enhanced by the Raikoke volcanic eruption. The optical constants are for a temperature of 243 K, although the retrieved v.4.1/4.2 atmospheric temperature is 195 K. The parameter values for the simulation were  $r_m = 0.47(7)$  $\mu$ m,  $N\ell = 1.0(1) \times 10^8$  particles/cm<sup>2</sup> and A = 0.975(3), with *R* and *S* fixed to 1. STSs (Fig. 7) have characteristic nitric acid bands at 1420 cm<sup>-1</sup> (actually part of a doublet as shown in the simulation) and 1720 cm<sup>-1</sup>, a sulfuric acid band at 1120 cm<sup>-1</sup> and a strong broad OH stretching band at 3300 cm<sup>-1</sup> [38].

#### 12. Polar stratospheric clouds: Ice

An infrared spectrum of PSC ice in the Antarctic polar vortex is presented in Fig. 8. The simulation in orange (Fig. 8) uses the optical constants of Clapp et al. [23] with a temperature of 183 K from the ACE-FTS retrievals. The parameter values for the simulation were  $r_{\rm m} = 2.22(6) \ \mu\text{m}$ ,  $N\ell = 1.05(11) \text{x} 10^7 \ \text{particles/cm}^2$ ,  $A = 0.66(3) \ \text{and} \ R = 4.97(9)$ , with *S* fixed to 1. PSC ice has two characteristic upward features at 1000 cm<sup>-1</sup> and 3550 cm<sup>-1</sup> and a slope between them. These two features are similar to those found in cirrus clouds which are also ice (Fig. 3). Indeed, some PSC ice spectra have spectra very similar to cirrus clouds.

# 13. Conclusions

The "residual" spectra from the ACE-FTS provide a unique set of measurements of clouds and aerosols. These infrared spectra can be used to reliably speciate the particles at a glance, using the sample spectra provided in this paper. In many cases, particles can be characterized in detail; that is, particle properties such as composition, particle size and particle shape can be determined using calculated extinction with T-matrix and Mie scattering codes. The infrared spectral region provides characteristic absorption features that provide quantitative information on particle composition.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **CRediT** authorship contribution statement

Michael J. Lecours: Formal analysis, Writing – review & editing. Peter F Bernath: Conceptualization, Resources, Funding acquisition, Writing – original draft. Jason J Sorensen: Writing – original draft, Supervision. Chris D Boone: Formal analysis, Writing – original draft. **Ryan M Johnson:** Formal analysis, Writing – original draft. **Keith LaBelle:** Formal analysis.

# Data availability

Data will be made available on request.

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