

# **Infrared Optical Constants of Particles in the Lower Stratosphere and Upper Troposphere**

## **Project Personnel:**

PI: Margaret A. Tolbert

Co-PI: Owen B. Toon

Post-Doctoral Associate: Bhavani Rajaram

Graduate Student: David L. Glandorf

## **Progress Report for Work Performed 6-15-00 through 9-6-01 on Project #NAG5-8127**

### **I. Introduction**

There is currently a great deal of interest in the optical properties of atmospheric aerosols. This interest is generated by the uncertain role that aerosols play in the Earth's radiation balance. It is also the result of the need for various sensors to detect aerosols, or remove their interfering signals from the observations. In particular, numerous EOS instruments need the optical properties of aerosols to reduce the data properly. Current attempts to retrieve aerosol properties from EOS instruments have met with only limited success due to a lack of optical constant data obtained under conditions that are relevant to the atmosphere.

In the last year, we have focussed on two major projects relating to the optical properties of atmospheric particles. First we have made laboratory measurements of infrared optical constants of water ice. Second, we have used the currently available optical constants of different aerosol species to analyze the new solar extinction spectra of type I PSCs (obtained during the January 2000 deployment of the Arctic Solve mission) in order to determine their composition.

### **II. Results**

#### **a) Temperature-dependent optical constants of water ice in the 4000-7000 $\text{cm}^{-1}$ region.**

The optical constants of water ice have been determined in the near infrared from 4000-7000  $\text{cm}^{-1}$ . Polycrystalline ice films with thickness up to  $\sim 1.2$  mm were formed by condensing water vapor on a cold silicon substrate at temperatures of 166, 176, 186 and 196 K. The transmission of light through the ice films was measured during their growth from 0-1164  $\mu\text{m}$  over the frequency range from about 500-7000  $\text{cm}^{-1}$ . The optical constants were extracted by fitting simultaneously the calculated transmission spectra of films of varying thickness to their respective measured transmission spectra using an iterative Kramers-Kronig technique. Equations were presented to account for reflection losses at the interfaces when the sample is held in a cell. These equations were used to re-analyze the transmission spectrum of water ice (358  $\mu\text{m}$  sample at 247 K) recorded by Ockman in 1957 [1]. Our imaginary indices for water ice have been compared with those of Gosse et al. [2], Kou et al. [3], Grundy et al. [4] and Warren [5] and the new indices

from Ockman's spectrum [1]. The temperature-dependence in the imaginary index of refraction observed by us between 166 and 196 K and that between our data at 196 K and the data of Gosse et al. [2] at 250 K are compared with that predicted by the model of Grundy et al. [4]. Based on this comparison, a linear interpolation of the imaginary indices of refraction between 196 K and 250 K was proposed. We believe that the accuracy of this interpolation is better than 20 %.

This work has been published in the September 2001 issue of the journal Applied Optics. A copy of this article [6] entitled, "*Temperature-dependent optical constants of water ice in the near infrared: New results and critical review of the available measurements*" has been enclosed.

#### **b) Analysis of PSC spectra from the January deployment of the Arctic SOLVE mission.**

Stratospheric ozone loss at both poles has focused attention towards understanding the properties of polar stratospheric clouds (PSCs). While Type II PSCs are known to be water ice, the compositions of Type I PSCs are not well understood. Possible compositions include crystalline nitric acid trihydrate (NAT), nitric acid dihydrate (NAD), supercooled binary solutions of  $\text{HNO}_3/\text{H}_2\text{O}$ , and supercooled ternary solutions of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  (STS).

High resolution FTIR occultation spectra collected on the DC-8 on January 27, 2000 during the SOLVE mission were analyzed to identify Type I PSCs. The spectra cover the 2 - 13 micrometer region with solar zenith angles between 78 and 92 degrees. Spectra were processed and analyzed from two flights - one in which PSCs are thought not to exist, and one in which PSCs were present. The ratio of the cloudy portions to the clear portions were examined in newly defined spectral windows between regions of atmospheric gas absorptions. The resulting extinction data were fit with spectra calculated from NAT optical constants using a Mie scattering code, providing direct field evidence for non-lee wave NAT PSCs. However, the best fit resulted from a mixed phase cloud containing mostly NAT particles mixed with smaller diameter supercooled  $\text{HNO}_3/\text{H}_2\text{O}$  particles.

This work has been submitted for publication in a special SOLVE-THESEO issue of the Journal of Geophysical Research under the title "*Identification of nitric acid trihydrate (NAT) in the Arctic stratosphere using infrared extinction measurements*". The submitted version of this article has been enclosed.

### **III. Future Work**

1. Steve Massie, the chair of the aerosol working group for AURA, has requested that we reexamine the infrared optical constants of sulfuric acid. Currently, there are values determined by three different groups [7-9], each using a different technique, and differing significantly from one another. We will attempt to determine the cause for these differences and make new measurements as needed.

2. We will work on improving the scheme for extracting PSC composition from the solar extinction data, possibly by accounting for and thus removing the gas phase features.

3. Other lab measurements:

There is a significant amount of thermal radiation in the earth's atmosphere beyond a wavelength of 20  $\mu\text{m}$ , but few data are available on the optical constants of water ice in the far IR. Further, the available data are in poor agreement with each other. Hence, temperature dependent optical constants of water ice will be determined in this wavelength region.

Optical constants of supercooled binary solutions of  $\text{HNO}_3/\text{H}_2\text{O}$ , ternary solutions of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  (STS), and of ammoniated sulfates covering the entire range of compositions and temperatures that prevail in the lower stratosphere and upper troposphere also need to be measured in the laboratory. An interpolation scheme could then be developed to provide optical constants for compositions that may not have been measured.

## References

1. N. Ockman, "The infrared spectra and raman-spectra of ice", *Phil. Mag. Supplement*, **7**, 199-220 (1858).
2. S. Gosse, D. Labrie and P. Chylek, *Refractive indices of ice in the 1.4-7.8  $\mu\text{m}$  spectral range*, *Appl. Opt.*, **34**, 6582-6586, (1995).
3. L. Kou, D. Labrie and P. Chylek, *Refractive indices of water and ice in the 0.65-2.5  $\mu\text{m}$  spectral range*, *Appl. Opt.*, **32**, 3531-3540, (1993).
4. W. M. Grundy and B. Schmitt, *The temperature-dependent near-infrared absorption spectrum of hexagonal  $\text{H}_2\text{O}$  ice*, *J. Geophys. Res.*, **103**, 25809-25822, (1998).
5. S. G. Warren, *Optical constants of ice from the ultraviolet to the microwave*, *Appl. Opt.* **25**, 1206-1225, (1984).
6. Bhavani Rajaram, David L. Glandorf, Daniel B. Curtis, Margaret A. Tolbert, Owen B. Toon and Nathan Ockman, *Temperature-dependent optical constants of water ice in the near infrared: New results and critical review of the available measurements*, *Appl. Opt.*, **40**, 4449-4462, (2001).
7. Robert T. Tisdale, David L. Glandorf, Margaret A. Tolbert and Owen B. Toon, *Infrared optical constants of low-temperature  $\text{H}_2\text{SO}_4$  solutions representative of stratospheric sulfate aerosols*, *J. Geophys. Res.* **103**, 25353-25370, (1998).
8. R. F. Niedziela, M. L. Norman, R. E. Miller and D. R. Worsnop, *Temperature- and composition-dependent infrared optical constants for sulfuric acid*, *Geophys. Res. Lett.* **25**, 4477-4480, (1998).
9. U. M. Biermann, B. P. Luo and T. Peter, *Absorption spectra and optical constants of binary and ternary solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  in the mid-infrared at atmospheric temperatures*, *J. Phys. Chem.*, **104A**, 783-793, (2000).