Complex refractive indices in the infrared of nitric acid trihydrate aerosols

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Abstract. The refractive indices of nitric acid trihydrate (NAT) have been determined from the infrared spectra of laboratory generated aerosols. The aerosols are formed via homogeneous nucleation in a flow cell with separate regions for nucleation and observation, allowing for independent control of the temperature conditions in these regions. A spectrum of small, non-scattering particles is recorded to determine the frequency dependent imaginary refractive index, within a scaling factor. A subtractive Kramers-Kronig routine is then used to calculate the real index. The scaling factor for the imaginary indices is determined by fitting a spectrum associated with larger, scattering particles, which depends on both the real and imaginary portions of the refractive indices. The complex refractive indices of NAT are reported over the range 700 cm^{-1} to 4000 cm^{-1}. While in good qualitative agreement with previously reported results, there are significant quantitative differences which are discussed.

Introduction

It is now clear that heterogeneous chemistry occurring on Polar Stratospheric Cloud (PSC) particles is responsible for setting up the necessary conditions in the polar stratosphere for massive ozone depletion [*Solomon*, 1988; *Crutzen and Arnold*, 1986; *Poole and McCormick*, 1988]. As a result, a great deal of attention has recently been directed towards the characterization of these particles, both *in situ* and in the laboratory. Much of the attention has focused on nitric acid trihydrate (NAT), which is thought to be the most stable hydrate phase under stratospheric conditions. Direct observations of these clouds in the infrared region of the spectrum has proven difficult to simulate [*Kinne et al.*, 1989], and although the implications of this are still not clear, there is obvious need for detailed studies of the optical constants of NAT and related species. Recently, there have been several laboratory studies of the refractive indices for both the crystalline and amorphous hydrates of nitric acid. These thin film measurements provided both the real refractive index at 632 nm [*Berland et al.*, 1994; *Middlebrook et al.*, 1994] and the complex refractive indices in the mid-infrared region of the spectrum [*Toon et al.*, 1994].

In this study, we use a newly developed method for deriving optical properties directly from the infrared extinction spectra of aerosols to determine the wavelength dependent complex refractive indices of α-NAT. The advantages of this technique as discussed by *Clapp et al.* [1995], lie primarily in the fact that the aerosols are unsupported, and so unlike thin films, their formation is free of the interference of a substrate. Although in qualitative agreement with the previously published work, the present data show some quantitative differences that are discussed below.

Experiment

The nitric acid hydrate aerosols of interest were generated in two low temperature flow cells, described in detail elsewhere [*Dunder et al.*, 1993; *Clapp et al.*, 1995]. As the gases of interest, which are entrained in a buffer gas of helium or nitrogen, flow into the cooled cell, the vapor becomes supersaturated and particles nucleate and grow by condensation. In the present experiments, a mixture of approximately 1% combined nitric acid and water in nitrogen was formed by bubbling the nitrogen gas through a solution of variable composition. The best NAT spectra were obtained when the gas phase water:nitric acid ratio was approximately 5:1, as determined by high resolution infrared spectroscopy of the flowing vapors at room temperature. Two mass flow controllers (MKS) were used to regulate the flow of the buffer gas into the cell and the pumping speed on the exit from the cell. As discussed in detail elsewhere [*Clapp et al.*, 1995], the size distribution of the aerosols formed in the cell is determined by the temperature in the region where nucleation occurs. The small cell [*Dunder et al.*, 1993] has the advantage that it can be cooled to very low temperatures (80 K), while the larger flow cell allows us to have independent control of the temperatures in the nucleation and observation regions [*Clapp et al.*, 1995]. In both cases, the temperatures of the various parts of the cells were controlled to ± 1 K. Infrared spectra were recorded using a Bomem DA3.02 FT-IR at a resolution of 2 cm^{-1} over the range of 700 cm^{-1} to 4000 cm^{-1}.

Calculations

A detailed description of the method for determining the optical constants from the spectra of aerosols, as well as a comparison with more traditional bulk methods, is given elsewhere for the case of water ice [*Clapp et al.*, 1995]. In the present case, the first step is to record the

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spectrum of small NAT aerosols ($r_{med} \gg 0.1$ μm), which do not scatter light of wavelengths greater than 2 μm and, thus to first order, are insensitive to the real index of refraction. This spectrum provides us with an estimate of the frequency dependent imaginary indices since the absorbance for a non-scattering aerosol is directly proportional to the imaginary index (k). Since the optical "thickness" of our aerosol sample is unknown, this procedure only gives the relative indices, making it necessary to independently determine the absolute scaling factor. This is done with the aid of spectra obtained for NAT particles with larger mean size, which both absorb and scatter the light. Using a subtractive Kramers-Kronig transform, real indices (n) can be determined from the originally unscaled imaginary indices. The large particle spectrum can then be modeled using these indices in conjunction with Mie theory. If the original scaling is incorrect, the relative contribution to the large particle spectrum from absorption and scattering will also be in error. Thus we can use an iterative fitting procedure, adjusting the two parameters defining the lognormal size distribution (r_{med} and σ) of the particles and the scaling factor, to determine a self consistent set of optical constants. The method is very stable and gives rise to a unique value for the scaling factor as displayed in the case of water ice and shall also be shown in the present study.

Although the absorbance at any frequency is directly proportional to the imaginary refractive index, the proportionality constant is a weak function of the real index at every frequency. As a result, the original determination of the imaginary refractive index from the small particle spectrum involves an approximation, particularly in regions of strong absorption. This can be accounted for, however, by using the refractive indices determined from the first set of calculations to fit the original small particle spectrum, making adjustments to the imaginary indices in the regions of strong absorption until the calculation agrees with experiment. If necessary, the entire procedure can then be repeated until an overall self consistent set of refractive indices are obtained.

In the above procedure we used the subtractive Kramers-Kronig FORTRAN code written by Palmer et al. [1981] to calculate the complex refractive indices. The anchor point for this program was chosen to be 4000 cm⁻¹, a position outside of the absorption region, where n is independent of the scaling of k. At this frequency we used the published value for n (1.41) from Toon et al. [1994]. The aerosol spectra were modeled using the Mie theory FORTRAN program published by Bohren and Huffman [1983], which has been modified to average over a lognormal distribution of particle sizes [Kerker, 1969]. While Mie theory is strictly accurate only for spherical particles, for small values of the size parameter, (the ratio of the circumference of the particle to the wavelength) the spectra of non-spherical particles, and especially size dispersions of these particles, are modeled well by Mie theory [Holland and Draper, 1967; Perry et al., 1978]. Particles in this study exhibited a size parameter of less than 2, even for the largest particles, which validates the use of the Mie theory calculations.

Results

Figure 1 shows a small particle NAT spectrum obtained in the small cell at 150 K. This spectrum is quali-
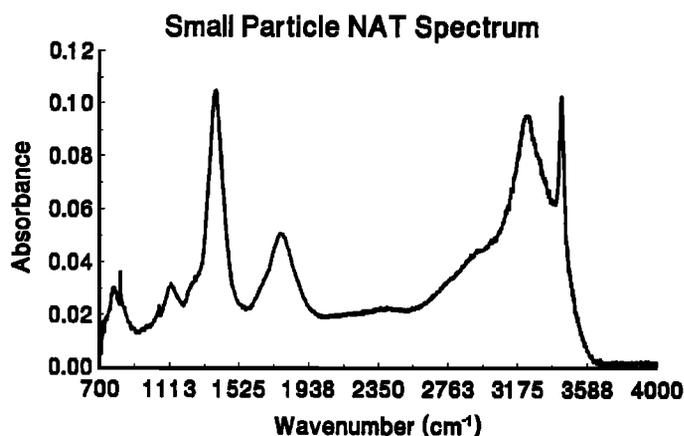
Figure 1. The infrared spectrum of a NAT aerosol composed of small particles which do not scatter light. This spectrum was used to construct the initial k spectrum used in the iterative procedure described in the text.

tatively similar to previously published spectra of α-NAT [Koehler et al., 1992; Barton et al., 1993; Ritzhaupt and Devlin, 1991; Tolbert et al., 1992]. Nevertheless, there are several quantitative differences in the relative intensities of the dominant absorption features of these spectra as compared to the films of the Tolbert group [Koehler et al., 1992; Tolbert et al., 1992] which will be discussed below. The primary difference is a shift in the peak position of the v_3 nitrate band at 1414 cm⁻¹ in comparison with the thin film studies of both Ritzhaupt and Devlin [1991] and Tolbert et al. [1992], which show this peak at about 1380 cm⁻¹. Nevertheless, the present spectrum agrees very well with the NAT aerosol spectra of Barton et al. [1993], both for the nitrate band frequency and in the relative intensities. The agreement in the relative intensities of the major absorptions between the present data and the bulk spectra of Ritzhaupt and Devlin [1991] suggests that the observed differences between the aerosol spectra and the thin film data of Tolbert et al. [1992] are not due to differences between the particles and bulk. Rather these differences are most likely due to differences in the structure of aerosols from that of the films published by Tolbert, either in the degree of crystallinity or in the crystal structure itself.

As noted above, the v_3 nitrate band of the aerosol at 1414 cm⁻¹ is shifted somewhat from the thin film studies. It is possible that a portion of the shift in the frequency is due to a temperature dependence of this nitrate band as evidenced by the fact that Tolbert et al. [1992] report a peak frequency of 1380 cm⁻¹ for this band measured at 183 K while Ritzhaupt and Devlin [1991] give a peak frequency of 1393 cm⁻¹ at 50 K. It is important to note however, that a Mie calculation of the aerosol spectrum based upon the Toon et al. [1994] refractive index data reproduces the peak position observed for NAT aerosols at 175 K, as observed in Figure 2. The fact that Mie theory predicts this peak shift clearly shows that it is a result of the finite size of the aerosol particles relative to the bulk, and that a temperature dependence cannot be used solely to explain it. In fact, this shift can be attributed to the strong dispersion in this region of the spectrum, which changes the proportionality between the imaginary index and the absorbance [Bohren and Huffman. 1983] as discussed in the Calculations section of this paper. To account for this shift, it was
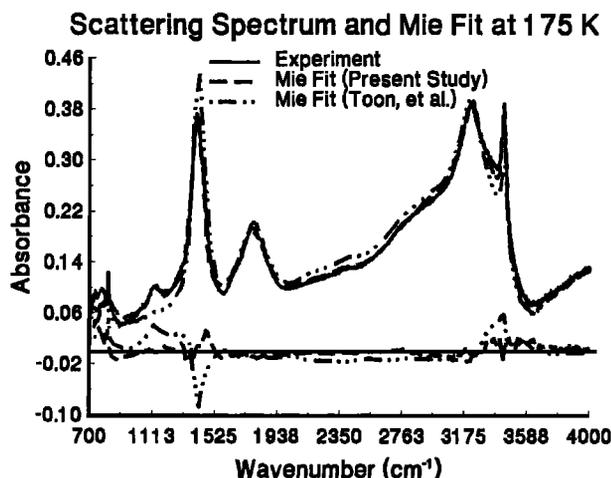
Figure 2. Fits to a scattering NAT aerosol spectrum using the refractive index data of *Toon et al.* [1994] and the data set determined in the present study. The residuals are shown in the lower panel of the figure.

necessary to translate the nitrate v_3 band in the aerosol k spectrum 32 cm^{-1} to the red of its position in the aerosol spectrum. Using the corrected data set for the Mie calculations not only gave results which reproduced the aerosol data quantitatively, but also resulted in a center frequency for this band in excellent agreement with the results of *Toon et al.* [1994].

Figure 2 shows a typical spectrum of a NAT aerosol with larger mean size. The rising baseline at the high frequency end of the spectrum is the result of non-resonant scattering. It is interesting to note that while the spectrum in Figure 1 appears to have resulted from "pure" NAT aerosols, i.e. no NAD absorptions are apparent, larger particles showed, under essentially all conditions, some slight contamination from the dihydrate (NAD). Fortunately, there are several very sharp and unique features attributable only to the dihydrate that can be used to quantify its contribution to the large particle spectrum [*Barton et al.*,1993; *Wooldridge et al.*, 1995]. Under the conditions used for recording the spectrum shown in Figure 2 the dihydrate contributed approximately 5% to the absorbance, while no NAD features were observable in the aerosol spectrum in Figure 1. We used a template spectrum of dihydrate aerosols from work to be reported elsewhere to remove the dihydrate component from the scattering spectrum. This subtraction has already been carried out for the spectrum shown in Figure 2. Also shown in the figure are two fits to this spectrum, the first based upon the refractive indices of *Toon et al.* [1994] and the second using the data set determined in the present study. It is clear from this that the *Toon et al.* data reproduces the peak positions quite well, while there are significant differences in the relative intensities of the three main peaks. The fit obtained from the present data set is clearly much better throughout the spectral range. The quality of the two fits can best be compared through their normalized residuals, namely 5.46 X 10^{-4} for the *Toon et al.* data set and 9.29 X 10^{-5} for the present work. Nevertheless, the two sets of data are clearly in rather good quantitative agreement, giving further confirmation that the present method for determining refractive indices is valid. The size distri-

bution parameters for the fit using the current data were $r_{med}= 0.17$ µm and $\sigma = 0.58$. While these sizes are not necessarily characteristic of Type II PSC's, the refractive index data determined from these measurements should be valuable in modeling spectra corresponding to aerosols of more realistic sizes.

The uniqueness of the present method for determining refractive indices has been checked in several ways. The first test is simply to start the fitting with very different initial values for the median radius, standard deviation, and scaling factor in the iterative procedure. In all cases, the parameters converged to the same values regardless of their starting values. A more significant test is to use different scattering spectra in the fitting procedure. The stability of the method is illustrated by the fact that the resulting median radius, r_{med}, and the standard deviation, σ, (using a lognormal distribution, see *Clapp et al.* [1995]) are different for each spectrum, in a way that was characteristic of the relevant size distribution, while the resulting k scaling factor was always the same within ± 3%. This coupled with a small local uncertainty for the absorption coefficients, places the overall accuracy within ± 5%.

Figure 3 shows the refractive indices of the present study compared to those of *Toon et al.* [1994]. As expected from the above fits, the two data sets are quite similar throughout the spectrum. The agreement is especially good above 1500 cm^{-1}, with the exception of the discrepancies in the relative intensities of the two high frequency peaks. The differences at lower frequencies are clearly more pronounced. In particular, the intensity of the 1380 cm^{-1} peak is considerably larger in the *Toon et al.* data set.

Additional differences are present between the aerosol spectra presented here and the films reported by *Toon et al.* [1994] and *Tolbert et al.* [1992]. For instance, the weak band that we observe at 1120 cm^{-1} is completely missing from the *Toon et al.* [1994] data set, yet it is clearly discernible here and in the spectra published by Devlin [*Barton et al.*, 1993; *Ritzhaupt and Devlin*, 1991]. There are also two very sharp features in the data set determined here at 820 cm^{-1} and 1050 cm^{-1} that are not present in the *Toon et al.* data set. While the NAT film spectra of the Devlin group appear to be contaminated with either NAD or an amorphous hydrate, they also re-
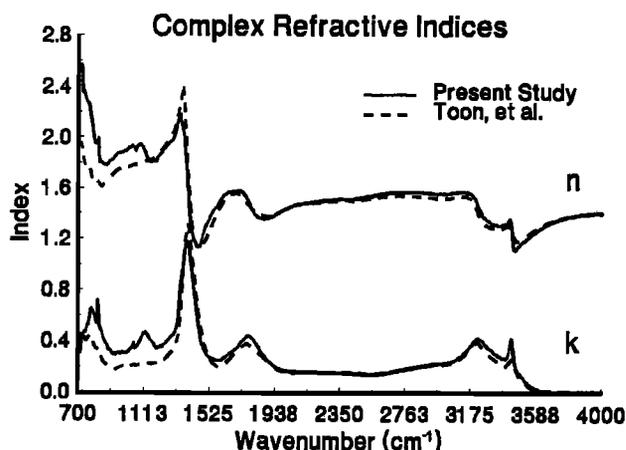
Figure 3. A comparison of the refractive index data sets of *Toon et al.* [1994] and that obtained in the present study.

port peaks at 820 cm^{-1} and 1120 cm^{-1}. We feel that these three peaks present in these aerosol spectra are NAT features since they are prevalent in the pure NAT spectrum but not in the pure NAD spectrum [Barton et al., 1993; Ritzhaupt and Devlin, 1991]. Therefore, the presence of these peaks further supports the idea that there are differences in the crystal structure of the thin films of Tolbert et al. [1992] and the aerosols studied here. In addition, these peaks are not attributable to particle absorptions for the rason that, with the exception of the peak at 1050 cm^{-1}, they are present in the NAT films published and assigned by Devlin. While our aerosols were nucleated around 155 K, the Tolbert films were deposited at warmer temperatures, which makes it tempting to assign this difference to an effect of the formation temperature. This seems unlikely given the fact that NAD aerosol spectra from our laboratory, as well as from Barton et al. [1994], display similar differences from the bulk films, even when nucleated near 180 K.

A complete listing of the refractive indices determined here are available from the authors.

Conclusion

Using a recently developed technique for determining the complex refractive indices of crystalline particles, we have derived the optical constants for a-NAT. The results derived here are in qualitative agreement with the recently published data of Toon et al. [1994]. Nevertheless, there are some important quantitative differences in the two data sets, particularly in the region of the v_3 nitrate band. We observe that the infrared spectrum of the aerosols are somewhat different from that of the bulk due to dispersion effects in the regions of strong absorptions. The resulting shift in the band positions is accounted for by both the present data set, which was constructed to do so, and the data set of Toon et al. [1994]. Given that the intensities of the various bands in these nitric acid hydrates are important in modeling spectroscopic studies of PSC's, the differences observed here should be of considerable practical importance.

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