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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A quantitative test of infrared optical constants for supercooled sulphuric and nitric acid droplet aerosols" *by* R. Wagner et al.

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General comments

This paper reports the results of a careful study whose aim is to evaluate the quality of optical constant data sets for sulfuric acid and nitric acid systems that are currently available in the literature. Recently, several groups have published complex refractive index data sets for these compounds, all of which were obtained using a variety of laboratory techniques under conditions relevant to the upper troposphere and lower stratosphere. Aside from inter-comparisons between the individual data sets by their respective authors, to wit there has not been an independent laboratory assessment of which set, or sets, of optical constants should be used in the analysis of aerosols

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containing these important chemical species. Such an assessment is of critical importance to a number of remote sensing applications whose principal job is to accurately determine the composition, size, and phase of aerosols containing sulfuric and nitric acid.

The authors carried out their evaluation by generating binary sulfuric acid/water and binary nitric acid/water aerosols, injecting them into a large, temperature-controlled chamber, and then recording the mid-IR extinction spectra of the particles. The spectra were then subjected to a least-squares Mie analysis using published optical constants to determine their composition and mass density which in turn were compared to independent measurements of the same quantities. The authors find relatively good agreement in the results of the optical analyses using the different refractive index data sets as far as the replication of aerosol composition and mass density, but do note a few discrepancies in the spectral structure of the optical constant data sets, particularly in wavelength regions of importance to those involved in remote sensing measurements. The authors do a somewhat thorough job at explaining some of the reasons for these spectral differences and provide several sample calculations. Their results should be of help to those attempting to interpret extinction measurements of actual atmospheric aerosols.

Specific comments

The authors have responded to a previous comment regarding the accuracy of the sulfate and nitrate concentrations within their aerosols. The explanation seems reasonable but should be incorporated within the text of the paper. For example, lines 8 and 9 on page 2225 in the paper's present form can give the reader an unnecessarily dismal view of the ability to measure nitric acid concentrations.

The authors discuss the fact that the particle size distribution parameters (i.e., CMD and (sigma)g) are not necessarily unique for small aerosols that are in the Rayleigh limit of Mie scattering theory, and as a result, they use retrieved volume densities since

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they are "... the least ambiguous." (line 10, page 2227) It is not clear from the text what this means. Perhaps the authors wish to make comparisons on a basis that is conceptually easier to grasp and certainly more applicable to atmospheric applications than the log-normal parameters! If so, the discussion should be framed in this manner.

Continuing with the topic above, the authors do not give any indication of just how different N, CMD, and (sigma)g can be for their small particle spectra. Based on experience, the uniqueness issue is probably more important for their nitric acid aerosols since they show much less scatter (Figure 4) than do the sulfuric acid aerosols (Figure 3). In previous work on nitric acid hydrate crystallization kinetics, Disselkamp, et al. (J. Phys. Chem., 100(21), 9127, (1996)) found that Mie fits to one of their small particle spectra yielded both monodisperse (CMD = 0.51 um, (sigma)g = 1.001, N = 8.7 x 10ˆ5 cmˆ-3) and polydisperse (CMD = 0.12 um, (sigma)g = 2.0, N = 5.7 x 10ˆ5 cmˆ-3) results with identical root-mean-squared deviations from the observed spectrum. While there is only a factor of 4.25 difference in the diameters in this example, there is a factor of 13.5 difference in the volume densities using the current authors' Equation (3). Given that multiple sets of N, CMD, and (sigma)g can produce the same least-squares results, how did the authors choose which set to use in comparison to the independently-measured DMA/CNC results?

The authors provide a nice commentary on the role of Kramers-Kronig truncation errors in the overall discrepancies between the sulfuric acid optical constant data sets (starting on page 2231). They review the concerns of Myhre, et al. with regard to the effect of neglecting the far infrared. It should be pointed out however that Niedziela, et al., while only reporting optical constants between 825 cmˆ-1 and 4700 cmˆ-1, did take into consideration activity towards the far infrared by including imaginary index data from Palmer and Williams (Appl. Opt., 14, 208, (1975)) in their Kramers-Kronig calculations.

Technical Corrections

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Page 2224, Line 25: Place a comma after the word temperatures.

Page 2227, Line 4: Replace get with are.

Page 2227, Line 7: "... independent of their sizes." seems redundant.

Page 2228, Line 3: The text between the colons is unnecessary. Some rewording will be necessary.

Page 2229, Line 4/5: Italicize n and k.

Page 2232, Line 7: Italicize n and k.

Page 2234, Line 18: Eliminate comma after the word particles.

Page 2239, Line 20: For consistency, use (sigma)g instead of (sigma).

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2219, 2003.