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

R. Wagner et al.

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First of all, we would like to thank R. Niedziela for his detailed comments to our paper.

Following the referee's suggestion, we will incorporate our previous comment regarding the accuracy of the sulphate and nitrate mass concentrations obtained from filter analyses within the text of our paper. This section of the paper (page 2224, line 17 et sqq.) will be changed as follows:

"Total aerosol sulphate and nitrate mass concentrations were determined by ion chromatographic analysis of nylon filter samples (type Nylasorb®, GelmanSciences). Unexposed filters were analysed in the same manner as loaded filters for background correction. The filter holders were located outside the cold housing. Sulphuric acid was collected on a Nylon filter through a stainless steel tube of 1.5 m length and 4

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Discussion Paper

mm inner diameter. Less than 1% sulphuric acid aerosol is lost in the cold sampling line for this configuration. Sulphuric acid is partially lost by evaporation when sampled on Teflon filters at room temperature under very dry conditions. However, this breakthrough effect does not occur on Nylon membrane filters, a was shown by using Nylon back-up filters. Since HNO_3 adsorbs on stainless steel, a PFA Teflon tube maintained at 293 K was used to sample this compound. Neuman et al. (1999) reported that significant adsorption of nitric acid on Teflon occurs only above 60% relative humidity at this temperature. Under our conditions (relative humidity $<$ 1% at 293 K) nitric acid is quantitatively passed to the Nylon filter. We could show by detecting HNO_3 with a chemical ionisation mass spectrometer that significant adsorptive losses occurred only when the Teflon tube temperature drops below 240 K. The Nylon filters collect nitric acid vapour from particles evaporating in the sampling tube, residual particles, and interstitial HNO_3 vapour in equilibrium with the particles from the aerosol vessel. However, due to the low temperatures interstitial HNO_3 vapour represents a very small fraction ($\sim$ 1%) of the predominantly particle-bound HNO_3 content of the chamber. To correct for breakthrough effects, HNO_3 was collected on two Nylon filters in series. Goldan et al. (1983) reported no measurable breakthrough of HNO_3 for filter loadings up to 2.2 μg/cm^2. However, in our experiments up to 10% nitric acid was recovered on the back-up filters at loadings up to 3 μg/cm^2. Thus, the total loss was of the order of 1% in our experiments. Including the uncertainty of the ion chromatographic analysis we estimate the relative uncertainty in the sulphuric and nitric acid mass concentration to be 10% or better, as confirmed by a good agreement between sulphate volume concentrations derived from filter analyses and from size distribution measurements in recent AIDA experiments (Fig. 4 in Möhler et al., 2003)."

In the following, we will address the "uniqueness issue", i.e. the fact that the particle size distribution parameters are not necessarily unique for particle radii being small in comparison with the incident wavelength. Let us give a numerical example (referring to Case 1 of our study, 80 wt% H_2SO_4) to illustrate what we mean by our statement that "... the retrieved volume densities are least ambiguous" (page 2227, line 10). We

choose two different size distributions, 1) N_1 = 11580 cm^{-3}, $\sigma_{g,1}$ = 1.9929, CMD_1 = 0.2257 μm and 2) N_2 = 3760 cm^{-3}, $\sigma_{g,2}$ = 1.6889, CMD_2 = 0.4419 μm, which differ by a factor of two in the count median diameter and a factor of three in the particle number density. When using these size distributions as input for the Mie calculations with the optical constants for 80 wt% H_2SO_4 (240 K) from Niedziela et al. (1999), our measured spectrum is in both cases nicely reproduced by the Mie calculation with only slightly different summed squared deviations. The relative difference between the two calculated extinction spectra is within $\pm$ 5% over the complete wavenumber range from 4700 to 900 cm^{-1}, and even within $\pm$ 2% in the wavenumber regime of the strong OH and sulphate extinction bands. Given that the assumed accuracy of the optical constants n and k is in the order of $\pm$ 2-3% (Niedziela et al., 1999; Myhre et al., 2003), both size distributions represent an equivalent solution of the retrieval problem. But the two different combinations of the size distribution parameters lead to nearly the same volume density V of the aerosol (V_1 = 592 μm^3/cm^3 and V_2 = 585 μm^3/cm^3), i.e. volume densities can be retrieved unambiguously from our measured FTIR spectra. So there is no problem to choose which set of parameters is used in comparison with the independently measured aerosol mass concentrations with the filter sampling technique because the different sets of size distribution parameters resulting in identical summed squared minima correspond to almost the same aerosol volume density (see also Echle et al., 1998). As mentioned by the referee, the uniqueness issue will be even more important in the nitric acid aerosol systems since these spectra show much less light scattering than the spectra of the sulphuric acid droplets. Hence the range of different size distribution parameters leading to identical summed squared minima will be larger (extending from monodisperse to polydisperse aerosol size distributions, σ_g = 1 - 2).

Regarding the two different size distributions quoted by Disselkamp et al. (1996), we cannot understand that both result in identical root-mean-squared deviations from the measured spectrum if there is a factor of 13.5 difference in the aerosol volume densities. This will also lead to completely different aerosol extinction coefficients when

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using the size distribution parameters in a Mie calculation. Hence we strongly suppose that some of the published values are mistaken.

To clarify the "uniqueness issue" in our paper, page 2227, line 7 et sqq. will be changed as follows:

"Therefore, since the radii of the supercooled H_2SO_4/H_2O and HNO_3/H_2O droplets studied in this work were in the sub-μm size range, well below the wavelength range of the FTIR spectra, we can obtain different sets of N, σ_g, and *CMD* which lead to almost the same summed squared minima. These sets of size distribution parameters, however, correspond to the identical aerosol volume density V. Consequently, only volume densities can be retrieved unambiguously from our measured FTIR spectra."

We will incorporate in our text that Niedziela et al. (1999) have included the room-temperature optical constants from Palmer and Williams (1975) in the wavenumber range from 825 to 400 cm^{-1} in the Kramers-Kronig integration to derive sets of optical constants n for the sulphuric acid aerosols. Page 2231, line 21 et sqq. will be changed as follows:

"Therefore, the authors have argued that the observable discrepancies between their data set of optical constants with the Niedziela et al. (1999) and Biermann et al. (2000) sets are due to the fact, that (a) Niedziela et al. (1999) only investigated the 4700 - 825 cm^{-1} region (but including the room-temperature optical constants of Palmer and Williams (1975) in the 825 - 400 cm^{-1} region), and that (b) Biermann et al. (2000) have assumed a monotonous decrease in the far infrared absorption in contrast with the measurements of Myhre et al. (2003) which even showed an increase of reflectance in this spectral region."

We will adopt all technical corrections in the final version of our paper except from page 2227, line 7: For clarification, we would like to keep up the statement "...independent of their sizes." Page 2228, line 3 et sqq. will be rewritten as follows: "The results of the retrieval procedure are presented in the following order: Cases 1, 2, and 3 refer to

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the experiments with supercooled H_2SO_4/H_2O solution droplets, cases 4 and 5 to the HNO_3/H_2O system."

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