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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Probing ice clouds by broadband mid-infrared extinction spectroscopy: case studies from ice nucleation experiments in the AIDA aerosol and cloud chamber" *by* R. Wagner et al.

R. Wagner et al.

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The authors would like to thank referee 2 for his thoughtful annotations. Please find below our answers to the individual comments.

1) Some figures are too small.

Yes, we agree - but also think that this is a specific problem of the PDF file generated for the ACPD publication where essentially two manuscript pages are merged into a single A4 page. We will pay attention that in the final PDF file for the ACP publication especially Figures 5, 8, and 13 (which are definitely too small in the current PDF file)

will be embedded as double column graphics in the manuscript text. This will make them much easier to read. Also, Figures 2, 11, 14, and 15 can be scaled up to the maximum page width in the final PDF file. As suggested by your comments below, further improvements will also be made to Figures 12 and 15.

2) Dependence of the ice particle shapes on variations in temperature, pressure, and ice saturation ratio. Did you attempt to model the particle shape and size based on your experimental conditions?

This issue has also been addressed by referee 1; we would therefore like to refer to our reply to referee 1. We think that it will also appropriately answer your comments/questions concerning this topic. In summary, we think that the detailed investigation of the dependence of the ice crystal habits on temperature and ice saturation ratio has to be postponed to future chamber studies, where more accurate information about the ice crystal shape might be available from additional instruments like the SID2 device. Numerical simulations of the ice nucleation experiments in the AIDA chamber of course complement our experimental work; see e.g. the paper by Haag et al. (2003), addressing the homogeneous freezing of supercooled H2SO4/H2O solution droplets (already cited in the manuscript). But modelling efforts specifically relating to the shape of the nucleated ice crystals have not been performed so far.

3) Hexagonal versus cylindrical particle shape in the T-matrix calculations.

We here refer to the work by Lee et al. (2003).

Lee, Y. K., Yang, P., Mishchenko, M. I., Baum, B. A., Hu, Y. X., Huang, H. L., Wiscombe, W. J., and Baran, A. J., Use of circular cylinders as surrogates for hexagonal pristine ice crystals in scattering calculations at infrared wavelengths, Appl. Opt., 42, 2653-2664, 2003.

The authors show calculations of the optical properties of hexagonal ice columns at infrared wavelengths using the finite-difference time-domain method and compare them

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to results of T-matrix computations for various equivalent circular cylinders. Figure 3 of their paper shows a comparison of the computed extinction efficiencies at a weakly-absorbing infrared wavelength (8.5 μm, k = 0.037) and Figure 6 the corresponding results for a strongly absorbing wavelength (11.0 μm, k = 0.3). The relative errors between the hexagon and cylinder results are clearly below 10% for the complete particle size range. In particular, the interference structure in the extinction plot at 8.5 μm for ice hexagons is well reproduced by the calculations for ice cylinders. Based on these results and our own computations (some of them shown in Fig. 5 of the manuscript), we considered it justified to employ the simpler cylindrical shape in our calculations. In the bottom right panel of Fig. 5 we show calculations of the extinction efficiencies at 1226.5 cm-1 (8.15 μm) for ice cylinders of different aspect ratios, revealing pronounced differences (> 10% relative error) in the extinction efficiencies in the regime of the first interference maximum. The optical constants for ice at 8.15 and 8.5 μm are very similar. So we can directly compare this panel with Figure 3 in Lee et al. (2003). Especially in the regime of the interference structure, a changing aspect ratio of the ice crystals thus leads to a much stronger variation in the extinction efficiencies than a change from hexagonal to cylindrical shape.

We have only briefly mentioned the Lee et al. (2003) study in our manuscript (page 5728, line 7), and propose to add a further reference to this work in our revised manuscript. We want to add the following brief paragraph to the discussion of our T-matrix calculations on page 5733, line 11:

“Note that, particularly within the regime of the interference structure, the changes in the extinction efficiencies for cylindrical ice crystals due to varying aspect ratios are much larger than the relative errors introduced by approximating hexagonal ice crystals with equivalent circular cylinders (Lee et al., 2003). Lee et al. (2003) have compared the extinction efficiencies for hexagonal columns and various equivalent circular cylinders, both at a strongly absorbing (11.0 μm, 909 cm-1, k = 0.3) and a weakly absorbing infrared wavelength (8.5 μm, 1176 cm-1, k = 0.04); see Figs. 3 and 6 in their paper. The

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relative error in Qext when approximating the ice hexagons with e.g. equivalent volume circular cylinders of the same aspect ratio as the hexagonal columns was clearly below 10 % for the complete considered particle size range. In particular, the habitus of the interference structure in the Qext plot at the weakly absorbing 8.5 μm wavelength for ice hexagons was also accurately reproduced by the calculations for equivalent circular ice cylinders. We therefore consider it justified to have employed the simpler circular cylinder geometry in our calculations."

4) Formation of crystalline sulphuric acid hydrates in the homogeneous freezing experiments with supercooled H2SO4/H2O solution droplets?

First of all, no - we have never seen any evidence or indication for the formation of a crystalline hydrated form of sulphuric acid like SAT. The homogeneous freezing experiments, covering the temperature range from 235 to 195 K, are described in detail in the two papers by Möhler et al. (2003) (experimental results) and Haag et al. (2003) (modelling results) (already cited in the manuscript). The initial aerosol composition of the sulphuric acid solution droplets ranged from about 32 wt% H2SO4 at 235 K to about 38 wt% H2SO4 at 195 K, following the (metastable) coexistence line of the liquid H2SO4/H2O solutions with ice in the phase diagram, according to the model of Carslaw et al. (1995).

Carslaw, K. S., Clegg, S. L., and Brimblecombe, P., A Thermodynamic Model of the System HCl-HNO3-H2SO4-H2O, Including Solubilities of HBr, from < 200 to 328 K, J. Phys. Chem., 99, 11557-11574, 1995.

This applies because the water vapour partial pressure inside the chamber (and thus the aerosol composition) is determined by the temperature of the ice-coated chamber walls. The accuracy of the Carslaw model was tested in a former AIDA study by comparing the model-calculated compositions of the H2SO4/H2O solution droplets with independent measurements of the aerosol composition with the ACMS Aerosol Composition Mass Spectrometer (Zink et al., 2002). Within this study, the sulphuric acid

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droplets were observed to remain liquid over long time scales of several days under conditions of strong supercooling with respect to solid hydrates like SAT, indicating that there is no sulphuric acid hydrate formation above the ice frost point.

Zink, P., Knopf, D. A., Schreiner, J., Mauersberger, K., Möhler, O., Saathoff, H., Seifert, M., Tiede, R., and Schurath, U., Cryo-chamber simulation of stratospheric H2SO4/H2O particles: Composition analysis and model comparison, Geophys. Res. Lett., 29, 46-49, 2002.

One might speculate that during a freezing experiment the nucleated ice crystals could offer a surface to nucleate e.g. SAT. But there are several indications that this did not happen in our experiments, based on the assumption that eventually generated SAT particles should “survive” a cooling cycle due to their relatively high melting point, i.e., remain present at the end of an AIDA expansion after all ice crystals have completely evaporated when Sice finally dropped below 1; see e.g. Figure 6 in Möhler et al. (2003). The fourth panel of this figure shows two traces recorded with our in situ laser scattering device during a selected expansion experiment: (i) the intensity and (ii) the depolarisation ratio of the back-scattered laser light. When only liquid (i.e., spherical) sulphuric acid droplets are present before the start of the expansion, the depolarisation ratio is at a low, constant background value. After the onset of pumping, the sulphuric acid droplets grow by the uptake of water vapour from the gas phase. This leads to an enhanced back-scattered intensity but the depolarisation ratio stays low and constant because the aerosol particles are still liquid (spherical). Only after the onset of ice nucleation the depolarisation ratio rapidly starts to increase, thus being a sensitive marker for the freezing onset. But note that the depolarisation ratio drops to its background value after all ice crystals have evaporated, meaning that there do not remain any crystalline, aspherical particles. Also, we have performed several repeated cooling cycles with the same aerosol, i.e., after the complete evaporation of the previously formed ice crystals. Especially at the lowest temperatures (< 195 K) the critical ice saturation ratio for the homogeneous freezing of supercooled sulphuric acid droplets is quite high (up

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to 1.7). In none of the repeated cooling cycles we have detected a significantly lower critical ice supersaturation in the second or third repetitive expansion run compared to the first expansion run. As e.g. SAT has shown to be an efficient ice nucleus with a critical ice saturation ratio of 1.3 - 1.02 (169.8 -194.5 K) (Fortin et al., 2003), this also indicates that no SAT crystals have formed and survived from a previous cooling cycle.

Fortin, T. J., Drdla, K., Iraci, L. T., and Tolbert, M. A., Ice condensation on sulfuric acid tetrahydrate: Implications for polar stratospheric ice clouds, Atmos. Chem. Phys., 3, 987-997, 2003.

And finally, if a sufficient volume fraction (at least 10 %) of the sulphuric acid droplets had frozen to SAT, this also should have been detectable in the infrared spectra, given the very sharp, prominent extinction band of SAT at around 1070 cm-1 in comparison with the rather broad extinction band of liquid sulphuric acid droplets in this wavenumber regime (e.g.: Zhang et al., 1993). But we have not detected this spectral feature of SAT.

Zhang, R., Wooldridge, P. J., Abbatt, J. P. D., and Molina, M. J., Physical Chemistry of the H2SO4/H2O Binary System at Low Temperatures: Stratospheric Implications, J. Phys. Chem., 97, 7351-7358, 1993.

5) Different arrangement of the FTIR and OPC measurements.

Yes, you are right - we should have addressed this point in our manuscript. The FTIR spectra are recorded in situ at medium height of the aerosol chamber whereas the OPCs operate in an ex situ mode by sampling chamber air from a distant point near the bottom of the aerosol vessel. But we have strong evidence that the mixing fan of the chamber (Fig. 1), which is operating at constant speed throughout the expansion, ensures that both measurements are indeed sizing particles of the same size. Within the large set of AIDA expansion runs, we have also performed several expansion experiments which resulted in the formation of micron-sized supercooled cloud droplets. For spherical droplets, the OPC sizing is of course correct and can directly be compared to

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the infrared retrievals of the cloud droplet diameters, using accurate infrared refractive indices for supercooled water. We have always observed a good agreement between the cloud droplet diameters from the FTIR retrieval and the OPC measurements, e.g. shown in Fig. 5 of Benz et al. (2005) or Fig. 13 of Wagner et al. (2005a).

Benz, S., Megahed, K., Möhler, O., Saathoff, H., Wagner, R., and Schurath, U., T-dependent rate measurements of homogeneous ice nucleation in cloud droplets using a large atmospheric simulation chamber, J. Photochem. Photobiol. A, 176, 208-217, 2005.

Wagner, R., Benz, S., Möhler, O., Saathoff, H., Schnaiter, M., and Schurath, U., Mid-infrared extinction spectra and optical constants of supercooled water droplets, J. Phys. Chem. A, 109, 7099-7112, 2005a.

We will insert the following paragraph on page 5726, line19 (in the context where we have already discussed an expansion experiment resulting in the formation of a droplet cloud to underline the insignificance of the forward-scattering correction).

“AIDA expansion runs which resulted in the formation of clouds of supercooled water droplets also prove valuable to check whether it is in principal justified to directly compare size distributions of micron-sized cloud particles retrieved from the FTIR spectra to independent OPC measurements, given that the location of these two probes is fundamentally different. Whereas the infrared extinction spectra are recorded in situ at medium height of the AIDA vessel, the OPCs operate in an ex situ mode by sampling chamber air from a distant point near the bottom of the chamber. In the case of spherical droplets, sizing by the OPCs will be correct and the comparison with the FTIR retrieval results with respect to the cloud droplet diameters will reveal whether both techniques are actually sizing particles of the same size. We have always observed good agreement between the cloud droplet diameters deduced from the FTIR retrievals and the OPC measurements; see e.g. Fig. 5 in Benz et al. (2005) and Fig. 13 in Wagner et al. (2005a). This illustrates that the operation of the mixing fan (see

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Fig. 1) provides for sufficiently homogeneous cloud properties throughout the chamber volume."

And we will add the following statement to the caption of Fig. 1: "A mixing fan is operating at constant speed throughout an expansion experiment."

6) Additional infrared refractive indices for ice.

Rajaram, B., Glandorf, D. L., Curtis, D. B., Tolbert, M. A., Toon, O. B., and Ockman, N., 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.

We have already employed the data set from Rajaram et al. (2001) in our calculations; see page 5729, line 13.

Curtis, D. B., Rajaram, B., Toon, O. B., and Tolbert, M. A., Measurement of the temperature-dependent optical constants of water ice in the 15-200 μm range, Appl. Opt., 44, 4102-4118, 2005.

Yes, thank you for the reference. So far, we have not probed the far-infrared spectral region, but we are planning to upgrade our IR equipment for this purpose.

7) Discussion of Fig. 12, differences between the various data sets of optical constants.

At first, we propose to add a sixth panel to Fig. 12, showing a comparison between our measured spectrum at 211 K and the best fit result for $\phi = 1$ using the Warren n & k data set. We think that it might be important to illustrate that these frequently employed refractive indices (already briefly addressed in the manuscript text on page 5742, line 7) also fail to reproduce our recorded spectrum. Then we will add a separate figure (Fig. 12b) which will show an expanded view of the 1500 - 800 cm-1 regime - as you suggested with each calculation on the same plot to better underline the differences. Also, we will extend the discussion of Fig. 12 in the revised manuscript and propose to include a separate paragraph for discussing the differences between the various refractive index data sets, as follows:

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The second paragraph from page 5742 (lines 9 - 21) will be appended to page 5741, line 23. Thereafter, we will insert the following paragraph:

"The good match of the $\phi = 1$ spectrum must indeed be emphasised, since it also points to the accuracy of the employed infrared refractive indices over the complete wavenumber regime, keeping in mind that the pronounced interference structure provides little scope to correct for potential mistakes in the optical constants by transforming them into the retrieved particle size distribution. This can be seen in the fifth and sixth panel of Fig. 12a, where we have repeated the fit for $\phi = 1$ with different refractive index data sets as input for the T-matrix calculations. In panel five, we have used the original Clapp et al. (1995) refractive indices instead of replacing them in the 1500 - 800 cm-1 regime with the recent Zasetsky et al. (2005) data. For the fit shown in panel six, we have employed the popular compilation of optical constants for ice by Warren (1984). Note that this compilation includes only a single measurement at T $=$ 266 K for the mid-infrared regime. Both modified refractive index data sets lead to a poorer agreement between measured and calculated spectra compared to the fit result shown in the top panel, particularly in the atmospheric window region from 1500 to 800 cm-1. This regime is shown in expanded view in Fig. 12b, covering the Christiansen band of ice at around 970 cm-1, i.e., a minimum in the extinction coefficients which can be ascribed to reduced scattering cross sections because the real part of the complex refractive index approaches unity (Arnott et al., 1995). When using the Clapp et al. (1995) data set, the magnitude of the Christiansen effect at 970 cm-1 is underestimated by almost 30% compared to the measured spectrum. When employing the Warren (1984) compilation, even the spectral habitus of the Christiansen band is not accurately reproduced. The minimum in the extinction coefficients is shifted by > 30 cm-1 to lower wavenumbers in comparison with the measurement. As stated in Sect. 2.3, the poor match with the Clapp et al. (1995) data at wavenumbers below 1500 cm-1 can be traced back to a procedural inaccuracy when deriving the refractive index data sets via the Kramers-Kronig integration. The poor quality of the Warren (1984) fit just reflects the pronounced temperature dependence of the optical constants of ice.

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In view of the tremendous efforts which are made for calculating shape-dependent extinction properties of ice crystals (Baran, 2005; Kokhanovsky, 2004; Yang et al., 2005), the results from Fig. 12b make clear that the same attention should also be paid to the appropriate choice of the employed infrared refractive indices."

8) Discussion of Fig. 15, differences between the unimodal and bimodal fit results.

Concerning Fig. 15, we will add the spectral residuals of the unimodal and bimodal fits to the bottom left and right panels - this will certainly help to compare the quality of the two different fit scenarios. Our statement "distinctly poorer than the bimodal one" on page 5747 refers to spectrum b of the spectra series shown in the top left panel of Fig. 15. Spectrum b is the first recording where the additional nucleation mode due to homogeneous freezing of the sulphuric acid solution droplets becomes visible. As will be evident in the final version of Fig. 15, the quality of the bimodal fit is indeed better than that of the unimodal one, but you are correct, it is not distinctly better; at best it is slightly better. Also, the unimodal fit is not particularly poor at wavenumbers between 1500 and 800 cm-1; there is also some disagreement in the 2800 - 2200 cm-1 regime. We will modify these statements. In the following, we state that spectrum b in principle represents an ideal scenario for distinguishing between uni- and bimodal size distributions in the FTIR retrieval: there is one mode of larger ice crystals (formed by early deposition ice nucleation) and there is a second mode of small, freshly nucleated ice crystals from the homogeneous freezing of the sulphuric acid droplets. At the early stage of the homogeneous freezing event, both ice modes hold approximately the same ice water content (thus are contributing with equal weight to the overall extinction spectrum) and are still clearly separated in size. Only here, the different quality of the uni- and bimodal fits indicates that it might be possible to deduce the modality of the size distribution from the FTIR spectrum. Our statement "impossible to distinguish between uni- and bimodal size distributions" on page 5748 refers to the subsequent recording (spectrum c). In this case, the "ideal" fit scenario of spectrum b is altered because the additional homogeneous ice nucleation mode has

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become the dominant part, now containing a substantially larger ice water content than the ice crystal mode formed by early heterogeneous ice nucleation. Here, the quality of the uni- and bimodal fits is indistinguishable; the FTIR retrieval does not allow for assessing the modality of the size distribution in this case.

We will try to make these points clearer in the revised manuscript and want to modify the discussion of Fig. 15 as follows (beginning with line 21 on page 5747):

"The unimodal fit, which yields a rather broad distribution of smaller ice crystals, N = 13.2 cm-3, σ_g = 2.0, and D = 2.1 μm, is also acceptable, but slightly poorer than the bimodal one, especially at wavenumbers between 2800 and 2200 cm-1 and in the range 1500 - 1000 cm-1. Note that spectrum b represents so to speak an ideal scenario to distinguish between uni- and bimodal size distributions in the FTIR retrieval. Two distinct ice crystal modes are known to be present: one mode of larger ice crystals (formed by early deposition nucleation on the mineral dust particles) and a second mode of still small, freshly nucleated ice crystals from the homogeneous freezing of the sulphuric acid droplets. At the early stage of the homogeneous freezing event, both ice crystal modes are clearly separated in size and hold approximately the same ice water content, thus are contributing with equal weight to the overall infrared extinction spectrum. But still, the quality of the bimodal fit is only slightly than the unimodal fit, indicating that it is extremely difficult to deduce the modality of the size distribution from the FTIR retrieval. This is further evidenced by considering the fit results for spectrum c. When leaving behind the early stage of the homogeneous freezing event (spectrum b), the additional homogeneous ice nucleation mode successively becomes the dominant part of the overall ice cloud. For spectrum c, the ice water content of the homogeneously nucleated ice crystals is already substantially larger than that of the heterogeneously nucleated ice particles, making it even more difficult to clearly identify two modes in the FTIR retrieval. Here, the quality of the unimodal fit (N = 20.7 cm-3, σ_g = 1.8, and D = 2.5 μm) and of the bimodal fit (N1 = 9.5 cm-3, $\sigma_{g,1}$ = 1.26, and D1 = 4.0 μm as well as N2 = 0.54 cm-3, $\sigma_{g,2}$ = 1.23, and D2 = 10.2 μm)

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is comparable, rendering it entirely impossible to distinguish between uni- and bimodal size distributions and to retrieve the correct number concentration of ice crystals."

9) Relative importance of the different input parameters for the retrievals?

You are right that we should not include the input parameter "quality of the refractive indices" in this listing on page 5749. We have shown in the context of Fig. 12 that a "wrong" refractive index data set (like the one from the Warren (1984) compilation) fails to accurately reproduce our recorded low-temperature extinction spectrum of ice, but we have not quantitatively investigated the retrieval errors with respect to the ice particle number concentration and number size distribution when using e.g. the Warren (1984) data set in the T-matrix fits. As for the remaining two items in the listing, the modelled asphericity and the modality of the size distribution, we have shown that erroneous assumptions for both of these two input parameters can severely distort the actual ice particle number size distribution. Some quantitative examples for this are given in the subsequent part of the Summary and outlook section.

So we propose to change our first statement on page 5749 as follows:

"As a principal conclusion, we want to emphasise that the basic input parameters for the retrieval, i.e., (i) the choice of the model to account for the asphericity of the ice crystals, and (ii) any prior assumption about the modality of the unknown number size distribution of the ice crystals, have to be carefully reconsidered for each single retrieval problem. Erroneous assumptions for both of these two input parameters may cause strong distortions of the actual ice particle number size distribution."

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5711, 2006.

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