

Interactive comment on “High variability of the heterogeneous ice nucleation potential of oxalic acid dihydrate and sodium oxalate” by R. Wagner et al.

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The authors would also like to thank referee #2 for the careful manuscript reading. Our answers to the individual comments are given below.

Comment: Specific comments: Page 11514, line 11: Can the rapid crystallization be a problem, that you don't form a pure crystal, but a poly-crystalline or an amorphous particle? Would it be possible to change the rate, which likely will lead to slightly different surface and thus different ice nucleation ability?

Answer: We would not call it a problem but just an observation that the rapid crystallisation leads to the formation of highly ice-active oxalic acid dihydrate particles. As stated
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in the introductory remarks of section 3.3 on page 11543, we have then deliberately increased the AIDA temperature to study the crystallisation of less supersaturated oxalic acid solution droplets in Exp. 6 (and later on also in Exp. 7). Here, the overall crystallisation process indeed proceeded on a much longer time period and provoked a marked change of the ice nucleability of the oxalic acid dihydrate particles. To further emphasise our intention with these experiments, we will extend our introduction on page 11543, line 10 as follows:

“Having observed a fast crystallisation of highly supersaturated oxalic acid solution droplets to oxalic acid dihydrate at $T = 244$ K, we decided to inject the aerosol particles into AIDA at a much higher temperature ($T = 266$ K) in order to probe whether less concentrated solution droplets would remain in a supercooled liquid state or whether oxalic acid dihydrate crystals of a different surface structure and ice nucleability would nucleate under the modified saturation conditions.”

As indicated e.g. on page 11549, line 9 ff, we intend to pursue the subject of particle morphology in future chamber studies to directly evidence that different surface structures are formed at different saturation conditions which, in the present study, is only indirectly apparent by means of a modified ice nucleation ability.

Comment: Page 11520, line 9: Why only roughly equal? Is the AIDA chamber not homogeneously distributed?

Answer: This is outlined in detail the experimental section on page 11525, line 8 ff: The actual ice saturation ratio is slightly below one due to some internal heat spots that lead to a slight increase of the gas temperature in comparison with the temperature of the ice-coated chamber walls. We propose to keep this information in the experimental section, but we will extend our statement on page 11520, line 9, as follows:

“The initial composition of the injected oxalic acid solution droplets adjusts to the prevailing relative humidity which is close to the saturation pressure over ice because the inner walls of the AIDA chamber are coated with a thin ice layer in the preparation of

an expansion run, as outlined in detail in section 2.”

Comment: Page 11525, lines 10-15: How do you get the “exact” Sice values? I clearly matters how much the gas temperature is higher, since Sice is very sensitive to the temperature. Isn't it?

Answer: This is absolutely true. As stated on page 11532, line 15, the exact Sice values are obtained as quotients of the in situ measured water vapour concentrations (TDL absorption), $p_w(T)$, and the saturation water vapour pressure over ice, $p_{w,ice}(T)$, for the given mean AIDA temperature (measured by arrays of temperature sensors, page 11522, line 27), as calculated from the equations from Murphy and Koop (2005). We agree that it would be better to include this information directly into the experimental section when describing the TDL setup. Following the referee's comments below, we will also address the uncertainty of the TDL measurements and include a reference where the TDL data analysis is described in somewhat more detail. The paragraph on page 11525, line 25, will be changed as follows:

“Accurate time profiles of the water vapour pressure $p_w(T)$ during the expansion cooling cycles are deduced from direct tuneable diode laser (TDL) absorption measurements. The employed room-temperature, near-infrared (1370 ± 2 nm) telecommunication-type diode laser is coupled via an optical fibre into an open-path White-type multiple reflection cell whose mirrors are directly mounted onto the interior walls of the AIDA chamber. The optical path length of the White cell is currently adjusted between 23 and 84 m, depending on the water vapour concentration. By modulation of the diode laser current, the entire absorption line profile of a selected rovibrational water vapour transition is scanned, integrated, and converted to water vapour mixing ratios at a temporal resolution of about 1 s. As a major benefit, the interstitial water vapour concentration can be inferred even in the presence of dense clouds of supercooled water and/or ice particles. By dividing the recorded $p_w(T)$ time profiles through the saturation water vapour pressures over ice and liquid water, calculated with the equations from Murphy and Koop (2005) for the measured spatial means

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of the AIDA gas temperature, the time evolutions of the saturation ratios with respect to ice (Sice) and supercooled water (Sliq) are obtained. The absolute accuracy of the TDL measurements is dominated by the line strength uncertainty of $\pm 3\%$ (Wagner et al., 2008). Supplementing the TDL humidity measurements, the total water mixing ratio, i.e., the sum of interstitial water vapour and evaporated condensed water from the aerosol and/or cloud particles, is measured with a fast high-precision chilled mirror hygrometer (MBW, model 373) at a time resolution of 1 s. The hygrometer is arranged outside the thermostated housing of the AIDA chamber and samples pass through a stainless steel tube that is heated to 303 K.”

New reference:

Wagner, R., Benz, S., Bunz, H., Möhler, O., Saathoff, H., Schnaiter, M., Leisner, T., and Ebert, V., Infrared Optical Constants of Highly Diluted Sulfuric Acid Solution Droplets at Cirrus Temperatures, *J. Phys. Chem. A*, 112, 11661-11676, 2008.

Accordingly, we will state on page 11532, line 13:

“In the second row, the time evolution of the saturation ratios with respect to ice (Sice, black line) and supercooled water (Sliq, red line) from the TDL absorption measurements are plotted.”

The following sentence on page 11532, line 15, will be deleted.

Comment: Page 11531, line 9: Could it be that the particles are even glassy or (semi)-solid? I guess no, because of the data shown in Fig. 4. Do you know the glass temperatures of oxalic acid solutions?

Answer: We would expect that the glass transition temperatures of oxalic acid solutions are much lower than the temperatures encountered in our experiments. Zobrist et al. (2008) have measured the state diagram of a five-component dicarboxylic acid mixture (M5, Fig. 5d in their publication), showing glass transition temperatures well below 200 K for the humidity levels that are covered by our experiments. All individual compo-

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nents of the mixture M5 have a higher molar mass than oxalic acid, so we consider it highly unlikely that glassy particles were formed in our experiments. Similar to previous literature studies, Zobrist et al. (2008) have found a linear relationship between T_g' (intersection between the ice melting point and glass transition curves) and the inverse molar mass of the solute (Eq. 3). For $M_w = 90 \text{ g mol}^{-1}$ (oxalic acid), a T_g' value of 166.5 K would be obtained.

For those experiments with oxalic acid where reliable FTIR extinction measurements were available (Exp. 1-3 and Exp. 6), we would indeed exclude that semi-solid phases were formed because the infrared signature at around 3500 cm^{-1} is indeed characteristic of crystalline hydrates – it is also e.g. apparent in the spectrum of sodium chloride dihydrate (Schiffer, J., and Hornig, D. F., On a Reported New Form of Ice, *J. Chem. Phys.*, 35, 1136-1137, 1961). The recorded spectrum also matches the library spectrum for oxalic acid dihydrate. For semi-solid particles, we would expect that the spectral habitus in the O-H stretching regime is more similar to the broad-band feature observed for liquid water. Concerning Exp. 7 where no information from the FTIR spectra recordings was available, we have indeed speculated in our manuscript (page 11551, line 29 ff) that also amorphous particles might have been formed, thereby explaining the modified ice nucleation ability that was observed in the expansion cooling cycles of this experiment. We propose to include a reference to the Zobrist et al. (2008) work in this context to underline that amongst the various types of amorphous particles (see e.g. Fig. 1 in Mikhailov et al., 2009), glassy particles were most probably not formed.

Modified manuscript text on page 11551, line 29:

“One cannot completely exclude that a species different from crystalline oxalic acid dihydrate, like anhydrous crystals, amorphous particles, or the recently discovered dimorphic sesquihydrates of oxalic acid (Wenger and Bernstein, 2007), has been formed during the various droplet activation runs in Exp. 7 due to the lack of information from the infrared spectra recordings. Only the formation of glassy particles can most proba-

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bly be ruled out due to the low molar mass of oxalic acid. According to the relationship found by Zobrist et al. (2008), the glass transition curve will intersect the ice melting-point curve at about 166 K (T_g') for solutes with a molar mass of 90 g mol^{-1} ; see Fig. 7 and Eq. (3) in their publication. Even when considering the estimated confidence interval of $\pm 25 \text{ K}$ that reflects the sensitivity of T_g' to the chemical structure and hydrophilicity of a particular solute, the expected glass transition temperatures of oxalic acid solutions are well below the temperature range covered by our experiments. More likely, the modified ice nucleability that was observed in Exp. 7 is related to the high variability of the surface microstructure of the crystallised oxalic acid dihydrate particles that have been generated and cloud-processed in different ways.”

New reference:

Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T., Do atmospheric aerosols form glasses?, *Atmos. Chem. Phys.*, 8, 5221-5244, 2008.

Comment: Page 11534, line 15: What about the accuracy of S_{ice} ? Is the variation of S_{ice} between 1.03 and 1.05 in Exp. 1 and 2, respectively, already significant? Could that difference result from a slightly different temperature?

Answer: According to the added information about the accuracy of the TDL humidity measurements (see our answer to referee 1), the variation in $S_{ice,crit}$ between the two repetitive expansion runs is indeed less than the absolute accuracy of the TDL measurements which is mainly determined by the line strength uncertainty of the selected rovibrational water vapour transition. In each individual expansion cooling cycle that was started at $T \leq 244 \text{ K}$, however, we have scanned the same water vapour absorption line. Therefore, the relative changes in $S_{ice,crit}$ between repetitive expansion runs might indeed be significant. Of course, these subtle variations should not be over-interpreted but, nevertheless, they point to a reduced ice nucleation ability due to the removal of the most ice-active particles from the first expansion run, as suggested in the manuscript text. The time profile of the temperature in the two repetitive expansion

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cooling cycles was highly reproducible (the same pumping speed was employed) and, therefore, temperature does not account for the difference in $S_{ice,crit}$.

To account for this issue, we will modify our manuscript text as follows (page 11534, line 12):

"Then, another expansion run with the same time profiles of pressure and temperature was performed. The AIDA records from run 2 closely match those from run 1 and are therefore not explicitly shown. During the second expansion cycle, the critical ice saturation ratio at the onset of ice formation, $S_{ice,crit}$, amounted to about 1.05. For $S_{ice,max}$ and f_{ice} , values of 1.11 and 0.12 were observed. The slightly higher activation threshold during run 2 might be due to the fact that the most efficient ice nuclei from run 1 were no longer present. Early activation will go along with growth to the largest ice crystals that will preferentially be removed by sedimentation. On the other hand, the increase in f_{ice} might be related to the slightly higher peak value for S_{ice} that was attained during run 2 compared to run 1. So, a part of less active ice nuclei that had no chance to become activated in run 1 can contribute to f_{ice} in run 2. Note that the slight variation in $S_{ice,crit}$ between run 1 and run 2 is less than the absolute accuracy of the TDL measurements which, as stated above, is mainly due to the line strength uncertainty. In the two repetitive expansion runs as well as in all subsequently described expansion cooling cycles that were started at $T \leq 244$ K, however, the same water vapour absorption line was scanned. Small relative variations in the critical ice saturation ratios might therefore indeed point to a modified ice nucleation ability of the investigated particles."

Comment: Page 11534, lines 16-17: Is it possible that the most efficient oxalic dihydrate particles are the largest ones? Can you prove that by your measurements?

Answer: We indeed consider a size-dependency of the ice nucleation ability to account for the increase of f_{ice} from 0.1 % (Exp. 3, 30 nm particles) and 0.5% (Exp. 2, 100 nm particles) to 10 – 22% in Exp. 1 (0.8 micron particles), see our manuscript text on

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page 11537, line 29 ff. In each individual ice nucleation experiment, however, we have only probed the ice nucleation ability of the complete, polydisperse aerosol sample and have not performed size-selected measurements.

Comment: Page 11535, line 1: What about the variation of S_{ice} between 1.06 and 1.08 for Exp. 3 and 4, respectively? See comment above.

Answer: Addressed above.

Comment: Page 11536, line 19: Is it fair to state that the possible gel-like amorphous particles in the Prenni et al. 2001 study were not effective IN. In a recent study in the AIDA (Murray et al. 2010) glassy citric acid particles are efficient IN. Both particles are amorphous (see e.g., Mikhailov et al. 2009), but obviously only the citric acid particles act as IN. You might state on that.

Answer: It was not our intention to generally rule out the possibility that gel-like, amorphous particles may act as efficient ice nuclei. We have just referred to the results from the Prenni et al. (2001) work – and those investigated oxalic acid particles were indeed only ice-active when reaching water saturation. For clarification, we will add the following statement on page 11536, line 23:

"Assuming that the oxalic acid particles probed by Prenni et al. (2001) were indeed amorphous, we emphasise that their comparatively low ice nucleability in relation to the oxalic acid dihydrate crystals from experiments 1 – 3 should not be interpreted as a common attribute of the amorphous state. For example, a recent AIDA study has shown that amorphous citric acid aerosol particles in a glassy state heterogeneously nucleated ice below the freezing threshold for homogeneous nucleation in liquid droplets, partly revealing threshold $S_{ice,crit}$ values as low as 1.2 (Murray et al., 2010)."

Comment: Page 11539, line 27-28: How are you sure that the sodium oxalate is not dissolved again and that you observe homogeneous ice nucleation instead of con-

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densation nucleation? I don't see the connection between the possible dissolving of sodium oxalate and the homogeneous ice nucleation (see also comment of Referee 1 concerning the temperature sensitivity.). I believe that the authors should discuss their uncertainties (Temperature, Sice) more clearly. See also comment above. Page 11541, line 20: See comment above. I'm not fully convinced that sodium oxalate does not fully dissolve. What about solubility data?

Answer: As stated in the manuscript, our results at least indicate that not all sodium oxalate particles are instantly and fully dissolved due to the continuous increase in the ice particle number concentration that was observed after the formation of the droplet cloud at $t = 90$ s. Note that the gas temperature at $t = 90$ s was still above 240 K, so homogeneous nucleation cannot account for this early ice formation. As outlined in detail in our answer to referee 1, we are also convinced that the second ice crystal mode that was formed at $t = 270$ s is not due to homogeneous droplet freezing because the droplet cloud had already evaporated to leave behind solid sodium oxalate particles, as can be clearly seen by the increase in the depolarisation ratio. We have no information on the degree of dissolution of the sodium oxalate particles during the droplet activation. To explain their modified ice nucleation ability that is evident in the formation of the second ice crystal mode in the later period of the first expansion run and in early deposition mode ice activity in the second expansion run, we have speculated that at least the outer particle shell must have been dissolved and re-crystallised (page 11541, line 18 ff). In our answer to referee 1, we have already proposed extensions to the original manuscript text to address the concern about the potential influence of homogeneous freezing.

Comment: Page 11541, line 23: The re-crystallization took a longer time than the first crystallization, right? If so, could it be that there was no crystallization in the first case, but rather the formation of an amorphous particle?

Answer: Upon aerosol injection, the relative humidity in AIDA was about 70%, i.e., below the efflorescence relative humidity of 72 – 75% that was found by Peng et al.

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(2001) (page 11539, line 1), thereby leading to the immediate crystallisation of the aerosol particles. When pumping was stopped at $t = 210$ s during the first expansion run, the relative humidity was close to water saturation (a liquid water cloud was present in AIDA). With slowly increasing gas temperature, it just takes some time for the droplet cloud to evaporate and for the relative humidity to level off, thereby explaining the gradual (and not stepwise) increase in the depolarisation ratio between $t = 210$ and 270 s (re-crystallisation).

The information from the FTIR spectra recordings (Fig. 7) might be suitable to assess whether amorphous or crystalline particles were present. We have indicated in the manuscript text that the observed band positions from the particles generated in Exp. 4 closely matched those recorded for sodium oxalate crystals in a KBr matrix and that no condensed-phase water signature was present (page 11538, line 20). Based on these observations, it is unlikely that semi-solid particles were formed.

Comment: Page 11553, line 12: Which form of oxalic acid would probably crystallize in the atmosphere? It would be great when the authors could address somewhat deeper the atmospheric implications.

Answer: With the aid of the supplementary FTIR extinction measurements, we could at least demonstrate that oxalic acid dihydrate was formed via different pathways, i.e., both by crystallisation of supersaturated solution droplets and by nucleation of a gaseous oxalic acid/air mixture. One might therefore speculate that also coating layers of oxalic acid which were formed by physical and chemical processing on solid particulates would consist of this species. It would be a challenging task to directly simulate this process in AIDA chamber experiments - also because coating layers of a considerable thickness (mass concentration) must be formed to analyse their chemical composition by FTIR extinction spectroscopy. We have therefore refrained from proposing such type of experiments in the summary section. But we will include the following statement on page 11553, line 12:

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"Concerning the atmospheric implication of our findings, the presented experiments are relevant to the scenario where by way of physical and chemical processing a coating layer of organic material may have formed on prevalent particulates such as soot and mineral dust. With the aid of the FTIR extinction measurements, we have demonstrated that oxalic acid in form of its dihydrate was generated under various conditions, i.e., by crystallisation of supersaturated oxalic acid solution droplets of different acid concentrations and by nucleation from a gaseous oxalic acid/air mixture. One might therefore assume that also coating layers of oxalic acid would consist of this species. Given the high variability of the heterogeneous ice nucleation potential of oxalic acid dihydrate, it is not straightforward to anticipate in which direction the ice nucleability of the pure compounds will be modified by the organic coating layer."

Comment: Page 11560, Table 1: Could you also add a column with the size of the particles or link it to Figure 3.

Answer: We will include a link to Fig. 3 into the description of Table 1:

"SMPS and APS number size distributions of the aerosol particles generated in Exp. 1, 2, 3, 4, and 6 are shown in panels a, c, e, b, and d of Fig. 3, respectively."

Comment: Page 11561, Figure 1: It would be helpful to include also RH with respect to ice, since that's the quantity, which one is interested in.

Answer: Fig. 1 already contains the T-dependent oxalic acid concentrations for $S_{ice} = 1$, i.e., the ice-melting point curve and the corresponding relative humidity with respect to supercooled water (right x-axis, only valid when moving along the ice-melting point curve in the phase diagram). We will add two additional traces calculated for $S_{ice} = 1.2$ and 1.4 .

Comment: Page 11563, Figure 3: The oxalic acid dihydrate particles are clearly larger when they are produced by rapid cooling (panel a) compared to panels c and e? Why? Is it only a size difference or also is the composition different, e.g. is some water

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remaining in the particles in panel a?

Answer: The different particle sizes are due to the different methods for the aerosol generation. The oxalic acid dihydrate particles whose size distribution is shown in panel (a) were generated by ultrasonic nebulisation (injection at 244 K), panel (c) shows the size distribution of particles generated with the atomizer (also injected at 244 K), and panel (e) shows a SMPS measurement of the particles formed by nucleation from the gaseous oxalic acid/air mixture (injection at 228 K). This is outlined in section 2, and after having added the link to Fig. 3 in Table 1 (see above) it will be easier to assign the size distribution measurements to the experiments.

Comments: Minor comments: Page 11515, line 8: replace "... of tropospheric aerosols" by "... the tropospheric aerosol." Page 11533, line 3: replace "forth" by "fourth"

Answer: Will be corrected.

Comment: Page 11533, line 8, Shouldn't you refer to Fig 5 instead of Fig. 4.

Answer: The reference to Fig. 4 just refers to the definition of time zero that is outlined in the caption of Fig. 4. We will replace "see Fig. 4" by "see caption of Fig. 4".

Comment: Page 11534, line 3: replace "forth" by "fourth"

Answer: Will be corrected.

Comment: Page 11535, line 15, Panel e means the fifth panel. Why do you refer to that one?

Answer: The fifth panel indeed shows the size distribution measurement of the nanometre-sized particles from Exp. 3 (see page 11525, line 1, and the newly added link to Fig. 3 in Table 1).

Comments: Page 11540, line 10: replace "forth" by "fourth" Page 11547, line 1: replace "forth" by "fourth"

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Answer: Will be corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11513, 2010.

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