Atmos. Chem. Phys. Discuss., 6, S433–S437, 2006
www.atmos-chem-phys.org/acpd/6/S433/
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Homogeneous nucleation rates of nitric acid dihydrate (NAD) at simulated stratospheric conditions – Part I: Experimental results” *by* O. Stetzer et al.

Anonymous Referee #2

Received and published: 3 April 2006

General Comments: Stetzer and co-workers present new data on the nucleation of nitric acid dihydrate (NAD) particles which may contribute to the formation of polar stratospheric clouds (PSCs). The formation of NAD from supercooled aqueous nitric acid aerosols at typical stratospheric conditions (temperature and saturation ratios) has been observed. A large aerosol chamber has been used to study the phase transition of these aerosols providing a new experimental setup compared to previous techniques to determine homogeneous and surface induced nucleation rates. The formation of NAD could be unambiguously determined by in situ FTIR spectroscopy. Nucleation of NAT has not been observed for nitric acid mole fractions of 0.26 to 0.28. Rapid conversion of NAD to NAT, although high supersaturations with respect to NAT were present, has not been observed. In addition, the surface induced nucleation rates derived from these experiments are significantly smaller than predictions using a parameterization suggested recently. This paper is within the scope of ACP and should be published. It provides new data relevant for our understanding of the formation of PSCs. The experimental methods are sound. However, the authors should address the comments below.

Specific Comments:

Page 2093, first paragraph (-line 4): It would be beneficial to know which PSC particles have been conclusively observed within PSCs.

Page 2094, first paragraph: The discussion of the possible nucleation mechanisms would gain if results of PSC modeling studies applying both nucleation mechanisms would be briefly mentioned.

Page 2094, line 13: The particle diameters applied in the study by Duft and Leisner have been larger than 38 μm.

Page 2094, line 22: Tabazadeh and coworkers, Science, 2001, already applied the assumption to convert immediately NAD to NAT in their modeling studies.

Page 2095, line 25: Since the determination of the size distribution is crucial for the derivation of the nucleation rates it would be beneficial to elaborate on this. What kind of correction factors have been used and how have they been derived?

Page 2096, 1st paragraph of ”Experimental Implementation” and page 2097, first paragraph: Does the cold wall of the chamber influence the particle production (composition changes)? The particle production proceeded for 30 minutes: how long does it take for the overall system, i.e. aerosol, gas phase, and wall to be in equilibrium? What kind of coating do you expect on the chamber walls?

Page 2096, line 24: Could you specify ”dry” conditions?

Page 2097, line 12-17: How large is the uncertainty of the aerosol composition derived from FTIR?

Page 2098, line 4: The solid phase is more stable than the supercooled liquid droplets. You could mention that the growth of the crystals is due to differences in the HNO_3 and H_2O vapor pressures between solid and liquid droplets. Is the growth of the NAD crystals due to NAD deposition/condensation?

Page 2100, line 11-14: I assume that the maximum time α-NAD was observed to be stable is given by the experiment time? Is there any observation which indicated conversion of NAD after more than one hour? Experiment E1 indicates that NAD was observed for longer time periods (about 2 hours, see Fig. 3). Additionally, the proper references should be added and discussed. E.g. Worsnop and co-workers, Science, 1993, also observed that NAD was stable for long time periods.

Page 2100, line 24: Could you elaborate briefly on the determination of the threshold limit? Why do the threshold diameters vary so much? Why do these different diameters do not influence the threshold detection limit? In the beginning it is stated that the particle background within the chamber is 0.1 particles cm^{-3}. How can you define a threshold of 0.02 NAD particles cm^{-3}?

Page 2101, 1st paragraph: How long does it take for ice particles with the observed particle diameters to evaporate completely? Could a possible NAT coating of the ice as suggested by Biermann et al, 1998 extended the lifetime of ice crystals with very small diameters?

Page 2102-2103: Since the WELAS spectrometer can only determine a small fraction of the overall size distribution, an additional figure which shows the lognormal fit to the data and which indicates the uncertainty of the fit would be helpful to understand the derivation of the particle surface area and subsequent uncertainty in the surface nucleation rate. I agree that the uncertainty with respect to measured and predicted surface induced nucleation rates is negligible, however, to possibly derive a correct surface induced nucleation parameterization and homogeneous nucleation parameterization data with corresponding uncertainty should be provided.

Page 2104, line 15: Is it obvious that this data fits well with the other data? In a J vs. T plot you may only compare nucleation data derived from liquid droplets of equal compositions. Different compositions will result in different saturation ratios, thus, the droplets may freeze at different temperatures. Maybe you elaborate on this point.

Page 2104, line 16: Could you elaborate on ”...to lower J as one would expect form classical nucleation theory”? Is this a trivial conclusion? The relationship between J and the Gibbs free energy for activation of a critical nucleus is not given.

Page 2105, line 5: In Fig. 6 it appears that the mole fraction of the data of Salcedo et al. range from 0.3-0.33 whereas the mole fraction of the new data range between 0.26-0.28. Can you simply compare these observations (see previous point)?

Page 2105, line 14: This stduy shows that NAD nucleation is a volume dominated process for particle sizes between 25 μm and 0.25 μm. Surface induced ice nucleation has yet not been studied for particle diameters of 0.25 μm. Since the particle sizes and the particle composition (and subsequent nucleated phases) differ substantially, I do not see that the presented data is a complement observation to the study of Duft and Leisner.

Page 2105, line 17: see comment about droplet diameters applied in Duft and Leisner.

Page 2106, 2nd paragraph: Could you derive an upper limit of the nucleation of NAD and NAT on ice due to the knowledge of the lifetime of the ice particles, and their size?

Page 2106: One important result is missing in the discussion and conclusion section: NAD did not convert to NAT immediately. How does this finding compare with field observations and modeling studies?

Technical corrections:

Page 2094, line 2: change ”parameterize” to ”parameterise”.

Page 2097, line 5: a comma is missing in front of ”respectively”.

Page 2100, line 9: ”Please note that...” could be set in brackets.

Page 2100, line 20: change ”2h” to ”2 hours” or ”2 hrs”.

Page 2101, line 4: ”as evidence by...these...”change ”these” to ”those”.

Page 2101, line 24: Missing space in ”gcm^{-3}”.

Page 2102, 2103: Missing period behind equation 1, 2, 6, and 7. Missing comma behind equation 4.

Page 2106, line 11: ”In particular...” may be rephrase this sentence for an easier understanding.

Page 2106, line 18: Typo “respect”.

References: Some initials of authors are missing, e.g. page 2103, line 3, 10, 26, 28...

Figures:

Figure 3-5: Panel F indicates ”C$_{\mathrm{NAD}}$”, however, the figure captions speak about ”ice crystal concentrations”. In addition, on page 2100, line 29.: ”...data point which were zero are set to 0.02.” However, in figures 3-5 they are set to 0.01.

Figure 7: It would be beneficial to know the experimental runs (E1-E3) which correspond to the single triangles.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2091, 2006.