Author response to comments of referee #1: "Spectroscopic evidence for large aspherical β-NAT particles involved in denitrification in the December 2011 Arctic stratosphere"

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We would like to thank referee #1 for his/her time and helpful comments and suggestions to improve the manuscript. In the following, we provide the original referee comments (italic letters) followed by our responses. Text added or modified in the revised manuscript is colored in blue.

Woiwode et al. analyze infrared limb emission spectra that were recorded with the airborne MIPAS-STR instrument during a flight above northern Scandinavia in December 2011. The spectra reveal a "shoulder-like" signature at 820 cm-1 which (in a slightly different manner, i.e., more "peak-like") has already previously been observed in spaceborne infrared PSC observations and has been assigned to beta-NAT particles. Ambient conditions like temperatures around flight altitude during the PSC encounter support the presence of NAT (temperature is above the existence temperatures of ice and STS). Additionally, a local maximum of gaseous HNO3 was detected just below the PSC encounter which could result from nitrification. From simulations with Mie theory, the authors confirm that only with the refractive indices of beta-NAT it is possible to at least roughly reproduce the observed signature at 820 cm-1. But only when considering highly aspherical particle shapes with aspect ratios of 0.1 and 10 in T-matrix computations, a satisfactory agreement between MIPAS-STR measurements and simulations is obtained.

General comment

This is a very comprehensive study containing a wealth of information, not only the detailed spectral analysis of the PSC signatures, but also concomitant measurements of particle size distributions (in-situ), trace gas analyses, and space-borne observations. In my opinion, the analysis is sound and indeed gives evidence for the presence of highly aspherical beta-NAT particles due to the much better match of the T-matrix simulations compared to those with Mie theory. The manuscript is well-written, and I have listed only a few points that need further clarification. I therefore support the publication in ACP once the following specific comments are addressed.

We thank referee #1 for this clear summary and encouraging statement.

Specific comments

1) Page 2, line 27: Here and at some other places in the manuscript (in particular at page 10, line 23ff) no mention is made that there are two IR spectroscopically different modifications of NAD, the low-temperature alpha-NAD and the high-temperature beta-NAD phase (Grothe et al., 2004). The employed optical constants from Niedziela et al. (1998) closely correspond to the alpha-NAD spectrum shown in Fig. 6 in Grothe et al. (2004). In beta-NAD, the v2 (NO3-) band is slightly shifted to higher wavenumbers (811 cm-1, Table 1 in Grothe et al., 2004) and, judging from Fig. 6 (in Grothe et al. 2004), has a higher intensity compared to alpha-NAD. As far as I know, optical constants for beta-NAD have not yet been retrieved, and maybe the small wavenumber shift of the v2 (NO3-) band in beta-NAD would not lead to a better match with the measured MIPAS-STR signature at 820 cm-1 compared to alpha-NAD, but the existence of the high-temperature beta-NAD modification should at least be acknowledged. In annealing experiments, Grothe et al. (2004) observed that the low-temperature alpha-NAD modification first transformed into beta-NAD at about 200 K, and that decomposition of beta-NAD into beta-NAT and NAM then only occurred at a considerably higher temperature. This finding should also be addressed in the discussion on page 10, line 25.

Grothe, H., Myhre, C. E. L., and Tizek, H., Vibrational spectra of nitric acid dehydrate (NAD), Vib. Spectrosc., 34, 55-62, 2004.

We thank referee #1 for this hint and modified the manuscript as follows:

P2/L27: As discussed by Grothe et al. (2004), the spectroscopic data of NAD used in these studies closely corresponds with the α-NAD modification. Furthermore, another metastable high-temperature modification β-NAD has been identified by Grothe et al. (2004) in laboratory experiments at temperatures above ~200 K, which decomposes into β-NAT and NAM (nitric acid monohydrate) at considerably higher temperatures.

P8/L4-5: The signatures of NAD are simulated using the refractive indices by Niedzela et al. (1998), which closely correspond with spectroscopic data of α-NAD (Grothe et al., 2004).

P10/L23-27: While α-NAD shows a similar spectral signature with weaker amplitude centred at 808 cm^{-1} (Niedziela et al., 1998, Grothe et al., 2004), the signature is not capable of reproducing the residual dip slightly below 820 cm^{-1} (see Sect. 3.5). The same is expected for the high-temperature modification β-NAD, which was characterized by Grothe et al. (2004) in laboratory experiments and shows a similar spectral signature centred at 811 cm^{-1}. Furthermore, the observations indicate temperatures close to the threshold temperature of β-NAT and slightly too warm for NAD under stratospheric conditions.

P19/L31: Grothe, H., Myhre, C. E. L., and Tizek, H., Vibrational spectra of nitric acid dihydrate (NAD), Vib. Spectrosc., 34, 55-62, 2004.

2) Page 3, lines 4/5: Here and/or in the later discussion on page 13, lines 17-19, one could also explicitly mention that Grothe et al. (2006) observed a variety of morphologies for the beta-NAT particles, depending on the growth conditions, supporting the argumentation that a simplified shape assumption might contribute to the discrepancies between the simulations and the observation.

We modified as follows:

P3/L5: under laboratory conditions and obtained highly aspherical particles with different morphologies depending on the growth conditions.

P13/L19: This is supported by the experiments of Grothe et al. (2006), resulting in highly aspherical β-NAT particles (i.e. platelets and needles).

3) Page 8, line 4: See above, the data from Niedziela et al. refer to the signatures of alpha-NAD.

See above.

4) Page 8, line 14/15: So size distribution A is a bi-modal log-normal fit to the FSSP-100 observation? One could state this more clearly instead of writing "resembles approximately the size distribution ".

We clarified as follows:

P8/L14-15: The bimodal size distribution A (Fig. 9b, red) was adjusted manually to match the size distribution derived from the FSSP-100 observations in terms of shape and condensed HNO_3.

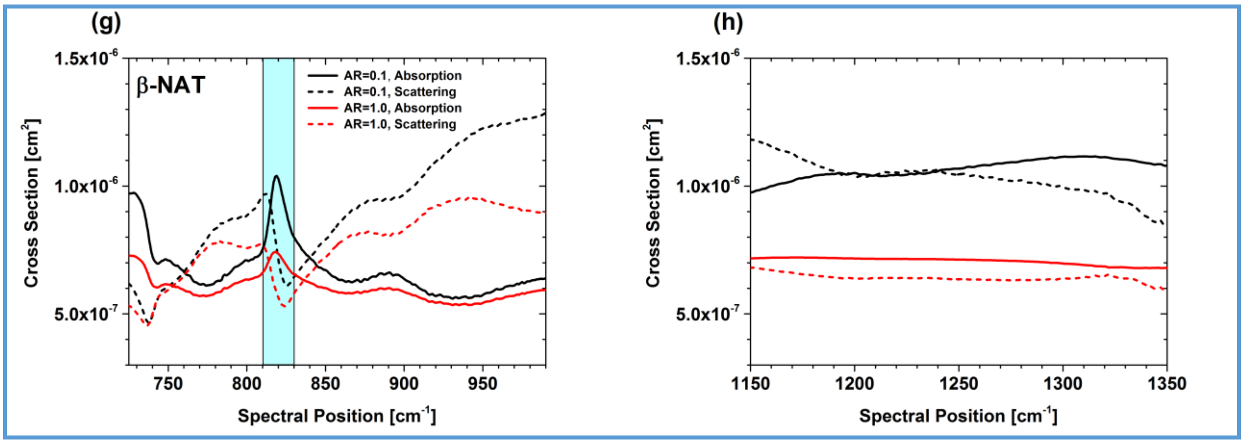
5) Page 12, line 21-24, discussion of Fig. 13: I am wondering whether one could elaborate the effect of particle asphericity on the emission/absorption and scattering of the particles more clearly. From the compilation of refractive indices plotted in Fig. 13 c-f it is clear that the "shoulder-like" signal at

820 cm-1 can only be reproduced by beta-NAT. But also large spherical beta-NAT particles would produce some sort of shoulder-like signal around that wavenumber from the interplay of "peak-like" emission and "steplike" scattering contribution. The important message is that only highly aspherical particles reproduce the correct amplitude of the measured signal. Obviously, the shape dependency is predominantly related to the scattering contribution, because the AR=1.0 and AR=0.1 scenarios without scattering only showed smaller differences. I would propose to include a more fundamental plot that shows the wavenumber-dependent ensemble-averaged absorption/emission and scattering cross sections for different aspect ratios, so that the reader immediately gets an impression about the change of these basic quantities with particle shape.

We thank referee #1 for this hint and included the absorption and scattering cross-sections of the optimized scenario for AR=1.0 and 0.1.

P12/L28: Figure 13g and 13h show the ensemble-averaged absorption and scattering cross-sections of β-NAT for the considered size distribution for AR=0.1 and AR=1.0, which determine the absorption/emission and scattering characteristics of the simulated particles. The T-Matrix scenario with AR=0.1 shows a much stronger peak in the absorption cross-section and a stronger step in the scattering cross-section in the spectral window around 820 cm^{-1} when compared to the Mie scenario, which together result in the characteristic "shoulder-like" signature in the simulated spectrum. Furthermore, the AR=0.1 scenario shows considerably higher values of the scattering cross-section towards higher wavenumbers, resulting in a relatively flat baseline of the simulated spectrum towards the upper end of channel 1. In the AR=0.1 scenario, higher absorption and scattering cross-sections in channel 2 result in higher radiances in the corresponding simulated spectrum.

Figure 13:



P39/L5: (g) and (h): ensemble-averaged absorption and scattering cross-sections of β-NAT for the discussed AR=0.1 and AR=1.0 scenarios.

To point out that the absorption cross-sections determine also the emission characteristics of the particles, we modified as follows:

P1/L31: absorption/emission and scattering characteristics

P12/L17: the absorption and emission characteristics of the particles

P12/L28: absorption/emission and scattering

P12/L31: absorption and emission

P13/L7: due to the net emission

P16/L13: absorption/emission and scattering characteristics

6) Page 12, lines 25-27: See above, no distinction between alpha- and beta-NAD.

From the modifications in P2/L27, P8/L4-5 and P10/L23-27 it should be clear now that the data used in this work and similar previous studies closely correspond with α-NAD.

7) Page 16, line 3-4: Is there any assessment of the influence of particle asphericity on the Mie theory-inferred diameters of the FSSP measurements? There is some discussion of this issue in the conclusion section, but I would propose to directly mention it here where the size distributions from the MIPAS-STR simulations and in-situ observations are compared.

We added:

P16/L5: We mention that Borrmann et al. (2000) investigated the effects of spheroids with AR=0.5 on FSSP observations. Similar to the infrared observations discussed here, the results were close to corresponding Mie calculations. However, the effects of highly aspherical particles on the interpretation of FSSP measurements are uncertain and might explain this discrepancy.

8) Conclusions section: I would like to see a statement/analysis whether there is a certain size threshold above which one can safely infer shape information for the beta-NAT particles from the signature at 820 cm-1. In the introduction, the authors refer e.g. to previous MIPAS-Envisat PSC observations of beta-NAT particles with smaller radii. Here, a "peak-like" rather than a "shoulder-like" signature at 820 cm-1 was observed, probably due to the reduced amount of scattering. When neglecting the scattering source function, however, the shape influence was observed to be less pronounced (Sect. 3.5). So I am wondering whether there are size limitations for the identification of highly aspherical particles from the MIPAS observations.

We agree and analysed the transition from a "peak-like" to a "shoulder-like" signature starting with the simplified size distribution B1:

P14/L32: We furthermore perform a sensitivity study based on the scenario involving the simplified size distribution B1 to investigate the effect of decreasing mode radii on the observed spectral signatures when the total volume of β-NAT is kept constant. The results are reported in Appendix B and show that the transition from a "shoulder-like" to a "peak-like" signature occurs for AR=0.1 and the considered mode width at a mode radius of ~3.0 µm. For a mode radius of 1.0 µm, a "peak-like" signature is found in agreement with a corresponding Mie simulation. The results show furthermore, that a modified "shoulder-like signature along with further changes in the simulated spectra results for spherical particles with a mode radius of 3.0 µm.

P16/L20: Sensitivity calculations involving a simplified size distribution show that for AR=0.1 the transition from a "shoulder-like" to a "peak-like" signature occurs at a mode radius of ~3.0 µm. A developed "peak-like" signature as discussed by Höpfner et al. (2006a) is found for a mode radius of 1.0 µm, which is almost identical to the corresponding Mie simulation. Furthermore, a corresponding Mie simulation with a mode radius of 3.0 µm shows that a modified "shoulder-like" signature along with further changes in the modelled spectra can be simulated for spherical particles using the discussed size distribution.

P18/L4: Appendix B

The goal of the sensitivity study discussed in the following is to identify an approximate size threshold for particles with AR=0.1 for the transition from a “peak-like” (compare Höpfner et al., 2006a) to a “shoulder-like” signature in the spectral region around 820 cm^{-1}. Corresponding Mie calculations for spherical particles (AR=1.0) are shown for comparison. Starting point for the simulations is the simplified size distribution B1 (1-modal, r=4.8 µm, see Fig. 9a and Table 1, scenario 57g). Sensitivity calculations involve the same total volume of β-NAT (i.e. condensed HNO_3) and mode radii of 3.0 µm and 1.0 µm, respectively (Fig. 19).

The results show that for AR=0.1 the spectral signature around 820 cm^{-1} becomes increasingly “peak-like” for mode radii decreasing from 4.8 µm to 1.0 µm (Fig. 20a, 20c, and 20e, blue). While for r=4.8 µm the signature shows a characteristic “shoulder-like” pattern, a superposition of a “shoulder-like” and a “peak-like” signature results for r=3.0 µm. A developed “peak-like” signature as discussed by Höpfner et al. (2006a) is found for r=1.0 µm, and the simulated spectra are almost identical to the corresponding Mie scenario for both channels (Fig. 20e and 20f) except for slightly higher radiances below ~860 cm-1 in for the AR=0.1 scenario. Finally, the Mie calculations show that a modified “shoulder-like” signature around 820 cm^{-1} along with further differences from the AR=0.1 scenario can be modelled for spherical particles with r=3.0 µm.

P45/new Figure 19:

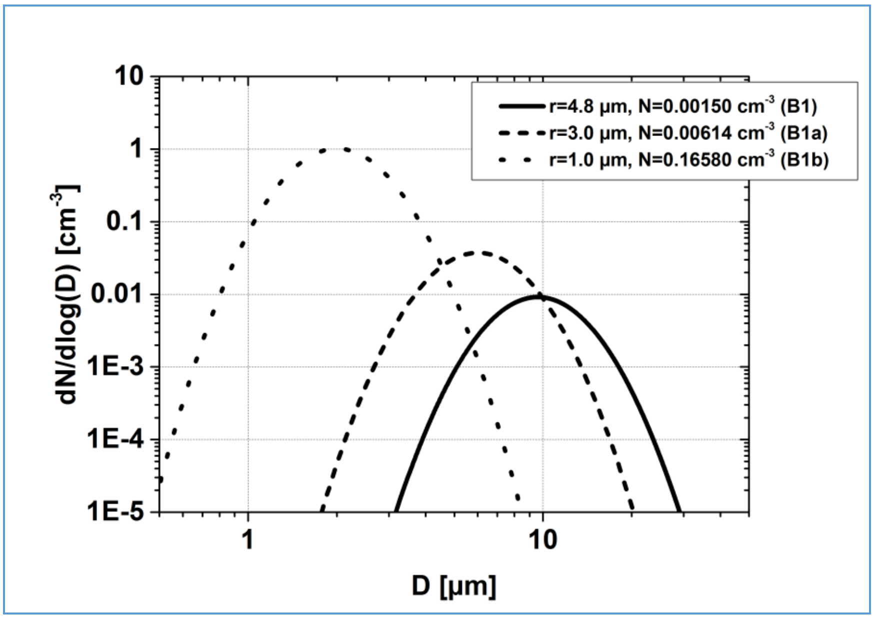


Figure. 19. Size distributions used for sensitivity simulations discussed in Appendix B. The total volume of condensed β-NAT is constant (corresponding with 8.4 ppbv of gas-phase equivalent HNO_3) and the mode with is 1.35 in all cases. For the binned size distribution used in the AR=0.1 scenario with r=1.0, the particle number density had to be scaled to 0.17342 cm^{-3} to match 8.4 ppbv of gas-phase equivalent HNO_3.

P46/new Figure 20:

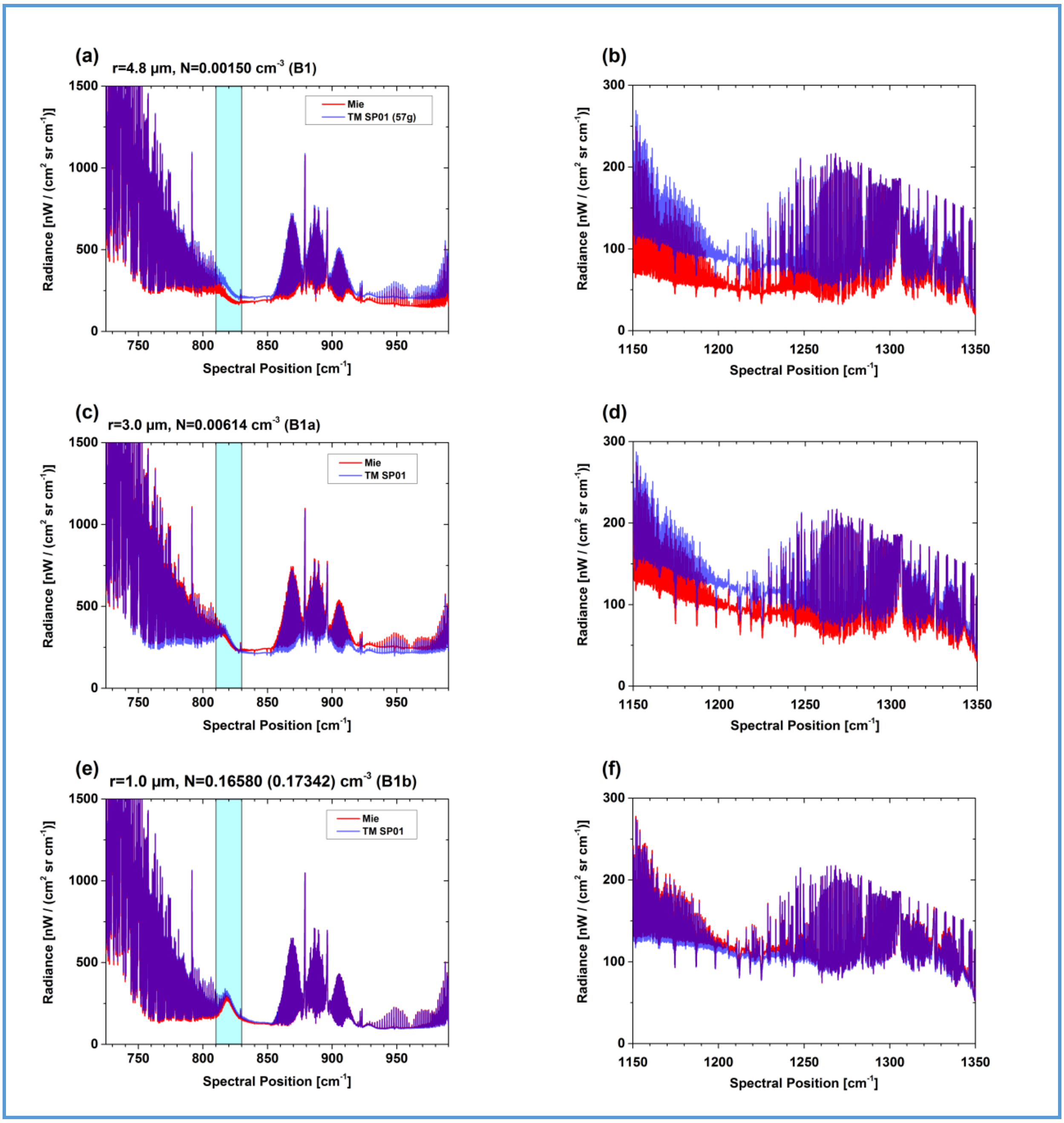


Figure. 20. Sensitivity simulations investigating the effect of decreasing mode radii on the simulated spectral signatures of β-NAT particles for a T-Matrix scenario with AR=0.1 (blue) and a corresponding Mie scenario (AR=1.0, red). (a) and (b): large particle mode, size distribution B1. (c) and (d): intermediate particle mode, size distribution B1a. (e) and (f): small particle mode, size distribution B1b. Numbers above (a), (c) and (e) indicate corresponding mode radii and particle number densities (see Fig. 19). 'TM' corresponds with T-matrix simulation and 'SP' with spheroid (numbers indicate AR).

Technical corrections

1) Page 2, line 11: typo in NO3-

Done

2) Page 5, line 11: CALIOP should be replaced by CALIPSO .

Done

3) Page 9, line 27: I suppose it is meant "by the simulated scattering of radiation", i.e., delete "to".

Done. We furthermore added at P9/L27: into the field-of-view.

4) Page 10, line 19: aspherical particles

Done

5) Page 11, lines 18, 23, 24: Please check the units for the given radiances. Shouldn't it be W cm-2 sr-1 cm?

Done. We furthermore corrected units at:

P4/L4: 11-19$\cdot 10^{-9}$ W cm^{-2} sr^{-1} cm

P9/L31: ~25$\cdot 10^{-9}$ W cm^{-2} sr^{-1} cm

6) Page 14, line 23: "the first mode is of minor importance"

Done

7) Page 16, line30: "of condensed HNO3."

Done