

Interactive comment on “Spectroscopic evidence for large aspherical β -NAT particles involved in denitrification in the December 2011 Arctic stratosphere” by W. Woiwode et al.

Anonymous Referee #1

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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

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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.

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 ν_2 (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 ν_2 (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

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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 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.

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

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 “.

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 “step-like” 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

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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.

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

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.

Technical corrections

1) Page 2, line 11: typo in NO₃-

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

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

4) Page 10, line 19: aspherical particles

5) Page 11, lines 18, 23, 24: Please check the units for the given radiances. Shouldn't

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it be $W \text{ cm}^{-2} \text{ sr}^{-1} \text{ cm}$?

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

7) Page 16, line30: “of condensed HNO_3 .”

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