**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Spectroscopic evidence for β-NAT, STS, and ice in MIPAS infrared limb emission measurements of polar stratospheric clouds" *by* M. Höpfner et al.

M. Höpfner et al.

We thank Hinrich Grothe for his comments on the paper which will help to improve especially the spectroscopic part. In the following we address them point by point:

1. The referee suggests to include relevant experimental parts of the referenced thesis [Biermann(1998)] into the manuscript to make it available to non-German readers.

We have added these as an appendix to the revised manuscript, including two figures of the experimental setup.

2. *From the MIPAS system the spectral range 685 - 2410 cm^{-1} is available, which*

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

in principle includes the following nitrate bands of β-NAT: $\nu_2(A_2'') = \delta_s = 820$ cm^{-1}, $\nu_3(E') = \nu_{as} = 1375$ $^{-1}$, $\nu_4(E') = \delta_{as} = 720$ cm^{-1}, as well as the oxonium and the water band: $\nu_4(H_3O^+) = \delta_{as} = 1830$ cm^{-1}, $\nu_2(H2O) = \delta = 1665$ cm^{-1}. The authors should more carefully justify why they have chosen just the symmetric deformation mode of the nitrate for their phase assignment. The criteria of the band selection should be explained: sufficient intensity, less interference with other bands (e.g. gaseous species), and reproducible band position and shape.

The 820 cm^{-1} band is identified in our paper as a means to identify NAT obser-vation in an efficient way from the MIPAS measurements, as done previously by [Spang and Remedios(2003)]. However, in our detailed analysis of broadband MIPAS spectra we do not, as the referee might have understood (and which, we admit, was not clear enough in the abstract and the original manuscript) rely only on that band but on the best fit over a broad spectra range, which does include the band at 1375 cm^{-1}. As can be seen from the Figure 4 of the paper, especially the range between 1350 and 1450 cm^{-1} shows distinct differences in the fits between simulation for the various refractive indices and measurement. Especially there, the worse fit of NAD compared to that of β-NAT is striking due to the nitrate ν_3 band of NAD at around 1450 cm^{-1}. We have emphasized the differences in this wavenumber region more clearly in the re-vised text and have illustrated the broad-band fitting quality by presenting a Table of the noise-weighted rms differences between simulation and measurement for the different refractive indices in each channel.

Nonetheless, for time-efficient identification, the 820 cm^{-1} band is especially suited be-cause it is a very narrow and prominent band in one of the few wavenumber regions which are nearly free of trace-gas signatures. Further, it is at the longer-wavelength range of the MIPAS observation and, thus, less affected by scattering effects. Unfor-tunately other bands are less/not suited for this purpose: 720 cm^{-1} is entirely covered by CO_2 emissions, 1375 cm^{-1} can be used in detailed radiative transfer simulations as shown, but is not suited well for fast detection due to some interference with CH_4.

1665 cm^{-1} and 1830 cm^{-1} are either strongly influenced by water vapour emission, and relatively broad bands. Additionally, at higher wavenumbers scattering effects blur the signals more strongly. As suggested by the referee we have stated the reasons for this band selection more detailed in the revised paper.

3. *Taking into account all these effects* (orientation, sample thickness, particle morphology, phase composition, interaction NAT-ice) *most literature data are reliable only to a certain extent, which is due to the very different procedures of sample preparation. In fact, none of the published sets of optical constants has ever reproduced a whole set of IR spectra (transmission, reflection, emission). The following references should be considered and quoted in order to describe the interfering effects which have a strong impact on the lab spectra ...*

In the revised version we have noted the uncertainty of the laboratory data and have added the references suggested by the referee.

However, many of the mentioned effects apparently influence band intensities rather than spectral positions. A strong effect on band position is shown in the paper by [Wagner et al.(2005)], but this analysis revealed mainly a red-shift of the major α-NAD absorption bands. Also, estimates for the α-NAD band at 810 cm^{-1} point at very weak shifts towards smaller wavenumbers (R. Wagner, pers. comm.). Thus, it is unlikely that the band will be shifted to 820 cm^{-1}.

In a new Table in the revised manuscript we have summarized papers where the position of the ν_2 of nitrate for NAD and NAT has been reported based on observations [Ritzhaupt and Devlin(1991)], [Toon et al.(1994)], [Richwine et al.(1995)], [Koch et al.(1996)], [Biermann(1998)], [Niedziela et al.(1998)], [Tisdale et al.(1999)], [Hudson et al.(2002)], [Grothe et al.(2004)]. >From these no indication for a strong shift of the position of this band can be deduced.

4. The referee concludes, that he is not convinced about our identification of β-NAT, *since it is based only on a single peak centred at 820 cm^{-1}*. As consequence he

suggests *changing the title, the abstract and the conclusion of the paper* towards *indications or clues*.

We do not agree with the referee in this regard because our conclusion does not rely on the single band only, but on comparison of a large spectral region with available optical constants of possible PSC candidates. We show that for the case where Lidar observed Type 1a PSCs, the measurements can best be fitted with the β-NAT data by [Biermann(1998)]. With these data the $820\,cm^{-1}$ band, which has not only been observed by MIPAS, but also by CRISTA (as stated in the text) and most recently also by the Atmospheric Chemistry Experiment (ACE) which works in limb solar absorption [Zasetzky et al.(2005)] could be simulated for the first time. There are large differences between the observed spectra and simulated ice, NAD or STS spectra not only around $820\,cm^{-1}$. Thus, we are convinced that we have shown evidence for NAT over a large spectral range, of course, based the available spectroscopic datasets.

The term 'Spectroscopic evidence' in the title has also been chosen intentionally as contrast to one of the first spectroscopic work to identify PSC composition published by O. B. Toon and M. A. Tolbert in Science, 1995, entitled: 'Spectroscopic evidence against nitric acid trihydrate in polar stratospheric clouds' [Toon and Tolbert(1995)].

We admit, however, that the differentiation between α- and β-NAT is not as clear as between NAT and the other species. Thus, we agree to skip 'β-' in the paper title.

In the search for NAD we use the $810\,cm^{-1}$ feature as a fast indicator if there is any signal of the $810\,cm^{-1}$ band of NAD visible in MIPAS observations, which is not. Of course this does not exclude the possibility that NAD still exists there. We have changed the related passages of the text accordingly.

5. *Additionally, it has been ignored that there are two modifications of NAD (α-NAD and β-NAD), of which single crystal data, infrared and Raman spectra already exist.*

We have stated in the text that the optical constants used have probably been the ones

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

of α-NAD [Grothe et al.(2004), Wagner et al.(2005)]. We have not tested β-NAD since to our knowledge no optical constants have been published. However, as stated in Table 1 of [Grothe et al.(2004)], the ν_2-bands of nitrate of α- and β-NAD are centred at 809 and 811 cm^{-1}, respectively, which is in agreement with the optical constants used here. Further, the NO$_3^-$ ν_2-band at around 1450 cm^{-1} which is the other spectral feature that does not fit our measurements is also present in case of β-NAD.

6. *Related to the STS analysis a mixing rule has been considered as an adjusting tool, which has been developed by Biermann 1998. In this context, the authors have to mention that only recently two papers appeared which have disputed this rule due to the temperature dependence of the density and of the dissociation equilibrium. Additionally, both dissociation equilibria (nitric acid and sulphuric acid) interfere. In order to be objective, you should quote Lund Myhre 2005 and Minogue 2003 when using this method.*

We have used this mixing rule since there is no other scheme available. It is not clear at the moment, how large the errors induced by application of the mixing rule are. [Norman et al.(2002)] found that the differences between their measurements of ternary solutions and calculations based on the [Biermann et al.(2000)] data and mixing rule are mainly caused by the binary data of [Biermann et al.(2000)]. This has also been suggested by [Wagner et al.(2003)]. Using their own data, [Norman et al.(1999)] for HNO$_3$/H$_2$O and H$_2$SO$_4$/H$_2$O by [Niedziela et al.(1999)], combined with the mixing rule by [Biermann et al.(2000)], the agreement between calculation and measurement of ternary solutions improved considerably [Norman et al.(2002)]. Remaining differences were attributed to the mixing rule. As the referee mentioned, also [Lund Myhre et al.(2005)] report on differences between their ternary spectra and calculations based on their own datasets of binary solutions. Unfortunately, the differences which are explained by interference of the dissociation equilibria of HNO$_3$ and H$_2$SO$_4$, are not shown in the paper. As the referee suggested, we have cited the related publications in the revised manuscript.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

7. *The Kramer Kronig Transformation assumes that the spectral cut-off falls in a moderately flat unstructured region - control that. What is the impact on the results when the region below 500 cm-1 has not been considered (see Lund Myhre et al., 2003, Lund Myhre et al., 2005)?*

[Lund Myhre et al.(2003)] have explained differences between their data of optical constants for the H_2SO_4/H_2O system and those by [Biermann et al.(2000)] by the fact that [Biermann et al.(2000)] had assumed a monotonous decrease in the far infrared absorption below 500 cm^{-1} while in the far infrared region [Lund Myhre et al.(2003)] had measured an increase. However, as [Wagner et al.(2003)] noted, such an application of the Kramers-Kronig transformation only influences the real part of the refractive indices in [Biermann et al.(2000)] while the imaginary part is directly obtained from the transmission spectra. This is also the case for the β-NAT refractive indices from [Biermann(1998)] used in our paper. Since (1) the imaginary part (i.e. the absorption part) mainly determines the MIPAS infrared spectra and since (2) the real part (i.e. the refractive part) is shown to be much less affected ($< 5\%$ [Lund Myhre et al.(2003)]) by neglecting the far-IR region, we are convinced that the influence on our comparison between MIPAS observations and simulations is negligible.

8. *In Fig. 4 the text box with the captions overlaps the spectra - please, change that.*

Done. Also for Fig. 5 and 6.

9. *What is the assignment of the narrower bands beside the band at 820 cm-1 (see Fig. 4–6)? Where are the other bands of nitrate in the MIPAS spectrum?*

The signal between 830 and 860 cm^{-1}) is the caused by CCl_3F (CFC-11), at 809 cm^{-1} by $CHClF_2$ (HCFC-22), at 798 cm^{-1} by O_3, CO_2, and CCl_4. The peak at 792 cm^{-1} is due to CO_2. This information has been included in the revised paper.

As stated above, the other particulate nitrate bands are partly covered by trace gas interference and are broad compared to the 820 cm^{-1} feature. Thus, these can best

be identified by detailed radiative transfer calculations including all interfering species as has been done in the paper.

10. *It isn't clear from the text why the band intensity at 792 cm-1 has been chosen for the colour-ratio method.*

The $792\,cm^{-1}$ wavelength region as a reference band with medium optical depth has been used successfully for the first time in cloud detection for CRISTA measurements [Spang et al.(2001a), Spang et al.(2001b), Spang et al.(2002)]. By calculating the ratio between a wavenumber region with very small trace gas interference ($832\,cm^{-1}$) and one with medium interference ($792\,cm^{-1}$) the temperature dependence of the resulting quantity is reduced compared to the use of only the $832\,cm^{-1}$ radiances to detect clouds. The colour-ratio procedure has been shown to provide compact relationships also when applied to PSC observations showing the $820\,cm^{-1}$ signature [Spang and Remedios(2003)] and is used in the standard processing of MIPAS data by ESA [Spang et al.(2004)]. Thus, in the paper we investigate this established method by use of radiative transfer simulations quantitatively. In the revised version we have described the colour-ratio method in more detail.

References

[Biermann(1998)] Biermann, U. M.: Gefrier- und FTIR-Experimente zur Nukleation und Lebensdauer stratosphärischer Wolken, Ph.D. thesis, Universität Bielefeld, cuvillier Verlag, ISBN 3-89712-212-X, 1998.

[Biermann et al.(2000)] Biermann, U. M., Luo, B. P., and Peter, T.: Absorption spectra and optical constants of binary and ternary solutions of H_2SO_4, HNO_3, and H_2O in the mid infrared at atmospheric temperatures, J. Phys. Chem. (A), 104, 783–793, 2000.

[Grothe et al.(2004)] Grothe, H., Lund Myhre, C. E., and Tizek, H.: Vibrational spectra of nitric acid dihydrate (NAD). Vibr. Spectrosc., 34, 55-62, 2004.

[Hudson et al.(2002)] Hudson, P. K., Zondlo, M. A, and Tolbert, M. A.: The interaction of methanol, acetone, and acetaldehyde with ice and nitric acid-doped ice: implications for cirrus clouds, J. Phys. Chem. (A), 106, 2882–2888, 2002.

[Koch et al.(1996)] Koch, T. G., Holmes, N. S., Roddis, T. B., and Sodeau, J. R.: Low-temperature reflection/absorption IR study of thin films of nitric acid hydrates and ammonium nitrate adsorbed on gold foil, J. Chem. Soc., Faraday Trans., 92, 4787–4792, 1996.

[Lund Myhre et al.(2003)] Lund Myhre, C. E., Christensen, D. H., Nicolaisen, F. M., and Nielsen, C. J.: Spectroscopic study of aqueous H_2SO_4 at different temperatures and compositions: variations in dissociation and optical properties, J. Phys. Chem. A, 107, 1979–1991, 2003.

[Lund Myhre et al.(2005)] Lund Myhre, C. E., Grothe, H., Gola, A. A., and Nielsen, C. J.: Optical constants of HNO_3/H_2O and $H_2SO_4/HNO_3/H_2O$ at low temperatures in the infrared region, J. Phys. Chem. A, 109, 7166–7171, 2005.

[Minogue(2003)] Minogue, N., Riordan, E., and Sodeau, J. R.: Raman Spectroscopy as a Probe of Low-Temperature Ionic Speciation in Nitric and Sulfuric Acid Stratospheric Mimic Systems, J. Phys. Chem. A, 107, 4436–4444, 2003.

[Niedziela et al.(1998)] Niedziela, R. F., Miller, R. E., and Worsnop, D. R.: Temperature- and frequency-dependent optical constants for nitric acid dihydrate from aerosol spectroscopy, J. Phys. Chem. (A), 102, 6477–6484, 1998.

[Niedziela et al.(1999)] Niedziela, R. F., Norman, M. L., DeForest, C. L., Miller, R. E., and Worsnop, D. R.: A Temperature- and Composition-Dependent Study of H_2SO_4

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

Aerosol Optical Constants Using Fourier Transform and Tunable Diode Laser Infrared Spectroscopy, J. Phys. Chem. (A), 103, 8030–8040, 1999.

[Norman et al.(1999)] Norman, M. L., Qian, J., Miller, R. E., and Worsnop, D.: Infrared complex refractive indices of supercooled liquid HNO_3/H_2O aerosols, J. Geophys. Res., 104, 30 571–30 584, 1999.

[Norman et al.(2002)] Norman, M. L., Miller, R. E., and Worsnop, D.: Ternary $H_2SO_4/HNO_3/H_2O$ Optical Constants: New Measurements from Aerosol Spectroscopy under Stratospheric Conditions, J. Phys. Chem. (A), 106, 6075–6083, 2002.

[Richwine et al.(1995)] Richwine, L. J., Clapp, M. L., Miller, R. E., and Worsnop, D. R.: Complex refractive indices in the infrared of nitric acid trihydrate aerosols, Geophys. Res. Lett., 22, 2625–2628, 1995.

[Ritzhaupt and Devlin(1991)] Ritzhaupt, G. and Devlin, J. P.: Infrared spectra of nitric and hydrochloric acid hydrate thin films, J. Phys. Chem., 95, 90–95, 1991.

[Spang et al.(2001a)] Spang, R., Riese, M., Eidmann, G., Offermann, D., and Wang, P. H.: A detection method for cirrus clouds using CRISTA 1 and 2 measurements, Adv. Space Res., 27, 1629–1634, 2001.

[Spang et al.(2001b)] Spang, R., Riese, M., and Offermann, D.: CRISTA–2 observations of the south polar vortex in winter 1997: A new dataset for polar process studies, Geophys. Res. Lett., 28, 3159–3162, 2001.

[Spang et al.(2002)] Spang, R., Eidmann, G., Riese, M., Offermann, D., Preusse, P., Pfister, L., and Wang, P.-H.: CRISTA observations of cirrus clouds around the tropopause, J. Geophys. Res., 107(D23), 8174, doi:10.1029/2001JD000698, 2002.

[Spang and Remedios(2003)] Spang, R. and Remedios, J. J.: Observations of a distinctive infra-red spectral feature in the atmospheric spectra of polar stratopsheric clouds measured by the CRISTA instrument, Geophys. Res. Lett., 30, 2003.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

[Spang et al.(2004)] Spang, R., Remedios, J. J., and Barkley, M. P.: Colour indices for the detection and differentiation of cloud types in infra-red limb emission spectra, Adv. Space Res., 33, 1041–1047, 2004.

[Tisdale et al.(1999)] Tisdale, R. T., Prenni, A. J., Iraci, L. T., Tolbert, M. A., and Toon, O. B.: Variation of the infrared spectra of nitric acid hydrates with formation conditions: Impact on PSC identification, Geophys. Res. Lett., 26, 707–710, 1999.

[Toon et al.(1994)] Toon, O. B., Tolbert, M. A., Middlebrook, A. M., and Jordan, J.: Infrared optical constants of H_2O, ice, amorphous nitric acid solutions, and nitric acid hydrates, J. Geophys. Res., 99, 25 631–25 654, 1994.

[Toon and Tolbert(1995)] Toon, O. B. and Tolbert, M. A.: Spectroscopic evidence against nitric acid trihydrate in polar stratospheric clouds, Nature, 375, 218–221, 1995.

[Wagner et al.(2003)] Wagner, R., Mangold, A., Möhler, O., Saathoff, H., Schnaiter, M., and Schurath, U.: A quantitative test of infrared optical constants for supercooled sulphuric and nitric acid droplet aerosols, Atmos. Chem. Phys., 3, 1147–1164, 2003.

[Wagner et al.(2005)] Wagner, R., Möhler, O., Saathoff, H., Stetzer, O., and Schurath, U.: Infrared Spectrum of Nitric Acid Dihydrate: Influence of Particle Shape, J. Phys. Chem. A, 109, 2572–2581, 2005.

[Zasetzky et al.(2005)] Zasetzky, A., Eremenko, M., and Sloan, J.: Characterization of aerosols and clouds by ACE-FTS measurements, Presentation at the 12th ASSFTS workshop, Quebec, May 18–20, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10685, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper