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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.

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This is a very interesting and well-written paper. It is the first attempt to identify in detail a particular nitric acid hydrate phase (NAT) by the aid of infrared spectroscopy directly in the stratosphere. Höpfner et al. have analyzed mid-infrared limb-emission measurements of PSCs by the MIPAS system during the Antarctic winter 2003. They have investigated a single IR band at 820 cm^{-1} comparing the MIPAS spectra with new refractive index data from lab measurements. They claim that this band gives spectroscopic evidence of β-NAT but not of NAD.

Since my competence is more on lab IR spectroscopy than on field measurements, I have concentrated my report particularly on the respective spectroscopic statements presented in this manuscript. However, I would like to point out that IR spectroscopy is much more reliable for the estimation of a phase composition of a solid aerosol than aerosol mass spectroscopy. This is due to the fact that the chemical composition of a particle (analysed by the mass spectrometer) is not a priori the same as its phase stoichiometry. Although, one should also take into account that for the estimation of an exact phase assignment diffraction techniques would be the more adequate methods monitoring the long range order of a solid while IR spectroscopy exhibits only the short range order (i.e. the direct environment of ions and molecules). Since diffraction techniques are not applicable in the present situation, a careful correlation between IR spectra from the field and confirmed spectra from the lab is the method of choice – as carried out by the authors. However, the spectroscopic part of this paper is hampered by some serious inadequacies, which have to be corrected before publication.

The experimental part of this paper is incomplete. The experimental procedure to obtain the two sets of indices is not described in the text but is only available in the thesis of Uta Biermann (*Biermann 1998*, written in German). Although I have a copy of this thesis, I think that the important information of sample preparation (from chapter 4 of the thesis) should be available to all readers of this article. Therefore, I strongly recommend outlining them in the text.

From the MIPAS system the spectral range 685 - 2410 cm^{-1} is available, which in principle includes the following nitrate bands of β-NAT: ν_2(A$_2$”) = δ_s = 820 cm^{-1}, ν_2(E’) = $\nu_{\rm as}$ = 1375 cm^{-1}, ν_4(E’) = $\delta_{\rm as}$ = 720 cm^{-1}, as well as the oxonium and the water band: ν_4(H$_3$O$^+$) $= \delta_{\rm as}$ = 1830 cm^{-1}, ν_2(H$_2$O) = δ = 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. However, the chosen deformation mode is

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in comparison to the asymmetric stretch of nitrate of rather small intensity (see Fig. 1). In general, deformation modes are less specific to the molecular arrangement in its next environment (additionally, in nitrate δ_s is not degenerated and therefore is not so sensitive to anisotropy) than the asymmetric stretching mode but depend much more on distortions of the overall structure, which changes the angle of the ion and therewith the position of the band. Therefore, the authors have to take into account certain interlinked effects like sample texture (orientation), sample thickness, crystal morphologies, and phase composition:

Sample texture: One receives a perfect polycrystalline sample when assuming 3-D aerosol particles, homogeneous nucleation and undisturbed crystal growth. However, if the crystalline phase grows on a 2-D sample support or nucleates heterogeneously on the surface of a foreign phase, then the volume expansion of the crystals might be disturbed. Comparing the aerosol spectra of NAT (*Richwine 1995*, *Niedziela 1998*) with the layer spectra of NAT (*Toon 1994*), one may recognize serious differences in the optical indices between aerosol and layer spectra in the wave number region below 1500 cm^{-1}. Even among the optical indices collected by *Biermann 1998* there are several differences, which are not in coincidence with the literature data of Toon. This fact also suggests that the optical indices in the literature are to some extent “sample dependent”.

Orientation: NAT crystals tend to align preferentially along a given optical axis. The orientation was found with the C_3 symmetry axis of nitrate and oxonium perpendicular to the substrate surface. This is roughly the same as orientation of the NAT polycrystals with their *ab* plane approximately parallel to the substrate. This orientation effect changes the intensity and shape of particular absorption bands.

Sample thickness: Optical indices measured at films of different thickness exhibit prominent differences caused by anisotropy and orientation effects. Predominantly, in thin films (100–800 nm) the orientation of NAT crystals is due to the substrate on which the layer has been deposited.

Particle morphology: The absorption spectrum of a solid (layer and aerosol) depends not only on absorption but also on the loss of light caused by Mie scattering of the crystal particles. Herein, the morphology of the particles has an important impact. A particular phase may exhibit different particle morphologies depending on the sample preparation or on the presence of coexisting phases.

Phase composition: It is conceivable that vapour deposition and subsequent annealing might not have led to a homogeneous NAT crystalline sample (particular in the case of thick layers). Also other techniques such as aerosol quenching or liquid layers, which are sandwiched between two windows, might change the phase composition. Thus, different phases can easily be found depending on the experimental conditions. Since most groups did not countercheck their samples by a diffraction technique, the phase composition remains a serious uncertainty which also inflects the published optical constants. X-ray diffraction measurements of 25 mol% HNO_3 evidence not only the NAT modifications but also small portion of NAD co-crystallizing. This is due to the different nucleation processes depending on the temperature gradient and local concentration gradients.

Additional uncertainties of the optical constants are related to the interaction between NAT and ice. Tizek et al. (*Tizek 2004*) have identified an impact of the ice on the α-NAT spectrum, on the phase transition temperature (shifting from 180K to more than 200K) and on the morphology of the β-NAT crystals (platelets change into needles) – see poster at the General Assembly of the EGU (`http://imc.tuwien.ac.at/staff/grothe/grothe_2005.pdf`).

Taking into account all these effects, 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: for the orientation effects of NAT see *Mate 2004*, *Koch 1996*;

for the impact of crystal morphology (demonstrated with NAD) see *Wagner 2005*; for the impact of film thickness on the refractive indices (demonstrated with NAM) see *Fernandez-Torre 2005*; for the sample composition (NAT in a mixture with ice) see *Delaval 2005*, *Tizek 2004*.

Taking into consideration the before mentioned arguments one might have serious doubts if the identification of β-NAT is conclusive, since it is based only on a single peak centred at 820 cm^{-1}. All phases discussed in this paper, namely α-NAT, β-NAT, NAD and NAM, can all contribute to a peak at this frequency. The peak of α-NAT at 820 cm^{-1} is even rather narrow see *Mate 2004 – figure 3*. Thus, it is not clear if a unique NAT phase has been analysed or if a mixture of both NAT modifications or with other hydrates exist. 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 (*Lebrun 2003; Tizek 2002; Grothe 2004; Wagner 2005*). By no means, I can see any convincing argument, which would exclude NAD from this phase assignment.

Finally, I may summarize that this paper includes interesting data and spectroscopic evaluation, but the central conclusion is not convincing. I understand that a pronounced symmetric deformation band of nitrate has been identified in solid PSC particles. This is a good hint to nitric acid hydrates in general, but I would not claim a “spectroscopic evidence” for β-NAT in particular. I agree with “indications” or “clues” for such assignment but it is definitely not “evidence”. Therefore, I recommend changing the title, the abstract and the conclusion of the paper. If possible a second β-NAT band should be correlated with the one at 820 cm^{-1}. Furthermore, the above-mentioned arguments on the optical constants should be included into the discussion. When a careful revision has been completed, this paper should be published in the ACP journal.

Additional comments

- 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.

- 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} hasn't been considered (see *Lund Myhre 2003, Lund Myhre 2005*)?
- In Fig. 4 the text box with the captions overlaps the spectra – please, change that.
- 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?
- It isn't clear from the text why the band intensity at 792 cm^{-1} has been chosen for the colour-ratio method.

References

Biermann, Gefrier- und FTIR-Experimente zur Nukleation und Lebensdauer stratosphärischer Wolken, thesis, Universität Bielefeld 1998.

Delval, Christophe; Rossi, Michel J. Influence of Monolayer Amounts of HNO_3 on the Evaporation Rate of H_2O over Ice in the Range 179 to 208 K: A Quartz Crystal Microbalance Study. Journal of Physical Chemistry (A), 109(32), 7151-7165, 2005.

Fernandez-Torre, D.; Escribano, R.; Herrero, V. J.; Mate, B.; Moreno, M. A.; Ortega, I. K. Theoretical Calculations of Refractive Indices and Optical Effects in Spectra of Nitric Acid and Nitric Acid Monohydrate Crystals. Journal of Physical Chemistry (B), 109(38), 18010-18017, 2005.

Grothe, Hinrich; Myhre, Cathrine E. Lund; Tizek, Heinz. Vibrational spectra of nitric acid dihydrate (NAD). Vibrational Spectroscopy, 34(1), 55-62, 2004.

Koch, Thomas G.; Holmes, Nicholas S.; Roddis, Tristan B.; Sodeau, John R. Low-temperature reflection/absorption IR study of thin films of nitric acid hydrates and ammonium nitrate adsorbed on gold foil. Journal of the Chemical Society, Faraday Transactions, 92(23), 4787-4792, 1996.

Lebrun, N.; Mahe, F.; Foulon, M.; Gors, C.; Petit, J. C. Thermal behaviour of nitric acid dihydrate in 1:2 HNO_3/H_2O solutions. Canadian Journal of Physics, 81(1/2), 61-69, 2003.

Lund Myhre, Cathrine E.; Christensen, Daniel H.; Nicolaisen, Flemming M.; Nielsen, Claus J. Spectroscopic Study of Aqueous H_2SO_4 at Different Temperatures and Compositions: Variations in Dissociation and Optical Properties. Journal of Physical Chemistry (A), 107(12), 1979-1991, 2003.

Lund Myhre, C. E.; Grothe, H.; Gola, A. A.; 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. Journal of Physical Chemistry (A), 109(32), 7166-7171, 2005.

Mate, Belen; Ortega, Ismael K.; Moreno, Miguel A.; Escribano, Rafael; Herrero, Victor J. Investigation of orientation effects in films of nitric acid trihydrate. Physical Chemistry Chemical Physics (A), 6(15), 4047-4055, 2004.

Minogue, Nicholas; Riordan, Eoin; Sodeau, John R. Raman spectroscopy as a probe of low-temperature ionic speciation in nitric and sulfuric acid stratospheric mimic systems. Journal of Physical Chemistry (A), 107(22), 4436-4444, 2003.

Niedziela, R. F.; Miller, R. E.; Worsnop, D. R. Temperature- and Frequency-Dependent Optical Constants for Nitric Acid Dihydrate from Aerosol Spectroscopy. Journal of Physical Chemistry (A), 102(32), 6477-6484, 1998.

Richwine, L. J.; Clapp, M. L.; Miller, R. E.; Worsnop, D. R. Complex refractive indices in the infrared of nitric acid trihydrate aerosols. Geophysical Research Letters, 22(19), 2625-2628, 1995.

Tizek, Heinz; Knoezinger, Erich; Grothe, Hinrich. X-ray diffraction studies on nitric acid dihydrate. Physical Chemistry Chemical Physics, 4(20), 5128-5134, 2002.

Tizek, Heinz; Knoezinger, Erich; Grothe, Hinrich. Formation and phase distribution of nitric acid hydrates in the mole fraction range $x_{HNO3} < 0.25$: A combined XRD and IR study. Physical Chemistry Chemical Physics, 6(5), 972-979, 2004.

Toon, Owen B.; Tolbert, Margaret A.; Koehler, Birgit G.; Middlebrook, Ann M.; Jordan, Joseph. Infrared optical constants of H_2O ice, amorphous nitric acid solutions, and nitric acid hydrates. Journal of Geophysical Research, [Atmospheres], 99(D12), 25,631-54, 1994.

Wagner, Robert; Moehler, Ottmar; Saathoff, Harald; Stetzer, Olaf; Schurath, Ulrich. Infrared Spectrum of Nitric Acid Dihydrate: Influence of Particle Shape. Journal of Physical Chemistry (A), 109(11), 2572-2581, 2005.

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