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Atmospheric Measurement Techniques
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Interactive comment on "The MIPAS/Envisat climatology (2002–2012) of polar stratospheric cloud (PSC) volume density profiles" *by* Michael Höpfner et al.

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We would like to thank H. Grothe, F. Weiss and M. J. Rossi for their helpful comments related to recent laboratory work on polar stratospheric clouds. Our answers are given below. The original comment is repeated in **bold** and changes in the manuscript text are printed in *italic*.

Höpfner et al. present a global data set of vertical profiles of volume densities of PSCs. They have derived their data from MIPAS measurements. They use beta-NAT optical constants in the wavenumber range around 830 cm-1 in order to interpret the profiles of volume density. Strong variability of PSC parameters

in different Artic stratosphere winters has been observed.

Unfortunately, the authors ignore the fact that more than one NAT phase (i.e. alpha and beta NAT) is known from literature [1] and that both phases in combination with ice can occur in the lower polar stratosphere [2]. For both phases, optical constants have not only been calculated, but have also been measured in the laboratory with high precision [3, 4]. The morphology of the crystalline particles can have an important impact on the spectra as well [5, 6].

We thank the team for pointing out the important issue of several NAT phases having been observed in the laboratory. We have to stress here that the goal of the presented work has been to introduce a first climatology on PSC volume densities over the whole MIPAS period. The retrieval approach is based on extensive studies by Höpfner et al., 2006b, where a variety of available optical constants have been tested on their compatibility with the MIPAS observations in combination with ground-based LIDAR measurements. In that work we have shown that a certain set of refractive indices for beta-NAT, STS and ice fitted the spectra over a broad range of wavelengths. Thus, it seems quite certain that PSCs of this composition are present in the stratosphere. This was the reason to use the optical constants related to those best-fits as baseline for the general climatology dataset. This, of course, does not mean that we generally exclude a possible existence of other phases/compositions of PSC particles. This will be pointed out more clearly in the revised version of our paper. However, since up to now those have not been shown to exist in the atmosphere, we have decided not to consider those in the present work. An extensive search for different compositions is, thus, beyond the scope of this paper.

We highly appreciate the work performed on spectroscopy in the laboratory. It is an indispensable prerequisite for meaningful analysis of remote-sensing data. However, since our work (Höpfner et al., 2006b) we are not aware of any new sets of refractive indices available for NAT or NAD and their different phases. The quoted papers do provide spectra of absorption (i.e. the imaginary part of the refractive index), however, both, the real and imaginary part of the refractive indices are not provided. As described in our work, for simulation of the MIPAS infrared limb emission observations we have to consider also scattering, even at wavelengths around 12 μm. Therefore, we would like to take this opportunity to formulate a 'wish list' for possible future spectroscopic studies on particles to be used for analysis of remote sensing data: (1) as mentioned, the real and imaginary parts of the refractive indices are needed and, (2), generally, laboratory IR data of particles are recorded with a spectral resolution of a few wavenumbers. However, since hyperspectral remote sensing IR measurements are often much better resolved, optical constants with less than one wavenumber are requested for the analysis of very sharp aerosol bands in the IR (this related especially to the ν_2-band of NO_3^-, which is very characteristic for NAT and NAD and which is situated in a spectral region not much affected by trace-gas interference).

Beside NAT also NAD is a possible phase in PSCs [7ab]. Also NAD exhibits two crystalline modifications (alpha and beta NAD) [8]. Cold chamber experiments show that the metastable low temperature phase is more likely [9].

As reported in Höpfner et al., 2006b we had performed an extensive search for the characteristic feature of NAD at 810 cm^{-1} in all available MIPAS observations up to that date. However, we found no clear indication for such a spectral signature (while the NAT-signature is found frequently). For the reasons given above, we have not considered NAD in the development of the retrieval scheme. Again this will be pointed out more clearly in the revised version of our paper.

The authors should include these latest spectroscopic and mechanistic results from the literature into their discussion. Eventually, this will help to understand the reported large variabilities.

We agree. As suggested, we will add a paragraph in the discussion pointing to the latest laboratory work, which might be relevant for our retrieval results. However, we do not believe that the observed large variability in PSC volume density between differ-

ent Arctic stratospheric winters is due to some errors in the optical constants we have utilized in our analysis. E.g. as reported by Pitts et al., 2018, CALIPSO observed very similar patterns of Arctic variability which is mainly caused by the variable meteorological stratospheric conditions between the different years.

In addition to the points raised above it behooves the authors to compare the complex index of refraction with absorption cross section data recently published in the literature [4]. The authors should use information from laboratory experiments to calibrate, or at least validate the field observations using independent verification. Retrievals do not mean anything unless the optical data are validated using information external to the retrieval cycle. Table 6 of reference 4 displays quantitative data on optical constants of alpha- and beta-NAT as well as NAD (exact phase unknown). The associated spectra also show that all three nitric acid hydrates absorb around 830 cm-1 such that basing the assessment of the occurrence frequency solely on a single wavelength region is a losing proposition. It behooves the authors to make better use of published results from laboratory experiments in order to maximize the scientific insight (phase, frequency of occurrence, interconversion dynamics and the like) to the benefit of the readers who will appreciate a break-out from the beaten path from time to time.

As outlined before, the intension of this work was not to perform detailed scientific investigations on particle composition, as has been performed previously. Instead we provide a first dataset over ten years, e.g. for the validation of atmospheric models, limiting the possible range of PSC vertical profiles of volume density being in accordance with the MIPAS limb radiance observations. In the selection of the spectral range, which minimizes retrieval errors, we had to balance out various side conditions, as trace gas interference, low sensitivity to scattering, and various refractive indices. With respect to the variability of refractive indices at 830 cm^{-1}, for the sensitivity analysis we have used refractive indices of those data which are definitively observed as composition of

PSC particles in the stratosphere (beta-NAT, STS, ice). The variability of these optical constants at 830 cm^{-1} is similar to the variability of laboratory observations also for phases like alpha-NAT, beta-NAT and NAD (see e.g. Woiwode et al., 2016, Fig. 13; Ortega et al., 2006, Fig. 3).

The following text has been added in the manuscript:

A further assumption we have made during the development of the retrieval was the choice of the optical constants. Our baseline was to use only those refractive indices of PSC composition and phase which have already been observed in the atmosphere and shown best compatibility with infrared limb observations, i.e. beta-NAT, STS, and ice (Höpfner et al., 2006b). This may lead to the following uncertainties: (1) the optical constants themselves are not perfect (Ortega et al., 2006; Iannarelli and Rossi, 2015). (2) particles may be present with different phases and composition (e.g. alpha-NAT, alpha-NAD, beta-NAD) as laboratory studies indicate their possible existence under polar stratospheric conditions (Grothe et al., 2008; Stetzer et al., 2006; Möhler et al., 2006). And (3), PSC particle shapes different from spherical ones, as seen in the laboratory (Grothe et al., 2006), can have an effect even at wavelengths in the thermal infrared (Wagner et al., 2005; Woiwode et al., 2016). We have implicitly accounted for those errors by the large variability of optical constants of beta-NAT, STS, and ice during the optimisation of the retrieval baseline configuration. Still, the use of one specific set of refractive indices leads to systematic retrieval errors which strongly depend on the atmospheric scene. A validation of infrared limb observations by in-situ measurements, especially of such cases where solid nitric acid containing particles are present, would be helpful to get a better grip on those uncertainties.

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