

Manuscript entitled:

MIPAS database: new HNO<sub>3</sub> line parameters at 7.6 microns validated with MIPAS satellite measurements" by A. Perrin, J.-M. Flaud, M. Ridolfi, J. Vander Auwera, and M. Carlotti.

We would like to thank Reviewer (1) for his very useful comments. Please find hereafter our answers.

Reviewer (1)

==> Q: ...when I read the Rothman et al. [2013] paper describing the HITRAN\_2012 linelist, it talks only about the addition of 15N lines of HNO<sub>3</sub> in the 11 micron region.

A: Yes, this is right. We changed "Rothman et al. [2013]" to "Rothman et al. [2009, 2013]".

==> Q: An usual feature of this work is the use of MIPAS atmospheric emission spectra (rather than lab spectra) to scale the 7.6 um line intensities to enforce consistency between HNO<sub>3</sub> retrievals performed using the 7.6 and 11.0 um regions. The danger with using atmospheric spectra is that some inadequately characterized absorber (e.g. ClNO<sub>3</sub>) may be biasing the MIPAS HNO<sub>3</sub> retrieval differently at 7.6 and 11 um. So I think that the authors need to explain in a little more detail their rationale for preferring MIPAS atmospheric spectra over lab spectra for this purpose.

We provide here two types of answers to the reviewer.

The availability of laboratory spectra:

Two type of laboratory spectra exist – and were used- during the present study.

☐☐ High resolution laboratory spectra:

To our knowledge, the only existing set of high resolution laboratory spectra of HNO<sub>3</sub> in the full 11 to 7.6 microns was recorded in 2004 (Perrin et al . J. Mol. Spectrosc., 228, 375–391, 2004). However since in 2004, the experimental study focused mainly on the 11 μm region the optical filter was not optimum at 7.6 μm, and the laboratory spectra are rather noisy for wavenumbers higher than 1350 cm<sup>-1</sup>. As a consequence we could not use these spectra to compare the 11 and 7.6 micron regions.

☐☐ Low resolution laboratory spectra (PNNL):

These low resolution laboratory spectra were recorded for various set of mixtures of HNO<sub>3</sub> and nitrogen. We used the PNNL spectra at 11 and 7.6 μm in parallel with MIPAS spectra to perform the present

calibration. Let us remind that a similar calibration with PNNL spectra was performed at 11  $\mu\text{m}$  during our previous investigation (Flaud et al. Atmos. Chem. Phys., 6, 5037 – 5048, 2006).

#### The MIPAS spectra:

It is true that, in principle, our calibration procedure is affected also by the error due to modeling the interfering species. However, as explained below, this error in our case is much smaller compared with the instrument calibration error (of 1.5%) mentioned in the paper.

The MWs used in our retrievals are selected with the MWMAKE algorithm of Dudhia et al. 2002.

(Dudhia, A., Jay, V. L., and Rodgers, C. D.: Microwindow selection for high-spectral-resolution sounders, Appl. Optics, 41, 3665-3673, 2002).

Out of a user-supplied broad spectral interval, this algorithm selects optimized narrow (less than 3  $\text{cm}^{-1}$ ) spectral intervals (called microwindows, MWs) that contain relevant information on the atmospheric target parameters to be retrieved ( $\text{HNO}_3$  VMR in our case). The selection is done with the aim to minimize the total retrieval error. This is evaluated taking into account the measurement noise, the error due to spectral interferences, instrument and forward model errors. The full list of the considered error components is reported in the following web page maintained by A.Dudhia at Oxford University: <http://www.atm.ox.ac.uk/group/mipas/err/>

At the end of the MW selection process the MWMAKE algorithm provides estimates of the various error components affecting the  $\text{HNO}_3$  profile retrieved with the selected MWs. At the altitude of 21km (the  $\text{HNO}_3$  VMR peak region), we get following estimates for the errors due to spectral interferences:

a) when using the 11 $\mu\text{m}$  MWs we have:

- error due to  $\text{H}_2\text{O}$  = 0.2%
- error due to  $\text{NH}_3$  < 0.1%
- error due to other non-retrieved species: smaller than the above contributions.

b) when using the 7.6 $\mu\text{m}$  MWs we have:

- error due to  $\text{H}_2\text{O}$  = 6.7 %
- error due to  $\text{N}_2\text{O}$  = 2.3 %
- error due to  $\text{CH}_4$  = 3.4 %
- error due to other non-retrieved species: smaller than the above contributions.

The error due to NH<sub>3</sub> interference is much smaller than the instrument calibration error, therefore it is negligible. Regarding the possible ClONO<sub>2</sub> interference error mentioned by the reviewer, while it is taken into account in the MWMAKE calculations, its amplitude turns-out to be much smaller than the above mentioned contributions. Regarding the interference errors due to H<sub>2</sub>O, CH<sub>4</sub> and N<sub>2</sub>O we can say that: since the VMR of these species is also retrieved from MIPAS spectra without any important biases (see ACP, 2006 special issue on MIPAS validation: [http://www.atmos-chem-phys.net/special\\_issue70.html](http://www.atmos-chem-phys.net/special_issue70.html)), the interference error caused by these species is random and therefore scales down with the inverse square root of the size of the set of averaged profiles. The contribution of these error components is therefore included in the error bars of the black curves in Figs 1 and 2. The additional test retrievals (mentioned in the paper) we performed exploring different seasons in the year also confirm this hypothesis.

In Sect.3 of the revised paper we now provide more details regarding the procedure used to select the MWs for the retrieval and we explain how the retrieval errors due to spectral interferences scale down in profile averages.

==> Q: Page 11646, line 17-19: At altitudes higher than 35-40 km tangent altitude, atmospheric H<sub>2</sub>O absorption lines are very narrow, and therefore not a major impediment to the retrieval of HNO<sub>3</sub> at 5.8 or 7.6  $\mu$ m, at least from high resolution spectra. At lower resolution the H<sub>2</sub>O will be more problematic at 5.8  $\mu$ m, but CH<sub>4</sub> will be problematic at 7.6  $\mu$ m. So the authors words don't satisfactorily explain why the 7.6  $\mu$ m band is the focus of this study, rather than the stronger 5.8  $\mu$ m band.

The error due to CH<sub>4</sub> interference at 7.6 $\mu$ m exists, however, since CH<sub>4</sub> is also retrieved from MIPAS spectra, this error is not very large. For example, the MW selection algorithm estimates the HNO<sub>3</sub> error due to CH<sub>4</sub> interference at 39 km to be 2.2% when using only the MWs in the 7.6 $\mu$ m region. This error is by far smaller than the noise error achieved at 39 km when using only the MWs at 11 $\mu$ m, therefore the MWs in the 7.6  $\mu$ m region can still be successfully used to decrease the total HNO<sub>3</sub> retrieval error above 35-40 km.

In the revised paper we expanded this Paragraph to make the point more clear.

Finally let us mention that there is no reason to update at 5.8  $\mu$ m the HNO<sub>3</sub> line parameters in the spectroscopic databases. Indeed, there exist, up to now, no new spectroscopic study in the literature concerning this 5.8  $\mu$ m region. The intercalibration between the 11  $\mu$ m and 5.8  $\mu$ m was already done in Flaud et al. paper [measurements, Atmos. Chem. Phys., 6, 5037–5048, doi:10.5194/acp-6-5037-2006, 2006.

==> Q: Page 11648: line 9: 20012 -> 2012

A: We changed to (2009).

==> Q: Page 11662, Table 3: Surprised to see \*fewer\* lines of the  $\nu_3/\nu_4$  bands in the new linelist than in the old one, despite a 20/25 times lower  $S_{min}$  threshold.

A: The "old" version of the HNO<sub>3</sub> linelist at 7.6 microns, was generated using a list of HNO<sub>3</sub> lines produced 20 years ago. In this old linelist a number of lines were written (for technical reasons) as "4- degenerate" or "2- degenerate" multiplets (lines at the SAME position, with the SAME lower state energy, and involving equivalent rotational quantum numbers). Each component of this "4- degenerate" or "2-degenerate" multiplet does not have any physical meaning by itself. Only the sum of the contributions of the 4- (or 2-) components is relevant. So, in the new linelist, we avoid these "non physical" clusters of lines. This is why the new linelist is shorter than the old one.

==> Q: Page 11663, Table 4: I don't understand why the  $R_{mean}$  for "This Work" is 0.95 and not 1.00. This implies that the laboratory FTIR spectra are not consistent with MIPAS

A: This is right ! As explained in Page 11, the intercomparison with the results of the FTS laboratory measurements is performed through a theoretical calculation of the experimental intensities. Unfortunately the model used for such calculations (Perrin, 2013) is not perfect. This represents a limit of this "line by line" intercomparison. However, owing to these difficulties, this line by line intercomparison gives reasonably good results: 0.95 instead of "1.00" is a reasonably satisfactory result. Finally, one has to mention that the intercomparison with the integrated band intensities (PNNL spectra) leads to an excellent agreement.

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