

Interactive comment on “MIPAS database: new HNO₃ line parameters at 7.6 μm validated with MIPAS satellite measurements” by A. Perrin et al.

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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 HNO₃ 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

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(rather than lab spectra) to scale the 7.6 μm line intensities to enforce consistency between HNO₃ retrievals performed using the 7.6 and 11.0 μm regions. The danger with using atmospheric spectra is that some inadequately characterized absorber (e.g. ClNO₃) may be biasing the MIPAS HNO₃ retrieval differently at 7.6 and 11 μm. 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. $\hat{\text{A}}\hat{\text{d}}\hat{\text{A}}\hat{\text{d}}$ High resolution laboratory spectra: To our knowledge, the only existing set of high resolution laboratory spectra of HNO₃ 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⁻¹. As a consequence we could not use these spectra to compare the 11 and 7.6 micron regions.

$\hat{\text{A}}\hat{\text{d}}\hat{\text{A}}\hat{\text{d}}$ Low resolution laboratory spectra (PNNL): These low resolution laboratory spectra were recorded for various set of mixtures of HNO₃ 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 μm 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-

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3673, 2002). Out of a user-supplied broad spectral interval, this algorithm selects optimized narrow (less than 3 cm^{-1}) spectral intervals (called microwindows, MWs) that contain relevant information on the atmospheric target parameters to be retrieved (HNO₃ 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 HNO₃ profile retrieved with the selected MWs. At the altitude of 21km (the HNO₃ VMR peak region), we get following estimates for the errors due to spectral interferences:

a) when using the 11um MWs we have: * error due to H₂O = 0.2% * error due to NH₃ < 0.1% * error due to other non-retrieved species: smaller than the above contributions.

b) when using the 7.6um MWs we have: * error due to H₂O = 6.7 % * error due to N₂O = 2.3 % * error due to CH₄ = 3.4 % * error due to other non-retrieved species: smaller than the above contributions.

The error due to NH₃ interference is much smaller than the instrument calibration error, therefore it is negligible. Regarding the possible ClONO₂ 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 H₂O, CH₄ and N₂O 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), 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 Fig.s 1 and 2. The additional test retrievals (men-

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tioned 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 H₂O absorption lines are very narrow, and therefore not a major impediment to the retrieval of HNO₃ at 5.8 or 7.6 um, at least from high resolution spectra. At lower resolution the H₂O will be more problematic at 5.8 um, but CH₄ will be problematic at 7.6 um. So the authors words don't satisfactorily explain why the 7.6 um band is the focus of this study, rather than the stronger 5.8 um band.

The error due to CH₄ interference at 7.6um exists, however, since CH₄ is also retrieved from MIPAS spectra, this error is not very large. For example, the MW selection algorithm estimates the HNO₃ error due to CH₄ interference at 39 km to be 2.2% when using only the MWs in the 7.6um region. This error is by far smaller than the noise error achieved at 39 km when using only the MWs at 11um, therefore the MWs in the 7.6 um region can still be successfully used to decrease the total HNO₃ 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 μm the HNO₃ line parameters in the spectroscopic databases. Indeed, there exist, up to now, no new spectroscopic study in the literature concerning this 5.8 μm region. The intercalibration between the 11 μm and 5.8 μm 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).

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==> Q: Page 11662, Table 3: Surprised to see *fewer* lines of the v3/v4 bands in the new linelist than in the old one, despite a 20/25 times lower Smin threshold.

A: The "old" version of the HNO₃ linelist at 7.6 microns, was generated using a list of HNO₃ 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 Rmean 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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Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/8/C5593/2016/amtd-8-C5593-2016-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 11643, 2015.

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