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## ***Interactive comment on “Heavy ozone enrichments from MIPAS limb emission spectra” by C. Piccolo et al.***

**Anonymous Referee #2**

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### **1 General:**

The article "Heavy ozone enrichments from MIPAS limb emission spectra" by C. Piccolo and her colleagues is an interesting and pioneering paper in that it seeks to gather a global picture of isotope enrichment in stratospheric ozone by means of satellite data. While the paper is generally well written and seems to be sound on the side of data retrieval, it is less convincing in terms of data interpretation, conclusions reached and, especially, the error analysis – a point that has been already pointed out by the first referee. Before the paper can be recommended for publication, the authors need to clarify which variations in delta (symmetric and asymmetric molecules) they attribute to measurement uncertainties and which they think are due to changes in the isotopic

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composition of ozone.

The lack of agreement with measurements based on the cryogenic collection of ozone samples, as well as the very large ( $\sim 100\%$ , uncorrelated in terms of symmetric and asymmetric ozone, but unconventionally correlated in terms of  $^{17}\text{O}$  and  $^{18}\text{O}$ ) variability of enrichments which is difficult to explain for a molecule that reacts rapidly, does raise some questions on the reliability of the observations. Given some recent atmospheric measurements (e.g. Haverd et al. (2005), Krankowsky et al. (2007), for a review of earlier results see Brenninkmeijer et al. (2003)) and the still ongoing work on photo-induced isotope effects (Miller et al. (2005), Liang et al. (2006)), I see obligation for the authors to present unequivocal evidence for their claims: How can a strong correlation  $\delta^{17}\text{O} > \delta^{18}\text{O}$  be explained? How can enormous enrichments  $> 50$  or  $100\%$  be explained? The paper also lacks some of the more recent publications in the field, such as the results of recent balloon born FTIR and mass spectrometer measurements (Haverd et al. (2005), Krankowsky et al. (2007)), which when included, will certainly change the argumentation of the manuscript.

## 2 Specific Remarks

### Error Analysis

While being presented clearly, the analysis of errors in  $\delta$  (section 3.2, Fig. 2) yields surprisingly small values ( $\leq 2\%$  between 20 and 50 km), which seem to be a lower limit, however. Given that systematic uncertainties in the spectroscopic data for the main isotopomer of ozone already are on the order of 3 - 4% (there is an ongoing discussion related to the compatibility of ozone data in different spectral regions in the community (eg. Picquelt-Varrault et al. (2005))), and that heavy isotope data are essentially based on a single spectroscopic study, an error in the 1% range seems completely out of the question.

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Uncertainties related to the spectroscopic data base need to be discussed more thoroughly, even more so as even larger systematic errors related to the heavy isotopomers are known to prevail (Flaud and Bacis (1998), Janssen (2005)).

With respect to the errors due to the spectroscopic data base, one of the more important contributions to the error should be that different lines with possibly very different degrees of accuracy are used for the analysis. In particular, the selection of a few suitable, and perhaps different ozone lines at different altitudes may lead to an artificial variability. In order to illustrate the uncertainties related to the ozone spectroscopic data base one might look at how line intensities have changed with updates of the HITRAN data base. When comparing the 2004 with the 1996 version, for example, intensities of  $^{16}\text{O}_3$  lines at  $10\text{ }\mu\text{m}$ , have decreased by 4 % on average due to a correction (see Rothman et al. 2005), but individual lines have been as much as 50 % higher or lower, mainly depending on the intensities.

The importance of undiscussed error sources seems to be reflected in the last sentence of the discussion (p. 25139, l. 18 - 20), where it is admitted that errors might be higher: "So, although the plots suggest that the zonal mean enrichments can be retrieved to accuracies of the order of 1% between 20–50 km, the error analysis cannot be regarded as definitive." This means that, finally, readers are left alone as to estimate the uncertainties of the measurements.

Despite the possibility that it might be very difficult to assess some of the systematic sources of uncertainties, the above statement in combination with the very small error indicated before is certainly not adequate. Without a meaningful error estimate, comparisons with previous measurements must become obsolete.

In similar veins, comparison of Fig. 5 with existing observations (Haverd et al. (2005) and Krankowsky et al. (2007)) seem to indicate the presence of large systematic errors (see discussion of Fig. 5 in the context of compatibility below).

In the context of systematic errors through the spectroscopic data base, it would be helpful to include some information on the lines used in each window in Ta-

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ble 1 (perhaps in a similar manner as Irion et al. (1996) have done). As it stands, the information given in Table 1 is not very helpful in understanding how the enrichment data has been obtained and how reliable it could possibly be. It would be interesting to know what and how many lines have been used for one particular isotope and which intensities are associated with these. Generally, there seems to be an anti-correlation between the  $O_3$  concentration (Fig. 8) and the variability of the enrichment (that may be explained by S/N due to line intensities or overlaps).

### Omission of and compatibility with previous measurements

Haverd et al. (2005) and Krankowsky et al. (2007) are two measurements that are particularly important in the context of the paper. Especially, Haverd et al. (2005) show that vertical gradients (stronger than predicted by temperature alone) exist, supposedly due to photolysis of ozone. This possibility has been discussed in detail by Liang et al. (2006) and Miller et al. (2005). Such a gradient (perhaps not observed at the same magnitude) is also evident from MS data (Krankowsky et al. (2007)), making the discussion in lines 19 to 26 on page 25142 obsolete. If these lines of text are to be retained, the source of the arguments presented need to be cited, however.

Fig. 5 is used to demonstrate that  $^{50}O_3$  enrichments are  $\sim 10\%$  and that asymmetric ozone is more enriched than symmetric (p. 25141 l. 10 - 16). Moreover agreement with previous measurements on these two issues is claimed (neglecting the issue of horizontal and vertical gradients) based on this figure. Unfortunately, the data in Fig. 5 are not 100 % compatible with the claim and they do not seem to justify the conclusion "MIPAS enrichments in stratosphere are consistent with those obtained by previous stratospheric observations and lab measurements. The asymmetric heavy ozone is significantly more enriched than the symmetric isotopomer" (p. 25144 l. 12 - 14). In particular, MIPAS seems to be ozone (isotope) blind in the lower equatorial stratosphere. Around the blank

area there are very high enrichments ( $> 35\%$  in Fig. 5, Fig. 8 shows equatorial asymmetric ozone at 21 km that is enriched even by  $> 50\%$ ), enrichments that have never been observed in the above mentioned studies. Mass spectrometer data are below 12 % at all Northern latitudes and FTIR data are smaller than 25 % for altitudes  $\leq 40$  km (Haverd et al. 2005). Do these elevated values thus indicate that something is wrong in the evaluation or do they imply that a deviation of  $\geq 10\%$  or even much more is in the margin of errors ?

## Presentation and discussion of results

Section 6 is devoted to the measurements of  $\delta^{17}\text{O}$ , which are presented in Fig. 9. The presentation discusses the compatibility with the early laboratory measurements of Thiemens and Heidenreich (1983), that are restricted to very low enrichments anyway. But enrichments that vary between  $-20$  and  $+60\%$  (a variation found at all altitudes from 21 to 33 km) have not yet been observed neither in a laboratory nor in an atmospheric environment. This is a very important point to make and to discuss, in particular when in section 5.1 an agreement with previous measurements has been claimed. It is not sufficient to mention this only in the conclusion section. The observation thus is truly remarkable or, perhaps, an artifact caused by the measurement. It seems that not all data points are shown in Figs. 8 and 9. Some data points might be off the graph. Here, it might be necessary to adjust the scale to show all data points.

A presentation of symmetric ( $S$ ) vs. asymmetric ( $A$ )  $\delta^{18}\text{O}$  in the same manner as Figs. 8 and 9 present  $^{17}\text{O}$  and asymmetric  $^{18}\text{O}$  would be desirable, because this could support the claim, which is yet based on one day of observation (Fig. 5) only: that asymmetric ozone is more enriched than symmetric ozone. It would also show that enrichments of symmetric ozone can possibly be tremendous ( $> 100\%$ ), a result either spectacular or due to yet unidentified errors. Enrichments of  $S > 100\%$  are not directly shown in the Figures presented, but seem to be implied by the data in Figures 8 and 9. For example, a dark yellow data point

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in Fig. 9 at 30 km shows  $E > 50\%$ . Because all dark yellow points in Fig. 8 have  $A < 20\%$ , we conclude that for reasons of mass balance ( $3E = 2A + S$ ),  $S > 110\%$ . Conversely, there is a green data point at 42 km with  $A \sim 60\%$  and  $E < 20\%$ , thus  $S \leq -60\%$ .

Currently, this enormous variability remains unexplained and requires clarification.

## References

Below is a list of publications that may be included. The first three publications are clearly missing in the manuscript.

- D. Krankowsky, P. Lammerzahl, K. Mauersberger, C. Janssen, B. Tuzson, and T. Rockmann. Stratospheric ozone isotope fractionations derived from collected samples. *J. Geophys. Res.*, 112(D8):D08301, Apr 2007.
- D. Krankowsky, F. Bartecki, G. G. Klees, K. Mauersberger, K. Schellenbach, and J. Stehr. Measurement of heavy isotope enrichment in tropospheric ozone. *Geophys. Res. Lett.*, 22(13):1713–1716, 1995.
- V. Haverd, G. C. Toon, and D. W. T. Griffith. Evidence for altitude-dependent photolysis-induced  $^{18}\text{O}$  isotopic fractionation in stratospheric ozone. *Geophys. Res. Lett.*, 32, 2005.
- C. Janssen. Intramolecular isotope distribution in heavy ozone ( $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ ). *J. Geophys. Res.*, 110:D08308, 2005.
- C. E. Miller, R. M. Onorato, M. C. Liang, and Y. L. Yung. Extraordinary isotopic fractionation in ozone photolysis. *Geophys. Res. Lett.*, 32, 2005.
- B. Picquet-Varrault, J. Orphal, J.-F. Doussin, P. Carlier, and J.-M. Flaud. Intercomparison of the ozone absorption coefficients in the mid-infrared (10  $\mu\text{m}$ ) and ultraviolet (300–350 nm) spectral regions. *J. Phys. Chem. A*, 109(1):1008 – 1014, 2005.

J. M. Flaud and R. Bacis. The ozone molecule: infrared and microwave spectroscopy. *Spectrochim. Acta A*, 54:3–16, 1998.

C. A. M. Brenninkmeijer, C. Janssen, J. Kaiser, T. Röckmann, T. S. Rhee, and S. S. Assonov. Isotope effects in the chemistry of atmospheric trace compounds. *Chem. Rev.*, 103(12):5125–5161, 2003.

### 3 Technical corrections

p 25128 | 5 allowing the variations in enrichment → allowing variations in enrichment

p 25128 | 10 in stratosphere → in the stratosphere

p 25128 | 19 contraddictions → contradictions

p 25129 | 3 transfered → transferred

p 25129 | 13 In line with previous studies in the present work → In line with previous studies

p 25130 | ? In stratosphere, the ozone chemistry is governed by the reaction cycle → In the stratosphere, ozone formation is governed by the following reaction

p 25131 | 18 Since then numerous → Since then, numerous

p 25132 | 14 - 16 → The pressure dependence in the stratosphere is insignificant however, because the formation rates of ozone are close to their low-pressure limits at pressures of interest, which are below 50 hPa (altitudes greater than 20 km).

p 25133 | 4 fourier → Fourier

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p 25134 | 19 - 24 Does this case apply here ? In the instrument description (p 25132 the authors speak about a comparatively low signal/noise). Please add a remark whether the limit of  $1/S_a \rightarrow 0$  does (approximatively) apply to this study

p 25135 | 1 - 24 The section 2.3 introduces sequential estimation and claims the advantage of the method as compared to two others. What is the price to pay ? Are there no inconveniences and how does this apply to the results ?

p 25135 | 9 There might be a comma required here : etc.) so  $\rightarrow$  etc.), so

p 25137 | 13 specifically the error  $\rightarrow$  specifically by the error

p 25137 | 19 retrieved profile  $\rightarrow$  retrieved profiles

p 25139 | 19 a zonally symmetric atmospheres  $\rightarrow$  a zonally symmetric atmosphere

p 25141 | 5 What is a large profile ?

p 25141 | 11 for the asymmetric isotopomer are apparently noisier than the symmetric  
 $\rightarrow$  for the symmetric isotopomer are apparently noisier than the asymmetric

p 25141 | 12 which suggest  $\rightarrow$  which suggests

p 25141 | 20 gradient  $\rightarrow$  gradients

p 25142 | 4 described in the sec. 2.3.  $\rightarrow$  described in sec. 2.3.

p 25142 | 8 day, resulted in  $\rightarrow$  day, which resulted in OR day, resulting in

p 25142 | 26 variantions  $\rightarrow$  variations

p 25143 | 15 Norther  $\rightarrow$  Northern

p 25143 | 15 noiser  $\rightarrow$  noisier



p 25144 | 10 The MIPAS observations → MIPAS observations

p 25147 | 6 O<sub>3</sub> → O<sub>3</sub>

p 25147 | 6 error is given by assuming horizontally homogeneous atmospheres → error is assuming a horizontally

p 25154 Fig 5 color scale is difficult to recognize due to the horizontal lines in the legend

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9, C9844–C9852, 2010

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