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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stratospheric $BrONO_2$ observed by MIPAS" *by* M. Höpfner et al.

M. Höpfner et al.

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We would like to thank the referee for the given comments and suggestions.

1. *If one tries to infer the total stratospheric bromine loading from the observations of bromine nitrate, possible systematic errors need to be addressed carefully. In this respect I find the discussion about possible systematic uncertainties in the integrated band intensity of bromine nitrate (section 3.4.1) particularly helpful. If I understand this correctly, the authors argue that any systematic bias in the IR cross section will also apply to the UV/visible cross section of bromine nitrate. Maybe the authors can expand a bit upon this to show how this would affect the comparison with the photochemical model and the comparison with BrO observations from SCIAMACHY: I expect that the results of the photochemical model shown in Fig. 6 are insensitive to the absolute cross section, if the IR and UV cross sections of bromine nitrate are scaled with the same factor?*

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We agree with the referee. The consistency of the infrared and the ultraviolet absorption cross-sections of $BrONO_2$ employed here is an important point when comparing the observed $BrONO_2$ concentrations with the predictions of the photochemical model: any systematic bias of the infrared cross-sections would also be present in the ultraviolet absorption cross-sections, leading to a rather robust comparison (i.e. insensitive of the absolute cross-section values). For example, higher infrared absorption cross-sections will not only lead to smaller $BrONO_2$ concentrations retrieved from the infrared spectra, but also to higher $BrONO_2$ photolysis rates (through the higher ultraviolet absorption cross-sections), so that the $BrONO_2$ concentrations predicted from the photochemical model would also be smaller. Therefore the most important parameter for the comparison of observed $BrONO_2$ concentrations with those predicted from a photochemical model (and based on the observed BrO concentrations) is the consistency of the infrared and the ultraviolet absorption cross-sections of $BrONO_2$, which has been established by the laboratory measurements of Burkholder et al. (1995).

We will mention this point also in the revised manuscript.

2. *p. 19681, l. 11: Br_2 is sometimes included in the list of inorganic bromine*

   We have added Br_2 in the revised manuscript.

3. *p. 19681, l. 19: I suggest to move the sentence with the reported decline of stratospheric bromine upward, following the estimated range of total inorganic bromine (l.14), and before the discussion of the partitioning of $BrONO_2$.*

   We have changed the manuscript accordingly.

4. *p. 19690, l. 5: Why is the error term due to "nlin" so much larger during day than during night? Is simply the concentration of $BrONO_2$ too low? According to Fig. 5, "nlin" is the dominating error above 30 km during day time.*

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Around 35 km altitude the "nlin" relative error term is in case of daytime retrievals with around 100% much larger than the corresponding error during night which is about 10%. However, the absolute "nlin" errors during day and night are of comparable size (1-2 pptv). Thus, the main reason for the large differences in relative units is the difference between day (about 2 pptv) and nighttime (about 20 pptv) values of bromine nitrate. This absolute systematic error is still in the range of the estimated error caused by spectral noise (about 2 pptv). Thus, as we state in the manuscript, for daytime retrievals $BrONO_2$ concentrations at altitudes above 30-35 km are in general below our detection limit. (In more detail, the absolute "nlin" errors at 35 km are for daytime retrievals still by about a factor of 1.5 larger than those during the night. From investigation of the behaviour of the retrieved profiles above this altitude it seems likely that the reason is an instability of the retrieval there caused by the very low daytime values of $BrONO_2$.)

5. *p. 19691, l. 13: Are the SCIAMACHY BrO measurements taken at the same (or at least similar) solar zenith angles as the bromine nitrate measurements? How critical is this?*

SCIAMACHY limb observations from Envisat are performed in flight direction while MIPAS ones are in rearward geometry. This means that both instruments view airmasses at the same latitude with a time difference of about 15 minutes. During day this results in solar zenith angle (SZA) differences of about 3.5° at the equator and about 0.2° at high latitudes (SCIAMACHY observations connected with larger SZAs than MIPAS ones). These differences in SZA lead to maximum changes of the photolysis frequencies of 0.8% which, in turn, would lead to about the same amount of increase in the derived $BrONO_2$ concentrations would the SCIAMACHY SZAs instead of MIPAS ones be used. Since this number is small compared to the estimated errors we decided not to discuss it in the paper.

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6. *p. 19691, l. 20: Heterogeneous reactions (in particular the reaction $BrONO_2$ + $H_2O(aq) \rightarrow HOBr + HNO_3$) can take place not only on polar stratospheric clouds, but also on background sulfate aerosol. (E.g., Lary et al., Heterogeneous atmospheric bromine chemistry, JGR, 101, 1489-1504, 1996.) I do not know if it would be easy to estimate by how much the calculated bromine nitrate profile would be influenced by this reaction, but at least in principle this reaction could be the reason why the calculated $BrONO_2$ is generally larger than the observed one in the 20 - 24 km region.*

   The referee is right: a further potential sink for $BrONO_2$ could be the hydrolysis of $BrONO_2$ at stratospheric background aerosol. Lary et al. (1996), estimated the influence on the $BrONO_2/BrO_y$ diurnal cycle at 37.9°N, 66.9 hPa for an aerosol surface area density of 6 $\mu m^2\,cm^{-3}$ (Figure 4 of Lary et al., 1996). Around noon this resulted in a reduction of $BrONO_2$ by about 25%. However, this aerosol surface area is valid for enhanced volcanic situations while background levels in 2002 were about a factor of 10 lower (e.g. Thomason and Peter, 2006). Therefore, the estimated effect on our comparison would be a reduction of the modelled $BrONO_2$ of only a few percent, which is too low to explain the overestimated values in the lower profile region. We will mention this in the revised version of the paper.

7. *p. 19691, l. 21: Modelled and measured $BrONO_2$ profiles agree well within the uncertainty range, but I would not call this agreement "very close".*

   We have changed this text passage accordingly.

8. *p. 19692, l. 15: Do you have any actual indications of whether or not a retrieval of $BrONO_2$ would be possible from ground-based IR experiments as well, or is this just a general assertion at this stage?*

   At present we do not have evidence for the possibility to retrieve $BrONO_2$ from ground-based IR observations. Thus this statement is only meant as

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a prospect for future work.

9. *Fig. 4, caption: please define the difference.*

   Done.

References:

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Lary, D. J., Chipperfield, M. P., Toumi, R., and Lenton, T., Heterogeneous atmospheric bromine chemistry, J. Geophys. Res., 101, 1489-1504, 1996.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19679, 2008.