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Interactive Comment

Interactive comment on "Balloon-borne Limb profiling of UV/vis skylight radiances, O_3, NO_2 and BrO: technical set-up and validation of the method" *by* F. Weidner et al.

F. Weidner et al.

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Please find our responses to the reviewers report in italic! For a full version of this comment including all figures go to http://www.iup.uni-heidelberg.de/institut/forschung/groups/atmosphere/stratosphere/publications/pdf/response_to_referee2.pdf

General comments

This is a very . . .
We hope that we can convince the reviewer that, stratospheric BrO profiles can sensitively be measured with the 'quasi in-situ' Limb technique (see below). At this point, we already would also like to provide a list of peer-reviewed publications concerning

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our UV/vis balloon measurements from which the reviewer my draw the necessary information about the employed techniques and methods. (Please see link above for list of peer-reviewed publications.)
In particular we would like to draw the reviewer's attention to the studies of Ferlemann et al., Harder et al., and Bösch et al., that describe the basics of our measurement technique, analysis methods and inversion techniques. In agreement with the statement of the reviewer (see below), we believe however, that all these studies should not be cited in the present paper, in order to not provoke the charge of 'trying to build up our "cited" statistics by self-referencing'.

Thus this work . . .
We investigated the spectrometer stray light in the laboratory, and it is found to be smaller than 1% for reasonable saturation levels, a value which is not uncommon for Czerny-Turner spectrometers) and it is in good agreement with previous studies (c.f., Bobrowski et al., Nature 423, 273–276, 2003). *However, the used software tools (WinDOAS, cited in the manuscript) allows us to largely account for stray light effects in the retrieval of atmospheric trace gases, primarily by including an additive polynomial (intensity offset) and Ring effect spectrum as pseudo-absorber in the fit. How this technique works is described in detail in the Aliwell et al., 2002 paper (J. Geophys. Res., 10.1029/2001JD000329, 2002) to which we contributed. Accordingly we agree with the reviewer's statement that stray light is of particular concern when using Ocean Optics spectrometers, but it can be dealt with when sufficient care is taken.*

The description of . . .
A more detailed description of the inversion algorithm than previously provided will bed in Sect. 2.6. For all the shown profile retrievals, the 'Maximum A Posteriori (MAP) solution as described by Rodgers (his book is cited in the manuscript) has been used. In retrieval exercises (which are not discussed in detail in the manuscript) SCIAMACHY O_3 profiles and/or outputs of the 3-D CTM SLIMCAT model output for NO_2 and BrO have been used as a priori. It is found that,

(a) *a priori' information is only necessary in all cases to infer profiles for altitudes above balloon float and*

(b) *at lower altitudes the inversions are totally independent of the used a priori primarily because of*
(i) sharply peaked weighting functions
(ii) high sampling frequency
(iii) small error bars of the measurements
This finding is also indicated by the measured large absorption in limb geometry and the well-behaved shapes of the averaging kernels (see Figs. 4, 5, 6 and 8). We have also convinced ourselves about the insensitivity of the result on the 'a priori' profiles in test exercises (not mentioned in the manuscript), c.f. by
i) setting the 'a priori' to zero in the relevant altitude range or by
(ii) inspection of the averaging kernels (see figure 8 in the manuscript) which are close to unity with a FWHM of the size of the altitude layers.

It is also found that for the inversions of the solar occultation observations, 'a priori profiles' are not necessary and thus have not been used.

The results presented . . .
First, our RT model Tracy is fully spherical (as it was written in the manuscript) and it does not use any plane parallel approximations. In our code the 1/cos(SZA) problem is more a numerical problem (and has nothing to do with the description of the RT in a spherical atmosphere at large SZAs) and it leads to a 20 % discrepancy (at most) in the measured and modeled radiances between 89.5–90.5° (see Fig. 3).
Unfortunately, all our limb scanning measurements have so far been undertaken around SZA=90° (which is not the typical condition under which limb scanning measurements are usually done) simply because the flight profile of the host payload (the LPMA/DOAS gondola) is optimized for spectroscopic observations around solar occultation. Certainly future flights (e.g. on the MIPAS payload) will have to show whether

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the measurements and model coincide better for higher sun that is easier to be handled by the RT and the photochemical codes. Noteworthy is that inversions of limb radical observations around SZA=90° are not at all trivial (and have never been done before), primarily due to the large (and 'a priori' unknown) concentration gradients across the terminator. Such investigations are not within the focus of the present study (see also your comments above), and future work will need to address this issue.

The measurements made. . .
We think that it does not matter to usage of the word limb whether the observations are horizontal or tangential or in any other direction, simply because,

1. *our viewing direction is explicitly given and,*
2. *we don't see any fundamental differences between the 3 mentioned geometries.*

Also it is a particular strength of our technique to obtain profile information by diving through the atmosphere (rather than scanning through it), a mode of observation that may sensitively provide profile information. We think by analyzing skylight received from the horizon in different viewing geometries provided during the balloon ascent, clearly justifies to refer to our observations as being done in 'limb' geometry.

I also would like to suggest that it would be more scientifically useful to show profiles of BrO, NO_2, and O_3 all from the same flight (namely Mar. 24, 2004).
We don't see any good reason to only show profiles for the 3 species from the same flight (even though we could do it) simply because the paper's primary intention is to show the feasibility of the technique and not to interpret the result with respect to stratospheric photochemistry. Also the atmospheric conditions of the 2 flights discussed were very similar (same location, same time of the year and well off the polar vortex).

I am concerned . . .
A more detailed discussion about how the trace gas amount contained in the solar

reference spectrum is determined is now added to Sect. 2.4 "DOAS evaluation". It primarily involves for

(a) ozone and BrO the retrieval the absorption for both gases in the measured solar Fraunhofer spectrum at float altitude using a folded Kurucz et al. spectrum as Fraunhofer reference, and a check of the inferred amounts with the absorption simultaneously measured by the direct sun observations. Noteworthy is here that in general the total residual amounts found in the solar Fraunhofer spectrum are small for both gases when compared with the amounts inferred from the actual limb measurements. Accordingly the errors in the determined residual absorption are small (and irrelevant) in the inferred profiles.

(b) NO_2 the same steps as described in (a). However, since a significant amount of atmospheric NO2 resides above float altitude, the uncertainty in the residual absorption in the solar Fraunhofer spectrum contribute somewhat more to the total error than for the gases discussed in (a).

It has to be stated that in all cases the inferred residual absorptions were found to result in a good agreement of the measured limb and direct Sun observations.
Noteworthy is, that once the residual absorptions in a particular Fraunhofer spectrum are determined, this spectrum with known residual absorption can be used in following measurements as a solar Fraunhofer reference.

Since O_4 and H_2O profiles are not shown, they should not be mentioned in this paper. Their scientific quality from limb scattering is not well established in your work or elsewhere.
We disagree because the absorptions of both gases are detected, but not shown here simply because their interpretation is not that trivial.
For the measured O_4 this is because of the predominance of Mie scattering due to aerosols and clouds in the troposphere which is not known, and for the H_2O

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absorption measured in the stratosphere due to 'skylight contamination' by skylight being backscattered from the troposphere (typically 1% of the total light according to our simulation) into the instrumental line of sight. This is particularly disturbing since the water load in the troposphere and hence absorption is a factor of 1000 larger than in the stratosphere, and hence significant in a 1:100 light mixture measured by the instrument in the stratosphere.
However, for your convenience an inter-comparison of measured and modelled O_4 and H_2O-SCDs is shown in Figs. 1&2 which can be found here: http://www.iup.uni-heidelberg.de/institut/forschung/groups/atmosphere/stratosphere/publications/pdf/fig2.pdf. Also, an O_4-profile is retrieved from the mini-DOAS limb measurements and compared to an O_4-profile obtained from direct sunlight DOAS observations and to an profile of the O_2-concentration squared (see Fig. 2). All these comparisons underline the quality of the mini-DOAS limb O_4 and H_2O measurements and the validity of the TRACY RT calculations even for complicated RT condition due to a priori unknown aerosol concentration and cloud covers.

The discussion contains . . .
We have done about 100 simulations on the various sensitivities of the limb observation to changing geophysical parameters, which are detailed in the first author's PhD thesis (in English). You may well receive a copy of it. The bottom lines of the simulations are the following.

(a) *Changing Sage III aerosol extinction in the lowermost stratosphere will not change anything simply because for volcanically quiet periods Rayleigh scattering in the UV/vis is by far more important than Mie scattering there. For example, considering NO_2 measurements at 440 nm for an ambient pressure of 150 mbar (n=4·10^{18}cm^2, $\sigma_{Rayleigh}$=1.1·10^{-26}cm^2). Accordingly, the extinction by Rayleigh scattering (ε) is ε=4.9·10^{-3}/km large when compared to Mie scattering ($\sim$10^{-4}/km for the time being at 13 km). This little calculation also demonstrates that once the observation geometry is well known nothing about scattering in the*

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visible spectrum has to be speculated on in the manuscript.

(b) *A good deal of the O_3 profile uncertainty is already demonstrated in our Fig. 7, and the following argument is probably even more important. Since stratospheric O_3 absorption in the visible spectral range is weak, the atmospheric RT (the path lengths) is hardly affected by (an assumed) O_3 profile uncertainty of 10% (a number which is much larger than c.f., typical errors of the ECC O_3 sonde measurements).*

Conversely, we wonder why the reviewer is asking to address all possible effects in our manuscript that are known to be unimportant for study. In fact unlike the reviewer feels, we strongly disagree to overload the paper with unnecessary and unfounded stuff that a skilled reader should be aware of. For further reactions see below.

Some work is needed to improve the grammar despite the efforts of the acknowledged M. Long. It is unlikely that all co-authors have proofread this manuscript based on some of the expressions used.
We hope we could identify and remove all grammatical error from the manuscript.

Specific comments

The title should be changed . . .
We think that given our results, the overall feasibility of the method to (a) retrieve stratospheric profiles of the 3 mentioned species from the limb scattering measurements during ascent and (b) the validity of the Tracy RT calculations under the given conditions is well proven. However, as stated above some smaller technical problems in the RT numerics (for morel details also see the comments of reviewer 1) may still exist which together with problems associated with the photochemistry of the probed radicals around SZA=90° rendered us cautious to retrieve profiles from the limb scanning measurements at twilight already. However, all this technical problem of Tracy does not affect the quality of the ascent measurements.

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p. 7633 SCIAMACHY measurements do not require novel methods...
The expression "novel" has been deleted.

line 24: DOAS does not give profiles. DOAS in combination with optimal estimation does.
This has been clarified in the text.

p. 7635 The period of a limb scan...
Assuming a typical integration time of 20–100 ms per scan (largely depending on illumination), 1000 co-added scans per spectrum and 14 spectra recorded per limb-scan would result in 15 min per limb-scan. Note that the integration time strongly depends on solar illumination and tangent height. It is also highly variable as our measurement software always keeps the number of scans per spectrum constant rather then the integration time. After each spectrum, the telescope is moved to the next elevation. Of course, no spectra are recorded during the movement of the stepper (which take a fraction of a second only).

p. 7636 Using the $\sim$2000 pixel detector to achieve a sampling ratio of $\sim$8 is commendable.
We concur to this statement!

p. 7637 Please write whether Tracy includes the SZA variation in 3-D and...
The Tracy simulations are 3D. The aerosol phase functions are calculated for standard scenarios using Mie-theory, however, this assumption is not relevant (see above). A more detailed discussion about aerosol parameters is unnecessary as the influence of stratospheric aerosols on the relevant RT is rather small as shown above.

p. 7638 "'conventional' profile inversion". Is this onion peeling?...
The term "convential profile inversion" refers to the afore mentioned optimal estimation method as introduced by Rodgers. Onion peeling is not used in any of the retrievals and not in the study at all. As the calculated box air mass factors are almost independent on the trace gas profiles (in fact they are for weak absorbers with which we deal here),

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any reasonably chosen profile to calculated them is suitable (in this case: ozone was taken from the ECC ozone profiling and NO_2 from the SLIMCAT model)

p. 7639 The hot pixels are a major issue for BrO. . . .
*We don't understand, why the dark current NOISE (which is also random) should not be inversely proportional to the number of coadded spectra. The mentioned hot pixels show a significantly higher dark current but no higher noise after dark current correction. All in all, the dark current noise is practically immeasurable for integration times below 10 s. For the typical integration times achieved during the balloon flight of 10-100 ms this would mean only 0.04–0.4 electrons out of 0.8*62500, i.e. 8*$10^{-5} - 8 * 10^{-4}$%. Because of this insignificant role the dark current plays in our measurements, a more detailed discussion of this issue is not included in the paper. The electronic offset and dark current is removed from all spectra prior to the DOAS evaluation (see also Ferlemann et al., 2000). For this correction, the same offset and dark current spectra, respectively, are used for all measured spectra. These correction spectra are obtained either on the ground shortly before the launch or, if possible, at float after sunset. Figure 1 shows that the total error is proportional to 1/sqrt(# of scans) for 1–10 000 co-added spectra and in the order of the photo-electron shot noise. This is all just conventional DOAS stuff, and discussed in length in the book by Stutz and Platt cited in the paper. As before we think here we should not invent wheels again that are just state-of-the-art.*

p. 7640 An absolute radiometric calibration of 35% at 380 nm is quite poor. Please discuss why this accuracy worsens so significantly in the field.
This is primarily due to 2 factors: (a) the much lower UV radiance of the used Ulbricht sphere and NIST lamp compared to the radiance in the visible spectral range, and (b) the lower sensitivity of the instrument in the UV compared to the visible region, which prevents us from calibrating the instrument equally good in all wavelength ranges. In future studies, however, we will use a newly bought deuterium lamp for calibration.

p. 7642 I suggest that you include some very small aerosols to see if this can account for the wavelength dependent bias (i.e. difference at 360 nm) and back up your speculated cause.

We repeated the RT calculation for several aerosol loads and phase functions and came to the conclusion that adding aerosols generally leads to a lower radiance compared to a pure Rayleigh atmosphere with our measurement geometry (i.e. 90° to the sun). So aerosols cannot explain the observed discrepancies between measured and RT modeled radiance. We will change the respective passage in the manuscript.

line 28: you should remove O_4, OClO and H_2O since you do not show profiles of these species. OClO may not be detectable given your instrumental issues.

For the response concerning H_2O and O_4 see above and Figs. 1&2 at the end. Further experiences gained in past field studies have shown that if one is able to measure BrO, a detection of OClO should also be possible. Unfortunately, for the time being we have no measurements inside the polar vortex to prove this.

p. 7643 Fitting windows etc. should be put in the method section. . .

The used cross section for every single species is now explicitly given and the DOAS evaluation section has been moved to Sect. 2 as Sect. 2.4. In part we concur, however, there are only a very limited number of ozone cross section available which totally cover our wavelength range, c.f. the Voigt et al. ozone cross section. We find that, outside the 400–450 nm wavelength range the Voigt et al., ozone cross section is reasonably good to be used in our study. Actually for 400–450 nm wavelength in which the NO_2 evaluation is performed, the O_3 absorption cross sections of Burrows et al. are used.

(Partly a technical comment). . .

Definitively simultaneous fits are better than fitting cross sections sequentially (see c.f., Platt and Stutz, 2004). You can convince yourself of this statement by writing down the equation of the measurement process and of the retrieval (which are similar but not the same). The only caveat to this statement is that all used cross sections have to be linearly independent, i.e., when you use 2 cross sections from the same gases recorded at different T, they have to be orthogonal.

Or how does your approach compare with fitting cross-sections...

We partly concur, but ! the problem primarily comes with the fact that the ozone Huggins band in general become optical thick in the atmosphere, and thus the linear approximations (good for many retrieval problems with optical thin absorbers) start to become really incorrect. For example, in most if not all retrieval processes the folding operation which accounts for the slit function is done with all cross section individually before their exponentials while it the real measurements process would recommend a reversed order of the mathematical operations. This approach thus poses a clear problem when absorption becomes optically thick.

Correlation of cross sections from the same species can be avoided by making them orthogonal. This is just conventional linear mathematics and is not worth be proven in this manuscript since proves are found in any good text book.

Please provide evidence that this is not the case for you...

First we recommend to the reviewer to read carefully the Aliwell et al. paper because it contains all necessary information how to deal best with skylight BrO detection. Essentially we followed the approaches described therein with good reasons. We strongly believe that going that way would largely spoil the manuscript with wisdom already available in peer-reviewed literature.

In the new version of the paper it has been clarified which wavelength interval and cross sections are used for the DOAS evaluation of each absorber. In general, only one cross section is used for the trace gas of interest, while (sometimes) 2 temperatures are used for the other absorbers. In case of 2 cross sections of the same gas at different temperatures, always one cross section is used as base while the other one is orthogonalized with respect to that base. So the 2 cross sections do not correlate and the retrieved SCD values have no meaning. However, the fit is improved by removing additional structures originating from fitting a 'wrong' temperature. Generally, the optical density of the second cross section is rather small so adding a second cross section does not really improve (but neither worsen) the DOAS fit. The Ring spectrum is calculated directly from the solar reference spectrum, i.e. either from a self-recorded or

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from the Kurucz spectrum, using different codes (in some codes even a full treatment of Raman scattering is involved) that result in slightly different theoretical Ring spectra. In test retrievals we subsequently tested any of these Ring spectra but no systematic improvement or worsening of the spectral fits was found.

p. 7645 line 5 “It is a result..." → To what does “It" refer?. . .
It refers to the following:

1. *The solar occultation measurements have generally smaller air mass factors compared to the limb scattering measurements (a fact mentioned in the manuscript), and,*

2. *Limb measurements have lower signal to noise ratios compared to solar occultation measurements for detectors operated at the electron shot noise limit simply because the latter provide more light.*

Both effects trade-off in a manner to result in almost equal sensitivities of both techniques for trace gas detection. Accordingly the text has been corrected for.
“It” refers to “the same sensitivity of the limb and solar occultation technique”.
Tangent height determination is not a real issue in our study as the RT simulations only require the detector position, viewing direction and the solar zenith angle at the detector position as input. This essential information is known from the gondola attitude control and the ephemerids. The tangent heights shown in Fig. 12 are only a rough estimate to provide some impression to which altitudes the respective measurements correspond.

p. 7646 The agreement in limb scanning geometry is not “reasonably good”.. . .
No, we disagree, since the excellent validation (at least better than what was existing previously for stratospheric twilight observations) of the radiance measured in distinct directions (Limb scanning) clearly indicates that our approach is appropriate.
However, the agreement for individual measurements is also observed (not shown)

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when the gondola is forced to rotate in the azimuth. Accordingly we do not have reasons to assume that a 4pi integral necessary to obtain actinic fluxes should be much worth than the individual observations. For details how to integrate skylight radiances and solar irradiance to actinic fluxes we recommend to read the Bösch et al., 2001 study. However, we will change the text here in order to be more modest.

I suggest you revise this sentence...
For our responses see above, which clearly provides the reasons for the larger sensitivity of 'in-situ' vs. remotely probing the atmosphere! Probably the reviewer should contemplate over the good reasons why many research groups spend a lot of money to probe the atmosphere by going into it rather than look at it from outside.

p. 7663 Fig. 10 shows better agreement. . .
A different value for the NO_2 amount of the solar reference spectrum has been used. It was taken from a correlation of the measured dSCD and simulated SCD values using the direct sunlight DOAS measurements as input. Before, the NO_2 amount of the solar reference spectrum was taken from a Kurucz et al., fit (see above). The overall good agreement increases our confidence in both methods and shows the feasibility to retrieve stratospheric NO2 profiles from limb scattering observations with the same sensitivity as with the solar occultation technique.

Figs. 10–11 Photochemical scaling of the profiles is required to match the slight differences in local time. This is critical for BrO (and of less importance for NO_2), otherwise validation can only be considered qualitative.
Photochemical scaling to find an agreement between the solar occultation and the simultaneous limb measurements is not necessary here since

(a) *both measurements have been simultaneously performed from the same platform well (SZA=77°–83°) below SZA=90° and*

(b) *we know from our own and SLIMCAT (Chipperfield, JGR, 1999) photochemical*

> *simulations that the change in stratospheric BrO concentration is still very small for the relevant SZA range.*

we do not expect large spatial gradients for BrO in the probed air masses at least not to a level that would differently affect the direct sun and limb observations.

Technical comments

Thank you for the thorough proof-reading of the manuscript. Your corrections will be included in the new version of the manuscript.

Title: Limb should not be capitalized in mid-sentence. The title needs rewording. “limb" should immediately precede “radiances" instead of describing “profiling". How about the following: Balloon-borne profiling of O3, NO2, and BrO from UV/vis limb scattering:...
The proposed title does not say that we also measure limb radiance profiles so we prefer the initial title.

INTRODUCTION p. 7632 You need to use the term “limb scattering"...
– *The citation of Kerr et al. has been deleted.*
– *“METOP/IASI” has been deleted.*
– *SME has been added with Mount et al., 1983 as reference*

line 22 “...if available profiles of the atmospheric aerosol and cloud cover and ozone profiles..." → “..., if available, profiles of ozone and aerosol and cloud particle number density...". Does Tracy require particle number densities or simply extinction and absorption coefficient spectra?
Tracy requires concentration profiles of the relevant absorbers and their absorption cross section, aerosol extinction profiles and aerosol phase functions, and the fraction of cloud cover and a cloud altitude. However, tropospheric clouds have not been “switched on” in our simulations.

INSTRUMENT PERFORMANCE AND CALIBRATION

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p. 7638, line 26 “noise" → “noise level" (occurs twice in this line). You should call this “electronic offset noise" if that is what it is.

This noise contribution combines all noise contributions caused by the electronics, including read-out noise, amplifier noise and A/D conversion noise and will, thus, be called “total electronic noise”.

OBSERVATIONS AND FLIGHTS

p. 7641 line 9 “instrument" → "instrument and method" Sections 3 and 4 can be combined with Sect. 2. Sections 3 and 4 would become Sects. 2.3 and 2.4.

The numbering of the individual sections has been reworked. Section 3 is now part of Sect. 2. Section 4 has become Sect. 3, but remains a section of its own as it gives an overview about all the flights undertaken so far which is not part of the methods nor of the results.

Ackowledgements lines 15–16 “for English proof-reading the manuscript” → “proof-reading the manuscript with regard to the English”

Corrected (comment: English is an awesome language to be learned, since a standard is not available, and different native speakers tend to insist on conflicting versions of their mother tongue.)

p. 7656 (partly non-technical) Fig. 3 is difficult to understand. . .

For the first limb scan, some of the spectra were oversaturated and, thus, not included in the analysis.

All SZA information in the manuscript is local, i.e. of the payload.

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