General comments

The paper addresses relevant scientific questions within the scope of ACP. The paper presents novel data. Substantial conclusions are reached. Some but not all of the scientific methods are valid and clearly outlined. Some, but not all of the assumptions are clearly outlined. A better discussion is needed regarding why J and k are both likely to be in error (see below). The results are sufficient to support the conclusions, but more discussion of the results is needed (see below). The description of calculations is not complete and precise to allow their reproduction by fellow scientists. The authors give proper credit to related work and clearly indicate their own new contribution. The title clearly reflects the contents of the paper. The abstract provides a complete and concise summary. The overall presentation is well structured and clear. The language could be improved in some cases: there are run-on sentences with too many ideas. The number and quality of the references is appropriate. No supplementary material was found. No part of the paper should be reduced, combined, clarified or eliminated.

The paper presents high precision limb scattering (LS) and solar occultation (SO) observations of BrO, NO2, and O3. The authors have wisely chosen the azimuth difference angle in limb scattering measurements to be 90° to minimize diurnal effects along the line-of-sight. Figures 2-5 and 8 are particularly impressive. However, more should have been done along the lines of Figure 5 with the limb scattering data. As the authors appear to realize, one way to separate J and k is to exploit their different SZA-dependence, particularly at sunrise and sunset: J is dependent on SZA (or time), but k is not. Looking at the agreement of modelled and measured SCDs as a function of SZA will provide more information than the authors' approach of looking at the agreement as a function of the SCD magnitude (Figures 6-8).

In Figure 5, the 'k=0.75, J=1.3' simulation case clearly appears to best fit the data before the air mass change, which would be in agreement with the limb scattering best J/k ratio. Noticing this (and the authors should mention this), I am convinced by their data that the currently accepted values of J and k are probably both wrong, if we assume that each must lie within its respective uncertainty.

We find the reviewer's conclusions too strong given the error bars of the measurements.

The authors should explicitly state that a J/k ratio of 1.69 implies that both J and k must have opposite biases if the uncertainty on each is not to be exceeded. This would also help the reader understand why they did not try any cases with k=1 in Figure 6 and to understand the conclusion specific to BrONO2 formation in the troposphere. Ideally, different occultation data should be tried from previous and/or future flights in the hopes that the air mass will be more homogeneous. Also, I wonder if previous limb scattering campaigns would provide an additional dataset to verify the findings presented here (e.g. 23 Mar 2003, 24 March 2004 or 1 March 2006 as listed in Kritten et al. [2010], see also Weidner et al. [2006]). If so, the best J/k ratio for each sunrise or sunset could be found, and then the ratios from all twilight occultations could be analyzed for central tendency and variability to give an estimate along the lines of the J/k ratio of 1.xx ± 0.yy found in this paper. I have also found that inferred Bry from BrO tended to be high, e.g. using SAOZ-BrO data (Figure 9 of Sioris et al., 2006).

We checked SO data available from previous balloon flights. However as said in the text, SO measurements do not provide a good insight into the kinetics of the BrO photochemistry, since intrinsically they always probe the atmosphere for more or less the same J (at SZ = 90°). Moreover our previous balloon flights suffered from either (a) a bad overlap of the BrO and NO2 profiles (c.f., in the tropics or at mid-latitudes), or (b) were conducted at non-favorable conditions to study the NOx/BrOx photochemistry (e.g. polar winter), or (c) were dynamically perturbed (e.g. taken at the edge of polar vortex), and accordingly it couldn't be unambiguously concluded that the same air masses were actually probed. Moreover, since we only started LS measurements in 2004 (e.g., Weidner et al., 2005), LS measurements were previously not performed at high latitudes during late summer, which we could exploit for the study.

Attempting to simulate the correlation of BrO and NO2 as a function of height with a large (satellite) dataset might provide a method to determine k because of its M-dependence (see Figure 10 of McLinden et al., 2010 and related text).

Yes, satellite studies along these lines have already been performed. However, in satellite observations a tight interpretation of J/k from the satellite NO2 and BrO measurements may suffer from (a) the given accuracy of the measurements, (b) that subsequent measurements of NO2 and BrO can't be performed in same air masses (which is necessary to determine out J/k), and (c) instantaneous measurements of NO2 and BrO are not very suitable to figure out kinetic constants, which would require to observe the same air masses at different time (or illumination conditions).

The major outcome of this submitted paper is the conclusion that the accepted value of the ratio should be increased by 69±4%. The authors appear to discard the significance of a large difference between their two sets of quasi-independent measurements (limb scattering and solar occultation).

No, in essence the outcome of the Limb and SO measurements for J/k is the same (see below), with the caveat that a part of the departure of the measured and modeled BrO for the SO measurement was likely due to stratospheric dynamics (see the text).

They claim to merge the two sets of ratios (from LS and SO) and weight the former more heavily. However, they do not discuss the merging of the two sets of ratios, the weighting or anything else related to quantifying the uncertainty. Using the four ratios obtained from the LS measurements and averaging, I obtain 1.696±0.04 (1σ). This is almost exactly what they found in terms of the ratio (possible rounding error?) and exactly what they found in terms of the uncertainty, meaning that the SO values seem to be essentially discarded. Because this replicates their result, I presume that I have essentially replicated the method the authors used to obtain the ratio and its uncertainty. The fact that the colour coding in Figure 8 seems to be only for LS measurements points to the fact the SO measurements are ultimately discarded. If the SO data are discarded with regard to inferring the J/k ratio, this should be stated. Because, as shown in Figures 6-7, the slope is insensitive to kmod/kJPL (between 0.65 and 1) and Jmod/JJPL (between 0.9-1.4) for a near constant (Jmod/JJPL)/(kmod/kJPL) ratio, the authors could have essentially found an uncertainty of ~0 in the (Jmod/JJPL)/(kmod/kJPL) ratio, had they chosen the (Jmod/JJPL)/(kmod/kJPL) ratio to be identical for all 4 combinations tried in Figure 6 (if the uncertainty calculation is as I describe above).

The SO measurements are not discarded, but mainly taken to confirm the conclusions on J/k obtained from the Limb measurements.

Another method for obtaining the error on the J/k ratio from the data shown in this paper would involve positively and negatively perturbing the J/k ratio until the slope of the measured versus modelled SCDs is no longer unity within the uncertainty. If the authors did this, it should be described.

This could be tried for the different four J and k combinations in Figure 6 as starting points. The work has already been done given Figure 8. To be conservative, the global maximum and minimum J/k ratios (over the four starting points) that depart from unity should serve ultimately as the uncertainty on the J/k ratio. The perturbations should proceed in four directions (from the four starting points):

1) $+\Delta k$, J constant

2) $-\Delta k$, J constant

3) $-\Delta J$, k constant

4) $+\Delta J$, k constant.

This will provide the bounds on the J/k ratio that allows the measured and modelled LS SCDs to come into agreement. I take issue with discarding the solar occultation measurements because they should be should be more reliable because of the simpler measurement geometry. I believe the uncertainty in their current method is more appropriately the difference between the mean/median of the sets of ratios from the two measurement techniques (unless they consider limiting the SO dataset to the time period before the hump at SZA=92.5°). Otherwise, the ratio (weighting SO and LS equally) and its uncertainty would be 1.525±0.175, meaning that the uncertainty is >4 times larger than the 0.04 claimed by the authors.

Given the error of the measurements firm conclusions on the individual contributions to the uncertainty of J or k in the JPL-2011 compilation can unfortunately not be drawn from our data. Accordingly, we strongly feel that such an approach (see above) would exploit the data beyond the limits set by the errors of the measurement. Of course as it is documented in Figures 6, 7, and 8, J and k were independently varied in the photochemical model within reasonable ranges, but as already stated above the measurement errors prevented to determine J and k separately.

The authors attribute the different (Jmod/JJPL)/(kmod/kJPL) ratios from LS and SO measurements on air mass differences, but make no attempt to account for air mass differences using models or other measurements. Given SLIMCAT's horizontal resolution of 2.8°, this translates to 310 km in latitude, and less in longitude, so unless tracer observations are needed, the model could be used to test the air mass difference hypothesis. I wonder if the 3 profiles from LPMA (ascent, sunset, sunrise) could be used to determine any horizontal gradients in CH4 and N2O or auxiliary measurements (MIPAS, etc.) and then Labmos could help with the temporal sampling.

Unfortunately, this is also not possible since it is known (and mentioned in the manuscript), that SLIMCAT (as any CTM) is not particular strong in simulating the vertical transport. So when the vertical transport is integrated over longer time, it can be expected that a model based profile of total NOy, or inorganic Br$_y$ may strongly depart from reality. Therefore, before any usefully measurement vs model inter-comparison can be made, measured and modelled profiles of vertical transport tracers (CH4, N2O, …) need to be compared. In fact, this is what we did for air masses probed during SO.

The air mass differences are really a source of error in the (Jmod/JJPL)/(kmod/kJPL) ratio in this experiment. That is why J and k are historically measured in the controlled conditions of a laboratory.

In fact, we were waiting (being aware of the problem) for more than a decade to catch this unique condition which would allow us constraint J/k for BrONO2 from simultaneous NO2 and BrO measurements in the stratosphere.

Specific comments

P27823L15-16 The value of 1.4 is the combined uncertainty for the BrONO2 absorption cross section and the quantum yield. The J value uncertainty will be slightly higher because there are several sources of uncertainty in the actinic flux (see specific comment P27826 below).

As stated in the text, the value of 1.4 for the uncertainty factor of J is taken from the JPL compilation. Also from the agreement found between the measured and modelled radiances together with findings of Bösch et al., (2001), we are confident that the uncertainty of the actinic flux is much smaller than of the BrONO2 absorption cross section and the quantum yield.

ref: Bösch, H., C. Camy-Peyret, M. Chipperfield, R. Fitzenberger, H. Harder, C. Schiller, M. Schneider, T. Trautmann, and K. Pfeilsticker, Inter comparison of measured and modeled stratospheric UV/vis actinic fluxes at large solar zenith angles, Geophys. Res. Lett., 28, 1179 - 1182, 2001.

P27823L17 The authors have done a nice job of surveying the chemical kinetics literature and pointing out that low temperature data is not available for the rate of Reaction 1.

Thank you

P27824L20 It should be noted that all SZAs are defined at the sensor.

The following text was included into the manuscript (P27824L20). "Please note that in the following all SZA's refer to local SZA, i.e., for the balloon gondola position."

P27825 McArtim claims to be accurate for limb radiance to SZAs of 90-91° but not for larger SZAs, yet the model appears to be used at even larger SZAs at dusk on the first day of the flight. Also, if BrO SCDs from SZA>93° are used to determine the J/k ratio, a method to correct for stray light should be probably be included in the data analysis.

No data for SZA > 92° go into the comparison.

P27826 Labmos assumes 0.3 for the surface albedo, but with overcast cloud, the effective albedo might be 0.8, which could affect bromine partitioning, particularly at smaller SZAs (<80 deg). This should be tested given that BrONO2 dissociates at long wavelengths, if a suitable literature reference is not available.

A = 0.8 would be more than extreme even for a 100% cloud cover. In fact satellite imaginary and by eye inspection indicate that the cloud cover never exceeded 2/8 around the scene, which most optimistically would lead to an A = 0.3 for a forest covered land. Beyond that, using the RT model McArtim extensive tests addressing spectral radiances in the stratosphere were performed to ascertain the correct atmospheric conditions and no indication for an abnormally increased ground albedo was found.

P27827L11-13 Is diurnal variation of BrO along the incoming solar path taken into account in both solar occultation and limb scattering simulations? It sounds like the capability exists with McArtim, but this needs to be stated explicitly. Note that limb single scattering consists of two directions for photon transport, the incoming solar path and the path along the line-of-sight, whereas in solar occultation, these two paths are one and the same. Diurnal variation is an issue for solar occultation because only the tangent layer is at SZA=90°.

Yes, correctly considering spatial gradients of the studied radicals is of utmost importance for our study. Therefore, in the last paragraph of section 2 it is written: In order to support an inter-comparison of measured and modelled slant column densities (SCDs) of O3, NO2 and BrO, the simulated photochemical fields are fed into RT models McArtim and DAMF, where path integrals through the simulated photochemical fields are calculated and then compared with the measured SCDs.

P27827L17 "…elevation angles and tangent heights…" -> "…tangent heights…". Also the minimum tangent height of all BrO SCDs during the flight should be stated. I calculate it to be 7.8 km assuming the sensor is at 31 km and an elevation angle of -4.88.

The text is accordingly changed (P27827L20) replacing ", or " with "down to 14 km and"

P27828L1-2 "…samples are always taken at SZA=90°, i.e. at the tangent height from…" -> "tangent layer is always at SZA=90°, and this is…". Also, Reaction (1) should be omitted from "…less sensitive to Reactions (1), (2a), …" since Reaction (1) is not SZA-dependent.

The text is accordingly changed, see P27828L1
"by definition the samples are always taken at SZA = 90, i.e. at the tangent height from where most of the absorption (signal) comes from (Figure 5)." replaced with
"the tangent height is by definition at SZA=90°, and this is where most of the absorption signal comes from."
Reaction 1 omitted in P27828L1

Also, the authors should move the reference to Fig. 5 to follow immediately after "sunset" on P27827L26.

Reference to Figure 5 (P27828L3) shifted to P27827L26

P27829L1-2. I disagree with this statement. The best range of kmod/kJPL is stated to be 0.65 to 0.85, but this experiment is only truly sensitive to the (Jmod/JJPL)/(kmod/kJPL) ratio and the values of kmod/kJPL are somewhat arbitrarily chosen. For example, the combination kmod/kJPL=0.9 and Jmod/JJPL=1.5 would also be expected to produce a slope of 1 for LS measurements, based on Figure 8, but exceeds the uncertainty of JJPL. The stated, best kmod/kJPL and Jmod/JJPL should not be outside the uncertainty of kJPL and JJPL, to respect those uncertainties and thus the case with kmod/kJPL =0.65 should be omitted from Figures 6 and 8 and any subsequent calculations regarding (Jmod/JJPL)/(kmod/kJPL). This sentence should be changed, otherwise the authors' approach becomes difficult to comprehend.

Isn't this only semantics, since infinite pair of j and k values may lead to a J/K ratio of 1.69. In fact, taking the error estimates of J and k serious as given by JPL-2012, only those variations of J and k are reasonable which fall into the JPL-2012 uncertainty range.

P27829L7 The tangent points for limb scattering are much farther than "30-70 km" at low tangent heights.

…but not for those measurements which contribute to the study according to the RT simulations

P27829L24-27 I suggest this sentence is omitted since the normalized limb radiance is not as sensitive to the surface albedo as the flux, partly because of the normalization and partly because the former is not a large-solid-angle quantity, whereas the latter is (including the hemisphere below, see comment above regarding scene albedo). Furthermore, I understood that McArtim is not used to provide the fluxes to SLIMCAT or the Labmos facsimile. The argument in the next sentence regarding the direct beam is sufficiently convincing anyway.   Figure 1 – Is it possible to include the SZA as an alternate x-axis (along the top of this figure)? At the very least, it would be helpful to know the SZA at 3:55 UT and I assume the SZAs for the first day can be read from Figure 5. Note that the SZA at the tangent point would be more helpful in Figure 1 because as the authors have noted, most of the absorption occurs in the tangent layer and not at balloon altitude.

See above. Not really because then one may struggle with the definition of local SZA (is it at the ground or at the balloon altitude?) without drawing any useful information from it.

Also, the inserted text refers to dSCDs of BrO, O3 and NO2, but the SCD appears in the y-axis title and the caption. This should be cleared up (i.e. is a model estimated dSCD for the reference spectrum added to each underlying dSCD to make it an SCD?) Or, if measured dSCDs are really used throughout the paper, the McArtim model should also calculate dSCDs by subtracting off the SCD for the simulated reference spectrum.

Measured are first dSCDs, so it is appropriate to show them in the first place. Secondly, the remaining absorption signal (calculated by the RT) is added to the reference spectrum which is taken at the smallest elevation angle (+1°) for the smallest (local) SZA.

Why is the LS time series longest for ozone and shortest for BrO on the first day?

The reason is first since O3 is measured in the visible and BrO in the UV spectral range and second the O3 absorption is much larger (by a factor of 10) than the BrO absorption. Also at sunset due to Rayleigh scattering and absorption, the UV radiances degrade earlier than the visible radiances at least to a degree to prevent an accurate detection of the targeted gases.

In a way, it is good that the BrO SCD time series cuts off since data in the lower stratosphere for SZA>90 should be discarded anyway if there were high tropospheric clouds. Do the authors have info on this from nadir observations? It seems that the last BrO measurement in Figure 1 occurs at 17:49 UT, but the last measurement shown in subsequent figures was at 17:48 UT.

Is it so? We don't see it.

At this time, given an estimated latitude of 67.9° and a longitude between Kiruna and the Finnish/Russian border, the SZA would equal or exceed 91.8°. If the SZA≥91.8°, the measured BrO SCD becomes sensitive to high tropospheric clouds, because the sun appears to be below them at the balloon and the radiative transfer becomes very complicated.

No, by then the balloon was seen overhead Esrange/Kiruna (67.9°N, 20.25°E) since the sky was mostly cloud free. Further, the Finnish border is located at (67.9°N, 24°E), so the difference in SZA (3.75°) is due to the difference in geo-location of the balloon. Beyond that, there were no high tropospheric clouds.

For overcast cloud with top at 8 km (within 4 degrees of latitude of the sensor), the height of the cloud's shadow at the tangent point can reach 11.2 km at SZA=91.8° and 22.8 km for SZA=93.9°. With the lowest tangent height (TH) at 7.8 km, clearly, the authors need to be careful about data at SZA>90 deg. The LS measurements on the next morning appear to be after sunrise and do not need to be filtered. However, the diurnal variation along the line-of-sight, should be considered in the modelled SCDs even if the authors have wisely chosen an azimuth difference angle of 90°, I estimate the SCD error at SZA=89° may be a few percent at the lowest THs based on McLinden et al. [2006] (relates to specific comment re:

See the comment regarding the cloud cover.

P27827L11-13).

Figure 2- Why are there missing points in only the 350 nm radiance time series? Figure 1 shows BrO measurements that are not discontinuous, which seems impossible given discontinuous 350 nm radiance measurements. Perhaps the lines should not be included in Figure 1 (i.e. point-markers only). Why is only 350 nm affected? Are the missing points due to anomalous data caused by shadowing of the tangent point by broken high tropospheric clouds? Figure 4- dSCDs in Figure 1 are larger than SCDs shown in Figure 4. This probably means that some SZA cutoff or other filter has been applied. Please describe.

In Figure 1 dSCDs of BrO range up to $3 \cdot 10^{14}/cm^2$ (discarding the last limb scan with large errors associated to it) and in the Figures 4 and 6 the SCDs for BrO range up to $3.5 \cdot 10^{14}/cm^2$ which is larger due to the offset of the absorption signal of the reference spectrum ($0.5 \cdot 10^{14}/cm^2$) being added.

Figure 8- State in the caption that the colour coding is appropriate to limb scattering measurements. Technical corrections

The caption of Figure 8 is accordingly changed from
"The colour coding indicates the resulting slopes of the modelled vs measured BrO SCD regression, when forcing the regression line through zero." to
"The colour coding indicates the resulting slopes of the modelled vs measured BrO SCD regression of the limb observations, when forcing the regression line through zero."

Please consider in the following that ACP demands for British and not American English

p27822L4 "turn-over" -> "turnover"

Correct in British English

p27822L7 "…indicates that,…"-> "…indicate that…"

Done

p27822L10 "…reasons likely…" -> "…reasons are likely…"

Done

p27822L25 "…with the amount…" -> "with the underestimated amount…" (see p27832L14-5 as well, where I suggest: "Also the overestimate of stratospheric Bry from the inorganic method due to… models by an underestimate of reactive bromine.")

Is not changed in the manuscript since the statement would then be incorrect.

p27823L14 (and elsewhere) "uncertainty" -> "uncertainty factor"

The text is accordingly changed in P27823L15 and the following instances.

p27824L10 "skylight"-> "sunlight"

Here we disagree, mainly in order to avoid confusion with the SO measurements

p27824L25 "Finish" -> "Finnish"

Done

p27825L28 "…evaluated." -> "…evaluated, respectively."

Done

p27825L29 "…both,…" -> "…both…"

Done

p27826L9 "…lab-owned 1-D Facsimile code…" -> "…1-D facsimile code…"

Done

p27826L10 "neccessary" -> "necessary"

Done

p27826L21 "are" -> "is"

Done

p27827L22 (and throughout) "higher" -> "larger"

Done

p27828L21 "size" -> "magnitude"

Done

p27829L1 "…regression measured vs. …" -> "…regression of measured versus …"

Done

p27829L24 "Incorrect modelled…" -> "Incorrectly modelled…"

Done

Figure1 It would help the reader to note (somewhere, perhaps in the 3rd paragraph of Section 2) that the malfunctioning of the scanning telescope only affects the limb scattering observations.

The text is accordingly changed (P27824L21), including the sentence "However, the scanning motor of the limb observation spectrometer malfunctioned and only spectra recorded after 03:50UT (SZA=86°) are used for analysis."

Figure1 "commenced" -> "continued"

Done

Figure1 "…down…" -> "…down to…"

Done

Figure 3 What is meant by "local angles"? Please state whether these are at the balloon or the tangent point.

The caption of Figure 3 is accordingly changed from "local SZA" to "local SZA at the balloon gondola" P27839.

Figure 5 caption: "k=0.075" -> "k=0.75"

The figure is accordingly changed. Corrected figure will be uploaded

P27828L27 "occulation" changed to "occultation"

P27829L4 "occulation" changed to "occultation"

References

McLinden, C. A., et al. (2010), Odin/OSIRIS observations of stratospheric BrO: Retrieval methodology, climatology, and inferred Bry, J. Geophys. Res., 115, D15308, doi:10.1029/2009JD012488.

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Sioris, C. E., et al. (2006), Latitudinal and vertical distribution of bromine monoxide in the lower stratosphere from Scanning Imaging Absorption Spectrometer for Atmospheric Chartography limb scattering measurements, J. Geophys. Res., 111, D14301, doi:10.1029/2005JD006479.