**Atmospheric
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Discussions**

Interactive comment on "Enhancement of the volcanogenic "bromine explosion" via reactive nitrogen chemistry (Kīlauea volcano, Hawai'i)" *by* G. G. Salerno et al.

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1   General comments

This paper presents measurements conducted with Differential Optical Absorption Spectroscopy (DOAS) at Kilauea volcano, Hawaii. The authors then go on to inter-

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pret the measurement results, suggesting an enhancement of the "bromine explosion" mechanism (e.g., Bobrowski et al., 2007) by the rapid titration of NO_2 in the volcanic plume into $BrONO_2$ and ensuing reaction with HBr in aerosols to release Br_2 into the gas phase. Unfortunately, while previous modeling studies have shown that there may be some merit to this mechanism, the measurement results reported in this manuscript are untrustworthy and the observed correlations between BrO and NO_2 are likely an artifact of a carelessly conducted DOAS retrieval. Thus all further conclusions can not be based upon this data. Aside from this most important point, the manuscript contains several further errors and should not be considered for publication in Atmos. Chem. Phys. in its current form.

2 Flaws in the DOAS retrieval of BrO

The retrieval of BrO in DOAS measurements in volcanic plumes is not straightforward. In contrast to SO_2, where high concentrations typically lead to measured differential optical densities (DOD) of 10% or more, BrO DODs are usually in the order of a few per mil. Aside from the typically weak signal, the absorption cross-section is also overlapped by those of O_3, NO_2, SO_2, HCHO, O_4 and several other less relevant species. Depending on the spectral range chosen for the DOAS retrieval, structured absorption of these gases must be taken into account in the BrO evaluation. However, care must be taken that the differential absorption cross-sections included in the fit are linearly independent, i.e. the absorption structures of one species cannot be reproduced by a linear combination of the other included cross-sections. Both the choice of retrieval wavelength range and the wavelength calibration of the individual spectra are of fundamental importance in this context.

2.1 Spectral range of retrieval

For the retrieval of BrO, the authors chose a spectral range of between 345 and 358 nm. This range encompasses only two absorption bands of BrO. While Aliwell et al. (2002) suggest a similar evaluation range, this study was performed specifically for zenith sky viewing DOAS measurements, in which O_3 absorption is the limiting factor. As the authors recorded a clear sky reference (CSR) before and after each volcanic data set and the evaluations were performed relative to these, only minor O_3 absorption structures should occur in the retrieval. Thus it is prudent to include additional absorption bands towards shorter wavelengths (e.g., Bobrowski et al., 2003, 2007; Bobrowski and Platt, 2007; Kern, 2009), and especially to include the band at 338.3 nm, which is twice as strong as those chosen by the authors and thus yields a doubled sensitivity towards BrO in the retrieval. The authors state that they checked their evaluation in the 330-370 nm range, but no results are mentioned. If the results obtained in this larger fit region do indeed match those of the narrow region (which is highly unlikely in light of the findings described below), the 330-370 nm range should be used for all the retrievals, and example fits from this fit window should be shown.

2.2 Wavelength calibration

Accurately calibrating all of the spectra and absorption cross-sections used in a DOAS retrieval is very important. For all measured spectra, this can be achieved by comparing the measurement to a high resolution solar emission spectrum (Kurucz, 1995) convolved to the spectrometer's resolution. The authors do not present any original spectra in their manuscript. However, the Ring spectrum shown in their Fig. 2. can be used as an indication for the true wavelength calibration of their instrument. Although it is usually calculated from a CSR, a Ring spectrum can also be calculated from the Kurucz spectrum after this has been convolved to the spectrometers resolution. The

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black spectrum in Fig. 1 of this comment is a Ring spectrum calculated from the Kurucz spectrum after having convolved it with a 0.44 nm FWHM Gaussian slit-function. It contains several fine structures not seen in the Ring spectrum in Salerno et al. Fig. 2. Therefore, the optical resolution of 0.44 nm stated by the authors appears to be incorrect. The true optical resolution of the applied instrument is closer to 0.8 nm, as can be seen from the similarity of the blue spectrum in Fig. 1 to that shown by the authors. More importantly, however, a stretch of 5% has to be applied to the Kurucz-calibrated Ring spectrum to accurately reproduce the author's Ring spectrum (red spectrum in Fig. 1. As the Kurcz spectrum exhibits a very precise calibration (reported vacuum wavelengths where converted to air assuming standard temperature and pressure as described by Morton (1991)), the fact that a stretch is necessary to reproduce the authors' results shows that their calibration is not completely accurate.

An inaccurate calibration is not uncommon for the miniature spectrometers often used for volcanic emissions measurements. A perfect absolute calibration is not necessary. However, it is of fundamental importance that the spectra and cross-sections used in the DOAS retrieval all exhibit the same calibration. To test this, the literature reference spectra used by the authors of O_3, NO_2, and BrO (Bogumil et al., 2003; Wahner et al., 1988) were each convolved and compared to the authors' Fig. 2. To obtain the spectra shown here, the O_3 cross-section had to be shifted by about 1.5 nm towards shorter wavelengths and stretched by 20 % (!), BrO had to be shifted by 1.5 nm towards shorter wavelengths and stretched by 15 %, while the NO_2 cross-section did not need to be shifted at all, and was only stretched by about 6%. Therefore, while the NO_2 cross-section was approximately on the same calibration as the Ring spectrum, the cross-sections of O_3 and BrO exhibited drastically different calibrations. Slight differences in absolute calibration between different literature absorption cross-sections are known to exist (e.g. Aliwell et al., 2002), but shifts are typically 0.1 nm and stretches are around 1%. Therefore, manipulating the cross-sections in such a drastic way is unfounded and violates basic principles of the DOAS method.

2.3 Linear dependency of BrO on NO_2 and O_3

The large discrepancies in wavelength calibration among the individual reference spectra combined with the relatively narrow DOAS retrieval region is cause for concern regarding the evaluation results. Another indication for an erroneous fit is the unreasonably high O_3 column density of 1.8×10^{20} returned by the fit shown in the authors' Fig. 2. The total vertical O_3 column over low latitudes is typically 300 DU, or about 8×10^{18} molec/cm^2. The change in solar zenith angle between measurement and reference spectrum (30 minutes apart) is of the order of a few degrees. Even if assuming that 100% of the total O_3 column is in the stratosphere, the associated change in light path in the O_3 layer can account for less than 1% of the measured O_3 column. If, on the other hand, the O_3 is located in the troposphere (as perhaps suggested by the authors' choice of O_3 cross section (293 K)), an unrealistic O_3 mixing ratio in the plume of over 100 ppm (!) would be necessary to explain the measured absorption signal.

Aside from the unreasonably high O_3 column, the high negative NO_2 values are conspicuous. While the authors state that a depletion of 50 ppb of NO_2 is not impossible, this argument is questionable at best, as NO_x created by thermal fixation of atmospheric nitrogen (the authors' suggested source) would be expected to be located mainly in the plume rather than in the background air.

By far the most likely explanation for the above mentioned observations is an error in the DOAS evaluation, as is shown in the following. A sensitivity study was set up to analyze the linear dependency of the chosen absorption cross-sections. First, the cross-sections of O_3, NO_2 and BrO were reproduced using the resolution, shifts and stretches obtained from Fig. 2. of the manuscript (as was described above) and kept fixed for all tests. Next, a noise spectrum was generated with pure Gaussian noise of the same order of magnitude as in the authors' example. Then, the cross-sections were fit to this noise spectrum under the condition that the O_3 column density should be 1.8×10^{20} molec/cm^2 (this value was found in the authors' example). The obtained fit result is shown in Fig. 2. The retrieval returned an NO_2 column density of -1.2×10^{17}

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molec/cm^2, a quite similar value to that found by the authors. Also, BrO seemed to be clearly identified by the two prominent absorption structures, and again a similar value of 5.8×10^{15} molec/cm^2 was retrieved.

The generation of results similar to the authors findings from a pure noise spectrum is explained by a linear dependency of the absorption cross-sections which is caused by the inaccurate relative wavelength calibration. To illustrate the effect, the O_3 cross-section was multiplied by 3.3×10^4, the NO_2 cross-section was multiplied by -22, and the two were added. In Fig. 3, the sum of these two spectra is compared to the BrO cross-section. Obviously, there is a strong similarity. Therefore, using the shift and stretch parameters chosen by the authors, any solution in which $[BrO]:[NO_2]:[O_3]$ is approximately equal to 1:-22:33000 is potentially just an artifact of cross correlations between these cross-sections. Which solution is chosen by the fit will depend on second order numerical effects and not on the actual column densities of the absorbers. Even if no BrO is present, the retrieved solution could e.g. correlate with the strength of the Ring effect, which in turn would likely correlate with SO_2 in a condensed plume. In this manner, the retrieved BrO column density could correlate with SO_2, but the results will not reflect the true column densities of the individual absorbers.

3 Other inconsistencies in the manuscript

A number of additional inconsistencies in the manuscript are listed below:

Page 10315, Line 18: BrO is not a primary volcanic emission product, but is rather thought to be formed to a large part in the plume itself (Bobrowski et al., 2007; v. Glasow, 2010; Roberts et al., 2008; Kern et al., 2009). Therefore, the calculation of total reactive bromine flux from BrO measurements conducted at a single point is not trivial, and assumptions about the amount of bromine still not released from aerosols or present in the form of other reactive bromine compounds must be made.

Page 10318, Line 25: Why was an NO_2 reference cross-section measured at 223 K

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used in the evaluation if the authors' hypothesis is that the measured signal originates in the depletion of tropospheric NO_2? A spectrum recorded at 293 K is available from the same source (Bogumil et al., 2003).

Page 10319, Line 1: It is known that a simple DOAS approach fails in cases where SO_2 optical densities exceed several percent (Kern, 2009; Kern et al., 2010). In the authors' evaluation range of 305-316 nm, the DOD exceeds unity at times. In such cases, the radiative transfer between the sun and the passive instrument is complex, and the SO_2 column density becomes dependent on wavelength (Mori et al., 2006). Accurate SO_2 column densities can only be retrieved by direct fitting and inversion of the radiative transfer problem. However, to approximate SO_2/BrO ratios, the evaluation of SO_2 can be performed in close spectral proximity to the evaluation of BrO. In this case, the radiative transfer can be assumed similar for both absorbers, thus canceling in the ratio. This would imply evaluating SO_2 as far towards long wavelengths as possible without sacrificing too much sensitivity. As the SO_2 columns reported by the authors are extremely high, a range of between 320 and 330 nm might e.g. be chosen.

Page 10319, Line 3: It is unclear how a simple DOAS evaluation performed in the region between 305 and 316 nm can yield a near random residual for SO_2 DODs larger than unity. As explained above, this approach typically fails for DODs above a few percent due to radiative transfer effects. A model run conducted for the authors' measurement geometry predicts absolute errors in the SO_2 column density on the order of 50%, and a structured residual correlating with the SO_2 cross-section with a DOD of close to 10%. It is possible that this effect is concealed by the linear offset allowed in the fit procedure. However, this offset should only be used to compensate for instrumental effects. Compensating for radiative transfer effects by using a linear offset will not give accurate results. The effect of omitting the linear offset from the evaluation should be investigated, and it should be determined whether the offset is really only compensating stray light.

Page 10319, Line 21: Again, a BrO emission rate is not well defined, as most BrO is formed after some time in the plume (see above).

Page 10319, Line 22: The presence of BrO in the CSR spectrum would lead to a positive ordinate intercept in the authors' Fig. 3. However, they find a negative intercept.
Page 10324, Line 6: This should read SO_2/BrO ratio, not vice versa. Of course the given number should be reevaluated in light of the above comments.
Page 10330, Table 1: Again, the BrO flux is not well defined.
Page 10331, Fig 1: The length scale in the lower right corner appears to be incorrect.
Page 10332, Fig 2: Why is the data point obtained from this evaluation ($BrO = 8.5 \times 10^{15}$ molec/cm^2) not shown in Fig. 3? Also see comments on the BrO retrieval itself.
Pages 10333 and 10334, Fig 3 & 4: These correlations need to be rethought in light of the above comments on the BrO retrieval.

4 Final remarks

The measurement results suggested by this discussion paper are ground-breaking in multiple ways. For one, the measured BrO column densities are the highest ever seen in a volcanic plume. Also, the extreme NO_2 depletion and tremendously high O_3 columns (on which the authors do not comment) have never been reported before. However, it has been shown in this interactive comment that the DOAS retrievals used to obtain these results are highly questionable, and a rigorous re-evaluation of the spectral data is necessary. In this re-evaluation, a larger wavelength range should be used encompassing additional BrO absorption bands, especially the strongest band at 338.3 nm. SO_2 and O_4 should also be included in the fit. Most importantly, care should be taken that all cross-sections used in the fit are on the same wavelength calibration as the measured spectra. Literature references taken by the same author and on the same instrument should not be shifted or stretched relative to one another. The absolute calibration of the spectrometer can be obtained by comparing the measured spectra to a convolved Kurucz spectrum. The relative calibration of the O_3 cross-section can be obtained by evaluating O_3 in CSR spectra obtained under different solar zenith

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angles. Only after re-evaluating all spectra can the results be discussed in a meaningful manner, and only then should the manuscript be considered for publication in Atmos. Chem. Phys.

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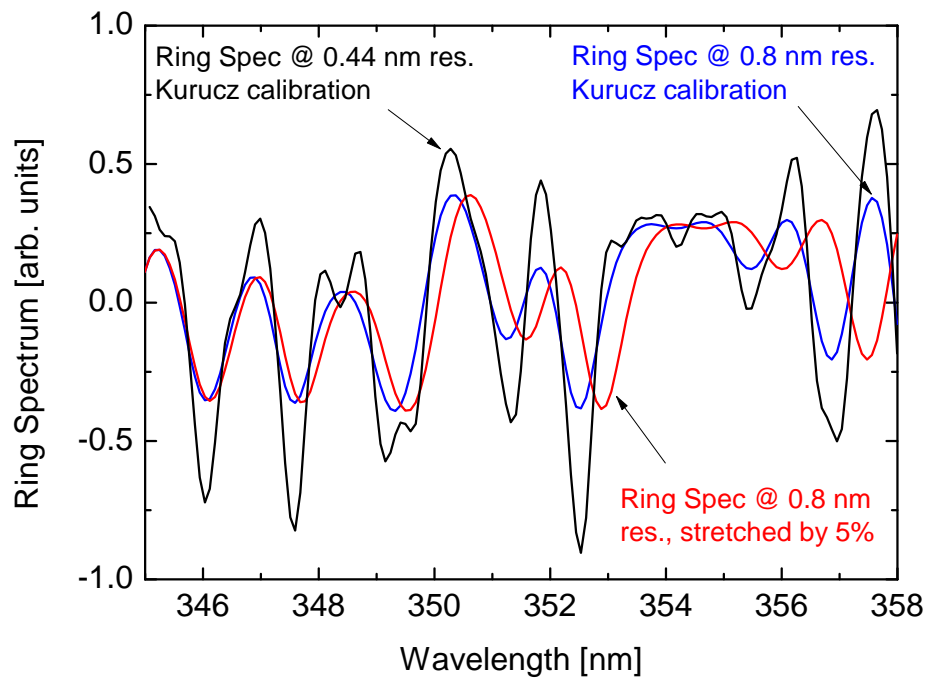Printer-friendly Version

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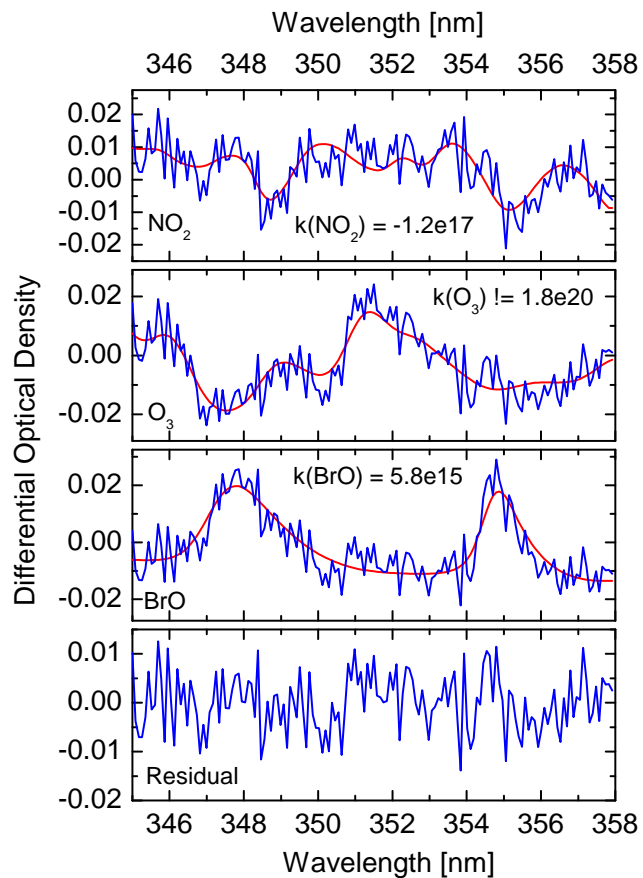
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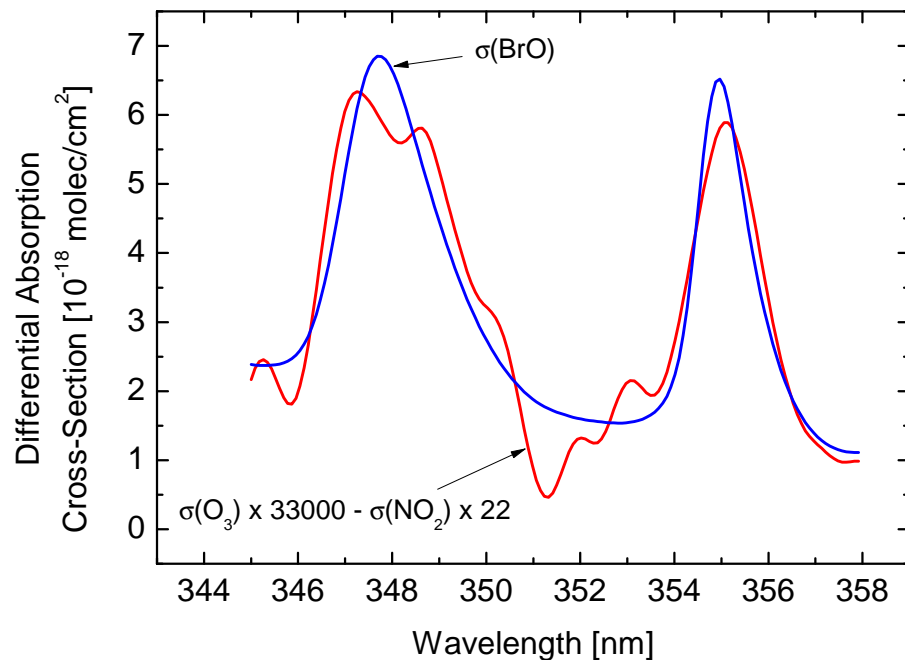
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Fig. 1. Ring spectra calculated from the convolved Kurucz spectrum. Black spectrum calculated using a resolution of 0.44 nm, blue at 0.8 nm, red at 0.8 nm and shifted by 5%.

Fig. 2. Reproductions of the authors' NO2, O3 and BrO cross-sections were fit to a pure noise spectrum. The O3 column density was fixed to 1.8e20molec/cm2.

Fig. 3. Plot illustrating the linear dependency between the BrO cross-section and a spectrum compiled by adding the O3 and NO2 cross-sections scaled by 33000 and -22, respectively.