Stratospheric BrO profiles measured at different latitudes and seasons: Instrument description, spectral analysis and profile retrieval

F. Ferlemann[1], C. Camy-Peyret[2], R. Fitzenberger[1], H. Harder[1,3], T. Hawat[2], H. Osterkamp[1], M. Schneider[1], D. Perner[3], U. Platt[1], P. Vradelis[1], and K. Pfeilsticker[1]

Abstract. Measurements of stratospheric BrO profiles are reported using a novel DOAS instrument (Differential Optical Absorption Spectrometry) operated on the LPMA/DOAS balloon gondola (LPMA/Laboratoire de Physique Moléculaire et Applications) during three flights (León, Nov. 23, 1996, Kiruna, Feb. 14, 1997, and Gap, June 20, 1997). BrO was detected by its vibrational bands (4-0 at 354.7 nm; 5-0 at 348.8 nm) of the $A(^2\pi) \leftarrow X(^2\pi)$ transition in direct sunlight spectra from balloon ascent, descent and during solar occultation at maximum (float) altitude. We show that our accuracy is about ±18% (1 σ) during balloon ascent (solar zenith angles, SZA < 88°), and about ±25% for solar occultation measurements. For altitudes above the balloon float our observations indicate average BrO mixing ratios of (14.4±2.5)ppt, (15.6±2.8)ppt, and (15.3±2.8)ppt above 30.6 km, 30.0 km, and 39.8 km, respectively.

1. Introduction

Presently stratospheric bromine, estimated to amount 20 ppt [*Schauffler et al.*, 1998], contributes ~25% to the anthropogenic O_3 depletion. The stratospheric key inorganic bromine species is BrO at daytime [*Lary et al.*, 1996a,b]. Unfortunately, only few stratospheric BrO measurements were conducted so far with a quite limited coverage of latitudes and seasons - and thus more BrO measurements appear to be warrant. BrO measurements rely on two techniques:

(1) In-situ observation of BrO (and ClO) by chemical conversion/resonance fluorescence previously employed in several aircraft (ER-2) and balloon-borne measurements [e.g., *Brune and Anderson*, 1986]. While a strong point of this technique is its capability of in-situ measurements, its absolute calibration is difficult, limiting its accuracy to ~30%.

(2) DOAS spectroscopy relies on the detection of vibrational absorption bands of the $A(^2\pi) \leftarrow X(^2\pi)$ UV transitions of the BrO molecule. The method can be employed by using zenith scattered Sun light or direct moon light [*Carroll et al.*, 1989; *Solomon et al.*, 1989; and others]. A major advantage of spectroscopy is its

[1] Institut für Umweltphysik, University of Heidelberg, Heidelberg/Germany

[2] Max-Planck-Institut für Chemie, Saarstr. 23, Mainz/Germany

[3] LPMA, CNRS, Université Pierre et Marie Curie, Paris/France

specifity, but due to the weakness of the BrO absorption (observed optical densities are of the order ~0.1%) and because of interference with tropospheric absorbers (warm O_3, NO_2, CH_2O, and others) and the necessary radiative transfer modeling in remote scattered skylight BrO measurements, the accuracy is also barely better than ±30% for the total vertical column.

Details on the measurement technique are reported here, while the measured BrO profiles are described by Harder et al. (this issue).

2. Measurements, Spectral Analysis and Profile Retrieval

Three balloon flights were conducted using a novel DOAS-instrument [Ferlemann et al., 1998]; (1) on Nov. 23, 1996 from León/Spain (42.6° N, 5.7° W), (2) on Feb. 14, 1997 from Esrange/Sweden (67.9° N, 21.1° E), and on June 20, 1997 from Gap/France (44.0° N, 6.1° E) (accordingly denoted flight 1, 2, and 3). The spectral retrieval of BrO was performed as previously described by e.g., *Stutz and Platt*, [1996] (Fig. 1 and Fig. 2) with a low air column "low" Sun spectrum (denoted FR) recorded at maximum altitude as reference. The spectral retrieval also included two reference spectra of O_3 at -20°C, and -80°C and NO_2 at -70°C recorded in the laboratory using our instrument, the O_4 spectrum of *Greenblatt et al.* [1990], the BrO spectrum (at T=223 K) of *Wahner et al.* [1988], and to account for the spectrometer's straylight a product of an "inversed" measured spectrum with the spectrometer straylight spectrum. The inclusion of a calculated Ring spectrum was also tested [*Fish and Jones*, 1995] but the amplitude of the Ring spectrum was found negligible except for spectra recorded at low tangent points ($\leq$ 20 km) not reported here. In a first step the wavelength shift of BrO reference was determined from measured spectra with a large BrO absorption (optical density some 0.1%). For the final spectral retrievals the whole set of reference spectra was allowed to shift and squeeze simultaneously against the measured spectrum. In all retrievals for all flights the shift never exceeded 0.014 nm. Once the wavelength calibration was established, the stability of the instrument permitted to perform all the other retrievals for all flights without wavelength recalibration of the reference spectra.

The amount of absorbing BrO in the FR was determined from the intercept of a regression of the measured BrO slant column density (SCD) and the calculated total airmass (air-SCD) seen at float for SZAs ranging from 86.4° to 89° (Fig. 3). It was found that the BrO-SCD is a linear function of the air-SCD mainly because there is only an insignificant photochemical change in stratospheric BrO above the gondola for our photochemical conditions (M. Chipperfield, priv. comm.).
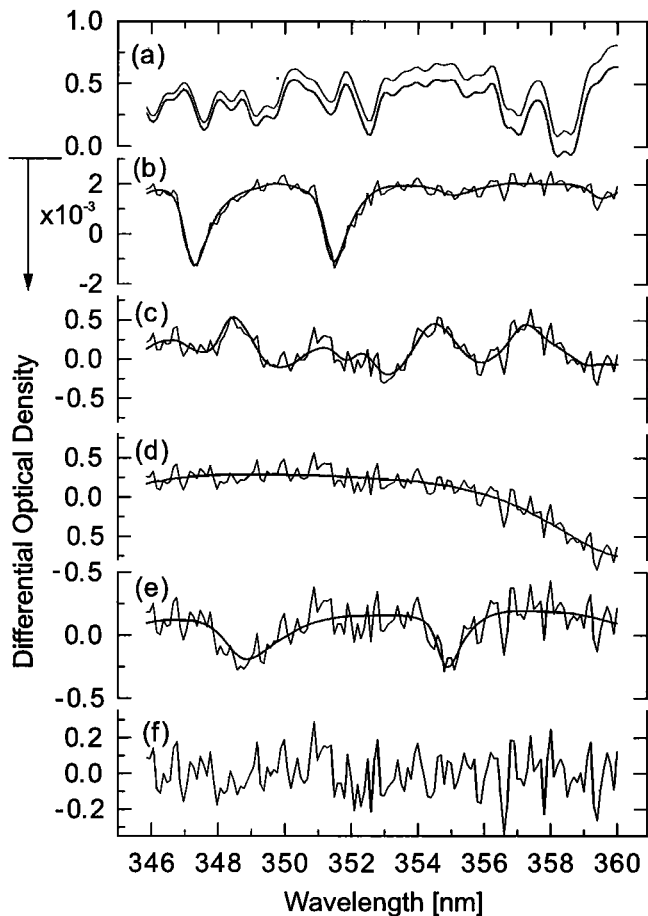
Figure 1. Retrieved trace gas absorptions (346 nm-360 nm) in a spectrum measured during the ascent of the León flight on Nov. 23, 1996. (a) Direct Sun spectrum measured at 7.7 km (SZA=74.8°) (thick line), and FR spectrum measured at 30.74 km (SZA=86.4°) (thin line); (b) fitted laboratory ozone absorption (thick line) and measured ozone absorption (thin line - fitted optical density plus residual o. d.); (c) same as (b) but for NO_2; (d) same as (b) but for O_4; (e) same as (b) but for BrO; (f) residual absorption.

The BrO profiles were derived from the measured BrO-SCDs using (1) the well known inversion technique described in *Rodgers* [1976], and (2) the so-called onion peeling technique (see below). Corrections due to the photochemistry of BrO at twilight were not applied. A more detailed discussion of possible photochemical effect is subject of a further study.

3. Discussion of Errors

In the following error discussion a clear distinction is made between statistical and systematic errors which determine the measurement precision and accuracy.
Spectral retrieval errors: Recent findings by *Aliwell et al.* [1997] indicate a potential sensitivity of the retrieved BrO-SCD to small wavelength alignment mismatches of the individual reference spectra. Accordingly, a similar test was performed by investigating the retrieved BrO-SCD as a function of the relative wavelength position of each individual reference spectrum with respect to all other reference spectra. In agreement with *Aliwell et al.* [1997] the largest sensitivity of the retrieved BrO-SCDs is found to be due to misalignments of the O_3 spectrum, but for our mode of observation the sensitivity is smaller than that reported (for a 0.05 nm shift of O_3 or NO_2 the BrO-SCDs changed by ±16% or
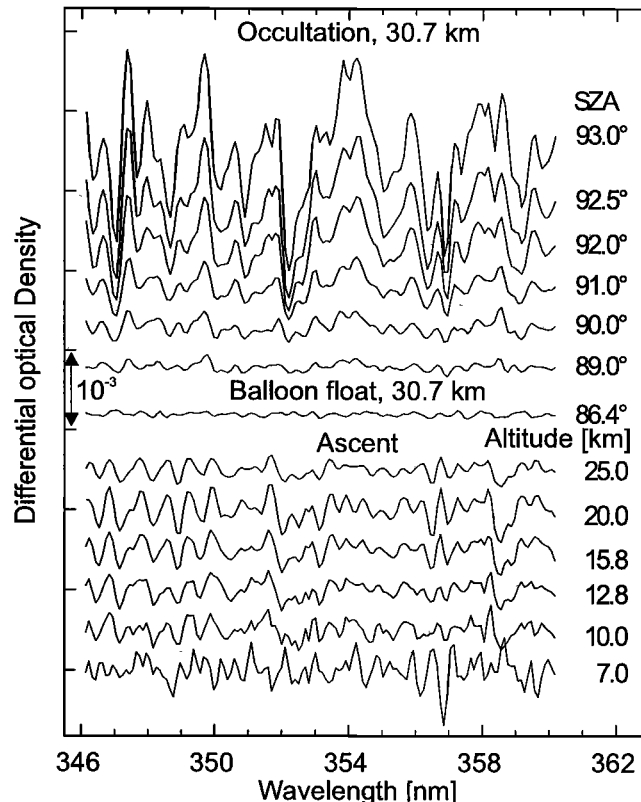
Figure 2. Residual optical density of the BrO fitting region as a function of the observation geometry during the León flight.

±5%, respectively). Assuming a misalignment of less than 0.01 nm for the individual reference spectra, this effect should only cause a systematic error of ±3%. The residuals from the fitting process show systematic featu-
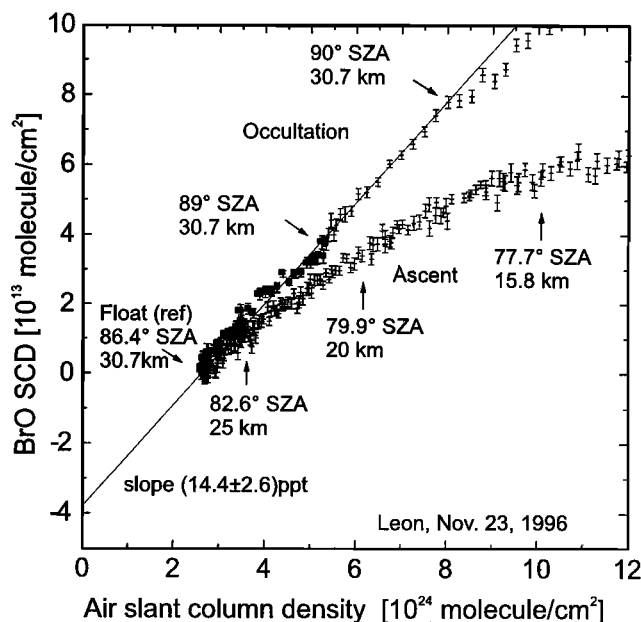
Figure 3. Retrieved BrO-SCDs as a function of SZA versus air-SCD for the measurements at balloon float during the León flight. The slope of the regression line (only the data marked as filled squares were fitted) indicates the BrO mixing ratio above balloon float altitude when assuming an uniform height distribution while the intercept determines the amount of BrO in the FR.

res, which appear to increase with the air-SCD (Fig. 2). Whether these features are due to improper reference spectra we tested other reference spectra than those actually taken for the BrO retrievals. For these tests the retrieved BrO-SCDs were found to agree within ±10%, but the residual structures were found to increase. Therefore, we ascribe to the remaining residual structures a systematic spectral retrieval error (ΔSSPE) of ±10%. The SCDs of successively recorded spectra were found to vary by ±3% from a 10 point running mean, which suggest a statistical error of (ΔRSPE=±3%).

Cross section: The absolute BrO cross section (σ_{BrO}) was taken from *Wahner et al.* [1988], which for the 7-0 vibrational transition was recently confirmed within -5% by *Laszlo et al.* [1997]. Still more recently *Gilles et al.* [1997] reported on an about 10% larger absolute σ_{BrO} (=1.63×10^{-17}cm^2) for T=298K and the same spectral resolution (0.5 nm) as used by *Wahner et al.* [1988]. Since the relative values of the differential σ_{BrO} for the different transitions are likely to scale accordingly, the different reported results for the 7-0 transitions may point to an uncertainty of ±10% in σ_{BrO}.

Since for our observation geometry stratospheric BrO is observed for a range of temperatures (T) spanning typically 30 K, another uncertainty may arise from the T dependence of the BrO cross section. When going from 223 K to 298 K *Wahner et al.* [1988] found a decrease of the differential BrO absorption cross section of about 31% for the 4,0 transition. This effect was corrected for by calculating an 'effective' BrO T for observations above float altitude and by applying a height dependent factor for the retrieved profiles. The BrO cross section for the 4,0 and 5,0 transitions were determined by linear interpolation between the Ts for which *Wahner et al.* reported their measurements. In conclusion, the uncertainties in the linear interpolation of the T dependent BrO cross section may introduce a systematic error of 2% (= ΔRCSE).

Errors in our determination of the **amount of BrO in the FR** (see above) may arise from (a) the uncertainties in the air-SCDs, (b) from possible photochemical changes in the BrO-SCD, or (c) from the spectral retrieval.

(a) The uncertainty in the air-SCDs is primarily due to the uncertainty in altitude, i.e., the instrumental errors of the onboard pressure sensor and GPS receiver. We estimate this error to ±2.5% (= ΔRPE) for flights 1 and 2 and ±8% for flight 3.

(b) The photochemical change of the BrO column above the gondola for the range of SZA used in the regression is still difficult to assess, mainly because of the uncertainties in the stratospheric BrO chemistry at twilight [*Lary et al.*, 1996a,b; *Fish et al.*, 1997]. However, SLIMCAT-model runs performed for our conditions (Chipperfield, priv. comm.) show that for our observation the change in BrO-SCD is likely smaller than 3%, or 3×10^{12}/cm^2.

(c) Since the amount of absorbing BrO in the FR is determined from measured spectra recorded during a short period (15 min for flight 1) at balloon float, spectral shifts due to possibly changing instrumental characteristics (e.g., the spectrometer optical adjustment or the detector T) are insignificant. Spectral interferences from other - at lower altitudes - more abundant absorbers (i.e., O$_3$, NO$_2$,..) should also be lower for the measurements at balloon float (for the residual traces see Fig. 2 for SZA=86.4° and 89°). Finally, the linear regression method relies on a set of independent BrO measurements (typically 50, the filled squares in Fig. 3), which further reduces the error. As a result the statistical error of the amount of BrO in the FR is estimated to $\sim0.7\times10^{12}$/cm^2.

When adding all these errors then the amount of absorbing BrO in the FR can be determined to a precision of ±3.5×10^{12}/cm^2. Since the contribution of the BrO absorption in the FR to the total BrO absorption is height dependent but usually low, this error (ΔFE) contributes about ±3% to the total error.

Photochemical profile corrections: Photochemical changes of the amount of absorbing BrO during the measurement, in principle, have to be considered in the
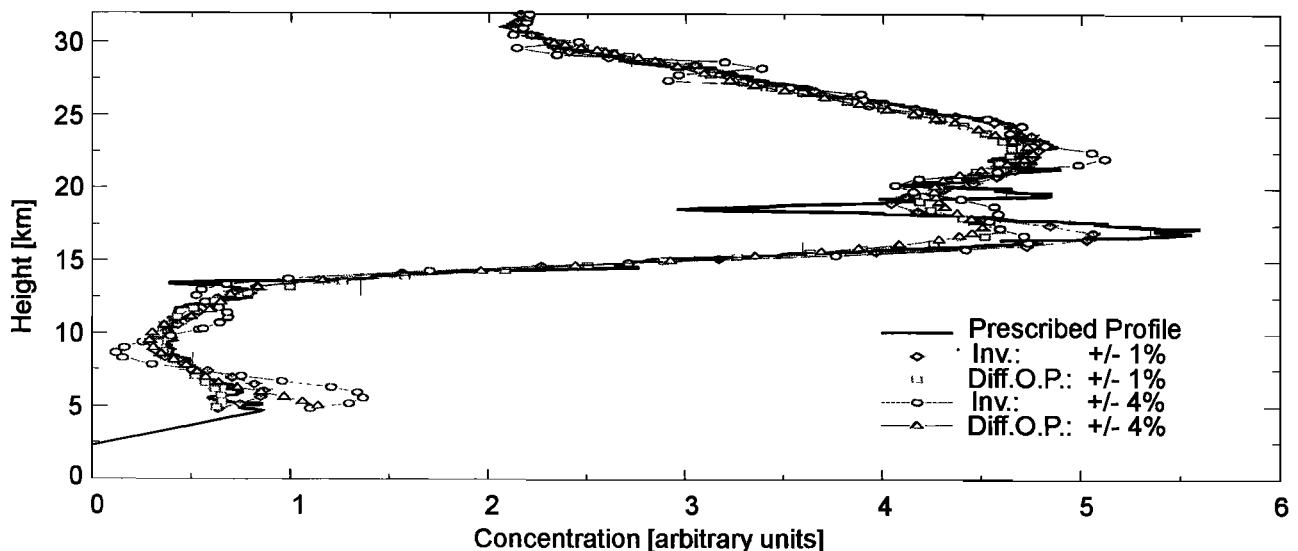
Figure 4. Sensitivity of how gaussian distributed random spectral retrieval errors propagate into the retrieved BrO profile; Prescribed profile (full thick line), retrieved profiles assuming 1 σ SCDs errors of ±1% (rhombs for the matrix inversion, 'Inv.' and squares for the onion peeling, 'Diff.O.P') and ±4% (circles for the matrix inversion, 'Inv.' and triangle for the onion peeling, 'Diff.O.P'), respectively. The statistical errors are not constant with height but can reach ±4% at most (see text). The deviations between retrieved and prescribed profile in the upper troposphere and around the profile maximum originates from the ill-conditioned inversion problem. The total 1 σ errors are height dependent but roughly ±18% or ±25% for ascent/descent or solar occultation observations.

profile retrieval. The photochemical model calculations [M. Chipperfield, priv. comm.] reveal insignificant photochemical changes (<5%) of the BrO-SCD for our ascent measurements. Also, our ground-based BrO observations at Kiruna suggest small photochemical changes of BrO for these conditions, and consequently we did not adopt any photochemical corrections to our profiles. Accordingly, the photochemical changes in BrO - not yet corrected for - are likely to cause a systematic error (=ΔPHCA) of -5% in the retrieved BrO for the ascents of the flights 1 and 2. A much larger systematic error of about ±10% (=ΔPHCO), however, is expected for the occultation profile retrieval neglecting any photochemical corrections [Roscoe and Pyle, 1987].

In summary the retrieved BrO-SCD's have a statistical error of ~4% (ΔRSPE=±3%, and systematic errors ΔRPE=±2.5%, ΔSSPE) = ±10% and ΔRCSE=±2%), excluding the systematic errors mainly from the absolute BrO cross section of the order of ±10%.

Profile retrieval error: The propagation of the BrO-SCD errors into the errors of the retrieved profile was investigated in a sensitivity test: A typical inversion was simulated by prescribing a profile similar in shape to the expected atmospheric BrO profile. After the apparent SCDs for a typical measurement were calculated, random errors of ±1% (for a O_3 retrieval) and of ±4% (for a BrO retrieval) were added to the prescribed profile. The deviations of the retrieved profile were taken as a measure of how the random SCD error propagates into the final profile (Fig. 4). For both inversion techniques ((a) with our profile matrix inversion routine and (b) with the onion peeling technique) from the prescribed profile (~ ±5% in the mid stratosphere) the overall shape of the profile was well recovered, although both techniques tend to smooth the vertical structures (see cf. the dip in the prescribed profile around 18 km). Since each of the inversion techniques has specific strenghts and shortcomings [Rodgers, 1976], both retrieval techniques are used further on.

In summary, our measured BrO profiles have a precision of about ±5%. When the possible systematic errors are simply added (ΔSSPE=±10%, ΔFE=±3%, and ΔPHCA=+5% for the ascent and ΔPHCO=+10% for the occultation measurements), our ascent/descent BrO measurements have an accuracy of about ±18% (or a 1σ rms error of 13%), and the solar occultation measurements have an accuray of about ±25%. The possible error in the differential σ_{BrO} is not included in the accuracy values given above.

4. Conclusions

Clearly, the spectroscopic direct sun balloon observations offer several advantages over zenith/nadir sky observations of BrO, e.g., profiles can be derived rather than total columns, the observation geometry is well defined, and due to larger BrO-SCDs and the larger photon flux a better signal to noise ratio can be achieved. We have shown that the remaining relative errors (1σ) for our BrO profile measurements are about ±18% (a rms error of 13%) for ascent/descent and about ±25% for solar occultation observations. For altitudes above the balloon float altitude, i.e., 30.6 km, 30.0 km, and 39.8 km, our observations indicate average BrO mixing ratios of (14.4±2.5)ppt, (15.6±2.8)ppt, and (15.3±2.8)ppt, respectively. Thus, the BrO mixing ratios above balloon float appear to be consistent with the known stratospheric bromine burden and photochemistry.

References

Aliwell, S.R., R.L. Jones, and D.J. Fish, Mid-latitude observations of the seasonal variation of BrO, 1. Zenith-sky measurements, Geophys. Res. Lett., 24, 1195, 1997.

Brune, W. H., and J. G. Anderson, In-situ observations of mid-latitude stratospheric ClO and BrO, Geophys. Res. Lett., 13, 1391, 1986.

Carroll, M. A., R. W. Sanders, S. Solomon, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo station, Antarctica: 6. Observation of BrO, J. Geophys. Res., 94, 16633-16638, 1989.

Fish, D., and R.L. Jones, Rotational Raman scattering and the Ring effect in zenith-sky spectra, Geophys. Res. Lett, 22, 811, 1995.

Fish, D. J., Aliwell, S. R., and R. L. Jones, Mid-latitude observations of the seasonal variation of BrO, 2. Interpretation and modeling study, Geophys. Res. Lett., 24, 1199, 1997.

Gilles, M.K., A.A. Turnipseed, J.B. Burkholder, A.R. Ravishankara, and S. Solomon, Kinetics of the IO radical, 2. reaction of IO with BrO, J. Phys. Chem., A, 101, 5526-5534, 1997.

Greenblatt, G.D., J.J. Orlando, J.B. Burkholder, and A.R. Ravishankara, Absorption measurements of oxygen between 330 and 1140 nm, J. Geophys. Res., 95, 18577-18582, 1990.

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

Lary, D. J., Gas phase atmospheric bromine photochemistry, J. Geophys. Res., 101, 1505-1516, 1996b.

Laszlo, B., R. E. Huie, M. J. Kurylo, and A. W. Miziolek, Kinetic studies of the reaction of BrO and IO radicals, J. Geophys. Res., 102, 1523-1532, 1997.

Rodgers, C.W., Retrieval of Atmospheric Temperature and Composition from Remote Measurements of Thermal Radiation, Rev. of Geophys. and Space Phys., 14, 4, 609-623, 1976.

Roscoe, H.K., and J. Pyle, Measurements of Solar Occultation: the Error in a Naive Retrieval if the Constituent's Concentration Changes, J. Atmos. Chem., 5, 323-341, 1987.

Schauffler, S.M., E.L. Atlas, F. Flocke, R.A. Lueb, V. Stroud, and W. Travnicek, Measurement of bromine-containing organic compounds at the tropical tropopause, Geophys. Res. Lett., 25, 317-320,, 1998.

Solomon, S., R. W. Sanders, M. A. Carroll, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at Mc Murdo Station, Antarctica: 5. Observations of the diurnal variations of BrO and OClO, J. Geophys. Res., 94, 11393-11403, 1989.

Stutz, J., and U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least squares methods, Appl. Optics, 35, 6041-6053, 1996.

Wahner, A., A. R. Ravishankara, S. P. Sander, and R. R. Friedl, Absorption cross section of BrO between 312 and 385 nm at 298 and 223 K, Chem. Phys. Lett., 152, 507-512, 1988.

Ferlemann et al., Institut für Umweltphysik, Universität Heidelberg, D-69120 Heidelberg, Germany (e-mail fe@uphys1.uphys.uni-heidelberg.de)