Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement

S. R. Aliwell, 1 M. Van Roozendael, 2 P. V. Johnston, 3 A. Richter, 4 T. Wagner, 5 D. W. Arlander, 6 J. P. Burrows, 4 D. J. Fish, 7 R. L. Jones, 1 K. K. Tornkvist, 6 J.-C. Lambert, 2 K. Pfeilsticker, 5 and I. Pundt 5,8

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[1] The analysis for BrO using the technique of differential optical absorption spectroscopy as applied to spectra of light scattered from the zenith sky has historically presented something of a challenge, leading to uncertainty about the accuracy of measurements. This has largely been due to the large sensitivity of the measurement to many analysis parameters and due to the small size of the absorption features being measured. BrO differential slant columns have been measured by six different groups taking part in an intercomparison exercise at Observatoire de Haute-Provence in France from 23 to 27 June 1996. The data are analyzed in a collaborative attempt to improve the overall analysis for BrO through investigation of a series of sources of errors in the instrumentation, calibration, input to the analysis, and the spectral analysis itself. The study included comprehensive sensitivity tests performed using both actual measurements and synthetic data. The latter proved invaluable for assessing several aspects of the spectral analysis without the limitations of spectral quality and instrument variability. The most significant sources of error are identified as the wavelength calibration of several of the absorption cross sections fitted and of the measured spectra themselves, the wavelength region of the fitting, the temperature dependence of the O3 absorption cross sections, failure to adequately account for the so-called I0 effect, inadequate offset correction, and inadequate measurement of the individual instrument slit functions. Recommendations for optimal analysis settings are presented, and comparing the results from the analysis of the campaign data shows BrO differential slant column observations from the various groups to be in agreement to within 4% on average between 87° and 90° solar zenith angle, with a scatter of 16%.

INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: bromine, monoxide, optical, absorption, spectroscopy

1. Introduction

[2] A number of studies of BrO measured by ground-based zenith-sky spectroscopy at middle and high latitudes have been reported [e.g., Carroll et al., 1989; Arpag et al., 1994; Fish et al., 1995; Eisinger et al., 1997; Aliwell et al., 1997; Kreher et al., 1997; Otten et al., 1998]. The analysis for BrO by the technique of differential optical absorption spectroscopy (DOAS) as applied to spectra of light scattered from the zenith sky is a difficult measurement owing to the small absorption of BrO relative to the other absorbers in the same wavelength region (especially O3) and thus requires considerable attention to the detail of the analysis. The measurement is somewhat easier in polar regions during winter when NO2 and O3 are at significantly lower concentrations than at midlatitudes and the interference in the analysis is thus reduced [e.g., Kreher et al., 1997]. Additionally, the temperature dependence of the O3 cross section is less marked at the lower temperatures. Small discrepancies between values for BrO measured in situ on board airplanes or balloons [e.g., Brune and Anderson, 1986; Avallone et al., 1995; McKinney et al., 1997] and ground-based [e.g., Arpag et al., 1994; Fish et al., 1995, 1997; Eisinger et al., 1997] or balloon-borne UV-visible measurements [Harder et al., 1998; Pundt et al., 2000] point to the need for an examination of the accuracies of the
analysis techniques. In addition, any coordinated measurement campaign requires that the instruments be shown to retrieve similar values under similar conditions.

[1] An intercomparison exercise was held at Observatoire de Haute-Provence (OHP) (43.9°N, 5.7°E) in France from 23 to 27 June 1996 in order to gather measurements for an analysis workshop to be held later. The conditions were not ideal for a BrO intercomparison, resulting in relatively low differential slant columns of BrO when compared to most middle and high latitude studies due to lower latitude and midsummer conditions. However, this time and place were chosen in order to take advantage of the presence of a number of instruments taking part in a Network for Detection of Stratospheric Change (NDSC) NO₂ and O₃ measurement intercomparison [Roscoe et al., 1999]. In contrast to the NDSC intercomparison, the BrO exercise had no level of blind intercomparison but was rather an opportunity to improve the analysis for each group by consensus and to highlight the sources of errors in the instrumentation, calibration, input, to the analysis, and the spectral analysis itself. The groups contributing measurements were University of Cambridge (UCam), University of Bremen (Bremen), University of Heidelberg (Heidelberg), National Institute of Water and Atmospheric Research (NIWA), Norwegian Institute for Air Research (NILU), and Institut d’Aéronomie Spatiale de Belgique (IASB). Service d’Aéronomie du CNRS (CNRS) and Heidelberg make balloon-borne measurements of BrO using UV-visible type spectrometers that employ a DOAS technique similar to the ground-based measurements groups [Pundt, 1997; Pundt et al., 2000; Harder et al., 1998]. Such measurements were not part of the measurement intercomparison; however, CNRS did contribute analysis of synthetic spectra.

[2] What follows is a detailed analysis of several factors aimed at improving the analysis for BrO in zenith-sky spectra. A brief discussion of the actual measurements made is presented along with a preliminary analysis that highlights the scope of the problem. This is followed by the analysis of a set of synthetic spectra that allows the testing of a variety of effects without the constraints of spectral quality and differences in ability to accurately wavelength calibrate the measured spectra. These tests isolate the analysis parameter effects from the individual instrument effects. A comprehensive set of sensitivity studies were then carried out on actual measured spectra, thus allowing an optimization of the agreed analysis parameters and a measurement of each instrument’s sensitivity to particular parameters. The agreed analysis parameters (summarized as recommendations for quick reference) were then used as the basis for comparing all spectral measurements over the intercomparison period.

2. Instrumentation

[3] All participating instruments are of the UV-visible zenith-sky viewing type used in the DOAS technique. A summary of each instrument’s characteristics is given in Table 1. The instruments, as set up to measure BrO, are oversampled with resolutions ranging from 0.6 to 0.9 nm. This compromise between resolution and sampling in each case gives a reasonable sensitivity to the vibrational absorption structures of BrO as well as minimizing interpolation errors and allowing a reasonable wavelength range to be measured. Temperature stabilization of instruments also helps to minimize drifts in wavelength calibration and changes in instrumental line shape. Further details of the individual instruments can be found in the relevant references given in Table 1.

3. Measurements at OHP

[4] Spectra were recorded by each group in the UV for the twilight periods of 23–27 June 1996 and were analyzed for BrO in terms of slant column differences between a particular solar zenith angle (SZA) and the reference spectrum. Differential slant columns are the natural product of the zenith-sky DOAS technique and have generally been reported as such in previous studies on BrO because of the significant uncertainties in the vertical profile of BrO that would affect the conversion to vertical column amounts [Fish et al., 1995]. A reference spectrum measured by each instrument for each twilight period at a solar zenith angle of 70° was agreed upon. This is lower than the 80° reference that has generally been used for midlatitude measurements.
are aimed at assessing the extent to which these factors may influence the differences in retrieved BrO and, therefore, are also aimed at improving the analysis and our understanding of it.

5. Synthetic Spectra

In addition to the analysis of atmospheric spectra, a set of synthetic spectra with known amounts of various absorbers was analyzed by each group. These spectra were produced using a forward model where the Beer-Lambert law is applied to a high-resolution solar atlas [Kurucz et al., 1984] using a standard set of cross sections, and the resulting transmitted intensity is smoothed to the typical instrumental resolution of 0.65 nm full width at half maximum (FWHM) (P. V. Johnston, personal communication, 1996). No noise was added to the synthetic spectra. Such analyses were found to be invaluable for assessing the effects of calibration without the limitations of spectral quality. In addition, they provided a check that each group was carrying out the analysis in the same manner, thus eliminating a further variable from the eventual intercomparison of actual measured data.

The synthetic atmospheric spectra and the cross sections were provided with wavelength calibration, so this study should omit the differences between the various groups’ selections of cross sections and instrument functions and therefore should concentrate on the effects of the different analysis packages. These tests may also indicate any limitations in the analysis. Analyses were carried out in the wavelength region 346–359 nm using the cross sections and wavelength calibration provided and, where applicable, using a second-order polynomial. Polynomial terms are usually applied in the DOAS technique to account for the smooth, unstructured part of the atmospheric attenuation. The choice of a relatively short wavelength interval has been commonly adopted so as to minimize the interference from adjacent O₃ bands at short wavelength and to minimize the impact of the O₄ absorption to the longer-wavelength side. The region is wide enough to incorporate two BrO bands, sufficient for the fitting process. As will be explained later in this section, the calibration was allowed to vary in some tests. Two O₃ cross sections measured at different temperatures (221 and 241 K) were fitted in order to account for the temperature dependence of the O₃ cross section over the range of temperatures covered by the altitudes at which O₃ absorbs most strongly.

Table 2 shows the retrieved slant columns of the various absorbers for each group when non-I₀-corrected

![Figure 1. Comparison of the initial analyzed BrO slant column differences for the evening twilight of 26 June 1996 at Observatoire de Haute-Provence (OHP). Analysis used groups’ preferred parameters. Some groups gave two different analyses. (Read 2.5e + 14 as 2.5 \times 10^{14}, etc.)](image-url)
cross sections were used and the wavelength calibrations of the cross sections and reference spectrum were accepted as given. The analyzed spectrum was allowed to shift and stretch with respect to the reference spectrum to minimize the residual. This provides some test of the relative convergence techniques of the groups. Also included in Table 2 are the slant column amounts used in constructing the synthetic spectra. When using uncorrected cross sections, the relative concentrations fitted by the two different ozone cross sections are incorrect, while the sum of the fitted ozone does approximately equal the sum of the two used in generating the synthetic spectrum. It appears that this effect causes an erroneously high column amount of the retrieved BrO in the non-I₀-corrected case. This is probably chiefly due to misalignment of the O₃ absorption features as a result of not including a correction for the solar I₀ effect. The fit tries to compensate for the less than optimum alignment by fitting more 241-K O₃ and less 221-K O₃. The residual is still unacceptably fitted absorption features due to the inadequacies of this compensation, and should be correlated with BrO absorptions, they will be fitted as such, resulting in higher BrO. This strongly supports the arguments that inadequacies in the O₃ fit are the major source of errors in the BrO retrieval. The majority of groups are able to retrieve approximately the same values of each absorber, indicating that the analysis packages perform similarly with the given restrictions. The notable exceptions are Heidelberg and the CNRS. A different approach to the analysis by each of these groups is believed to be the cause of the differences. Heidelberg includes the fitting of a “Fraunhofer coefficient,” which is a scaling factor for the log of the Fraunhofer spectrum in the log ratio forming the differential spectrum [Wagner et al., 1996]. The CNRS analysis does not use polynomials for the generation of differential spectra and cross sections but instead uses Fourier transform high-pass filters (a 15-nm filter in this instance). These filters are applied over a region somewhat wider than the fitting region, and though this seems to work reasonably well for a wide fitting region, it is apparently not suitable for a narrow region as used here. CNRS is currently considering changing to the use of polynomials for the BrO analysis. Nevertheless, the BrO retrieved by both Heidelberg and CNRS is very close to that of the other groups.

Table 3 summarizes the results of a number of sensitivity tests carried out by IASB on the synthetic spectra. These results are representative of those achieved by the other groups. Table 3 gives the analysis type, and reference to this is made in the discussion below. These tests essentially address the issue of the combined impact of spectral shift and solar I₀ effects on the accuracy of the BrO retrieval. Table 3 is subdivided into three classes of test cases: A-type, B-type, and C-type cases. A-type tests are for calculations using standard (non-I₀-corrected) cross sections. Analysis A2 is given in Table 2, while A1 has all
parameters the same as A2 but has an analysis spectrum that is not allowed to shift and stretch onto the fixed reference spectrum. Since both spectra were constructed using the same solar spectrum, it might be expected that this shift and stretch would be unnecessary. However, results show that the calibration of the spectrum applied a shift of $4.9 \times 10^{-4}$ nm and a stretch of $-7 \times 10^{-5}$ when allowed this freedom. The reasons for this are unclear; however, it is obvious that this has a significant effect on the balance of the two O₃ cross sections fitted and on the retrieved amounts of NO₂ and BrO as well. This less restrictive analysis case is in fact a step closer to the analysis that must be performed on the measured spectra. Analysis A3 further shows that it is possible to get significantly closer to the correct BrO column amount if the non-I₀-corrected cross sections are allowed some freedom to move. In this case the cross sections are allowed to shift and stretch by the same amount to find the minimum residual of the fit. Evidently, the shift and stretch process compensates to some extent for the lack of I₀ correction. However, this compensation is not total, as the incorrect O₃ and NO₂ column amounts show. In effect, it turns out that the I₀ correction shifts the peaks of the O₃ maximum absorption so that a better match is reached. B-type analyses, which are similar to A-types but use I₀-corrected cross sections rather than uncorrected ones, evidently lead to much improved results. Still, small discrepancies between the actual and retrieved O₃ columns are observed with the B1 and B2 analyses. Further tests showed that this was largely due to the fixed scaling factor used in the I₀ correction of the cross sections (see Appendix A). B3 shows that adjusting the scaling factor in the calculation of the I₀-corrected cross sections to the true values of the different column amounts does account for the small discrepancies with the actual column amounts used for O₃. Originally, values of $1.0 \times 10^{20}$ molecules cm⁻² were used for each O₃ cross section, and values of $1.0 \times 10^{17}$ molecules cm⁻² were used for NO₂. Clearly, for measured spectra the exact amount of scaling for each I₀ correction will vary and will be unknown. However, given the accuracy of the BrO columns retrieved in analyses B2 and B3, this should not be a significant source of error. Finally, C-type analyses show by comparison to A2 and B2 that small changes in the analysis wavelength window used can have a significant effect on the retrieved BrO if non-I₀-corrected cross sections are being used.

The ability of each group to produce approximately the same values, especially for the I₀-corrected case, where agreement was almost perfect for each group, suggests that any differences between the various groups’ retrieval of their own data are largely due to differences in calibration, cross sections, instrumental factors, and, in some cases, differences in the method of the analysis (e.g., Heidelberg and CNRS).

The importance of using I₀-corrected cross sections is clearly illustrated in Figure 2. Figure 2a shows the fit to BrO after the removal of all other absorbers when using non-I₀-corrected cross sections (analysis A1), and Figure 2b shows the same when using I₀-corrected cross sections (analysis B3). Relatively large residual structures are left in Figure 2a that are not evident in Figure 2b. Different values for the BrO slant column difference are produced in the two different analyses (see Table 3), with the correct value being retrieved in the I₀-corrected case. As will be shown in section 6.5, the use of I₀-corrected cross sections has a significant effect on the retrieved BrO column amount when analyzing real atmospheric spectra, though the differential spectra are often too noisy to readily reveal the effect on the residual absorption. Smoothing of the spectra prior to analysis does, however, enable these changes in the residual features to be seen.

6. Sensitivity Studies

Since there were some large discrepancies between the results of the various groups (see Figure 1), examinations of the sensitivity of the analysis to a variety of analysis parameters were carried out. Initial tests having indicated that sensitivity to the various changes may be different from group to group, the study was conducted on a representative set of data from five instruments out of the six involved in the intercomparison: Bremen, Heidelberg, IASB, NILU, and UCam, all treated with the IASB software. The data analyzed are those measured simultaneously by the five instruments, i.e., on 24–25 June and

![Figure 2](image-url). Bremen group fit of BrO to the optical depth after removal of absorptions due to O₃, NO₂, and O₄ in the synthetic differential spectrum, using (a) non-I₀-corrected cross sections and (b) I₀-corrected cross sections.
on 26 June 1996 after noon. The NIWA spectrometer was not optimized for BrO observations during the campaign, suffering from poor transmission at 350 nm resulting in noisy results not representative of measurements usually performed by the NIWA group. Therefore data from this latter instrument were not included in this part of the study.

[17] This work largely builds upon initial sensitivity tests carried out for BrO analysis by the UCam group [e.g., Aliwell et al., 1997]. The standard case used for comparison was analysis using the Harder et al. [1997] 227-K NO2 cross section, the Global Ozone Monitoring Experiment (GOME) [Burrows et al., 1999] O3 cross sections (221 and 241 K) with shifts of +0.03 nm, the Wahner et al. [1988] BrO cross section (223 K) with a shift of +0.17 nm, and the Greenblatt et al. [1990] O3 cross section (298 K) with a shift of −0.0868 nm and a stretch of 5.22 × 10−3. A second-order polynomial was used in deriving the differential cross sections and spectra, and the fitting procedure was carried out over the wavelength region 346–359 nm. The O3 and NO2 cross sections were corrected for the I0 effect. The Ring cross section was derived from rotational Raman scattering calculations according to the simplified yet accurate method described by Chance and Spurr [1997].

A more elaborated method treating infilling of molecular structures and atmospheric radiative transfer effects is described by Vountas et al. [1998]. Wavelength calibration of the measured atmospheric spectra used the Kitt Peak solar spectrum [Kurucz et al., 1984], the accuracy of which is quoted to be better than 0.001 nm. Correction for a linear offset in the measured intensities was allowed in the fitting procedure.

[18] What follows is a discussion of the various sensitivity tests performed and of their significance. Results of test analyses are summarized in Figures 3a and 3b in Tables 4 and 5. In total, 14 test cases have been considered, each described in brief in Table 4, column 2. Figures 3a and 3b display, for each test case and as a function of the solar zenith angle, the percent difference in retrieved BrO differential slant columns relative to the standard case. Different symbols are used to identify the various data sets, so that instrument-related differences in sensitivity can be easily detected. Mean deviations calculated in the most commonly used range of solar zenith angles, 87°–90°, are given in Table 4. The last column represents, for each test case, the net impact of the analysis change considered, averaged on all instruments. Table 5 shows percent differences in BrO slant columns relative to values obtained with the UCam instrument (also in the range 87°–90° SZA). This gives an indication of how the various instruments may be affected differently by the changes in analysis settings. The overall agreement is quantified in a single number for each test case by calculating the standard deviation of all BrO differential slant columns retrieved between 87° and 90° SZA (last column of Table 5).

6.1. Accuracy of BrO Absorption Cross Section

[19] Systematic errors in the retrieved BrO slant columns as a result of inaccuracies in the shape and wavelength calibration of the absorption cross sections used are likely to be a significant problem. Previous work suggested that the 223-K BrO cross section of Wahner et al. [1988] required a shift of +0.17 nm [Aliwell et al., 1997]. The direction and approximate magnitude are confirmed by comparison with Fourier transform spectrometry (FTS) measurements of the relative and absolute BrO absorption cross sections made at Harvard University [Wilmouth et al., 1999] and at the University of Bremen (O. Fleischman et al., Measurements of the spectroscopy and kinetics of BrO by time-resolved Fourier transform spectroscopy, manuscript submitted to Journal of Photochemistry and Photobiology, 2001; data available from http://www.iup.physik.uni-bremen.de/gruppen/molspec/index.html), respectively. Although previous results indicated that relatively small shifts (on the order of 0.05 nm) do not affect the retrieved BrO slant column greatly, results from test 1 (see Table 4 and Figure 3a) show that the shift of +0.17 nm leads to a significant difference in the BrO slant column retrieved relative to the unshifted case. The difference as a result of not including the shift in BrO is a systematic overestimation of the retrieved BrO columns by 23% on average between 87° and 90° SZA (see Table 4). As can be seen, some instruments show larger sensitivity than others to the shift applied. The reason for this behavior is unclear. It is probably related to the fact that BrO and O3 shifts are in effect not independent (see section 6.2). Note, however, that not shifting BrO results in a significant increase of the scatter between groups (see Table 5).

[20] The resolution of the Wahner et al. [1988] cross section is ~0.4 nm and so is somewhat too low for the resolution of the instruments taking part in this study. In smoothing the cross sections to instrument resolution, falsely high values of BrO will be recorded depending on the resolution in the range used by the instruments tested here. This effect has been investigated in test case 3, where BrO differential slant columns have been retrieved using the recent Wilmouth et al. [1999] BrO cross section. The resolution of this data set is 0.12 nm FWHM at 350 nm, which is sufficient to enable accurate smoothing to the various instrument resolutions. Results of test 3 given in Table 4 show that incorrect smoothing of the Wahner et al. [1988] BrO cross sections may account for only a few percent difference between the different groups’ analyses. As expected, the smallest difference with the reference evaluation is obtained with the NILU instrument, which has the poorest resolution (0.9 nm). Note also the very good consistency between the two sets of cross sections resulting in almost identical BrO values when smoothed at this low resolution.

6.2. Accuracy of O3 Absorption Cross Sections

[21] The BrO analysis was previously found to be quite sensitive to the wavelength calibration of the O3 cross sections when fitting over the 345- to 360-nm wavelength range [Aliwell et al., 1997]. In that case, using non-I0-corrected cross sections over the 345- to 360-nm range, the unshifted analysis was found to give BrO values some 28% higher than the correct shifted analysis. Repeating the test using the standard conditions specified above (i.e., 346–359 nm and I0-corrected cross sections) shows a reduced sensitivity to shift of some 5% on average between...
and 90° SZA but, again, with significant differences when looking at individual instruments (see results from test 2). Note that instruments showing large dependence to O₃ shift (e.g., IASB) generally show comparatively smaller dependence to BrO shift, which suggests that the two effects may not be independent. Note also in Table 5 that the similar increase in the scatter of BrO results for test cases 1 and 2.

[22] Previous work [Aliwell et al., 1997] had suggested that a shift of +0.02 nm in the calibration of the GOME O₃ cross sections was appropriate when analyzing spectra measured at Aberdeen, Scotland, during the winter of 1994/1995. This shift was derived from attempts to minimize the residual of the fit. Work during this intercomparison has shown that for the measurements made at OHP, a shift of approximately +0.03 nm was most appropriate based on minimizing the residual of the fit. FTS measurements of the O₃ cross sections by the Bremen group [Voigt et al., 2001] have since confirmed that a +0.03-nm shift of the GOME O₃ cross sections is required. This shift is within the known accuracy of the wavelength calibration of the GOME flight-model instrument made during the preflight measurements of the O₃ cross sections [Burrows et al., 1999]. The reasons for the different shifts from the GOME...
for the analysis of the Aberdeen and OHP data are not clearly understood at present. They are probably at least partially the result of nonlinearities in the O₃ cross-section temperature dependence, which would affect the proportions of each of the two O₃ cross sections fitted when the atmospheric temperatures are so different.

6.3. Temperature Dependence of O₃ Absorption Cross Sections

[23] Since the O₃ cross section has a strong temperature dependence in the UV [e.g., Brion et al., 1993], it was previously suggested that two different temperature cross sections fitted simultaneously be used in order to account for the effect of having O₃ at different temperatures in the stratosphere. The cross sections chosen were at 221 and 241 K, which should be approximately representative of stratospheric temperatures. Although it has proven to be useful in practice, the method of fitting two cross sections in order to describe O₃ at different temperatures is clearly an approximation that, to correctly describe a temperature profile, would require the temperature dependence of the cross sections to be linear. As mentioned earlier, nonlinearities in the temperature dependence may be the origin of some unanswered problems such as, for example, the different O₃ cross-section shifts derived from Aberdeen and OHP data (see section 6.2). The impact of not accounting for the temperature dependence has been investigated in test case 10, where BrO was retrieved with one O₃ cross section (241 K) instead of two. Results shown in Figure 3b and Table 4 indicate a strong and
consistent impact for all tested instruments except the Heidelberg instrument. On average for the OHP conditions, the effect of not accounting for the $O_3$ cross-section temperature dependence is an overestimation of the BrO slant columns by 25% between 87° and 90° SZA.

### 6.4. Selection of the Wavelength Interval

[24] The selection of the wavelength interval over which the analysis is to be carried out was found to be a significant source of systematic differences in the BrO slant column retrieved. This has been investigated for a selection of wavelength intervals considered in test cases 4, 5, and 6. We see that even small adjustments to the width of the analysis window can cause significant differences in the retrieved BrO slant columns. This is probably indicative (at least partially) of the effects of interference by correlating and/or poorly fitting other absorbers. By shortening the interval, it is possible to exclude some absorption features that would otherwise interfere with the quality of the fit; however, at the same time, the degree of correlation of the cross sections fitted is increased. We also see that the sensitivity to changes in the width and position of the fitting interval varies significantly from instrument to instrument (compare, for example, the results obtained for UCam and Heidelberg). This large instrument-dependent variability in sensitivity leads to increased scatter of BrO results as seen in Table 5, especially for test case 6. Such a behavior points to the role of instrumental effects that may differently interfere with the quality of the BrO fit, depending on the wavelength region considered for the fit. In the cases investigated here the analysis is less sensitive to small changes on the long-wavelength side of the interval than to similar changes on the short-wavelength side where $O_3$ differential structure is largest. The largest change is seen when extending the interval from 346 to 345 nm. Clearly, the selection of a suitable wavelength region that minimizes interference from poorly characterized “absorption” features but nevertheless allows sufficient wavelength range

### Table 4. Summary of BrO Retrieval Sensitivity Tests Carried Out Using the DOAS Software From IASB Applied to Spectra From Bremen, Heidelberg, IASB, NILU, and UCam Instruments

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Description</th>
<th>Bremen</th>
<th>Heidelberg</th>
<th>IASB</th>
<th>NILU</th>
<th>UCam</th>
<th>Mean</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>standard analysis</td>
<td>−17</td>
<td>26</td>
<td>17</td>
<td>18</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>BrO cross section [Wieder et al., 1988], not shifted</td>
<td>−16</td>
<td>39</td>
<td>8</td>
<td>31</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$O_3$ cross sections (GOME 221 K and 241 K), not shifted</td>
<td>−26</td>
<td>32</td>
<td>30</td>
<td>1.6</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BrO cross-section [Wilmouth et al., 1999]</td>
<td>−17</td>
<td>21</td>
<td>17</td>
<td>22</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>fitting interval: 345–360 nm</td>
<td>−10</td>
<td>−71</td>
<td>−18</td>
<td>−29</td>
<td>4.2</td>
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<td>15</td>
<td>20</td>
<td>16</td>
<td>3.3</td>
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<td>fitting interval: 346–365 nm</td>
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<td>no $I_s$ correction</td>
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<tr>
<td>9</td>
<td>wavelength-dependent air mass factor corrected</td>
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<td>24</td>
<td>17</td>
<td>17</td>
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<td>fit only one $O_3$ cross section (241 K)</td>
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<td>1.9</td>
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<td>−67</td>
<td>−29</td>
<td>−10</td>
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<td>shift spectra by −0.01 nm relative to all cross sections</td>
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<td>30</td>
<td>19</td>
<td>12</td>
<td>4.0</td>
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<td>slit function determined by DOAS algorithm</td>
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<td>2.7</td>
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<tr>
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<td>same as test 13, but using Wilmouth et al. [1999] BrO cross section</td>
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<td>−4</td>
<td>0.1</td>
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</tbody>
</table>

*Applied to spectra from Bremen, Heidelberg, IASB, NILU, and UCam instruments. Table shows the evolution of the overall agreement between instruments for the different test cases considered. Percent difference in BrO slant columns relative to UCam results, and standard deviations of BrO slant columns (all groups together), are calculated in the solar zenith angle range 87°–90°.

### Table 5. Summary of BrO Retrieval Sensitivity Tests Carried Out Using the DOAS Software From IASB

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Description</th>
<th>Percent Difference in BrO Slant Column Relative to UCam</th>
<th>BrO SD Molecules cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>standard analysis</td>
<td>−17</td>
<td>3.4</td>
</tr>
<tr>
<td>1</td>
<td>BrO cross section [Wieder et al., 1988], not shifted</td>
<td>−16</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>$O_3$ cross sections (GOME 221 K and 241 K), not shifted</td>
<td>−26</td>
<td>4.3</td>
</tr>
<tr>
<td>3</td>
<td>BrO cross-section [Wilmouth et al., 1999]</td>
<td>−17</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>fitting interval: 345–360 nm</td>
<td>−10</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>fitting interval: 346–360 nm</td>
<td>−16</td>
<td>3.3</td>
</tr>
<tr>
<td>6</td>
<td>fitting interval: 346–365 nm</td>
<td>−62</td>
<td>7.4</td>
</tr>
<tr>
<td>7</td>
<td>no $I_s$ correction</td>
<td>−15</td>
<td>4.6</td>
</tr>
<tr>
<td>8</td>
<td>polynomial of degree 3</td>
<td>−12</td>
<td>2.9</td>
</tr>
<tr>
<td>9</td>
<td>wavelength-dependent air mass factor corrected</td>
<td>−17</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>fit only one $O_3$ cross section (241 K)</td>
<td>−15</td>
<td>3.7</td>
</tr>
<tr>
<td>11</td>
<td>no offset correction</td>
<td>−11</td>
<td>5.6</td>
</tr>
<tr>
<td>12</td>
<td>shift spectra by −0.01 nm relative to all cross sections</td>
<td>−18</td>
<td>4.0</td>
</tr>
<tr>
<td>13</td>
<td>slit function determined by DOAS algorithm</td>
<td>−5</td>
<td>2.7</td>
</tr>
<tr>
<td>14</td>
<td>same as test 13, but using Wilmouth et al. [1999] BrO cross section</td>
<td>−7</td>
<td>2.5</td>
</tr>
</tbody>
</table>
coverage to give a good degree of noncorrelation between the cross sections is of paramount importance.

6.5. Impact of Correcting Absorption Cross Section for the I₀ Effect

[25] The use of cross sections corrected for the solar I₀ effect has already been mentioned in section 5 (see also Appendix A). Test case 7 shows the effect of not using I₀-corrected O₃ cross sections in the analysis of real atmospheric spectra. The difference made by not using the I₀-corrected O₃ cross sections is consistently found by each instrument to be significant and variable with SZA. Between 87° and 90° SZA the effect of not using the I₀-corrected cross sections is to overestimate the BrO slant column by 35% on average (see Table 4 and Figure 3a). The dependence on the SZA is likely due to the fact that O₃ makes a larger contribution to the total differential absorption at large SZA than at small SZA (the O₃ slant column increases faster as a function of SZA than the BrO slant column), so the impact of the I₀ correction is expected to be larger at large SZA. As mentioned in section 5, while the use of the I₀-corrected cross sections makes a significant difference to the amount of BrO retrieved, improvements to the residual of the fit are not as readily visible as was the case with the synthetic spectra. Figure 4a shows the fit of the BrO cross section to the differential optical depth remaining after the removal of all other absorption features has been attempted using non-I₀-corrected cross sections. Figure 4b shows the fit where I₀-corrected O₃ cross sections have been used. Note the reduction by ~30% in the BrO slant column compared to results from Figure 4a. Clearly, the differential spectra are very noisy, especially when compared to previous observations at higher-latitude sites in winter [e.g., Aliwell et al., 1997; Eisinger et al., 1997; Otten et al., 1998]. This noise may have a variety of sources, including large interpolation errors due to larger temperature-dependent shifts of the wavelength registration or unaccounted for variability in the sensitivities of the various detector pixels to the signal measured. In the case of CCD detectors this interpixel variability effect is measured and accounted for. Diode array detectors exhibit this effect to a far smaller degree, so such corrections are not generally made. It is possible that at the detection levels required for BrO analysis, such effects are significant and have not been sufficiently well accounted for. It should be noted that the O₃ concentration in the synthetic spectra is approximately similar to those seen in measured spectra, so a smaller contribution of the I₀ effect is not likely. Some of the spectral features due to the use of non-I₀-corrected cross sections are expected to be of comparable amplitude to the spectral noise, so unlike the case of the noise-free synthetic spectra, these may be masked to some extent. In the analysis employed by NIWA the spectra are filtered prior to the analysis to remove some of the higher-frequency noise, and the improvement in the residual is clearly visible, with features similar to those seen in the synthetic case being evident. These differential fits for the uncorrected and corrected cases are shown in Figures 5a and 5b. It should be noted (see Appendix A) that this correction is not necessary where cross sections are measured using the zenith-sky instrument and a cell with the zenith sky as the light source (e.g., National Oceanic and Atmospheric Administration group).

6.6. Role of the Polynomial Order

[26] There is some sensitivity to the degree of the polynomial used in the fit and generation of the differential cross sections. This is illustrated in test case 8, where a polynomial of third order has been used instead of the second-order polynomial applied in the reference analysis. As mentioned in section 5, the role of the polynomial is to account for the unstructured part of the differential optical thickness (a complex combination of Rayleigh, Mie, and (residual) broadband attenuation terms). The approximation of a low-order polynomial is justified by the small width of the BrO fitting interval. Increasing the degree of the polynomial may account for larger curvatures, but at the expense of a reduction in the number of degrees of freedom of the problem and hence at a reduced precision. The relatively small sensitivity found in test 8 (8% change in BrO slant column on average) suggests that the choice of a second-order polynomial is in general close to an optimum for the selected BrO interval.
Note, however, that some groups’ results (see, e.g., Bre- 
men) are more sensitive to the choice of the polynomial 
order than others. The fact that the overall scatter of results 
is reduced when using a third-order polynomial (see test 
case 8 in Table 5) suggests that for these instruments, 
correction for greater curvature would be needed.

6.7. Wavelength Dependency of O₃ Air Mass Factors

The analysis was also tested for its sensitivity to the 
use of wavelength-dependent air mass factor (AMF) cor-
rections to the O₃ cross sections. Basically, what happens 
is that because the atmosphere is not optically thin in this 
part of the UV, due to strong absorptions by O₃, the average 
altitude from which comes the majority of light scattered 
down into the spectrometer varies according to the O₃ 
absorption cross section. At wavelengths where there is a 
strong absorption band the average scattering altitude is 
pushed down since most light from above has been 
absorbed. This effect has also been described as an optical 
path length filtering process [Marquard et al., 2000].

Accordingly, the O₃ cross sections need to be corrected 
for by multiplying by wavelength-dependent air mass 
factors as calculated using a scattering model [e.g., Fish et 
al., 1995]. These are then fitted in place of the actual cross 
sections and effectively fit the vertical column amount. 
Such corrected cross sections were calculated here using 
the UVSPEC software package (A. Kylling, UVSPEC: A 
program package for calculation of diffuse and direct UV 
and visible intensities and fluxes, available by anonymous 
ftp to kaja.gi.alaska.edu, cd pub/arve, 1995), which imple-
ments the pseudospherical radiative transfer model DISORT 
[Dahlback and Stamnes, 1991]. Air mass factor calculations 
included multiple scattering for a model atmosphere includ-
ing O₃ as well as Rayleigh and aerosol scattering. The 
temperature, pressure, and O₃ vertical profiles used in the 
calculation were obtained from sonde measurements made 
in support of this campaign at Gap (80 km from OHP) on 
the same day. The results of using the AMF-corrected cross 
sections are shown in Table 4 and Figure 3b (test case 9). 
The corrected analysis gives BrO values slightly smaller 
than the standard analysis, but the difference is definitely 
small. Between 87°/C176 and 90°/C176 SZA the AMF-corrected 
analysis is 3% less than the standard analysis. Given the 
other sources of error, however, this correction does not 
appear to be a significant improvement on the standard 
analysis. Previous work using this correction [Fish et al., 
1995; Richter et al., 1999] had shown greater improvements 
to the residual of the fit and significant changes to the 
amount of BrO fit. This was, however, prior to the use of 
two O₃ cross sections to account for the temperature 
dependency effect. The improvements due to the AMF-
corrected cross sections came largely from the treatment of 
O₃ temperature dependence in the radiative transfer model 
used in their calculation.

6.8. Offset Correction

An ideal spectrometer operated in an ideal atmos-
phere would measure that part of the sunlight that has 
been elastically scattered by air molecules and particles in 
the zenith direction. In a real experiment, however, a 
number of possible additional sources of signal may add 
to the ideal Rayleigh/Mie contribution, causing an “offset” 
to the measured intensity. To a first approximation, the 
Ring effect, which is mainly due to inelastic Raman 
scattering by O₂ and N₂ molecules [e.g., Solomon et al., 
1987], is a natural source of offset that has received much 
attention in the data analysis. In addition to the Ring 
effect, instrumental sources of offset also need to be 
considered, such as stray light in the spectrometer or 
imperfectly corrected dark current of the detector. The 
accurate characterization of these instrumental effects 
(e specially stray light) often proves to be difficult in the 
field, hence most analysis packages include the possibility 
of fitting an offset parameter. Note that because of a 
cancellation effect when taking the ratio of spectra, the 
analysis can only correct for a difference in the offsets 
possibly present in both spectrum and reference. A large 
offset that is present at the same level in both spectra 
would therefore not be detected even though it directly 
affects the accuracy of the retrieval. The reference evalua-
tion in this study used a linear offset correction for all 
 instruments. In test case 11 the impact of not including this

Figure 5. NIWA group fit of BrO to the filtered optical 
  depth after removal of the absorptions due to O₃, NO₂, O₄, 
  Ring, and Rayleigh using (a) non-I₀-corrected cross sections 
  and (b) I₀-corrected cross sections. In contrast to Figure 4, 
  these spectral data are smoothed.
correction was investigated. Results in Figure 3b and Table 4 show quite clearly that the magnitude of offset effects is strongly instrument dependent. We see, for example, a rather small impact in the case of Bremen and NILU data, while the Heidelberg instrument requires a much larger correction. Evidence for poor scattered light rejection is also found when looking at the shape of the measured slit function of the Heidelberg instrument, which appears to have a signal that extends very large lambda-lambda nought values (see Figure 6). This points to the importance of careful instrument design and characterization in minimizing instrumental sources of offset.

6.9. Accuracy of the Wavelength Calibration of Measured Spectra

As mentioned in section 6.2, it was found that a shift of +0.03 nm of the GOME O₃ cross sections [Burrows et al., 1999] could be used to minimize the residual of the fit. However, if all the cross sections are then subject to further shifts simultaneously, the residual is sometimes found to reduce further. The minimum residual is clearly found after further simultaneous shift of all cross sections. This is in effect equivalent to a change in the wavelength calibration of the measured spectrum. For other spectra and on other days this shift was often either not necessary or was even in the opposite direction. A similar behavior is found by other groups when analyzing their own data.

[30] The accuracy of the wavelength calibration of measured spectra is a key issue because it determines how well measured spectra can be aligned with laboratory cross sections. Initial tests in this study have confirmed that excellent precision can be obtained by correlating measured atmospheric spectra with the Kitt Peak solar atlas [Kurucz et al., 1984]. The above results suggest, however, that there may still be a problem with the absolute wavelength calibration of the analyzed spectra, in addition to the already recognized shifts to the cross sections required. It is, in fact, likely that the wavelength calibration and resolution of the Fraunhofer spectrum used for the calibration is insufficient to fix the spectral calibration to much better than a hundredth of a nanometer, as would be required to match the size of the necessary shifts in the cross sections that cause such significant differences to BrO retrieval. The impact on the BrO slant columns of an uncertainty on the order of 0.01 nm on the calibration of spectra was checked in test case 12. Clearly, all instruments show a similar sensitivity to this error source (18% on average between 87° and 90° SZA for a shift of 0.01 nm).

6.10. Role of the Instrument Slit Function

A further limiting factor on the accuracy of the spectral evaluation is the correctness of the measured slit function in each case. A poorly representative slit function...
may be caused by measurement of a line source at an unsuitable wavelength or by incorrect filling of the instruments’ field of view when measuring the line source. Such inadequacies in the slit function will affect both the calibration of the spectra and the smoothing of the cross sections to match the absorption shapes in the differential spectra. The slit function has been shown to be sensitive to wavelength and temperature, depending upon the characteristics of the individual instrument. In order to try and help minimize these problems, an alternative technique for determining the slit function using the Fraunhofer features in the actual measured spectrum has been developed and implemented in the IASB analysis package. The technique consists of a nonlinear least squares procedure where a measured spectrum is fitted to a high-resolution solar atlas [Kurucz et al., 1984] degraded to the spectrometer resolution using a parameterized slit function that is adjusted as part of the least squares fit. Although limited in its accuracy by the need to use existing analytic functions to represent the various instrumental line shapes, the method is easily applicable and allows possible wavelength dependencies of instrumental slit functions to be identified. Figure 6 shows a comparison of the slit functions of the instrument tested here, as measured by each group (solid line) and as determined by the IASB algorithm (dotted line). Small but significant wavelength dependences (not shown in Figure 6) have been identified and considered for the Heidelberg instrument. These results have been used in test case 13 to investigate the impact of changing slit functions on the BrO retrieval. For this test case the calibration of the spectra and the smoothing of the cross sections were performed using the slit functions determined using the IASB algorithm. Results given in Table 4, showing differences in retrieved BrO slant columns ranging from 3 to 18%, confirm that the uncertainty on the slit function is likely to play a significant role in explaining the differences between groups. This is further confirmed by the analysis displayed in Table 5, which shows that the consistency between instruments is significantly improved for test case 13 compared to the standard analysis. As can be seen, the net effect of test case 13 is to decrease the values from Heidelberg, IASB, and NILU and to increase Bremen values so that better matching is obtained with UCam (results from this latter group being practically unchanged). The best overall agreement (<10% difference between each set of results) is finally obtained for test case 14, which is similar to case 13 except that BrO cross sections are from Wilmouth et al. [1999] (correctly smoothed to instrument resolutions) instead of Wahner et al. [1988].

6.11. False BrO Signatures

[32] An important test of the sensitivity of the analysis is the possibility of detecting false amounts of BrO in the absence of BrO. In order to test this effect, synthetic spectra were produced with no BrO contribution. The result is that applying the standard analysis with I₀-corrected cross sections were used, a positive slant column of 5.0 × 10¹³ molecules cm⁻² was detected, which is of the order of the errors in the synthetic data tests discussed in section 5. However, the quality of the erroneous fit is poor and would not in practice have been mistaken for the detection of atmospheric BrO. The use of I₀-corrected cross sections should therefore avoid any false detection of BrO.

7. Other Analysis Considerations

[33] OCIO was not included in the fit. This is different from the case for some higher-latitude winter studies where OCIO was present and therefore was analyzed for. In these summer measurements the fitting of OCIO tended to produce lower residuals by fitting to features like the O₃ temperature dependence, thus affecting these fits and giving false negative amounts of OCIO.

[34] The O₃ cross section of Greenblatt et al. [1990] measured at 298 K was used, with each group finding their own optimum shift and stretch due to differing definitions of how each group carried out spectral stretching within a particular wavelength region. This shift and stretch was necessary because the Greenblatt et al. [1990] measurements were made at a pressure of 55 atm and more recent measurements have shown that at atmospheric pressures the line shapes are slightly different [Hermans et al., 2001]. The cross section of Greenblatt et al. [1990] has recently been corrected in the UV region (J. B. Burkholder, private communication, 1996). In the corrected version the bands at 342 and 380 nm have been shifted by 0.38 nm, and the band at 360 nm has been shifted by 0.84 nm. Recent measured cross sections of O₃ in the UV match well with this corrected cross section [Hermans et al., 2001]. The corrected cross section and the Hermans et al. [2001] cross sections have not been used in the present study but are recommended for future use.

[35] The high-resolution NO₂ cross section of Harder et al. [1997] measured at 227 K was used. This cross section was used down to wavelengths shorter than the 350-nm published minimum wavelength, so the signal-to-noise ratio below this wavelength is relatively poor. The wavelength calibration of this cross section is expected to be very accurate, especially with respect to the Kitt Peak solar Fraunhofer spectrum. The low temperature was chosen to be approximately representative of the stratosphere. The use of more than one NO₂ cross section to describe any temperature dependence was not found to improve the analysis noticeably. This is most likely due to the low temperature dependence of the NO₂ cross section in this wavelength region. Additionally, it is necessary to keep the number of fitted variables to a minimum since, with the narrow wavelength range and the number of other fitted variables, the analysis may approach the limit of simultaneous equations relative to number of unknowns; that is, it eventually ceases to be an overdetermined solution. Thus a second NO₂ cross section would have added another parameter to be fitted for minimal return in analysis improvement.

[36] Spectra were analyzed in the SZA range from 70° to 91°. This includes the SZA of 90° that is generally reported when publishing daily values for seasonal studies. Above this SZA, spectra were often felt to be too noisy for accurate analysis. Significant divergence between the BrO slant column differences of the various groups was observed at
greater than $\sim 92^\circ$ SZA, probably as a result of this variation in spectral quality.

8. Recommended Analysis

[37] This study has shown that it is necessary to be very careful in the selection of the analysis parameters when attempting to fit BrO in the 345- to 360-nm wavelength region. Hence a recommended analysis at this stage with the available cross sections and other reference data is given below. This analysis has been adopted by the participating groups in the interest of uniformity of analysis, though further improvements are underway as, for example, improved absorption cross sections become available.

[38] It is recommended that for the BrO analysis the wavelength range of the fit should be 346–359 nm. Note that fitting results are by far more sensitive to changes on the short-wavelength side of the interval than on the longer-wavelength side. Measured spectra should be calibrated in wavelength by correlation to the Kitt Peak solar atlas [Kurucz et al., 1984]. The $O_4$ cross section of Greenblatt et al. [1990], after suitable shift and stretch, should be used along with the recent Wilmouth et al. [1999] BrO cross section or the cross section by Wahner et al. [1988] with a shift of +0.17 nm. A suitable NO$_2$ cross

![Figure 7. Comparison of BrO differential slant columns (90°–70° SZA) measured at OHP between 23 and 27 June 1996. Data are analyzed independently by each group using the constrained set of analysis parameters defined in the study (see text).](image-url)
section, used in the present study, is the 227-K cross section of Harder et al. [1997], because of its accurate wavelength calibration. However, the poor signal-to-noise ratio below 350 nm of this cross section is a drawback. It may therefore be worth considering the use of the more recent set of high-resolution (2 cm$^{-1}$) and high-precision wavelength calibration NO$_2$ cross sections measured using FTS by Van Daele et al. [1998]. These cover the wavelength range 240–1000 nm and have been measured at 220 K and at room temperature. The GOME O$_3$ cross sections at 221 and 241 K [Burrows et al., 1999] should be fitted simultaneously so as to account for the temperature dependence of the O$_3$ cross section, but both should be shifted by +0.03 nm. The correction of cross sections for the so-called I$_0$ effect should be applied where laboratory-measured cross sections are used. For higher-latitude studies, especially during the winter months, OCIO should be included in the fit as well.

9. Intercomparison of Results

[39] Comparisons of the analyzed BrO for each group when using the constrained set of analysis parameters are given in Figure 7. These plots include all twilight periods covered by the exercise to show the range of agreement obtained. In this and the following plots, when a particular

Figure 8. Comparison of BrO differential slant columns (90°–70° SZA) measured at OHP between 23 and 27 June 1996 by five out of the six participating groups. Data are analyzed by IASB using the same set of analysis parameters as in Figure 7.
The agreement between the results is greatly improved compared to initial comparison results (compare Figure 1), which suggests that the most significant causes of discrepancy have effectively been identified and minimized through this study.

For comparison purposes, Figure 8 shows the results of the standard case produced with the IASB analysis package described in section 6. This analysis was performed using the same constrained analysis settings and cross sections, except for the Ring effect where a Raman calculation was used in all analysis. In contrast, in the individual groups’ analysis shown in Figure 7, each group was allowed to use their own preferred method of generating a cross section to describe the Ring effect. Methods used included that of Solomon et al. [1987] using cross-polarization measurements and the calculation of a Ring cross section by simulation of rotational Raman scattering [e.g., Fish and Jones, 1995; Vountas et al., 1998; Bussem, 1993; Chance and Spurr, 1997]. After careful examination of the plots in Figures 7 and 8, one can see that in the IASB analyzed comparison the scatter of data is somewhat reduced compared to the individual analysis, despite the fact that both analyses used the same cross sections. Further reduction of the scatter is finally obtained in Figure 9, where results from the optimal IASB analysis using fitted slit functions (test case 14) are displayed. The overall level of agreement

Figure 9. Same as Figure 8, but showing results from test case 14 where fitted slit functions are used instead of measured ones (see text).
obtained in this latter case is illustrated in Figure 10, where the fractional differences in BrO slant column, relative to UCam values, are displayed. One can see that the average difference between all groups’ data (calculated between 87° and 90° of solar zenith angle) is on the order of 4% with a scatter of 16%.

Although moderately significant, the improved consistency of the IASB analyzed comparison points to the importance of features that are known to be treated differently by the individual analysis packages (e.g., wavelength calibration, Ring cross sections, offset corrections, and the Fraunhofer fit used by the Heidelberg group). Some groups appear to be more affected by this than others. In particular, the NILU and Heidelberg data appear to be brought more into agreement with the IASB analysis.

Remaining differences between the groups’ measurements are likely to be due to actual differences in the measured spectra rather than to the analyses. Part of the discrepancies between the groups may be due to different amounts of BrO in the reference spectra in each case. Although the specified reference spectrum was at a SZA of 70°, the closest available SZA spectrum was chosen by each group. In some cases this was as much as 0.5° SZA difference. Other more subtle factors are also likely to play a role, like differences in spectral quality, differences in the field of view that would lead to a different sensitivity to cloud effects and tropospheric ozone, and different sensitivities to factors like stray light and dark current. As mentioned in section 6.9, there is also probably a limit to the ability of the calibration routines to correctly determine the wavelength registration of the spectra. This may be on the order of 0.01 nm, which though small, is significant in an analysis as sensitive as that for BrO.

Note, finally, that in general, the afternoon data are more scattered than the morning data. This is probably the result of instrument temperature regulation problems during the hotter afternoons, combined with increased NO2 and cloud cover [Pfeilsticker et al., 1999; Winterrath et al., 1999].

10. Summary of Error Sources

The various sources of errors that have been identified in this paper are summarized in Table 6. This includes an approximate assessment of the likely significance that such sources of error may have and estimates of the size of the errors based on the results of the various sensitivity studies described in section 6. Note that errors given here are not meant as a full error budget of the BrO retrieval. They are merely representative of the case for slant column differences calculated in the range 87°–90° SZA using a reference spectrum taken at 70° SZA, as determined from a limited though representative sample of five different instruments. Possible differences in sensitivity depending on the choice of the standard conditions and on atmospheric conditions are not considered.

<table>
<thead>
<tr>
<th>Error Source</th>
<th>Comments</th>
<th>Error Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offset correction</td>
<td>moderate to large effect depending on individual characteristics of spectrometer</td>
<td>10–70%</td>
</tr>
<tr>
<td>Wavelength interval for fits</td>
<td>moderate to large effect</td>
<td>2–40%</td>
</tr>
<tr>
<td>I0 correction</td>
<td>large effect</td>
<td>35%</td>
</tr>
<tr>
<td>BrO cross-section shift (0.17 nm)</td>
<td>significant effect</td>
<td>23%</td>
</tr>
<tr>
<td>O3 temperature dependence</td>
<td>significant effect but well accounted for by fitting two O3 cross sections of differing temperatures</td>
<td>25%</td>
</tr>
<tr>
<td>Spectral wavelength calibration</td>
<td>moderately significant effect that is at present limited to an accuracy of ~0.01 nm</td>
<td>18%</td>
</tr>
<tr>
<td>Slit function determination</td>
<td>moderate effect</td>
<td>10%</td>
</tr>
<tr>
<td>Degree of polynomials used</td>
<td>small effect</td>
<td>8%</td>
</tr>
<tr>
<td>O3 cross-section shift (0.03 nm)</td>
<td>small if using I0 correction and 346- to 359- nm fit window</td>
<td>5%</td>
</tr>
<tr>
<td>Low BrO cross-section resolution</td>
<td>small effect</td>
<td>4%</td>
</tr>
<tr>
<td>Wavelength-dependent air mass factor corrected O3 cross sections</td>
<td>very small effect as long as accounting for O3 temperature dependence in some other way, such as two O3 cross-sections</td>
<td>3%</td>
</tr>
<tr>
<td>False fitting of BrO</td>
<td>very small effect provided I0 corrected cross sections are used</td>
<td>–</td>
</tr>
</tbody>
</table>

*Relative importance of the sources has been assessed. Error estimates are for slant column differences calculated between 87° and 90° SZA using a reference spectrum at 70° SZA, as derived from results of sensitivity tests given in Table 5.
conditions (temperature, NO₂ amounts, cloud cover, and aerosols) cannot be ruled out.

11. Further Requirements

[45] In this study the inaccuracy of the wavelength calibration of the GOME spectra, now resolved [Voigt et al., 2001], and of the O₄ spectra were shown to be significant sources of error in the retrieval of BrO. Even though for many of the gases, little rotational structure is expected in their vibronic spectra, this study indicates the need for accurate high spectral resolution measurements of the absorption cross sections of the gases covering a relevant atmospheric range of temperature and pressure. A database of accurate high-resolution gaseous absorption cross sections in the UV and visible spectral regions is expected to replace the GOME data set for remote sensing applications using the DOAS retrieval technique. New O₄ cross sections under more realistic atmospheric conditions have been measured and recently released [Hermans et al., 2001], so their suitability should be assessed and recommendations should be made.

[46] Further attention should be given to the determination of Ring cross sections and offsets, as these appear to be significant sources of differences between the groups. In addition, improvements may be obtainable if the measurement of instrument slit functions can be improved. As far as further improvements in the analysis by the method of intercomparison are concerned, it would be desirable to have another such intercomparison under more suitable conditions, perhaps at somewhat higher latitude in winter when there is more BrO present and the temperatures are more conducive to the instruments functioning optimally.

12. Conclusions

[47] This study has highlighted the difficulty of BrO measurement and the extreme sensitivity of BrO DOAS retrieval to very small changes in calibration of spectra and cross sections as well as to the wavelength fitting window used for the analysis. As a consequence, there is a need for high-resolution cross sections with very accurate wavelength calibration and high signal-to-noise ratio in this region. Additionally, cross sections should be measured over a range of temperatures both to measure differences in cross-section shape and magnitude and to check for wavelength shifts with temperature. Given the nonideal nature of the measurements, a reasonably good agreement (to within some 4% on average between 87° and 90° SZA with a scatter of 16%) has been found under carefully controlled analytical conditions. As a result of the investigations into the sensitivity of the analysis to a number of factors, recommendations have been made as to the best analysis with the presently available cross sections.

[48] This study has demonstrated that consistent observations of BrO columns by a series of instruments operated by different groups can be obtained as long as carefully controlled common analysis settings are used. As shown in a recent study by Sinnhuber et al. [2002], the gain in data consolidation is such that the technique is now approaching the level of accuracy needed to allow modelers to assess our current understanding of stratospheric bromine chemistry. Given that the intercomparison measurements were not made under the same conditions as the previously published measurements and that the error sources identified affect different instruments to different extents, the implications for the accuracy of previously published slant column measurements of BrO are difficult to assess. While it is likely that such data may be affected by a few percent to tens of percent, the error is not of an order of magnitude such that the main conclusions drawn in previous investigations should not be invalidated by the present study.

[49] Finally, an important application of the reported study might be the future development and exploitation of networked BrO observations as part of the Network for the Detection of Stratospheric Change (NDSC).

Appendix A

A1. Solar I₀ Effect

[50] The need to correct the convolved cross sections used in zenith-sky UV/visible spectroscopy actually arises because the I₀ spectrum in the zenith-sky measurements is the highly structured solar Fraunhofer spectrum, whereas the I₀ spectrum used to measure the laboratory absorption cross sections is usually nearly flat. In zenith-sky differential absorption spectroscopy, one removes the Fraunhofer

Figure A1. Results from a fit of NO₂ absorption cross sections to a NO₂ cell measurement performed in Lauder on 31 July 1996, using the zenith sky as a light source. The improvement in residuals obtained when applying a correction for the so-called I₀ effect (see text) is obvious.
structures by forming the log ratio of a twilight spectrum to a reference midday spectrum, thus retaining the absorptions by atmospheric absorbers. However, because both of the spectra forming the ratio are measured by the instrument and therefore have been filtered by the instrument slit function before the ratio is calculated, complete removal of the Fraunhofer structures is not possible. This can be seen by looking at the integral equations given here.

[51] Assuming no absorption, the midday reference spectrum measured and therefore filtered by the instrument is

\[ I_0(l') = \int I_0(\lambda) W(\lambda - l') \, d\lambda, \tag{A1} \]

where \( I \) is the spectrum measured by the zenith-sky spectrometer, \( I_0 \) is the solar Fraunhofer spectrum, and \( W(\lambda) \) is the normalized instrument slit function. Similarly, the twilight spectrum also filtered by the instrument (where \( h \) is the optical depth of absorbers such as \( O_3 \) and \( NO_2 \)) is

\[ I(l') = \int I_0(\lambda) e^{-h(\lambda)} W(\lambda - l') \, d\lambda. \tag{A2} \]

[52] The negative log ratio of the twilight to the reference spectra does not completely remove the \( I_0(\lambda) \) term unless \( I_0(\lambda) \) or \( h(\lambda) \) are constant over the integration interval (the full width of the instrument slit function). This essentially occurs for broadly structured cross sections such as, for example, those of \( O_3 \) for \( \lambda > 400 \text{ nm} \), but not for \( NO_2 \), BrO, OCIO, or \( O_3 \) in the Huggins bands. The significance of the solar \( I_0 \) effect has been quantified using synthetic spectra and real spectra, as shown in Figures 2 and 5, respectively, and as discussed in sections 5 and 6.

A2. Correcting Absorption Cross Sections For the Solar \( I_0 \) Effect

[53] In order to generate absorption cross sections that include the solar \( I_0 \) effect in their shape, the method adopted in this work is to calculate synthetic spectra with an optical depth \( h(\lambda) = \sigma(\lambda) X \), where \( \sigma(\lambda) \) is the absorption cross section and \( X \) is the corresponding column amount. The correction depends slightly on the value of \( X \), because of the nonlinear terms in the integral, so a value that is typical of the maximum measured is used. This leads to the following definition for the solar \( I_0 \)-corrected cross section:

\[ \sigma_{\text{corrected}}(\lambda) = -\frac{1}{X} \ln \left\{ \frac{\int I_0(\lambda) \exp[-h(\lambda)] W(\lambda - X) \, d\lambda}{\int I_0(\lambda) W(\lambda - X) \, d\lambda} \right\} \tag{A3} \]

[54] In this work the solar atlas by Kurucz et al. [1984] was used as the reference Fraunhofer spectrum \( I_0 \). The significance of the correction is demonstrated in Figure A1, where an \( NO_2 \) cell fit residual (obtained using the zenith sky as a light source) is shown using standard uncorrected \( NO_2 \) cross sections and \( NO_2 \) cross sections corrected using (A3).

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References


S. R. Aliwell and R. L. Jones, Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. (simon@atm.ch.cam.ac.uk; rjl1001@cus.cam.ac.uk)

D. W. Arlander and K. K. Tornkvist, Norwegian Institute for Air Research, Instituttveien 18, N-2007, Kjeller, Norway. (bill.arlander@nilu.no; kjersti.tornkvist@nilu.no)

J. P. Burrows and A. Richter, Institute of Environmental Physics, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany. (burrows@iup.physik.uni-bremen.de; richter@iup.physik.uni-bremen.de)

D. J. Fish, Department of Meteorology, University of Reading. Early Gate, PO Box 243, Reading RG6 6BB, UK. (D.J.Fish@reading.ac.uk)

P. V. Johnston, National Institute of Water and Atmospheric Research, Private Bag 50061, Omakau, Otago Lauderdale, State Highway 85, Central Otago, New Zealand 9182. (p.johnston@niwa.cri.nz)

J. C. Lambert and M. Van Roozendael, Institut d’Aéronomie Spatiale de Belgique, Avenue Circulaire 3, B-1180, Brussels, Belgium. (lambert@oma.be; michelv@oma.be)

K. Pfeilsticker and T. Wagner, Institute of Environmental Physics, University of Heidelberg, INF 366, D-69120 Heidelberg, Germany. (Klaus.Pfeilsticker@iup.uni-heidelberg.de; Thomas.Wagner@iup.uni-heidelberg.de)

I. Pundt, Service d’Aéronomie du CNRS, BP 3, F-91371 Verrières-le-Buisson, France. (irene.pundt@aevoj.jussieu.fr)