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Analysis of BrO Measurements from the Global Ozone Monitoring Experiment

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Abstract. The Global Ozone Monitoring Experiment (GOME), launched on the ESA ERS-2 satellite in April 1995, measures solar back scatter spectra from which atmospheric BrO columns may be derived globally with high precision (slant column uncertainties of $\pm 3\times10^{13}$ cm^{-2} or less). Obtaining such precision requires additional characterization of GOME spectra, reference spectra that are well calibrated in wavelength, and a fitting method capable of reproducing measurements to several parts in 10^4. This paper describes these elements of the data processing and gives examples of BrO distributions in the stratosphere and enhanced tropospheric BrO in the polar springtime.

Introduction

The importance of bromine chemistry to stratospheric ozone, including the synergy between bromine and chlorine chemistry which enhances O_3 destruction in the lower stratosphere, is well established [*McElroy et al.*, 1986]. GOME provides the first possibility to establish a global climatology of BrO. The capability of GOME to measure BrO globally was established by *Chance et al.* [1991] and has since been demonstrated [*Hegels et al.*, 1996, 1998]. This paper describes improvements in instrument characterization, in the reference spectra used for fitting, and in the fitting technique. The results are vertical columns with precisions of 0.5-1.5$\times10^{13}$ cm^{-2} for single radiances (1.5 s integration time), an order of magnitude improvement. Overall accuracy is currently limited by the 7% uncertainty in the absorption cross sections.

Data Analysis

Spectrum Fitting

Radiance spectra are directly fitted using nonlinear least-squares (NLLS), beginning with a GOME irradiance spectrum. Spectrum simulation includes Beer's law contributions from the reference spectra, a linear Ring effect correction, albedo, and polynomial closure terms. No high pass filtering or smoothing is applied. Fitting can be done after wavelength calibration of each radiance and irradiance spectrum. Since only the irradiances and radiances contain high frequency spectral information, and there are more than 2000 radiances per orbit, it is more usual to calibrate the irradiance and one radiance spectrum near the middle of the orbit, and then let the wavelength scale of the irradiance vary in the fitting to provide fine adjustment of the relative scales. This option has been carefully checked to insure that results are consistent with individual calibration and that artificially low residuals and fitting uncertainties are not obtained.

Reference spectra for BrO, O_3, NO_2, OClO, the O_2-O_2 collision complex, and the Ring effect are required. A major difficultly has been to assemble a sufficiently good set of reference spectra; substantial improvements remain to be made in both cross sections and wavelength calibration. The 223 K BrO spectrum of *Wahner et al.* [1988], with the stated intensity uncertainty of 7%, is used here. It is re-calibrated in wavelength using FTS spectra of BrO and SO_2 (D. Wilmouth, T.F. Hanisco, and J.G. Anderson, private communication, 1997; A.C. Vandaele, private communication, 1997). The Ring effect spectrum is calculated as described in *Chance and Spurr* [1997].

Wavelength Calibration

Operational calibration uses in-flight spectra of a PtNeCr reference lamp, transferring the calibration using temperature as a proxy for wavelength shift. This results in calibration of, usually, $\leq6\times10^{-3}$ nm in the BrO region ($\leq$0.05 GOME pixel). *Caspar and Chance* [1997] showed that wavelength calibration is improved by using a Fraunhofer reference spectrum [*Chance and Spurr*, 1997] and applying either spectral cross-correlation [*Kurtz et al.*, 1992] or NLLS fitting (used here) to adjust portions of GOME radiances or irradiances. For the BrO fitting region, these methods calibrate in vacuum wavelength to usually 0.001 nm or better.

Undersampling Correction

The wavelength calibration of the irradiance spectra also determines the instrument transfer function (ITF) independently to high accuracy. The ITF in the BrO fitting region was determined to be very close to a Gaussian of 0.097 nm HW1/e. The dispersion in this region is close to 0.11 nm/pixel, substantially short of that required to approach full sampling of the ITF [*Goldman*, 1953].

Undersampling should be the same for both radiances and irradiances, and thus cancel, in the limit that the atmospheric spectrum is dilute (the BrO region approaches this limit, as it contains mainly small absorptions plus the Ring effect contribution). Substantial residual structures, largely constant from spectrum to spectrum, were found in the initial radiance fitting. These did not have the character of either a known (or likely) molecular absorption or of a potential contribution from the Ring effect. (The Ring effect spectrum consists of gently-varying low-frequency structures.) Figure 1a shows the residual from a single radiance fit, compared with the average residual from fitting 101 spectra. Aliasing due to spectral undersampling can still contribute to residuals if the ITF is different for radiances and irradi-

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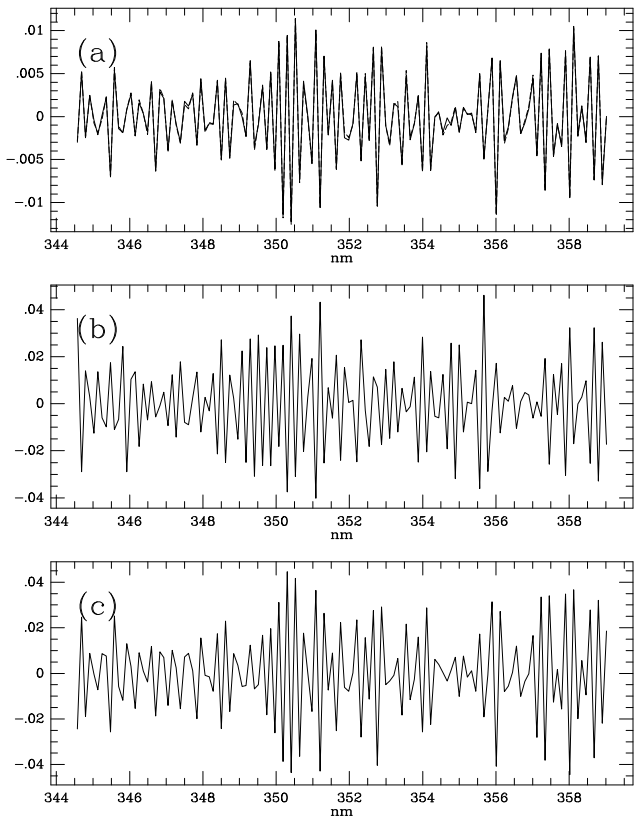

Figure 1. (a) Residuals from fitting 1 GOME spectrum (solid line) and the average from fitting 101 GOME spectra (heavy dashed line), in optical depth units. (b) Phase 1 of the undersampling correction. (c) Phase 2 of the undersampling correction. Undersampling accounts for more than 90% of the fitting residuals.

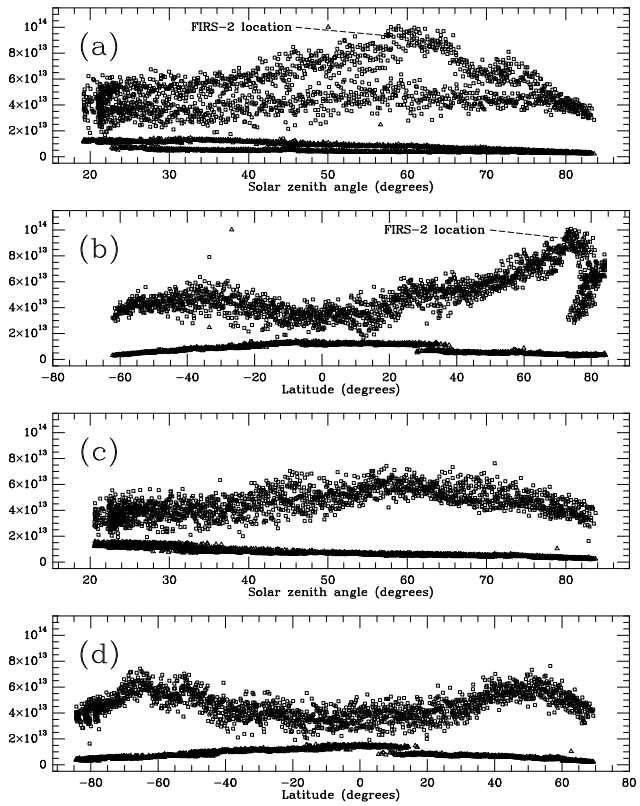

Figure 3. Vertical column amounts of BrO in cm^{-2} (squares) plus the 1σ fitting errors (triangles). (a) Orbit 70430224 (April 30, 1997) BrO vs. solar zenith angle. (b) Orbit 70430224 BrO vs. latitude. (c) Orbit 71030220 (October 30, 1997) BrO vs. solar zenith angle. (d) Orbit 71030220 BrO vs. latitude. The orbits are chosen to have approximately the same geographic coverage.

ances - for example, from non-uniform filling of the slit. This possibility was investigated by generating a synthetic undersampling spectrum using the 0.01 nm resolution Fraunhofer reference spectrum [*Chance and Spurr*, 1997]. It is convolved with the ITF determined as above and re-sampled to determine two phases of undersampling correction, shown in figures 1b and 1c. This synthetic undersampling correction accounts for more than 90% of the common residual in the radiance fitting, but does not entirely eliminate it. The remaining common residual, determined as an average from fitting a complete orbit, is still apparently an instrumental artifact. It does not have the character of either a molecular absorption or a Ring effect contribution. It is included in the final fitting, giving (approximately) an additional factor of two improvement in BrO uncertainty.

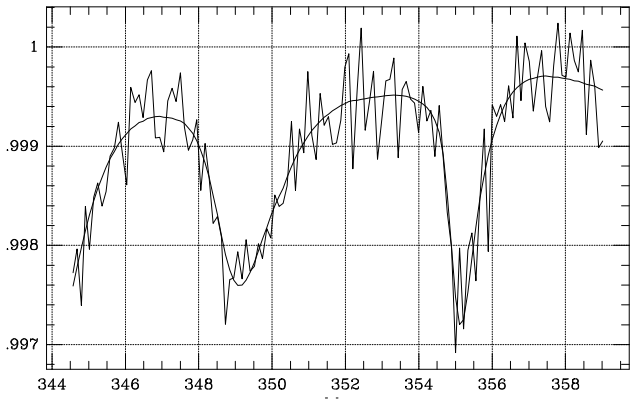

Figure 2. GOME BrO fitting for the FIRS-2 overflight on April 30, 1997. The integration time is 1.5 s. The fitting precision is 4.2% and the RMS is 2.7×10^{-4} in optical depth. Fitting and inversion gives a vertical BrO column of 9.3×10^{13} cm^{-2}.

Vertical Column Determination

Line-of-sight measurements are inverted geometrically to give BrO vertical columns. Radiative transfer calculations show this to be a reasonable approximation for BrO above 15 km (better than 20% for SZA up to 60° and albedo of 0.3 or greater). Tropospheric BrO is substantially underestimated except at low SZAs and high albedos because of reduced penetration of light at these wavelengths into the troposphere. Thus, tropospheric BrO amounts in the present work may be substantially (up to a factor of two) underestimated. GOME does include the necessary albedo and SZA information to correct BrO columns to high accuracy in those cases where the altitude of the BrO is known

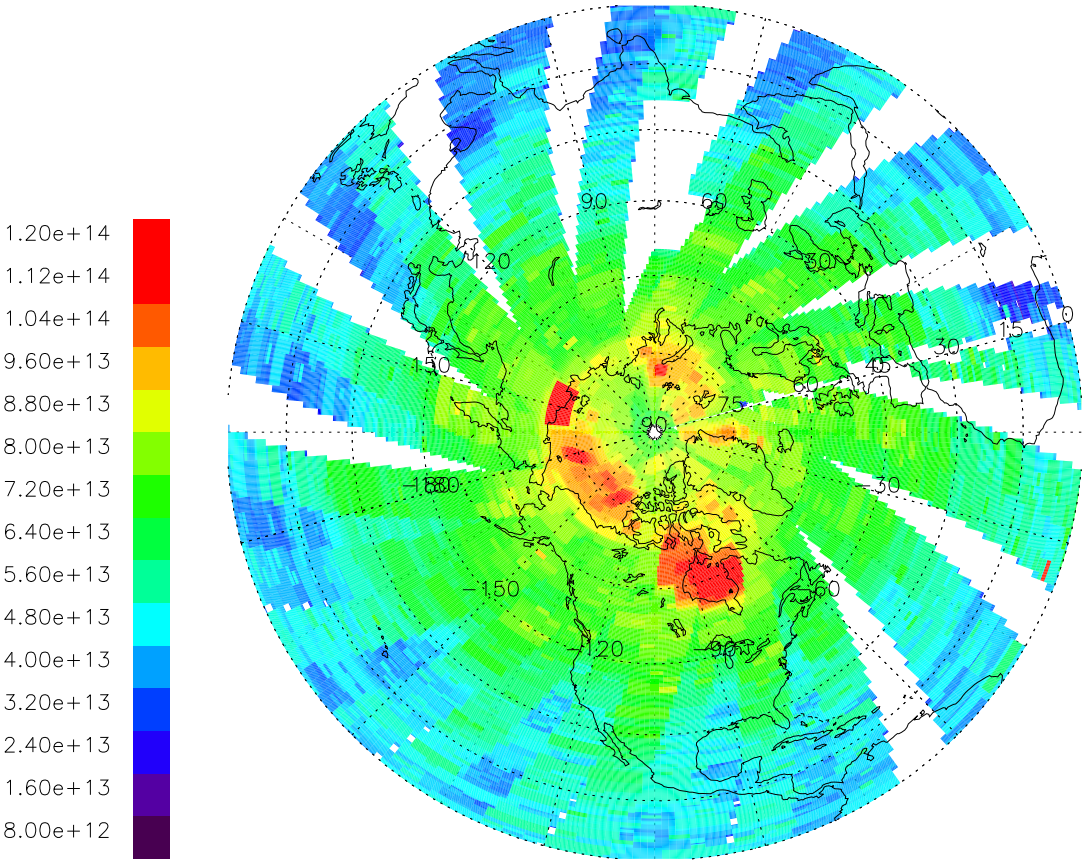

Figure 4. Vertical column BrO (cm^{-2}) in the northern hemisphere, April 30-May 2, 1997. Hudson Bay and the Arctic ice shelf have large enhancements, almost certainly due to tropospheric BrO.

(*e.g.*, when it is clearly stratospheric or clearly lower tropospheric). This correction is currently being developed in the analysis of enhanced BrO in the polar spring.

The first BrO measurements are from an orbit overflying the SAO FIRS-2 balloon-borne spectrometer on April 30, 1997. The fitting of the GOME spectrum overflying FIRS-2 is in figure 2; the fitting RMS (2.7×10^{-4} of full scale) and the column fitting uncertainty (4.2%) are typical values. BrO vertical columns and 1σ fitting uncertainties for this orbit are shown vs. SZA in figure 3a and vs. latitude in figure 3b. An orbit 6 months later at the the same geographical location is shown in figures 3c and 3d. BrO is smoothly distributed along the orbits, thus located primarily in the stratosphere (or at least above cloud height, since cloud blocking would induce significant apparent orbital), except for the highest northern latitudes of the April orbit. Comparison of figures 3a and 3c indicates that GOME BrO measurements may determine significant hemispheric differences in the global distribution.

Figure 4 shows the distribution of BrO in the northern hemisphere for April 30-May 2, 1997. Large enhancements are obvious over several areas, including Hudson Bay and the Arctic ice shelf. A cross section through this distribution is shown in figures 5a and 5b. Similar polar enhancements attributed to tropospheric BrO have been observed by ground-based techniques in both hemispheres [*Kreher et al.*, 1997]. Boundary layer processes involving autocatalytic release of halogens from sea-salt aerosol [*Vogt et al.*, 1996] and from the snow pack [*Tang and McConnell*, 1996] have been proposed to explain such BrO enhancement. The large enhancements of BrO measured by GOME (up to 10^{14} cm^{-2}

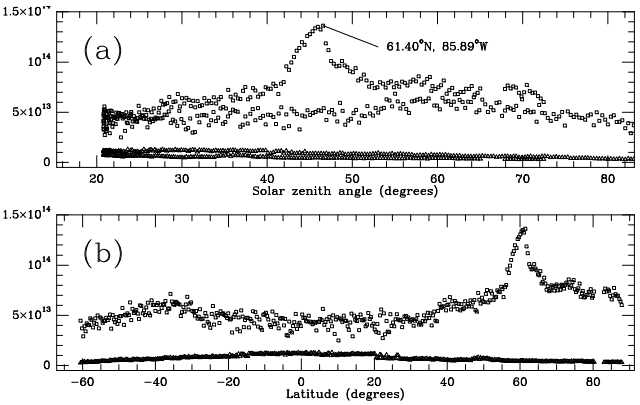

Figure 5. A cross section through the BrO distribution of Figure 4 vs. solar zenith angle (5a) and vs. latitude (5b). Squares are BrO vertical columns (cm^{-2}); triangles are 1σ fitting errors. The density of points is less than in Figure 3 because only the center spectrum scans of the orbit (#70502164), where the BrO maximum is located, are included. The maximum in BrO corresponds to northern Hudson Bay.

in such episodes) correspond more closely to release from the snow pack.

Conclusions

BrO columns can be measured globally from GOME data; the fitting method described here improves the precision by an order of magnitude. BrO that is clearly in the stratosphere and BrO that is clearly in the lower troposphere can be determined quantitatively.

Ongoing work with GOME BrO measurements includes: (1) Comparison of BrO vertical columns with FIRS-2 measurements of HBr, HOBr, and additional species to test stratospheric bromine photochemistry; (2) Development of the global climatology of BrO, including seasonal and interhemispherical differences; (3) Quantification of episodic production of tropospheric BrO, particularly in the polar spring in both hemispheres; (4) Radiative transfer calculations to improve the inversion of line-of-sight measurements to give vertical columns.

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