

Stratospheric BrO abundance measured by a balloon-borne submillimeterwave radiometer



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Introduction

Measurements of mixing ratio profiles of stratospheric bromine monoxide (BrO) were made using observations of BrO rotational line emission at 650.179 GHz by a balloon-borne SIS (superconductor-insulator-superconductor) submillimeterwave heterodyne receiver. The balloon was launched from Ft. Sumner, New Mexico (34N) on 22 Sept 2011. Peak mid-day BrO abundance varied from 16 ± 2 ppt at 34 km to 6 ± 4 ppt at 16 km. Corresponding estimates of total inorganic bromine (Br_T), derived from BrO vmr (volume mixing ratio) using a photochemical box model, were 21 ± 3 ppt and 11 ± 5 ppt, respectively. Inferred Br_T abundance exceeds that attributable solely to decomposition of long-lived methyl bromide and other halons, and is consistent with a contribution from bromine-containing very short lived substances, Br_T^{VLSL} , of 4 ppt to 8 ppt. These results for BrO and Br_T were compared with, and found to be in good agreement with, those of other recent balloon-borne and satellite instruments. Stratospheric bromine contributes to ozone loss through halogen catalyzed cycles analogous to stratospheric chlorine chemistry, except that the bromine cycles have a significantly greater potential to deplete ozone [2]. In the daytime upper stratosphere, BrO is the most abundant of the inorganic bromine species comprising up to 70% of Br_T , where



Stratospheric Br_T results from photodecomposition of naturally-occurring and anthropogenic bromine-containing source gases transported from the troposphere into the stratosphere. Although the total bromine loading of the stratosphere has declined by 1%/year since 2001 [3, 4, 13] due to reductions in surface emissions of CH_3Br and other halons with long photochemical lifetimes, some uncertainty remains in the quantitative closure of Br_T budget. Recent balloon-borne and satellite observations of BrO abundance indicate that Br_T levels in the mid- and lower stratosphere exceed that estimated by models based solely on long-lived organic bromine surface source gases [11, 8].

The additional source of Br_T needed to reconcile the stratospheric bromine budget is generally understood to be from decomposition of naturally occurring bromine-containing source gases with very short photochemical lifetimes (VLSL) such as $CHBr_3$, CH_2BrCl , and CH_2BrCH_2Br , with current estimates of Br_T^{VLSL} ranging from 2 to 8 ppt [8, 13, 1].

The SLS Instrument

The Submillimeter Limb Sounder (SLS) is a heterodyne radiometer that measures molecular rotational thermal emission spectra from a limb observing geometry. The SLS has been flown on numerous middle and high altitude flights since 1991 [9, 10]. Measured gases include ClO , O_3 , HCl , N_2O , HO_2 , and HNO_3 . In 2004, the instrument was upgraded with a superconductor-insulator-superconductor (SIS) mixer improving receiver sensitivity by 20 times compared to that with the Schottky diode mixer used on earlier flights. Spectrometers were also upgraded from analog filterbanks to a single digital polyphase filterbank spectrometer that provides uniform channels with high spectral resolution and significantly improved gain stability. Figure 1 is a block diagram of the radiometer. Radiance from the atmospheric limb, sky cold reference and warm calibration reference are selected by a scanning 30 cm diameter primary antenna and scan plate. The measured field-of-view is approximately 0.6 full width at half maximum. The double sideband down converter is a quasi-optic coupled SIS NbTiN junction mixer. The tunable local oscillator (620 GHz to 680 GHz) is generated by a synthesizer, amplifier, multiplier and coupled to the mixer by a Mylar beamsplitter. The SIS junction and HEMT low noise amplifier are maintained at 4.2 K in a liquid helium cryostat. Following downconversion in the SIS mixer, the output intermediate frequency (IF) band (4-8 GHz) is analyzed by the digital spectrometer.

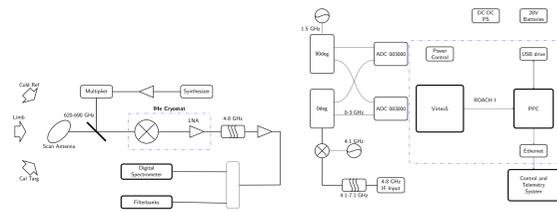


Figure 1: Diagram of the SLS instrument. Atmospheric radiance is collected by a scanning antenna system, combined by a Mylar beam splitter with a frequency tunable local oscillator, downconverted in an SIS mixer. The IF signal is amplified, filtered, downconverted in a second heterodyne stage to the input frequency range of the digital and analog spectrometers. Diagram of the digital spectrometer sub-system. Two interleaved National ADC083000 digitizers sample the input signal at 6 G samples/sec. Signal bitstream is converted to a power spectrum by an algorithm implemented in the Xilinx Virtex 5 FPGA. Code in a PowerPC collects spectra data, stores data onboard in a flashdrive, and transmits a real-time compressed sample of spectra to the ground.

The digital spectrometer (Figure 1) deployed on SLS was instrumental in obtaining excellent data quality. A digital polyphase spectrometer was implemented in a Reconfigurable Open Architecture Computing Hardware (ROACH) FPGA signal processing board developed by the Berkeley CASPER project [12]. Two 3 Gsps (gigasamples per second) analog to digital converter cards, sampling the IF down converted to base band at an aggregate rate of 6 Gsps, provided 3 GHz of bandwidth with 8192 channels and frequency resolution of 375 kHz. To our knowledge this is the most advanced digital spectrometer deployed in a field experiment. For the measurements discussed here alternate channels were co-added to provide a reduced data rate due to the limited on-board data storage system. Unlike autocorrelator and FFT digital spectrometers, the polyphase implementation provides channels with steep and deep skirts. A Power PC interfaced to the Virtex 5 on the CASPER board performs additional data processing, telemetry down-link, and data storage on a USB flash drive.

Balloon Flight Summary

Data presented here are from a high altitude balloon flight of the Jet Propulsion Laboratory (JPL) Submillimeterwave Limb Sounder (SLS) instrument from the Columbia Scientific Balloon Facility site at Ft. Sumner, New Mexico, USA (34N, 104W). On-board the gondola, in addition to the SLS, were the JPL MkIV solar occultation Fourier transform infrared spectrometer and *in situ* O_3 sensor. The balloon was launched on 22 Sept 2011, reached float altitude of approximately 39 km at 14:00 local time and remained above 37 km through the flight until flight termination the next day.

Observations and Analysis

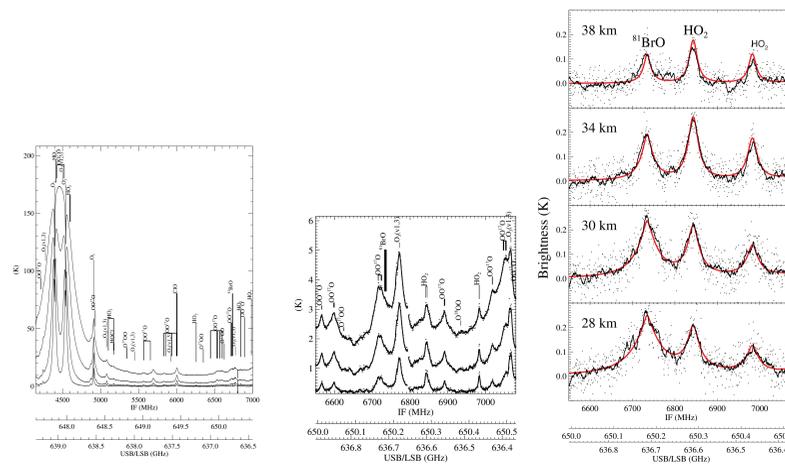


Figure 2: [Left panel] Measured double-sideband emission spectra with LO frequency 643.444 GHz. Sample spectra from the September 2011 balloon flight showing the full spectrometer bandwidth corresponding to limb tangent heights of 38, 36, 34 and 30 km. Region containing the ^{81}BrO lines is at the far right. Abscissa scales show frequency in an intermediate frequency (IF), and upper-lower sideband frequency prior to heterodyne down conversion. [Middle panel] Expanded scale plot showing the BrO emission features. [Right panel] Day-night difference emission spectra of the same spectral region shown in the middle panel. Spectrometer data are shown at 750 kHz (dots) resolution and boxcar smoothed (thick solid black line). Synthetic spectra calculated using retrieved BrO profiles are also plotted (red-solid). HO_2 line occurring in lower sideband is indicated by the san-serif font.

BrO Profile Comparisons

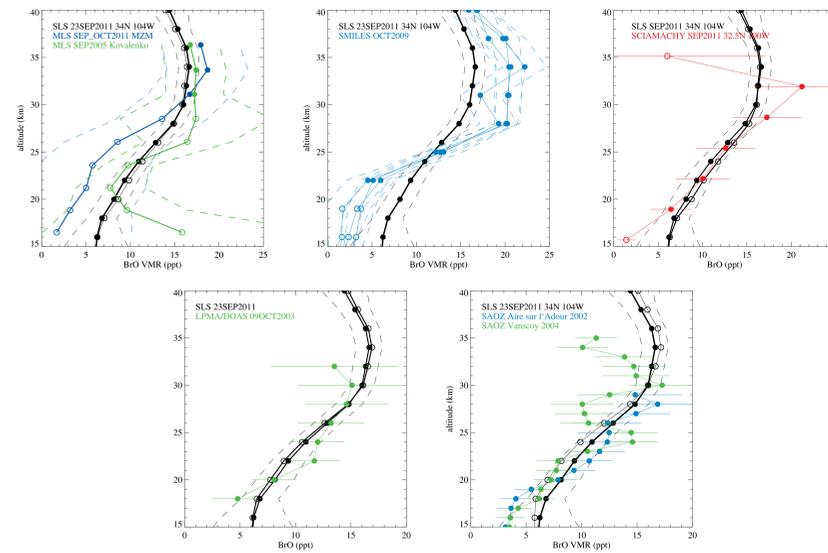


Figure 3: Comparison of SLS BrO with MLS [top left], JEM/SMILES [top middle], SCIAMACHY [top right], LPMA DOAS [lower left] and SOAZ [lower right] BrO profiles.

Inferred Total Inorganic Br_T

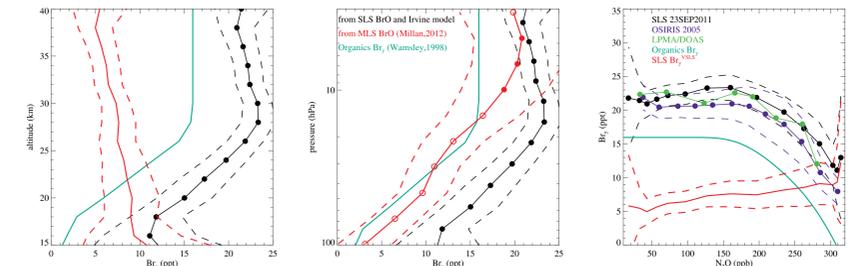
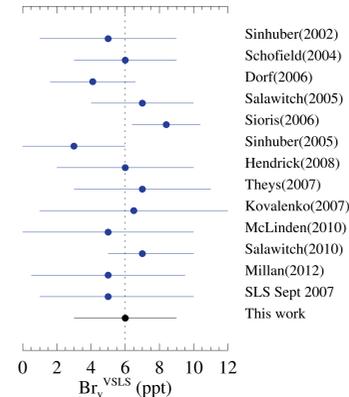


Figure 4: [Left panel] Br_T mixing ratio inferred from SLS measured BrO (black) using the U.C. Irvine photochemical photochemical box model. Br_T uncertainty range (black-dashed) is the BrO uncertainty scaled by Br_T/BrO from the photochemical box model. Abundance of Br_T from long-lived organic sources (cyan) is from [11] scaled to 16 ppt at peak. Estimated VLSL abundance is Br_T minus the estimate of inorganic bromine attributed to long-lived bromine source gases. [Middle panel] Comparison of Br_T mixing ratio scaled by SLS measured BrO (black) Br_T inferred from MLS BrO for 2005 [7]. Br_T from long-lived organic gases from [11] scaled to 16 ppt for an age-of-air of 5 years (2006) is also plotted (cyan curve) Correlation of Br_T mixing ratio inferred from SLS measured BrO against N_2O mixing ratio (black). [Right panel] The Br_T tracer correlation from monthly mean Odin-OSIRIS and the Odin/Submillimeter Radiometer instruments [6]. LPMA/DOAS Br_T correlation (green dots-line) is from a balloon flight in March 2003 from Kiruna, Sweden [5]. SLS Br_T uncertainty range (black-dashed) is the BrO uncertainty scaled by Br_T/BrO from the photochemical box model. Abundance of inorganic bromine (cyan) from long-lived source gases is from [11] scaled as in Figure 4. Estimated Br_T^{VLSL} abundance is Br_T minus the estimate of inorganic bromine attributed to long-lived bromine source gases.

Adapted from [13] Table 1-14 and [7], summary of recent estimations of the VLSL contribution to stratospheric inorganic bromine (Br_T^{VLSL}) from satellite, ground-based and balloon-borne instruments. Vertical dashed line marks 6 ppt, the central values for Br_T attributed to VLSL.



Summary

Balloon-borne remote sensing submillimeterwave emission measurements of BrO indicate mid-day abundances ranging from 16 ± 2 ppt at 34 km to 6.5 ± 4 ppt at 16 km. Total Br_T abundance, inferred from BrO and a photochemical model, is 21 ± 3 ppt. The inferred Br_T abundance profile was found to exceed the levels of Br_T attributable solely to photodecomposition of CH_3Br and other long-lived source gases throughout the stratosphere. These results are consistent with the view that decomposition of short-lived bromine-containing source gases deposits at least 4 ppt inorganic bromine in the lowermost stratosphere. Results are in good general agreement with other recent measurements and support the conclusions [13].

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