

## Stratospheric HBr concentration profile obtained from far-infrared emission spectroscopy

I. G. Nolt,<sup>1</sup> P. A. R. Ade,<sup>2</sup> F. Alboni,<sup>3</sup> B. Carli,<sup>4</sup> M. Carlotti,<sup>3</sup> U. Cortesi,<sup>4</sup> M. Epifani,<sup>4</sup> M. J. Griffin,<sup>2</sup> P. A. Hamilton,<sup>2</sup> C. Lee,<sup>2</sup> G. Lepri,<sup>3</sup> F. Mencaraglia,<sup>4</sup> A. G. Murray,<sup>2</sup> J. H. Park,<sup>1</sup> K. Park,<sup>5</sup> P. Raspollini,<sup>4</sup> M. Ridolfi,<sup>4</sup> and M. D. Vanek<sup>1</sup>

**Abstract.** Hydrogen bromide (HBr) is the principal bromine sink species for the ozone loss chemistry induced by bromine-containing gases in the stratosphere. We report a 1994 balloon-based measurement of the daytime stratospheric HBr profile between 20 and 36.5 km altitude. The average concentration result of  $1.31 \pm 0.39$  parts per trillion in volume (pptv) and an analysis for the concentration versus altitude profile are consistent with previously reported measurements. These results strengthen the evidence for a significantly higher HBr concentration than that predicted by current photochemical models which, on the basis of recent kinetics results, do not include significant HBr production by the reaction branch,  $\text{BrO} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_3$ .

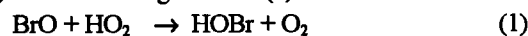
### Introduction

A concerted international study is underway to determine whether bromine-containing gases pose a significant threat to the Earth's protective ozone layer. A principal source gas of concern is methyl bromide which is emitted to the atmosphere from a number of natural and anthropogenic sources (Kurylo *et al.*, 1994). While the first exposition of possible bromine catalyzed destruction of ozone was made in 1980 (Yung, *et al.*), research has expanded recently with the recognition that regulation of methyl bromide production may be required, in addition to that of CFC, for the protection of the Earth's ozone layer (Kurylo *et al.*, 1994). The phase out of the use of methyl bromide as a major soil fumigant presents a potential impact to agricultural productivity.

The complex nature of upper atmospheric chemistry dictates that measurements be made in the atmosphere itself as a check on the modeling predictions of bromine-related ozone loss processes in the stratosphere. The atmospheric budget of bromine compounds can be categorized into source, reactive, and sink components. A critical determinant of methyl bromide's ozone depletion potential (ODP) is the relative fractions of bromine in the principal reactive and sink forms, i.e. BrO and HBr, respectively. *In situ* measurements of BrO have been reported from a polar balloon flight by Toohey

(1995), and from ER-2 aircraft flights in the ASHOE/MAESA program. Outside the tropics, the aircraft *in situ* BrO measurement is combined with other simultaneous measurements to infer that BrO comprises about 50% of total inorganic bromine Br<sub>y</sub>, HOBr about 30%, and BrONO<sub>2</sub> about 20%, where Br<sub>y</sub>=BrO, BrONO<sub>2</sub>, HOBr, Br, BrCl, and HBr (Stimpfle *et al.*, 1995).

A relatively inactive form of bromine in the stratosphere is hydrogen bromide (HBr) and, although a small fraction of Br<sub>y</sub>, uncertainty in its rate of formation has been a significant uncertainty in the calculated bromine ODP (Ko, 1993; Kurylo *et al.*, 1994). The following reaction (2)



has been proposed as a reaction pathway which could increase HBr and thus serve to reduce the bromine ODP. A recent laboratory measurement of this reaction set yielded an upper limit of 1.5% for reaction (2) compared to reaction (1) at stratospheric temperatures (Larichev *et al.*, 1995), while an earlier indirect measurement using the reverse of reaction (2) resulted in a much smaller branching limit of < 0.01% (Mellouki *et al.*, 1994).

An early workshop on methyl bromide in 1992 identified significant differences between model estimates of stratospheric HBr and the limited experimental data then available (Park *et al.* 1989; Traub *et al.*, 1992). As a result efforts were undertaken to improve the sensitivity for measuring the HBr content of the stratosphere. By 1995 the experimental measurements by two research groups were consistent in showing an average stratospheric HBr concentration of less than two pptv (Johnson, *et al.*, 1995, Carlotti *et al.*, 1995). This paper compares our 1994 flight results to these previously reported measurements.

The HBr molecule is well suited for detection by far infrared emission spectroscopy as it has a relatively large dipole moment which produces a strong emission intensity on a per molecule basis. Furthermore, as a consequence of having a nearly equal abundance of two bromine isotopes (<sup>79</sup>Br and <sup>81</sup>Br), its rotational line emission consists of closely spaced doublets which adds confidence to the HBr spectroscopic assignment. Instrument sensitivities were improved with development of narrowband photon-noise-limited photoconductive detectors (NB-PC) (Murray *et al.*, 1992). The first NB-PC system was incorporated in our Infrared Balloon Experiment (IBEX) flight of May 4, 1993, for detection of the HBr (J=2←3) transition doublet near 50 cm<sup>-1</sup> (200 μm wavelength). The essential result of the 1993 flight was a measured HBr concentration of  $1.6 \pm 0.6$  parts per trillion (pptv) between 25 and 36.5 km altitude (Carlotti *et al.*, 1995]. For

<sup>1</sup>NASA Langley Research Center, Hampton, Virginia.

<sup>2</sup>Queen Mary and Westfield College, London, UK.

<sup>3</sup>Dipartimento di Chimica-fisica e Inorganica, Università di Bologna, Italy.

<sup>4</sup>Istituto di Ricerca sulle Onde Elettromagnetiche, Firenze, Italy.

<sup>5</sup>University of Oregon, Eugene, Oregon.

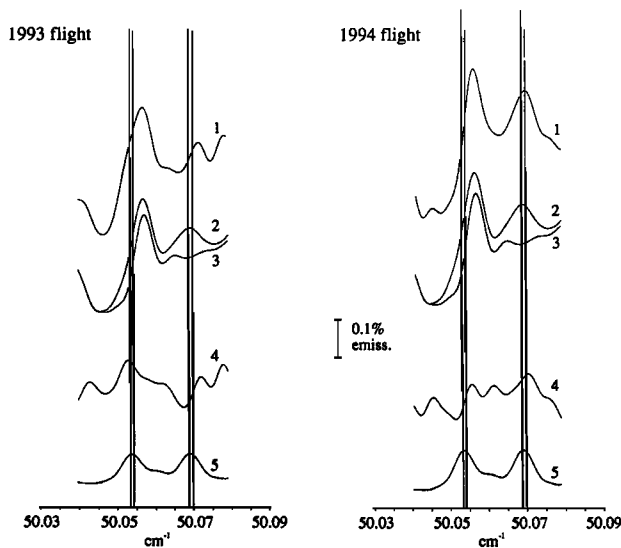


Figure 1. This figure compares the global fitting results for the 1993 and 1994 balloon flights for similar altitude and daytime conditions. This is a highly expanded display of the average emission spectrum of the HBr region, where curve 1 shows the average of 117 spectra obtained in 1993 (Case E of Table 1) and 108 spectra in 1994 (Case A), for the altitude range from 20 to 36 km. Curve 2 is the average of the simulated spectra after convergence by the global fitting algorithm, and curve 4 is the residual difference between curves 1 and 2. Curve 3 is the average of the simulated spectra as in curve 2 but with no HBr included in the simulations, so that curve 5, which is the difference between curve 2 and curve 3, represents the spectral component attributed to HBr emission of the two equally abundant isotopes,  $H^{79}Br$  and  $H^{81}Br$ . The apodized instrumental resolution of  $0.0035\text{ cm}^{-1}$  resolves the isotopic transitions where the lower frequency line shows interference by an isotopically substituted ozone transition. The vertical lines show the known frequencies and the hyperfine splitting of the  $J=2 \leftarrow 3$  rotational transition.

the 1994 campaign, the same detection system was flown with excellent system and balloon altitude performance.

## Measurements

The results reported here were obtained in a 1994 balloon flight campaign which was part of an international cooperative effort in support of correlative measurements for the Upper Atmosphere Research Satellite. The flight instrument combines a high resolution Fourier transform emission spectrometer developed in Italy (Carli *et al.* 1984), with advanced detector technology from the UK (Murray *et al.*, 1992). The data presented here were obtained May 14/15, 1994 on a balloon payload launched from Fort Sumner, NM, (34.5 deg N, 104 W). The flight maintained a float altitude of  $36 \pm 1.5$  km for a full 20 hrs of measurement, about equally divided between day and night.

The experimental data were obtained in the following fashion. From the balloon float altitude of 36 km, the optical instrument viewed the limb emission of the atmosphere at a sequence of elevation angles, with a typical tangent height increment of 1.5 km. At each elevation angle, the interferometer

Table 1. Mixing ratio of stratospheric HBr

Case	Altitude <sup>(1)</sup> (km)	Flight (m/d/y)	No. Scans	M. R. <sup>(2)</sup> ( $10^{-12}$ )	Ref
A	20 to 36.5	5/14/94	108	1.31 (39)	(3)
B	34.6	5/14/94	108	1.78 (1.42)	(3)
	28.0			2.43 (97)	
	21.2			0.85 (68)	
C	22 to 34	1988-94	7 flights	2.00 (80)	(4)
D	25 to 36.5	5/31/93	121	1.60 (60)	(5)
E	20 to 36.5	5/31/93	117	1.15 (46)	(6)

(1) A uniform mixing ratio is assumed when a range is specified for the altitude.

(2) The uncertainties in the right-most digits of mixing ratios (in parentheses) are the quadrature sum of the  $1\text{-}\sigma$  random errors (precision) from the global fit to unapodized data (Cases A, D, & E) and an estimated 15% systematic error. See Carlotti *et al* (1995) for a discussion of the systematic errors.

(3) This paper.

(4) Johnson *et al.*, 1995.

(5) Carlotti *et al.*, 1995.

(6) Modified Carlotti *et al.*, 1995.

moving mirror scanned an optical path difference of 2 m in a time of 2.7 min, providing an unapodized spectral resolution of  $0.0025\text{ cm}^{-1}$ . Periodically a black-body reference source replaced the limb beam for calibration and normalization of the limb spectra. The spectral bandwidth of the channel is defined by a cryogenically-cooled filter, which served to limit the photon flux, and hence fundamental photon noise, incident upon the stressed Ge:Ga photodetector. The spectral channel for this measurement was centered at  $50\text{ cm}^{-1}$ , with a bandwidth (FWHM) of about  $2\text{ cm}^{-1}$ . During the scan, the output signal comprising the interferogram is digitized and relayed by telemetry to the ground for recording. Each digitized interferogram had a nominal 158,000 points. Subsequently, Fourier transform spectra were computed and normalized relative to the black-body reference spectra. Additional details of the instrument can be found in Carlotti *et al.* (1995).

## Results

Our objectives were to extend our analysis using the same retrieval procedures as for the '93 flight data (Carlotti, 1988 & Carlotti *et al.*, 1995) and, in view of the better 1994 balloon and instrument performance, to evaluate the altitude dependence for HBr. All the retrieval analyses reported here were carried out at the University of Bologna and use the global-fit analysis described in Carlotti, *et al* (1995). Briefly in this procedure all the spectra are fit simultaneously but each with a synthetic spectrum calculated with the corresponding observing geometry. The ozone profiles, which are needed to model nearby features, were separately determined and treated as known inputs in the HBr fitting. The relatively weak water vapor features were adequately fit with a standard profile. Finally, a non-linear least squares fit was used to determine the HBr mixing ratio. The atmospheric line database used for modeling the simulated spectrum was the 1992 release of

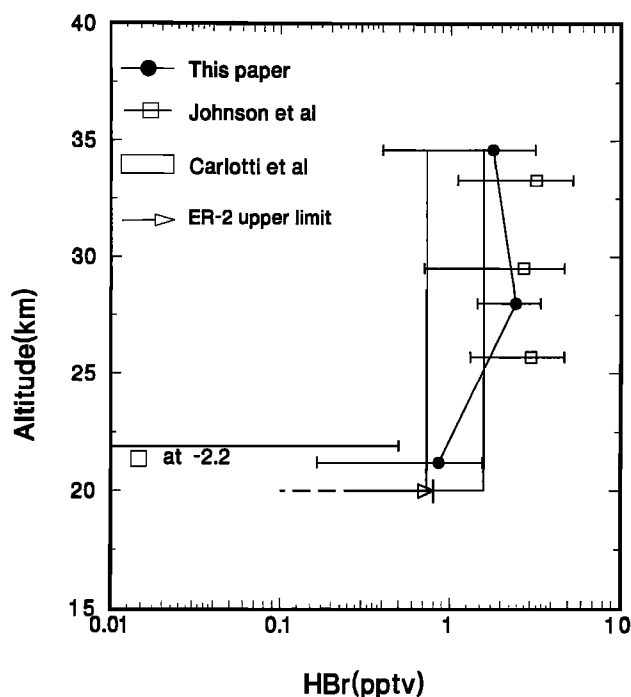


Figure 2. This figure compares the daytime mixing ratio profiles of HBr obtained in our 1993 and 1994 balloon flights, and the profile by Johnson *et al* (1995). The errors are the one-sigma estimate of the total uncertainty which in our cases includes the fitting error (precision) obtained for the global fit as described in the text, added in quadrature to an estimated systematic error of 15%. The retrieval for the 1993 measurement (case E in Table 1) assumed uniform mixing over the indicated altitude range. The upper limit estimate at 20 km altitude is inferred from *in situ* aircraft measurements as described in the text (Stimpfle, private communication, 1996).

HITRAN (Rothman *et al*, 1992) supplemented by the JPL catalog (Poynter and Pickett, 1985), and SAO database (Chance *et al*, 1994). The HBr frequencies are known to high accuracy (Di Lonardo *et al*, 1991).

Figure 1 compares the observed and simulated emission features of HBr for the 1993 and 1994 flights. These averages of apodized spectra on a highly expanded scale illustrate the HBr emission component relative to the residual of the fit. The spectral averages compared for the two flights in this figure encompass the same altitude range and are for daytime observations. In addition, the simulation uses an improved model for the instrument lineshape compared to that used in the Carlotti *et al* (1995) reference. The reproducibility of the two flights is quite good with a slightly smaller residual for the 1994 data.

In Table 1, we compare the 1994 flight results (Case A) to previously published results (Cases C & D). We also show the '93 data re-analyzed (Case E) to match the conditions of the '94 result (Case A).

In an attempt to extract information for the altitude dependence of the HBr mixing profile, we made retrievals relaxing the constraint of a uniform mixing ratio. Using unapodized spectra we had difficulty obtaining a statistically meaningful result, probably due to imperfect modeling of the large "ringing" features interfering with the very weak HBr emissions. Using linearly apodized spectra for the retrieval reduced the spurious interfering sidelobes or "ringing" from

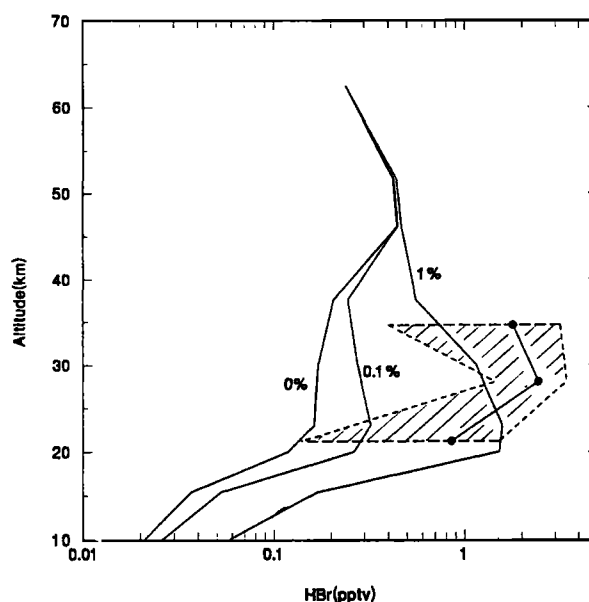


Figure 3. This figure compares the experimental measurement of HBr concentration to the calculated mid-latitude concentrations for local noon using a gas phase model as given in Lary (1996). The model results are shown for three values of the branching ratio for the yield of HBr in the reaction of BrO with HO<sub>2</sub> to produce either HOBr or HBr. The experimental data is case B in Table 1.

nearby lines, and resulted in good convergence of a fit for a three-point profile between 25 and 35 km altitude. However, apodization introduces correlation between adjacent spectral values, and the global-fit error estimate, which assumes linearly independent spectral values, is not correctly estimated in this case. To account for this correlation effect we have increased by 70% the errors estimated by the global fit using apodized data. The result is Case B in Table 1. In Figure 2 this result is compared to the 1993 average daytime concentration result (case E in Table 1), to the Johnson *et al* (1995) profile (obtained from HBr rotational lines at 99.9 and 116.4 cm<sup>-1</sup>), and to an upper limit for HBr at 20 km inferred from aircraft measurements. This latter model-based HBr upper limit is about 4% (0.8 pptv) of the total inorganic bromine (Br<sub>y</sub>) and is estimated from a BrO plus other *in-situ* measurements in the 1994 ASHOE campaign (Stimpfle, private communication, 1996).

## Discussion

An important test of our understanding of bromine chemistry and its ozone depletion potential is the comparison of active and reservoir concentrations in the stratosphere to model predictions. The recent study of the conversion of BrO to HBr by the reaction of BrO with HO<sub>2</sub> (Larichev *et al*, 1995) yielded an upper limit of 1.5% for the reaction branch for HBr (see eq. 2), but a study of the reverse reaction gave a branching ratio of less than 0.01% (Mellouki *et al*, 1994). In Figure 3 we compare the measured HBr concentration to model calculations for different values of this branching ratio. The model results are those calculated by Lary (1996) for mid-latitude, local noon using the 3-d transport model of Cambridge University. Similar results were also reported at an earlier workshop on methyl bromide (Ko, 1993). The model comparisons to the

experimental results constrain the reaction for the production of HBr by reaction (2) to have a branching ratio between one and two per-cent, taking into account the uncertainty in inorganic bromine ( $\approx \pm 15\%$ , Fish *et al.*, 1995). Alternately, in view of the kinetics evidence against a branching ratio of this magnitude, some other significant pathway may exist for the production of HBr in the mid-stratosphere or the HBr loss rate may be less than modeled. In any case, the effective sequestration of about 5% of total inorganic bromine as HBr implies about a 10% reduction in ODP compared to a model which assumes negligible HBr formation by reaction (2) (Ko 1993).

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I. G. Nolt, J. H. Park, and M. D. Vanek, NASA Langley, Hampton, VA.  
 P. A. R. Ade, M. J. Griffin, P. A. Hamilton, C. Lee, and A. G. Murray, Queen Mary and Westfield College, London, UK.  
 B. Carli, U. Cortesi, M. Epifani, F. Mencaraglia, P. Raspollini, and M. Ridolfi, IROE, Firenze, Italy.  
 F. Alboni, M. Carlotti and G. Lepri, University of Bologna, Italy.  
 K. Park, University of Oregon, Eugene, OR.

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