Detection of HBr and upper limit for HOBr: Bromine partitioning in the stratosphere

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Abstract

We determine mixing ratio profiles for HBr and upper limits for HOBr in the stratosphere with precisions up to 1.7 and 4.8 parts per trillion, respectively, using the combined data from 7 flights of our far-infrared spectrometer. The measurements suggest that in the range 22–34 km the average mixing ratio of HBr is 2.0 ± 0.8, and that the average mixing ratio of HOBr is less than 2.8 ppt. Our measurements of HBr are in reasonable agreement with a photochemical model which includes 0 or 2% production of HBr through the reaction of BrO with HO_2, but in strong disagreement with a model including 5 or 10% HBr production.

Introduction

Anthropogenic emission of methyl bromide and the halons has the potential to cause greater ozone losses than emissions of chlorofluorocarbons and hydrochlorofluorocarbons, in part because nearly 50% of the bromine released into the stratosphere is believed to exist in reactive forms, as compared to a few percent of the chlorine [*World Meteorological Organization (WMO)*, 1992]. Already, at a concentration of only 0.5% that of chlorine, catalytic cycles involving bromine account for 25% of the ozone loss in the Antarctic ozone hole and a few percent of the total ozone loss rate at mid-latitudes [*McElroy et al.*, 1992].

Accurate assessment of the ozone depletion potential (ODP) of brominated compounds requires an understanding of the partitioning of stratospheric bromine between reactive species (Br, BrO) and reservoir species (HBr, $BrNO_3$, and HOBr). Their low abundance has made measurement of bromine species difficult, which is unfortunate because there is still considerable uncertainty in the reaction rates used in photochemical models and comparison with observations would build confidence in model predictions.

For example, the reaction rate for $BrO + HO_2$ at 298 K was recently found to be 6 times faster than previously believed [*Poulet et al.*, 1992]. The effect of the faster reaction rate is to increase the abundance of HOBr at the expense of BrO, assuming that the only products are HOBr and O_2. Models which include some production of HBr through this reaction predict even less BrO, resulting in a smaller ODP for brominated compounds such as methyl bromide (CH_3Br) [*Poulet et al.*, 1992; *Ko et al.*, 1994]. While not observed at room temperature, the existence of an HBr channel is not ruled out at lower temperatures by the work of *Poulet et al.* [1992]. Recent observations of a lower than expected ClO/HCl ratio [*Stachnik et al.*, 1992; *Chance et al.*, 1995] could be explained by the existence of an analogous channel in the reaction of ClO with HO_2 or OH [*Tuomi and Bekki*, 1993; *McElroy and Salawitch*, 1989].

The measurements presented in this paper expand on earlier work [*Traub et al.*, 1992] in which we combined measurements from 3 balloon flights to produce an upper limit for HBr of 4 parts per trillion (ppt) at an altitude of 32 km. In the present work we combine data from 7 balloon flights to produce mixing ratio profiles of HBr and HOBr from 22–38 km.

Measurements

The FIRS-2 spectrometer and data reduction system are described in detail elsewhere [*Johnson et al.*, 1995]. We observe the stratosphere in thermal emission from a balloon platform, recording infrared spectra continuously during both day and night. The instrument scans the Earth's limb, making observations at 7 different elevation angles corresponding to tangent heights spaced by about 4 km in altitude. The spectrometer resolution is 0.008 cm^{-1}, apodized.

The launch dates and hours of data at float for the flights analyzed here are as follows: May 12, 1988, 16.6 hours; September 26, 1989, 23.1 hours; June 4, 1990, 28.1 hours (only the final 9 hours used here); May 29, 1992, 8.7 hours; September 29, 1992, 7.8 hours; March 23, 1993, 6.7 hours; and May 22, 1994, 22.0 hours. The 1988 flight was launched from Palestine, TX and the 1993 flight was launched from Daggett, CA; all other flights were launched from Ft. Sumner, NM. We bin the spectra by elevation angle, flight, and time of day to produce average limbscans for day and (or) night for each flight. For this analysis we formed 1 daytime average limbscan each for the May 1988, June 1990, May 1992, and September 1992 flights; and 2 daytime averages for the September 1989 and May 1994 flights (one for the first day and one for the second). We also formed 1 nighttime average each for the May 1988, September 1989, March 1993, and May 1994 flights. For a typical average limbscan each spectrum is the sum of 7 individual spectra, corresponding to 40 minutes of integration per elevation angle.

Spectroscopic parameters for the HBr lines used in this analysis are taken from the Smithsonian Astrophysical Observatory line database SAO92 [*Chance et al.*, 1994]. Line positions and strengths for HOBr were calculated at the Jet Propulsion Laboratory (E. A. Cohen, personal communication, 1995) using data from *Koga et al.* [1989] combined with unpublished measurements. Because the HOBr lines are very weak and unresolved in our spectra, we ignore the hyperfine splitting and use a default value of $0.06\,cm^{-1}atm^{-1}$ for the collisional broadening. The broadening preserves equivalent width for an unsaturated line, and so the choice of default value will not affect our results. Lines for both ^{79}Br and ^{81}Br are included.

We use the rotational lines near 99.9 and 116.4 cm^{-1} for HBr mixing ratio retrieval. Our average HBr sensitivity is 6 ppt for a single measurement (fitting a single line in a single averaged spectrum). The line strengths for HOBr are considerably weaker, but there are more lines in our spectra. We fit rotational lines of HOBr at 112.1, 116.3, 142.8, 143.5, 146.3, 147.7, 149.8, 155.3, 155.9, and 159.4 cm^{-1}, as well as the Q branch at 140.0 cm^{-1}. Our average sensitivity for HOBr is about 45 ppt per measurement of a single line or Q branch. For comparison, a photochemical model starting with 20 ppt of inorganic bromine and using reaction rates and photolysis cross sections recommended by *DeMore et al.* [1992] (including the faster rate for BrO + HO_2) predicts mixing ratios for HBr and HOBr of 0.2–0.4 and 1–6 ppt, respectively [*Ko et al.*, 1994]. Therefore the signal-to-noise ratio in an individual spectrum is roughly 0.05 for either species, and one does not expect spectral features of HBr or HOBr to be visible above the noise level in a single FIRS-2 spectrum. However, to the extent that the sensitivity is limited by random noise, we can average many measurements together to increase the sensitivity (as discussed below). While we carefully choose the fitting windows to avoid interfering lines of other molecules, there is always the possibility that uncatalogued lines are present which could bias the average towards high values. We reduce the risk of bias by using 2 or more spectral windows for each molecule and checking to see that the different windows give consistent results.

Analysis

We retrieve a mixing ratio profile for each average limbscan as follows. First, we select a small window centered on each spectral line used in the analysis. Next, mixing ratios are retrieved for each window by fitting a calculated spectrum to the observed spectrum as described in *Johnson et al.* [1995]. The mixing ratio for strong lines is retrieved in onion-peeling fashion, proceeding from the highest to the lowest tangent height and updating the mixing ratio profile as each spectrum is fitted. For the weak lines of HBr and HOBr the poor precision of each measurement makes it unlikely that such a procedure would converge. In this case, we do not update the profile until after all lines have been fit. The results for all lines are averaged together and compared to the initial profile, and the profile is modified if the difference is statistically significant. The errors in determining the mixing ratio at different altitudes are correlated, but we reduce this correlation by spacing the elevation angles such that for a uniformly mixed species, roughly 75% of the column density along the line of sight is in the atmospheric layer being fitted. Finally, the results from the different limbscans are averaged together to produce the final day and night profiles.

Before averaging together the results for individual windows we carefully check the estimated error for each fit. Our fitting procedure estimates the random error in each measurement from the variance of the residuals, the number of degrees of freedom, and the correlations between the parameters being fitted. Statistically one expects to underestimate the variance roughly half the time, and because of the small number of degrees of freedom the spread in the variance estimates can be quite large. In order to prevent a fit with an underestimated error from skewing the weighted average, we first compare the estimated variance to the noise level in nearby line-free windows in the spectrum. In cases where the residuals from the fit are less than the noise level the errors are adjusted accordingly.

Results and Discussion

We present the final HBr and HOBr mixing ratio profiles in Tables 1 and 2. All errors are 1σ, and include random errors as well as errors in pointing, atmospheric temperature determination, and intensity calibration. The random error dominates the estimated total error. Some of the mixing ratios are negative, which is not physically meaningful, but is certainly statistically meaningful. The weighted average mixing ratios in the range 22–34 km are 2.0 ± 0.8 and 0.6 ± 2.2 ppt for HBr and HOBr, respectively.

Averaging the mixing ratio profiles from many midlatitude balloon flights is equivalent to estimating a zonal mean profile, so our measurements can be compared to the results of 2-D models. We compare our average day and night profiles for HBr and HOBr to several different model calculations in Figures 1 and 2. The model profiles are labeled A, B, C, and D. Profile A was calculated using reaction rates and photolysis cross sections taken from the 1992 Jet Propulsion Laboratory (JPL) recommendation [*DeMore et al.*, 1992]; profile B uses the same reaction rates but includes a 2% yield of HBr from the reaction of BrO and HO_2; profile C includes a 5% yield of HBr; and profile D includes a 10% yield. Daytime and nighttime averages are shown. All model profiles were calculated using the Atmospheric and Environmental Research 2-D model (M. K. W. Ko, private communication, 1994), assuming

Table 1. HBr Mixing Ratio Profiles

Day		Night	
z, km	[HBr], ppt	z, km	[HBr], ppt
38.4	3.7 ± 6.5	38.4	-0.6 ± 8.2
33.3	3.2 ± 2.1	33.4	2.1 ± 2.6
29.5	2.7 ± 2.0	29.5	0.4 ± 2.6
25.7	3.0 ± 1.7	26.0	2.1 ± 2.8
21.9	-2.2 ± 2.7	22.8	2.6 ± 3.3

Table 2. HOBr Mixing Ratio Profiles

Day		Night	
z, km	[HOBr], ppt	z, km	[HOBr], ppt
38.4	13.4 ± 21.6	38.3	-3.0 ± 28.9
33.4	0.3 ± 6.4	33.3	-1.2 ± 8.2
29.4	0.1 ± 5.8	29.6	5.2 ± 7.5
25.8	0.5 ± 4.8	26.1	2.1 ± 7.2
21.9	-0.2 ± 6.1	22.9	-0.9 ± 7.0

19 ppt of total inorganic bromine. The profiles correspond to average conditions on May 15 at at a latitude of 38 degrees north (about 4 degrees north of Ft. Sumner). Results for 28 degrees north and for September are similar.

As shown in Figure 1, the measurements of HBr are in good agreement with profiles A and B. The data are not consistent with profiles C or D, indicating that the branching ratio for HBr is less than 5% and may be 0. This agrees with the work of *Mellouki et al.* [1994], who concluded that the HBr branching ratio is less than 0.01% under atmospheric conditions by measuring the rate of the reverse reaction, $O_3 + HBr$. Indeed, there seems to be little evidence for a large additional source of HBr, unlike the situation for HCl [*Stachnik et al.*, 1992; *Chance et al.*, 1995]. Simultaneous measurements of BrO and HBr would provide a more direct measurement of bromine partitioning by eliminating assumptions about the total bromine concentration. From Figure 2 it is clear that profiles A–D are all consistent with the HOBr data, but there is insufficient precision in the measurements to distinguish between them.

In recent laboratory work, *Hanson and Ravishankara* [1995] found that the hydrolysis of $BrONO_2$ on sulfuric acid solutions is extremely rapid, implying that a significant amount of the $BrONO_2$ in the stratosphere may be converted to HOBr at night by reacting on the surface of sulphate aerosols. Our measurements of HOBr are not consistent with a nighttime increase greater than 6 ppt at an altitude of 23 km.

Assuming that the errors are random, we can perform a more quantitative comparison of the models with the data by computing the χ^2 statistic. There are 10 degrees of freedom in the combined HBr data set (5 altitudes, and 2 times of day, with no free parameters). For model profile A, $\chi^2 = 9$, which indicates agreement at about the 53% confidence level (CL). Profile B is also in reasonable agreement with the data, with $\chi^2 = 8$ (CL = 64%). Profiles C and D, with $\chi^2 = 25$ and 67, respectively, are inconsistent with the data at a CL $> 99\%$.

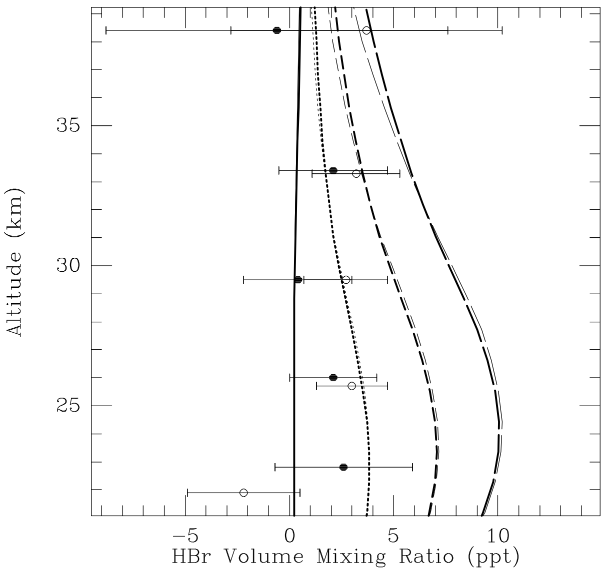

Figure 1. A comparison of the average daytime (open circles) and nighttime (solid circles) HBr mixing ratio profiles with calculated profiles A (solid), B (dotted), C (short dash), and D (long dash). Daytime average model profiles are indicated by the light lines, and nighttime averages by the heavy lines. The profile calculations are described in the text.

Conclusion

The HBr and HOBr measurements presented here are consistent with a model which assumes 19 ppt of total inorganic bromine and conventional chemistry. The data are also consistent with a model which includes 2% production of HBr through the reaction of BrO with HO_2, but are highly inconsistent with a 5 or 10% production of HBr.

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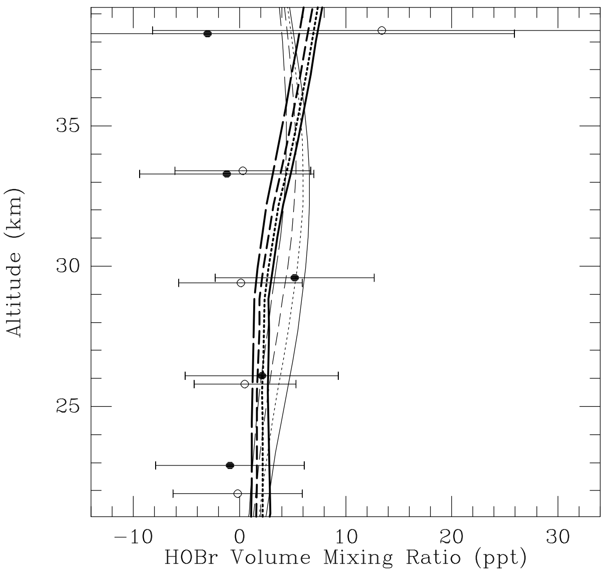

Figure 2. A comparison of the average daytime (open circles) and nighttime (solid circles) HOBr mixing ratio profiles with calculated profiles A (solid), B (dotted), C (short dash), and D (long dash). Daytime average model profiles are indicated by the light lines, and nighttime averages by the heavy lines. The profile calculations are described in the text.

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