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Search for HBr and bromine photochemistry on Venus

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Abstract

Search for the strongest HBr line at 2605.8/6.2 cm^{-1} using NASA IRTF and CSHELL spectrograph with resolving power of 4×10^4 resulted in an upper limit to the HBr mixing ratio of 1 ppb at 78 km. A simplified version of the bromine photochemistry is included into the photochemical model by Krasnopolsky (2012). Photolysis of HBr and its reactions with O and H deplete the HBr mixing ratio at 70-80 km relative to that below 60 km by a factor of ≈300. Reanalysis of the observational data with the calculated profile of HBr gives an upper limit of 20-70 ppb for HBr below 60 km and the aerosol optical depth of 0.7 at 70 km and 3.84 µm. The bromine chemistry may be effective on Venus even under the observed upper limit. However, if a Cl/Br ratio in the Venus atmosphere is similar to that in the Solar System, then HBr is ≈1 ppb in the lower atmosphere and the bromine chemistry is insignificant. Thermodynamic calculations based on the chemical kinetic model (Krasnopolsky 2013) predict HBr as a major bromine species in the lower atmosphere.

1. Introduction

The high temperature near the surface of Venus stimulates reactions between the rocks and atmospheric species that release HCl and HF, which looked unexpected and exotic when they were detected by Connes et al. (1967). No attempts have been made to search for HBr, and the only relevant result is an upper limit of 0.2 ppb to Br_2 near 15 km from the Venera 11 and 12 descent probes (Moroz et al. 1981). Search for HBr is the subject of this work.

2. Observations and analysis

We chose for our study the strongest line R2 of the fundamental band of HBr at 2605.8/6.2 cm^{-1}. Though the line is strong, it is weaker than the similar HCl and HF lines by factors of 8 and 36, respectively.

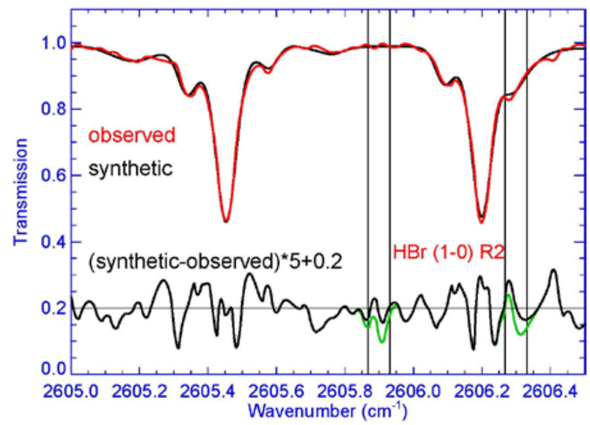

Fig. 1. Observed and synthetic spectra of Venus at the equator. Vertical lines show resolution elements at the expected positions of the Doppler-shifted HBr lines. The black line near the bottom shows a difference between the synthetic and observed spectra scaled by a factor of 5. The green line is for HBr = 10 ppb.

Venus was observed in July 2015 using NASA IRTF and a long-slit spectrograph CSHELL with resolving power of 4×10^4. We used our standard tools for observations and processing of the observed spectra. 101 spectra along the slit that crossed the bright crescent of Venus were analyzed and compared with best-fit synthetic spectra. A spectrum observed near the equator is shown in Fig. 1. The synthetic spectra were calculated in Fig. 1 for the best fit with HBr near zero and for HBr = 10 ppb, and the latter is close to the detection limit for an individual spectrum. Combinations of the HBr and CO_2 lines provide mixing ratios of HBr that refer to 78 km. Retrievals for all 101 spectra are shown in Fig. 2. The values scatter between -8 and 5 ppb with a mean value of -1.2 ppb and standard deviation of 2.5 ppb. According to the Gauss statistics, uncertainty of the mean of 101 values is smaller by a factor of 10 and equal to 0.25 ppb. Our observations result in an upper limit of 1 ppb for HBr at 78 km on Venus.

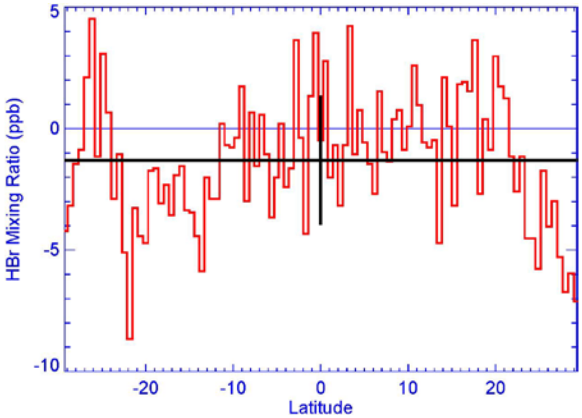

Fig. 2. HBr mixing ratio in the observed 101 spectra of Venus. The mean value and standard deviation are shown by black solid lines.

3. Possible HBr photochemistry

Quantitative assessment of the HBr chemistry on Venus is made by inclusion of ten major photochemical reactions of bromine (Table) into the photochemical model by Krasnopolsky (2012) and assuming HBr = 10 ppb below 60 km.

Table. Column rates (CR) of bromine reactions

#	Reaction	CR	CR (Cl)
1	$HBr + h\nu \rightarrow H + Br$	3.27+10	9.46+10
2	$HBr + O \rightarrow Br + OH$	1.15+10	1.60+9
3	$HBr + H \rightarrow Br + H_2$	1.30+10	2.31+9
4	$H + Br + M \rightarrow HBr + M$	1.47+10	-
5	$Br + HO_2 \rightarrow HBr + O_2$	4.12+10	6.71+10
6	$Br + O_3 \rightarrow BrO + O_2$	2.16+12	6.89+12
7	$BrO + O \rightarrow Br + O_2$	4.35+11	3.50+12
8	$BrO + NO \rightarrow Br + NO_2$	1.73+12	4.22+12
9	$Br + Br + M \rightarrow Br_2 + M$	1.04+14	1.64+13
10	$Br_2 + h\nu \rightarrow Br + Br$	1.04+14	3.18+13

3.27+10 = 3.27×10^{10} cm^{-2} s^{-1}. CR (Cl) is the column rate of the similar Cl reaction in the model by Krasnopolsky (2012)

Photolysis of HBr and its reactions with O and H strongly deplete the HBr mixing ratio above 65 km (Fig. 3). The fast photolysis of Br_2 and the reactions of BrO with O and NO convert these species to Br, which dominates above 67 km. The most significant effect of the bromine chemistry is in the production of H_2 (reaction 3), which exceeds that without Br by a factor of 5, and in the production of O_2, which is a third of that without Br.

Our upper limit of 1 ppb at 78 km is applicable to the uniform distribution of HBr. To constrain the HBr abundance below 60 km from our observation and the model, we use the Venus albedo of 0.028 at 3.66 μm (Krasnopolsky 2010). This low value is caused by the H_2SO_4 absorption, Single scattering approximation is reasonable for this black atmosphere in our observation at 3.84 μm. Assuming the aerosol scale height of 3 and 4 km above 70 km and a constant extinction coefficient at 60-70 km, the calculated upper limits to HBr below 60 km are 70 and 20 ppb, respectively, and $\tau \approx 0.7$ at 70 km, in accord with Cottini et al. (2015) and Fedorova et al. (2016). The bromine chemistry may be effective on Venus even under the observed upper limit. However, if a Cl/Br ratio in the Venus atmosphere is similar to that in the Solar System, then HBr ≈ 1 ppb in the lower atmosphere and the bromine chemistry is insignificant.

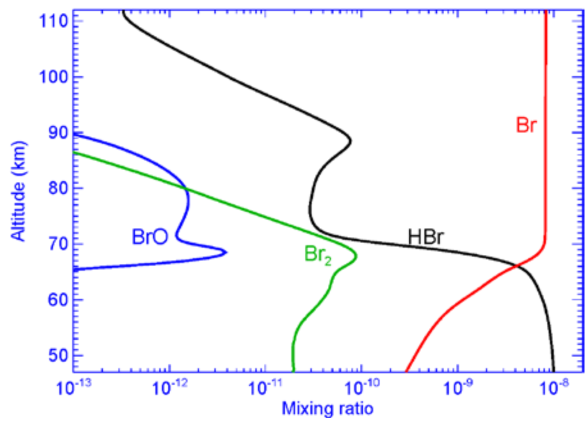

Fig. 3. Vertical profiles of bromine species in the photochemical model.

Acknowledgement

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