

The far infrared rotational spectrum of HOBr: line positions and intensities

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This paper is dedicated to Dr. Walter J. Lafferty, for his many contributions to science.

Abstract

The far infrared absorption spectrum of HOBr has been measured at high resolution between 100 and 400 cm^{-1} using high-resolution Fourier transform spectroscopy. It was possible to identify not only 1403 pure rotation lines within the vibrational ground state involving levels with rather high K_a quantum numbers (up to $K_a=9$) but also 457 pure rotation lines within the first excited vibrational state 3^1 up to $K_a=7$. The ground state lines, combined with 32 microwave transitions available in the literature, were used for a new determination of the rotational constants up to higher orders for both isotopomers HO^{79}Br and HO^{81}Br , by least squares fitting of the observed line positions using a Watson-type Hamiltonian for the calculation of rotational energy levels. In the same way the 3^1 rotational lines were fitted together with the few existing microwave transitions and the energy levels derived from the study of the ν_3 band (J. Orphal, Q. Kou, F. Kwabia Tchana, O. Pirali, and J.-M. Flaud, *J. Mol. Spectrosc.* 221 (2003), 239–243) leading to an improved set of Hamiltonian constants. Finally relative line intensities were measured and used for the determination of rotational corrections to the b -component of the permanent dipole moment. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

HOBr plays an important role in atmospheric chemistry [1–6]. It is formed in the stratosphere by the gas-phase reaction between the BrO and HO_2 radicals and by heterogeneous reactions of BrONO_2 with H_2O on Polar Stratospheric Cloud particles. In the stratosphere, HOBr is rapidly photolyzed by sunlight [7–9] releasing OH and Br radicals that destroy ozone in catalytic cycles [10]. In the troposphere, HOBr is formed by reactions including heterogeneous chemistry on sea salt aerosols, and—in addition to photolysis and gas-phase reactions—can be removed from the gaseous phase by dissolution in aqueous aerosol particles [11–15]. In the chemical cycles of

tropospheric bromine, HOBr is one of the most important intermediates [4,5,16].

However, atmospheric detection of HOBr is still difficult because of its rather low concentrations. Its sharp rotational Q -branches in the far-infrared region have been used to estimate an upper limit of 2.8 ppt for the HOBr mixing ratio in the stratosphere, using balloon-borne limb-sounding of atmospheric emission [17]. HOBr is also one of the target species of the SAFIRE-A remote-sensing experiment on the Geophysika M-55 high-altitude aircraft [18], and it is part of the potential scientific data products of future space-borne microwave limb-sounders [19]. With the increasing sensitivity of far-infrared instruments, the observation of atmospheric HOBr might become feasible in the future.

From the spectroscopic point of view, the electronic ground and excited states of HOBr have been characterized by several high-level ab-initio calculations [20–26], and the ground electronic state has been studied (together with DOBr) in the microwave region [27] as well as by high-resolution Fourier-transform infrared spectroscopy

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and rotational analysis of the fundamental bands ν_1 , ν_2 and ν_3 around 3615, 1163 and 620 cm^{-1} , respectively [28–30].

In this paper, we present the first high-resolution absorption measurements of the pure rotational spectrum of HOBr in the far infrared region between 100 and 400 cm^{-1} . A total of 1403 pure rotation lines within the ground state involving levels with rather high K_a quantum numbers (up to $K_a=9$) were observed and assigned. From these lines, together with 32 microwave transitions available in the literature [28], a set of new rotational and centrifugal distortion constants of the ground states was determined for both the HO⁷⁹Br and HO⁸¹Br isotopomers. Also a total of 457 rotation lines within the first excited vibrational 3¹ state were measured up to $K_a=7$. They were fitted together with the few existing microwave lines and the energy levels derived from the analysis of the ν_3 band [30] leading to an improved set of Hamiltonian constants. Finally measurements of individual line intensities for 585 lines were used to determine the rotational corrections to the b -component of the permanent transition moment.

2. Experimental

The experimental procedure has already been described in a previous paper [30]. To give only the most important facts: the far-infrared spectrum of HOBr was measured using a commercial Bruker IFS-120 HR Fourier-transform spectrometer, together with a White-type multi-pass absorption cell made of Pyrex glass, with gold-coated mirrors and equipped with polyethylene windows. The optical path length in the cell was adjusted to 400 cm (4 passes). The beamsplitter used was a 6 μm mylar foil, the broadband light source was a glowbar inside of the Bruker IFS-120 HR source chamber, and the detector was a He-cooled bolometer. The spectral resolution was 0.0032 cm^{-1}

(Full-Width at Half-Maximum FWHM), and the free spectral range was limited to 0–1128 cm^{-1} . The observed linewidth for unblended lines was about 0.005 cm^{-1} (FWHM).

HOBr was synthesized by flowing slowly gaseous bromine over dry yellow HgO powder, yielding gaseous Br₂O and significant amounts of HOBr by heterogeneous reactions with residual H₂O adsorbed on the cell's surfaces. The total pressure in the absorption cell was adjusted to 7 mbar, including Br₂O, HOBr, and residual Br₂. Spectra were recorded in blocks of 10 scans, each taking approximately 2 h. It was observed that the HOBr sample slowly decomposed inside the cell, reaching nearly zero absorption after 12 h. In order to minimize the effects of sample decomposition on the determination of relative line intensities, only the first block of data was used for the analysis described below.

Fig. 1 shows an overview of the recorded spectrum at high resolution. Note that, besides HOBr, there is absorption by residual H₂O inside the cell and the interferometer. In addition, weak absorptions due to the rotational spectrum of HOCl [31], probably resulting from an impurity in the chemical synthesis, were observed. Figs. 2, 3 and 4 show more details of the spectra. The signal/noise ratio is about 100 (root mean square, RMS), but significantly decreasing towards lower wavenumbers. Note that for the line intensity determinations, the spectrum was slightly apodized using the Norton-Beer 'medium' apodization function, to minimize the effects of the instrumental line shape (see Fig. 5). All line positions were determined using the Bruker OPUS software peakfinder routine, and were calibrated to absolute vacuum wavenumbers using the residual H₂O lines and the line positions of Ref. [32] recommended by the IUPAC [33]. The experimental uncertainty of the calibrated line positions is 0.00026 cm^{-1} (RMS deviation of 66 rotational lines of H₂O between 100–400 cm^{-1}).

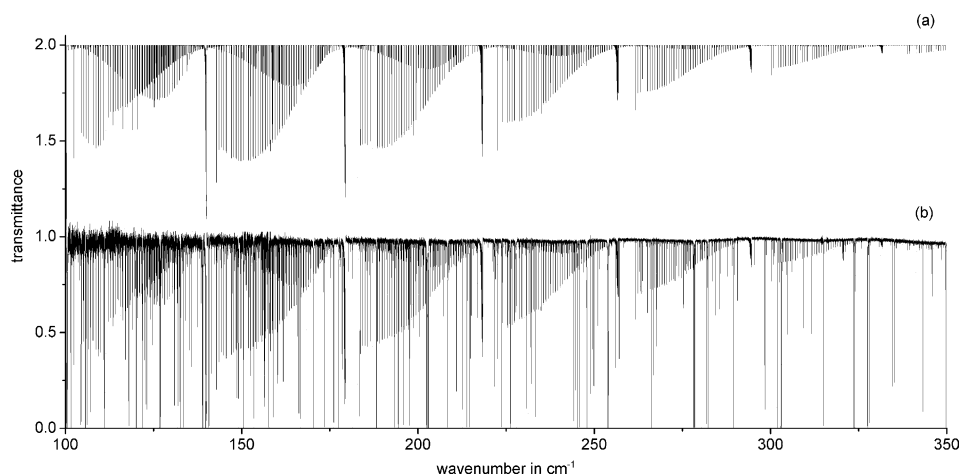


Fig. 1. Overview of the measured absorption spectrum of HOBr. The spectral resolution is 0.0032 cm^{-1} , the absorption path is 800 cm. One can see the distinct R-branches for different K_a values.

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