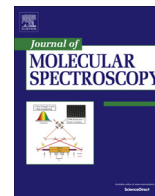




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New infrared spectroscopic database for bromine nitrate

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ABSTRACT

Fourier transform infrared measurements of bromine nitrate have been performed in the spectral region 675–1400 cm^{-1} at 0.014 cm^{-1} spectral resolution. Absorption cross sections were derived from 38 spectra covering the temperature range from 203 to 296 K and air pressure range from 0 to 190 mbar. For line-by-line analysis, further spectra were recorded at 0.00094 cm^{-1} spectral resolution at 223 and 293 K. The sample was synthesized from ClONO_2 and Br_2 . Band strengths of the bands ν_3 around 803 cm^{-1} and ν_2 around 1286 cm^{-1} were determined from three pure BrONO_2 measurements at different temperatures and pressures. Number densities in the absorption cell were derived from pressure measurements of the purified sample taking into account small amounts of impurities determined spectroscopically. Resulting band strengths are $S_{\nu_3} = 2.872(52) \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1} \text{ cm}^{-1}$ and $S_{\nu_2} = 3.63(15) \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1} \text{ cm}^{-1}$. Absorption cross sections of all measurements were scaled to these band strengths. Further data reduction was achieved with an interpolation scheme based on two-dimensional polynomials in $\ln(\text{pressure})$ and temperature. The database is well-suited for remote-sensing application and should reduce the atmospheric bromine nitrate error budget substantially.

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1. Introduction

There is about a factor 200 less inorganic bromine than chlorine in the stratosphere but bromine cycles have a 45 times greater ozone depletion potential [1]. While most of the chlorine is bound in ClONO_2 and HCl [2] most of the bromine is in active BrO during daytime. In contrast to ClONO_2 the analogous reservoir species BrONO_2 is almost completely photolyzed during daytime [3]. The reservoir species ClONO_2 and BrONO_2 , being chemically stable compounds when compared to the active species, are not directly involved in fast catalytic ozone depletion cycles. The measurement of stratospheric BrONO_2 is essential to determine the inorganic stratospheric bromine budget, gain insight to bromine partitioning in the stratosphere and validate photochemical models. Details on all atmospheric reactions of bromine compounds are given by Lary [4]. The current knowledge on the impact of bromine on ozone depletion is given in [5]. Bromine chemistry and BrONO_2 are also important for tropospheric ozone [6].

BrONO_2 has strong rovibrational bands in the thermal infrared. Since the total bromine load (and thus also the maximum BrONO_2 mixing ratio) of the stratosphere is only about 20 pptV [5] the infrared signatures in atmospheric spectra are very small. The weak features barely outside the noise and buried under stronger

lines have been detected in thermal limb emission spectra of the satellite instrument MIPAS/ENVISAT by Höpfner et al. [7] and the stratospheric balloon instrument MIPAS-B2 by Wetzell et al. [8], both using the ν_3 band with a strong Q branch around 803 cm^{-1} . The accuracy of the retrieved mixing ratio profiles was limited by the accuracy of the absorption cross sections [7] indicating the need for new laboratory measurements.

The first measurements of infrared absorption cross sections of BrONO_2 have been carried out by Burkholder et al. [9]. They made ambient temperature measurements of the ν_3 band with a stated band strength uncertainty of about 20%. Orphal et al. [10] measured relative absorption cross sections of the ν_3 band, the ν_2 band around 1286 cm^{-1} , and the ν_1 band around 1709 cm^{-1} . The band strength determined by Burkholder et al. was used to scale the absorption cross sections. HITRAN2012 [11] contains the scaled ν_3 data for 296 K determined by Orphal et al. For atmospheric retrieval the missing temperature dependence of the absorption cross sections was assumed to be a problem since it was expected that the Q branch intensity, being most relevant for analyzing atmospheric spectra, is strongly temperature dependent as in case of ClONO_2 . The temperature dependence was modeled with a Hamiltonian approach calculating rovibrational lines using the similarity to ClONO_2 [12]. The absorption cross sections of 296 K were scaled to obtain values for 218 K which were entered into HITRAN2012 [11]. These data were used in the BrONO_2 retrievals from MIPAS/ENVISAT by Höpfner et al. [7] mentioned above. In

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conclusion BrONO₂ laboratory spectroscopic measurements in the infrared are rather rare. There is only one determination of absolute absorption cross sections of BrONO₂ in the literature and the stated accuracy is rather low. No temperature dependence was ever measured. Improved spectroscopic data are needed to support atmospheric measurements.

The authors have already measured temperature and air pressure dependent absorption cross sections of the related ClONO₂ molecule [12]. Since ClONO₂ is a precursor of BrONO₂ and infrastructure and experience were available it was feasible to measure the even more challenging BrONO₂.

2. Experimental setup

All absorption spectra were recorded with the Bruker IFS 125HR interferometer located at DLR (German Aerospace Center) in Oberpfaffenhofen, Germany. Common measurement parameters are given in Table 1. Pressure measurements were carried out with thermostated MKS Type 127A/627A Baratron pressure transducers with an accuracy of 0.35%, as stated by the manufacturer. A coolable/heatable (190–350 K) 22 cm single pass absorption cell equipped with two window pairs, capable of quasi-simultaneous FIR (far infrared) + MIR (mid infrared) + UV (ultra violet) measurements was applied. This cell is mounted inside the evacuated sample compartment of the spectrometer and was built to measure bromine in the UV quasi-simultaneously with bromine nitrate in the MIR. The cell, together with the vacuum apparatus, can be moved from the outside by a screw mechanism to position either window pair in the beam path. The cell consists of a double-jacketed Duran glass body and two stainless steel flanges which were coated with PFA (perfluoroalkoxy-copolymer) by Impreglon, Germany. Cooling is achieved by flowing methanol from a bath cryostat through the glass cell double jacket and the flanges. Two glass tubes connect the cell to the outside of the Bruker interferometer allowing for gas flow. The cell can thus be filled from the outside without breaking the vacuum of the spectrometer. Seals are made from spring-loaded PTFE (polytetrafluorethylene). Thus only materials not susceptible to corrosive substances were in contact with the sample. Special care was taken during mechanical design to provide precise knowledge of window positions allowing accurate absorption path determination better than 0.1 cm. The temperature of the cell's walls was measured with 2 Pt100 sensors (class 1/10B). Another sensor was attached to one of the flanges. A LakeShore 218E temperature monitor instrument was used for temperature readout. High temperature homogeneity is achieved by operating the cell in vacuum, by special heat sinking of the windows to the flange, by minimizing the diameter of the windows, and by radiation shielding of the windows. A finite element thermal model of the windows was developed in the design phase. The temperature homogeneity was tested by measuring a N₂O

spectrum and analyzing the relative line intensities. The resulting average gas temperature differed from the cell body temperature by less than 0.1 K. Frequency calibration was achieved by separate N₂O measurements taken with the same field stop diameters as the measurements for ACS (absorption cross sections) and LBL (line-by-line). The reference line positions were taken from Maki and Wells [13]. The frequency precision from the standard deviation of the calibration factor at 1000 cm⁻¹ is 3 × 10⁻⁶ cm⁻¹ for LBL and 1.6 × 10⁻⁵ cm⁻¹ for ACS.

Synthesis and sample handling for spectroscopic measurements were carried out applying a Duran glass apparatus with several exits equipped with PTFE-sealed Normag stopcocks. Duran glass tubes, also with PTFE-sealed Normag stopcocks, were attached to the apparatus via Swagelok PTFE fittings and were used for trapping, evaporating, and storing samples at liquid nitrogen temperature. The apparatus was connected to the absorption cell inside the Fourier-transform spectrometer (FTS) by a short glass tube.

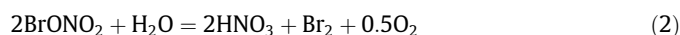
3. Sample synthesis

BrONO₂ was synthesized from ClONO₂ and Br₂ according to Orphal [14] and the reference (Schmeißer et al. [15]) cited in [14]:



ClONO₂ was synthesized from N₂O₅ + Cl₂O. A description is given in Ref. [12].

The synthesis of BrONO₂ required several iterations for optimization. About 1.3 mmol (52 mbar in 0.53 l) of ClONO₂ were condensed in a small trap with a few cm³ volume. 0.65 mmol Br₂ were added and the trap closed and agitated at 8 °C for 15 min. The small volume was needed to avoid complete evaporation of ClONO₂ since the reaction was expected to occur in the liquid phase. Br₂ disappeared completely due to the excess of ClONO₂. The reaction mixture was first cooled to 77 K, evacuated and then thermostated at -72.5 °C using an isopropyl-acetate slush. While the reaction vessel was connected to the vacuum apparatus the pressure rose due to evaporation of the more volatile BrCl and ClONO₂. At this temperature the vapor pressure of pure BrCl is about 20 mbar [16] and that of ClONO₂ 2.9 mbar [12]. The reaction vessel was closed and BrCl and excessive ClONO₂ were pumped off. Then the reaction vessel was opened again. This procedure was repeated until the pressure was ca. 0.5 mbar. The BrCl was thus mostly removed and a mixture of only BrONO₂ and small amounts of ClONO₂ and N₂O₅ remained. The sample was transferred into another tube at -48 °C. The vapor pressure of nearly pure BrONO₂ was 0.48 mbar at -44 °C which is somewhat less than 0.64 mbar reported by Spencer and Rowland [17]. UV measurements showed the absence of Br₂. BrONO₂ was found to be very stable in the absorption cell. The decomposition was 24% in 16 h at 223 K and 33% in 4.5 h at 293 K. The decomposition rate at 293 K was considerably slower (2 × 10⁻⁵ s⁻¹) compared to the value measured by Orlando and Tyndall [18] (10⁻³–10⁻² s⁻¹ at 320–340 K). While Orlando and Tyndall have indicated thermal decomposition to NO₂ and BrO in our case a contribution of hydrolysis with water from the walls of the cell forming HNO₃ was observed. At the beginning of the experiments the cell was not sufficiently pumped and a lot of HNO₃ was formed. UV Br₂ measurements indicated the correct stoichiometry ($-\Delta p_{\text{BrONO}_2} = 2 \times \Delta p_{\text{Br}_2}$) according to:



The amount of gaseous HNO₃ formed was too small, likely caused by wall adsorption. An example of a test spectrum of BrONO₂ at -40 °C is shown in Fig. 1. Beside the three strong rovibrational bands of BrONO₂ there is only minor absorption by HNO₃ (850–910, 1310–1350 cm⁻¹) and N₂O₅ (1230–1260 cm⁻¹). Three

Table 1

Common IR measurement parameters. ACS: absorption cross sections, LBL: line-by-line.

Source	Globar
Field stop diameter	2.5 mm for ACS 1.3 mm for LBL
Maximum optical path difference (MOPD)	36 cm for ACS 529 cm for LBL
Focal length of collimator	41.8 cm
Beamsplitter	Ge on KBr
Sample cell windows	AgCl
Absorption path	22.1(1) cm
Detector	HgCdTe (MCT), 40 K (achieved by pumping on liquid nitrogen)
Optical filter	Low pass 1400 cm ⁻¹

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