Journal of Quantitative Spectroscopy & Radiative Transfer 105 (2007) 264–302

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

A complete set of line parameters for CH_3Br in the 10-μm spectral region

D. Jacquemart[a,*], F. Kwabia Tchana[a], N. Lacome[a], I. Kleiner[b]

[a]*Laboratoire de Dynamique, Interactions et Réactivité, Université Pierre et Marie Curie-Paris6, CNRS, UMR 7075, Case courrier 49, Bât F 74, 4, place Jussieu, 75252 Paris Cedex 05, France*

[b]*Laboratoire Inter-Universitaire des Systèmes Atmosphériques, Universités Paris 12 et Paris 7, CNRS, UMR 7583, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France*

Received 15 September 2006; received in revised form 25 October 2006; accepted 29 October 2006

Abstract

Using FT spectra (Bruker IFS 120, unapodized FWHM resolution $\approx 0.001\,cm^{-1}$) of methyl bromide CH_3Br, absolute line positions and intensities, as well as self- and N_2-broadening coefficients have been measured for about 1200 lines, between 880 and $1050\,cm^{-1}$, in the ν_6 band of both $^{12}CH_3^{79}Br$ and $^{12}CH_3^{81}Br$ isotopologues. An absolute wavenumber calibration has been performed using the frequencies of the ν_2 band of NH_3. A multispectrum fitting procedure has been used to retrieve simultaneously the line parameters from six experimental spectra recorded at different pressures of CH_3Br and N_2. Average absolute accuracies of the measurements have been estimated to be equal to $\pm 0.0002\,cm^{-1}$ for line positions, to ±5% for line intensities, and to ±5–10% for broadening coefficients. A theoretical treatment of measured line positions permitted a prediction of positions and assignments for the whole 10-μm spectral region. Measured line intensities have been analyzed in order to predict the intensities for the whole ν_6 band. The J and K dependences of the self- and N_2-broadening coefficients have been observed and modeled. These measurements improve the precision of wavenumbers and line intensities previously obtained and lead us, for the first time, to a complete set of self- and N_2-broadening coefficients for which clear J and K dependences have been observed and modeled. A complete line list containing line positions, intensities, self- and N_2-broadening coefficients has then been generated for atmospheric purposes from 820 to $1120\,cm^{-1}$.

Keywords: Methyl bromide; Fourier transform spectroscopy; Infrared; Vibration–rotation; Line intensities; Broadening coefficients; Line list

1. Introduction

Methyl bromide (CH_3Br) is a trace gas with a tropospheric concentration of about 10 parts per trillion per volume [1] and a total atmospheric lifetime of 0.6–0.9 years [2]. CH_3Br has the highest tropospheric concentration among all long-lived organobromides, making it the primary source of bromine to the

*Corresponding author. Tel.: +33 1 44 27 36 82; fax: + 33 1 44 27 30 21.
E-mail address: jacquemart@spmol.jussieu.fr (D. Jacquemart).

0022-4073/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jqsrt.2006.10.006

stratosphere. Bromine radical in the stratosphere has been shown to contribute significantly to stratospheric ozone loss through coupled reactions with ClO, HO_2 and NO_2 radicals. Although the role of methyl bromide in the stratospheric ozone loss has been well documented, no spectroscopic data are available at the present time for methyl bromide in the atmospheric databases such as HITRAN [3] and GEISA [4]. Complete lists of spectroscopic line parameters are necessary to detect methyl bromide in atmospheric spectra and retrieve its concentrations in the atmosphere. Much work has been devoted to CH_3Br, almost all concerning line positions. An extensive review on this molecule was given by Graner [5] for works prior to 1981. References on more recent works can be found in Ref. [6].

The present paper follows a series of recent works devoted to the measurements of line positions and line intensities for the ν_6 band around 10-μm [6], and for the interacting ν_2 and ν_5 bands around 7-μm [7,8]. This work is dedicated to an extensive study of the line parameters of the ν_6 band of CH_3Br. A multispectrum fitting procedure [10] has been used to adjust simultaneously six experimental spectra recorded at different pressures of CH_3Br and N_2. Line positions, intensities, as well as self- and N_2-broadening coefficients have been measured for about 1200 transitions between 880 and 1050 cm^{-1} in the ν_6 bands of $^{12}CH_3^{79}Br$ and $^{12}CH_3^{81}Br$. The average accuracy of the line parameters obtained in this work has been estimated to be $\pm 0.0002\,cm^{-1}$ for line positions, ±5% for line intensities, and ±5–10% for broadening coefficients.

Measured line positions have been analyzed using the set of codes written by Tarrago [9] for C_{3v} symmetric-top molecules. Line intensities have been fitted using two different ways. The first one, in which all interactions have been neglected, led to the vibrational transition dipole moment for the ν_6 band as well as Herman–Wallis factors that describe the J and K dependences of the transition dipole moment. In the second one, the eigenvectors (determined previously from the calculation of line positions) have been used to model the dipole moment matrix with the set of codes written by Tarrago [9]. Both line intensity calculations are similar since the ν_6 band is isolated, and the ν_6 level presents weak l-type interactions. The extensive measurements for self- and N_2-broadening coefficients have been obtained for large sets of values of J and K, for which clear J and K dependences have been observed. Empirical polynomial expansions have been used to model the rotational dependence of the experimental widths. Such a study has, to our knowledge, never been done for CH_3Br.

The experimental procedure and the methodology of the analysis will be first presented, respectively, in Sections 2 and 3. Then, measurements and calculations of positions, intensities, and broadening coefficients will be presented in Section 4 together with comparisons of line positions and intensities obtained in Ref. [6]. The generation of a complete line list for the whole 10-μm spectral region will be described in Appendix.

2. Experimental procedure

The rapid scan Bruker IFS 120 HR interferometer of the Laboratoire de Dynamique Interactions, et Réactivités (LADIR in Paris) was used to record six spectra (see Figs. 1 and 2). The unapodized spectral resolution used for each spectrum was about $1.1 \times 10^{-3}\,cm^{-1}$ (FWHM), corresponding to a maximal optical path difference of 450 cm. The interferometer was equipped with a Ge/KBr beamsplitter, a MCT photovoltaic detector, a Globar source, and an optical filter covering the 800–1100 cm^{-1} spectral region. Because of the spectral density of the ν_6 bands of $CH_3^{79}Br$ and $CH_3^{81}Br$ (see Figs. 1 and 2) and of the strong values of the self-broadening coefficients, a line by line study could not have been possible with too high pressures of CH_3Br. The choice of the pressure for each spectrum has been done in order to have sufficient information on all the line parameters when analyzing a transition with the multispectrum fitting procedure. The experimental conditions of the six recorded spectra are summarized in Table 1. For all spectra the whole optical path was under vacuum. For five of them a multipass cell of 1 m base length was used for a total absorption path of 415 ± 1 cm. One spectrum was recorded using a 30 cm cell. These cells were equipped with KCl windows. The commercial gas sample, furnished by Fluka, with a stated purity of 99.50% in natural abundances, was used without further purification. Additional spectrum at low pressure of NH_3 has also been recorded with the multipass cell in order to measure line positions belonging to the ν_2 band of NH_3 and to be able to calibrate the wavenumber scale of the CH_3Br spectra.

The temperature of the gas in the cell was recorded with four platinum probes at different places in the cell. The uncertainty on the temperature measurements has been estimated to be ±1 K. The pressure of the gas was measured with a capacitance MKS Baratron manometer with an accuracy estimated to be ±1%. Every scan