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Absolute line intensities in methyl bromide: The 7-μm region

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Abstract

This work deals, for the first time, with the modeling of absolute line intensities in the fundamental v_2 and v_5 bands of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ at 7 μm. For that, four unapodized absorption spectra of CH_3Br (natural abundance, 99% purity, $P \times L = 0.082 - 0.165$ atm × cm, room temperature) were measured in the range 1260–1560 cm^{-1}, at a resolution of 0.002 cm^{-1} using a Fourier transform spectrometer Bruker IFS 120 HR. For both isotopomers, 313 line intensities were analyzed within the dyad system required to account properly for the strong Coriolis coupling between v_2 and v_5. The intensity fit of experimental data led to the determination of the dipole moment derivatives $d_2 = \partial\mu/\partial q_2$ and $d_5 = \partial\mu/\partial q_5$ relative to the v_2 and v_5 bands, as well as the first-order Herman–Wallis correction in K to d_5. The observed line intensities are fitted to 3.0% (3.3%) for v_2 at 1309.9 cm^{-1} and 2.6% (3.0%) for v_5 at 1442.9 cm^{-1}, respectively for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$. The values derived for the vibrational band strengths of v_2 and v_5 are 55.7(0.6) and 39.2(0.3) cm^{-2} atm^{-1} at 296 K, respectively. The corresponding assignments and line positions of the dyad from previous work [F. Kwabia Tchana, I. Kleiner, J. Orphal, N. Lacome, O. Bouba, J. Mol. Spectrosc. 228 (2004) 441] are combined with the present intensity study to provide an improved CH_3Br database for atmospheric applications.

Keywords: Methyl bromide; Infrared spectra; Dyad; Line intensities; Dipole moment

1. Introduction

Methyl bromide (CH_3Br) is an atmospheric trace gas of interest because of its contribution to stratospheric ozone depletion. Methyl bromide has both natural and anthropogenic origins. Its known sources include natural production from oceans [1] and biomass burning [2]. Methyl bromide is also industrially produced for use as an agricultural fumigant. With a tropospheric mixing ratio of 9–11 pptv in the Northern Hemisphere (with an increase of about 0.15 pptv per year) and about 8 pptv in the Southern Hemisphere, it is believed to be the single largest contributor of stratospheric bromide [3]. However, until present, no attempts have been made to determine atmospheric concentrations of CH_3Br using infrared spectroscopy. For this, accurate modeling of the infrared spectrum of CH_3Br, including line intensities, is indispensable.

There have been various investigations in the past on the infrared and microwave spectra of methyl bromide. An extensive review of the spectroscopy of this molecule was given by Graner [4]. The most recent infrared work on this molecule including line intensities was published in 2002 by Brunetaud et al. [5]. In that work, high-resolution spectra of the v_6 band of CH_3Br between 820 and 1120 cm^{-1} were recorded and line positions and intensities were predicted for atmospheric remote-sensing applications.

Although the line positions in the 7-μm region (containing the two interacting fundamentals v_2 and v_5) have been

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Table 1
Experimental conditions used to record the FTIR spectra of CH_3Br[a]

Spectrum No.	Path (cm)	Pressure[b] (mbar)	Temperature (K)	Resolution (cm^{-1})
Bruker IFS 120 HR at LADIR, Paris, Bandpass: 1150–1550 cm^{-1}				
1.	415 (1)	0.1991 (8)	297 (1)	0.002
2.	415 (1)	0.2778 (11)	296 (1)	0.002
3.	415 (1)	0.3415 (14)	298 (1)	0.002
4.	415 (1)	0.4028 (16)	296 (1)	0.002
5.[c]	27.0 (0.1)	4.693 (5)	296 (1)	0.004

Note. The resolution is equal to 0.9/(maximum optical path difference) and 1 atm = 1013 mbar.
[a] The numbers in parentheses represent the absolute uncertainty in the units of the last digit quoted.
[b] The absolute uncertainty is estimated to be 0.4% of the measured pressure.
[c] Recorded using the Bruker IFS 120 HR located at LPPM, Orsay (see [6] for more details).

reinvestigated recently at high spectral resolution [6], little is known about the line intensities in this region. The integrated band intensities of these two overlapping bands were measured in the past by different groups [7–10], using band separation techniques applied to low-resolution spectra. However, no line by line study of absolute intensities at 7 μm of CH_3Br is presently available. At the present time, no spectroscopic information (including line positions, intensities, and linewidths) on CH_3Br is available from either the HITRAN [11] or the GEISA [12] databases.

The purpose of the present study was to measure the absolute infrared intensities for the two fundamentals ν_2 and ν_5 of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$, and to provide a CH_3Br compilation at 7 μm for databases. The intensity parameters were derived by analyzing a set of individual line intensities accurately measured using a Fourier transform spectrometer Bruker IFS 120 HR. Modeling of the intensities was achieved within a two-interacting-band system, i.e., ν_2 and ν_5, such a model being required to account properly for the strong Coriolis coupling between ν_2 and ν_5. The formulation of the model was developed in [13] for a vibrational system including up to five interacting bands. The intensity fit of experimental data led to the determination of the dipole moment derivatives $d_2 = \partial\mu/\partial q_2$ and $d_5 = \partial\mu/\partial q_5$ relative to the ν_2 and ν_5 bands, as well as the first-order Herman-Wallis correction in K to d_5. A new evaluation of the individual band strengths S_2 and S_5 is made and compared with previous determinations [7–9].

The following sections present, respectively, the experimental details, the theoretical treatment leading to line intensity data, the procedure used for extracting the individual band strengths S_2 and S_5, and comparisons with previous works. From the resulting values of the dipole moment derivatives, a global line-by-line prediction is now available for atmospheric applications. For applications of our database to atmospheric remote sensing and retrieval of methyl bromide concentrations, we plan also to investigate line broadening in this region. That work is in progress.

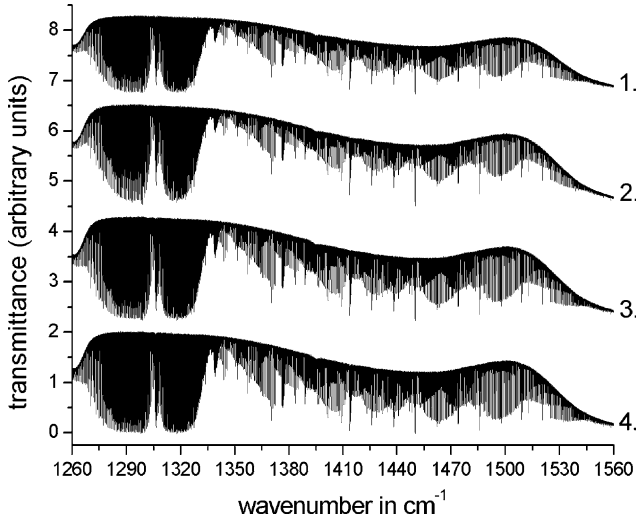

Fig. 1. Unapodized absorption spectra of CH_3Br between 1260 and 1560 cm^{-1}, recorded at a resolution of 0.002 cm^{-1} using a Bruker IFS 120 HR located at LADIR (Paris, France), with the experimental conditions reported in Table 1.

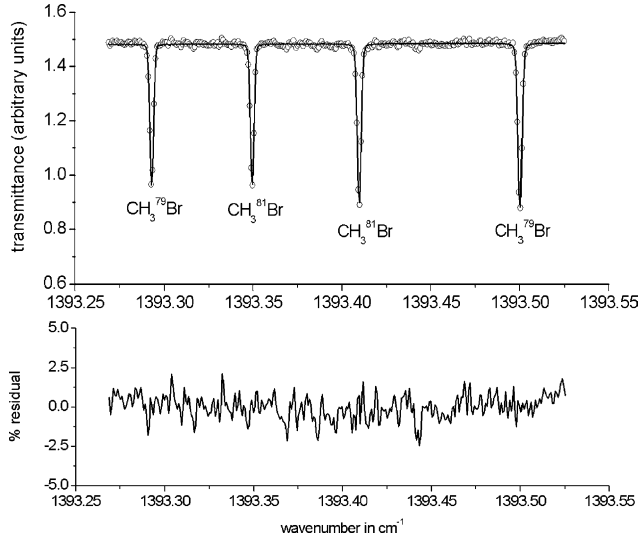

Fig. 2. Line-by-line retrieval of positions and intensities using non-linear least squares fitting technique at 1393 cm^{-1}. The differences are minimized by adjusting the assumed positions and intensities of lines in the synthetic spectrum. The methyl bromide gas pressure is 0.4028 ± 0.0016 mbar at 296 ± 1 K, the optical path 415 ± 1 cm, and the resolution is 0.002 cm^{-1}. Upper panel: observed (open circles) and synthetic (solid line) spectra overlaid. Lower panel: differences between the two spectra in percent.