Temperature dependence of N_2- and O_2-broadening coefficients in the v_4 band of $^{13}CH_4$

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ABSTRACT

Using a tunable diode laser spectrometer and an home made cooling cell, the N_2- and O_2-broadening coefficients of $^{13}CH_4$ were measured at room and low temperatures in the v_4 band near 1300 cm^{-1}. Fifteen transitions were studied for the $^{13}CH_4$ diluted in the nitrogen at room temperature and 11 of them were also studied at 273.0 K, 248.0 K, 223.0 K, 198.0 K and 173.0 K. Twenty-four lines were considered at room temperature for the gas-mixture $^{13}CH_4 + O_2$ and 10 of them were analyzed at low temperatures (273.0 K, 223.0 K and 173.0 K). The measurements at low temperatures allowed the determination of the temperature dependence parameter of the collisional broadening coefficients. The line parameters were obtained by fitting, to the experimental profile, the Voigt lineshape and the Rautian and Sobel'man model taking into account the collisional narrowing. In addition, air-broadening coefficients were calculated in the v_4 band of $^{13}CH_4$ for 10 transitions studied jointly for the mixtures $^{13}CH_4 + N_2$ and $^{13}CH_4 + O_2$. We compare, in this paper, the collisional broadening coefficients determined at room temperature with previous studies on the v_3 and v_4 bands of $^{13}CH_4$. The results are also confronted with N_2- and O_2-broadening coefficients determined in the v_4 band of $^{12}CH_4$. The air-broadening coefficients, based on a simple atmospheric composition, are compared with HITRAN values.

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1. Introduction

Methane is a gas present in the Earth atmosphere. Its concentration is on the increase for the last century and reaches today a mean value of 1.75 ppbv [1]. The determination of the line parameters is necessary to know precisely the methane concentration in our atmosphere and to rigorously analyze the atmospheric spectra. The isotopologue $^{13}CH_4$, which constitutes 1% of natural methane, contributes to a significant absorption in many regions of the infrared atmospheric spectra. Since the lines of the $^{13}CH_4$ isotope are often observed in atmospheric spectra, it is essential to know precisely the N_2- and O_2-collisional half-widths for the different conditions of the Earth atmosphere.

A lot of works have been realized on the v_4 band of $^{12}CH_4$ to study the intensity, broadening and shift parameters. Few investigations were dedicated to the study of spectroscopic parameters of the isotopic form $^{13}CH_4$ and only a few at low temperature. If we focus on the collisional broadening coefficients, we note that several works [2–7,?] have been devoted to the $^{13}CH_4$ form diluted in $^{13}CH_4$, He, H_2, N_2, O_2 and air. To our knowledge, only Devi and co-workers examined the half-widths of this isotope broadened by N_2, O_2 and air. Indeed in 1983, Devi et al. [2] measured, with a tunable diode

laser spectrometer, 11 transitions in the v_3 and $v_2 + v_4$ bands of $^{13}CH_4$ at room temperature. They used a Lorentz profile to determine self- and nitrogen-broadening coefficients. Two years later, Devi and her collaborators [3] measured in the same vibrational bands air- and nitrogen-collisional half-widths of 23 lines using Lorentz profile. In 1988, the same team reiterates their measurements on the v_4 band of $^{13}CH_4$ [4]. They used, this time, a Fourier transform spectrometer to record the spectra. They determined air-broadened Lorentz half-widths and pressure induced line shifts of 180 transitions and they compared their results with previous values obtained for identical transitions in the v_4 band of $^{12}CH_4$. They conclude that the $^{13}CH_4$ air-broadened half-widths are 5% smaller than the corresponding $^{12}CH_4$ half-widths and that the pressure shifts for $^{13}CH_4$ lines are 5–15% larger than those obtained for $^{12}CH_4$ lines. Finally, in 1991, Devi et al. [5] measured air-, N_2-, O_2-broadening coefficients and pressure induced line shifts in the v_3 band of $^{13}CH_4$. They studied 75 transitions at room temperature with a Fourier transform spectrometer (0.01 cm^{-1} resolution). Moreover, Fox et al. [6] measured, in 1985, H_2-broadened widths of $^{13}CH_4$ in the $3v_3$ overtone at 9030–9120 cm^{-1}. Margolis [7] studied experimentally the H_2- and He-broadening coefficients and collisional shifts of 266 lines in the v_4 band of $^{13}CH_4$. More recently, Gabard [8] calculated helium broadened line parameters in the same vibrational band.

In this work, we present the measurements of N_2- and O_2-broadening coefficients at room and low temperatures in the v_4

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band of $^{13}CH_4$. The temperature dependence parameters of the N_2- and O_2-broadening coefficients of $^{13}CH_4$ are also determined for 11 and 10 lines, respectively. Furthermore, we report the air-broadening coefficients of 10 lines at room temperature, determined from the results of N_2- and O_2-broadening coefficients measured in this work.

2. Experimental details

The measurements are realized with a tunable diode laser spectrometer with a high resolution of 5×10^{-4} cm^{-1}. The data acquisition system, enabling the record of 100 spectra in 8 s, confers a signal to noise ratio better than 1000. This experimental setup, described more in details in a previous paper [9], allows the study of individual lines. It means that the lines are measured independently of each other and we thus avoid systematic errors.

Two laser diodes were used to sweep the spectral region ranging from 1246 to 1364 cm^{-1}. A multipass White-type cell, with an optical path length of 4.17 m, was employed to perform the measurements at room temperature. In addition, an home made cooling cell was placed in the optical path in order to achieve the low temperature measurements. This cooling system, represented in Fig. 1, and more precisely described in the paper of Lerot et al. [10], is composed of two flasks. The small one (the absorption cell) contains the gaseous sample and is inserted in a large one. The external cell assures a primary vacuum to isolate thermally the internal cell. The cooling system is realized by a dry nitrogen flow, circulating around the absorption cell. A wire of copper allows to warm up the cell to regulate precisely the temperature. This absorption cell, with an optical path length of 40.43 cm, can be cooled down until 77 K with a stability of 0.1 K.

The $^{13}CH_4$ was supplied by "Sigma–Aldrich" with a state purity of 99% and the nitrogen and oxygen were provided by "Air Liquide" with a state purity of 99.999% and 99%, respectively. Except for two less intense lines in the R-branch (R12 A11–A21 and R13 A11–A21), the partial pressures of $^{13}CH_4$ were lower than 0.3 mbar for the measurements at room temperature and lower than 1.5 mbar

for those at low temperature, while the partial pressures of N_2 and O_2 were ranging from 20 to 90 mbar. All the pressures were measured with two MKS Baratron gauges with full scale readings of 1.2 and 120 mbar.

For each line under study, at each temperature, a set of 8 spectra was recorded. The first four spectra were the $^{13}CH_4$ line at a constant pressure, broadened by four increasing pressures of perturber. Secondly, a saturated line of pure methane was recorded to give the 100% of absorption. Then the Doppler line was acquired. This line, with a low pressure of pure methane, which represents an apparent Doppler profile, is used to determine the apparatus function. After that, the record of the diode emission profile with the cell evacuated was made, representing the 0% of absorption. Finally, the fringes of the confocal étalon were acquired and get a relative calibration scale. An example of these spectra is illustrated in Fig. 2 for the R10 A11–A21 line of $^{13}CH_4$ perturbed by oxygen at room temperature.

3. Data reduction

The Beer–Lambert law gives the absorbance ($\alpha(v)$) at wavenumber (v), from the initial intensity of the source transmitted through the absorption cell evacuated ($I_0(v)$) and from the intensity transmitted through the absorption cell filled with the gas sample ($I_t(v)$):

$$\alpha(v) = -\ln\left(\frac{I_t(v)}{I_0(v)}\right) \tag{1}$$

The determination of the experimental half-width of a line was realized by fitting a theoretical profile on the experimental absorbance. We used two different theoretical lineshapes: the Voigt profile [11,12] and the Rautian model [13]. The Voigt profile results from the convolution between a gaussian and a lorentzian, representing the Doppler and the collisional broadenings, and is used by the majority of the spectroscopists. On the three adjustable parameters of this profile, only two were adjusted by the computer: the intensity (S in cm^{-2}) and the collisional half-width at
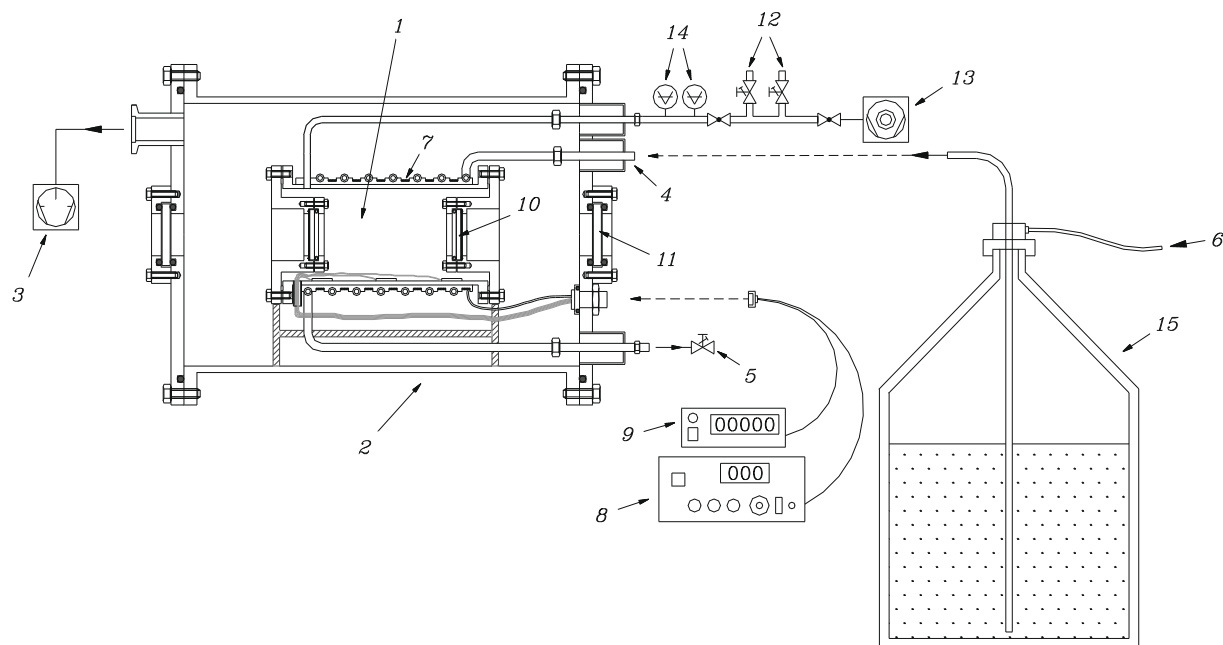

Fig. 1. Schematic view of the cooling system: (1) absorption cell; (2) vacuum flask; (3) rotary vane pump; (4) cold gaseous nitrogen inlet; (5) cold gaseous nitrogen flow controller; (6) dry nitrogen flow; (7) copper wire; (8) temperature controller; (9) digital thermometer; (10) ZnSe window; (11) BaF$_2$ window; (12) gas inlet; (13) turbomolecular pump; (14) pressure gauges; and (15) Dewar liquid nitrogen.