

## CO<sub>2</sub>-broadening coefficients in the $\nu_4 + \nu_5$ band of acetylene

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### Abstract

The CO<sub>2</sub>-broadening coefficients of 24 *P*- and *R*-branch transitions in the  $\nu_4 + \nu_5$  band of acetylene were measured at room temperature using a diode-laser spectrometer. These lines with *J* values up to 26, were located in the spectral range 1270 to 1400 cm<sup>-1</sup>. The collisional broadening coefficients were retrieved by fitting the experimental profiles to the Voigt, Rautian, and Galatry lineshape models. Two experimental values for the narrowing coefficient were determined from the spectra and compared with the theoretical narrowing coefficient. The calculations of these broadenings were also performed in the frame of a semiclassical formalism involving a simple intermolecular potential with an adjustable parameter. The theoretical results are in good agreement with the experimental results and reproduce well the *J* dependence of the broadening coefficients.

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### 1. Introduction

Acetylene is a minor constituent of several planetary atmospheres such as Earth [1], Jupiter [2], Saturn [3], Mars [4], and Titan [5] and has been the subject of several high resolution spectroscopic studies, especially on collisional broadening. We have previously determined N<sub>2</sub>-, O<sub>2</sub>-, H<sub>2</sub>-, He-, Ar-, Kr-, Xe-, and self-broadening coefficients in the  $\nu_5$  band of C<sub>2</sub>H<sub>2</sub> [6–17]. Other measurements were carried out for transitions in the same band as well as in other bands with broadening gases N<sub>2</sub> [18–20], O<sub>2</sub> [18], H<sub>2</sub> [18,20], He [18], Ne [18], Ar [18,19,21–23], Kr [18], Xe [18], and C<sub>2</sub>H<sub>2</sub> [18,19,24–26]. To our knowledge, no CO<sub>2</sub>-broadening coefficients of C<sub>2</sub>H<sub>2</sub> have been yet reported. However, these spectroscopic results are important for

studies of minor atmospheric constituents of Mars and Venus, where carbon dioxide predominates.

In this work, we have measured CO<sub>2</sub>-broadening coefficients of <sup>12</sup>C<sub>2</sub>H<sub>2</sub> at room temperature for 24 lines belonging to the  $\nu_4 + \nu_5$  band in the spectral range 1275–1394 cm<sup>-1</sup> using a diode-laser spectrometer [27].

We have also performed calculations of the broadening coefficients using the semiclassical formalism of Robert and Bonamy [28]. The intermolecular potential used in our calculations involves a simple anisotropic contribution in addition to the main electrostatic quadrupole–quadrupole interaction [17]. Finally, the theoretical results of broadening coefficients are compared with the experimental results.

### 2. Experimental details

The spectra of acetylene in mixture with carbon dioxide recorded for broadening measurements were performed with an improved tunable diode-laser spectrometer

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(TDL) Laser Analytics LS3 operating with lead salt IR diode-lasers, and described in a previous publication from our group [27]. The spectra result from an average of 100 scans in order to increase the signal to noise ratio. The relative wavenumber calibration was obtained by introducing in the laser beam a confocal étalon with a free spectral range of  $0.007958 \text{ cm}^{-1}$ . This confocal étalon with  $0.25 \text{ m}$  between mirrors was used in passive mode. The étalon fringe pattern allowed us to correct the slightly nonlinear tuning of the diode-laser with a constant step of the spectra and to check the laser mode quality.

Acetylene in natural abundance with a stated purity of 99.6% and carbon dioxide with a stated purity of 99.99% were supplied by *Air Liquide*. In order to reduce the pressure of  $\text{C}_2\text{H}_2$  in the gas mixtures, different optical path lengths were chosen (between  $4.17$  and  $24.17 \text{ m}$ ) in a White-type cell with  $1 \text{ m}$  between mirrors and with KBr windows. The partial pressure of  $\text{C}_2\text{H}_2$  in the gas mixtures was always chosen to be very small (pressures ranging from  $0.005$  to  $0.200 \text{ mbar}$ ). Nevertheless, the  $\text{C}_2\text{H}_2$  pressure was considered for all lines, and corrections were made to take into account the weak self-broadening contribution evaluated from the results given in [17] in the determination of the broadening coefficients. For each line, we recorded four spectra with a different pressure of  $\text{CO}_2$ , ranging from  $11$  to  $100 \text{ mbar}$ . The pressures of acetylene and carbon dioxide were measured with a relative uncertainty of  $0.5\%$ , using two MKS Baratron gauges with a full scale reading of  $1$  and  $100 \text{ mbar}$ . The sample temperature was measured by an electronic temperature probe fixed on the cell wall giving measurements with an accuracy of  $0.1 \text{ K}$ . All data were recorded at the room temperature i.e.,  $24.7 \pm 1.0 \text{ }^\circ\text{C}$ . Before recording the spectra we waited about  $15 \text{ min}$  for homogeneity of the  $\text{C}_2\text{H}_2 + \text{CO}_2$  gas mixture.

For each line, the following recording sequence was carried out: (a) a spectrum of the empty cell which represents the laser emission profile; (b) record the line at very low gas

pressure ( $\leq 0.004 \text{ mbar}$ ) and small absorption, which yields the Doppler profile convolved with the instrumental function (the ‘observed’ Doppler profile); (c) record the étalon fringes pattern with the empty absorption cell; (d) the spectra of the broadening lines at four different pressures of  $\text{CO}_2$ ; (e) the  $0\%$  transmission level. An example of the spectra obtained for the R(11) transition of  $\text{C}_2\text{H}_2$  at  $1356.8555 \text{ cm}^{-1}$  is shown in Fig. 1.

### 3. Data reduction

The measured absorbance  $\alpha(\nu)$  at wavenumber  $\nu$  of a homogeneous gas sample is determined for each spectrum using the Beer–Lambert’s law as

$$\alpha(\nu) = -\ln\left(\frac{I_t(\nu)}{I_0(\nu)}\right), \quad (1)$$

where  $I_0(\nu)$  and  $I_t(\nu)$  are transmitted intensities with the cell under vacuum and filled with the gas sample, respectively. Line parameters are obtained by fitting a theoretical line-shape to the measured absorbance. We first used the Voigt profile giving the line intensity parameter  $S$  and the collisional half-width  $\gamma_c$ . This profile [29,30] is defined by

$$\alpha_V(x, y) = A \frac{y}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{y^2 + (x-t)^2} dt = A \text{Re}[W(x, y)] \quad (2)$$

with

$$W(x, y) = \frac{i}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{x + iy - t} dt, \quad (3)$$

where

$$A = \frac{S\sqrt{\ln 2}}{\gamma_D\sqrt{\pi}}; \quad y = \sqrt{\ln 2} \frac{\gamma_c}{\gamma_D}; \quad x = \sqrt{\ln 2} \frac{\nu - \nu_0}{\gamma_D}. \quad (4)$$

Here  $S = S_0 p_1$ , with  $S_0$  (in  $\text{cm}^{-2} \text{ atm}^{-1}$ ) the line intensity;  $\nu_0$  (in  $\text{cm}^{-1}$ ) is the line center wavenumber (the pressure

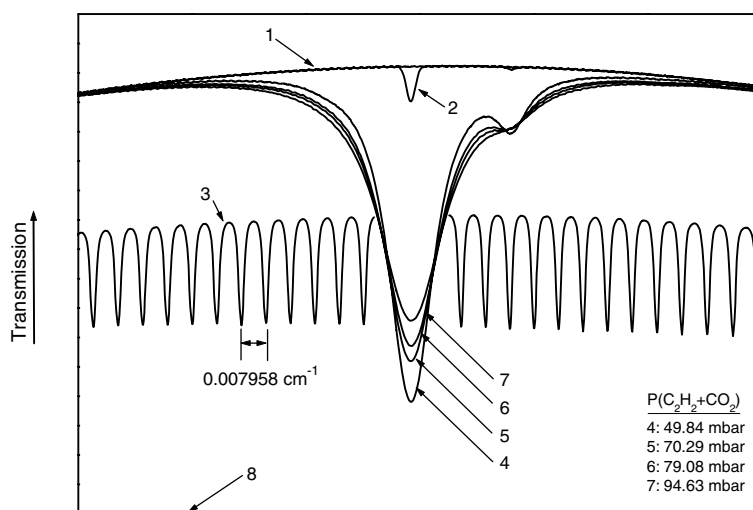


Fig. 1. Example of the spectra recorded for the R(11) line at  $1356.8555 \text{ cm}^{-1}$  in the  $\nu_4 + \nu_5$  band of  $\text{C}_2\text{H}_2$ . (1) Diode-laser emission profile recorded without absorption; (2) low-pressure ( $0.0012 \text{ mbar}$ ) line of  $\text{C}_2\text{H}_2$  (apparent Doppler line); (3) confocal étalon fringes; (4–7)  $\text{CO}_2$ -broadened line at different total pressures and a partial  $\text{C}_2\text{H}_2$  pressure of  $0.1630 \text{ mbar}$ ; (8)  $0\%$  transmission level.

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