



# O<sub>2</sub>-broadening coefficients of acetylene lines in the $\nu_4 + \nu_5$ band at room temperature



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## ABSTRACT

Room temperature O<sub>2</sub>-broadening coefficients were measured for 16 transitions, from P(23) to R(16), of the  $\nu_4 + \nu_5$  band of acetylene near 7.5  $\mu\text{m}$ . Absorption spectra of these lines were recorded at room temperature and various pressures, from 20.00 mbar to 66.21 mbar using a tunable diode laser spectrometer. The broadening coefficients were obtained by fitting the Voigt profile as well as the Rautian, the Galatry and the quadratic Speed Dependent Voigt models on the experimental spectra. The results were then compared with some previous studies realized for other bands of acetylene.

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## 1. Introduction

Acetylene is a minor component of our atmosphere [1] as well as in the atmospheres of Mars [2], Jupiter [3], Titan [4], Uranus [5,6] and Neptune [7]. In the Earth atmosphere, it has been suggested that by 2030 the concentration of C<sub>2</sub>H<sub>2</sub> (considered as a pollutant) would reach 150% of its value in the 1990s due to increased use of automobiles worldwide [8]. Retrieval of C<sub>2</sub>H<sub>2</sub> concentrations in these atmospheres from remote sensing requires precise knowledge of spectroscopic data of C<sub>2</sub>H<sub>2</sub>. These data are line position, integrated line intensity, line broadening and shifting coefficients.

Broadening coefficients of C<sub>2</sub>H<sub>2</sub> lines in the strong fundamental band  $\nu_5$ , in presence of various collision partners (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, He, Ar, Kr, Xe and C<sub>2</sub>H<sub>2</sub>) were previously determined at room and low temperatures [9–19]. Similar studies were investigated for the  $\nu_1 + \nu_3$  [20–25],  $\nu_1 + 3\nu_3$  [26–30],  $\nu_1 + \nu_5$  [31] and  $\nu_2$  [32] bands. Unlike other combination bands in near infrared spectral region, the  $\nu_4 + \nu_5$  band, located around 7.5  $\mu\text{m}$ , is fairly strong [33] and easily reachable by inexpensive tunable semiconductor laser diodes. Ro-vibrational transitions in this band are separated enough to be identified for the determination of individual spectroscopic parameters and they are therefore interesting for testing

theoretical approaches. The strengths and self-broadening coefficients of the transitions of this band were measured at room temperature [34,35]. Other studies were performed to obtain N<sub>2</sub>-, Ar-, He-, CO<sub>2</sub>-, and Xe-broadening coefficients at various temperatures [36–41]. To the best of our knowledge, no O<sub>2</sub>-broadening coefficients of C<sub>2</sub>H<sub>2</sub> in the  $\nu_4 + \nu_5$  band have been reported yet.

In this work, absorption spectra of sixteen transitions belonging to the  $\nu_4 + \nu_5$  band of <sup>12</sup>C<sub>2</sub>H<sub>2</sub> diluted in O<sub>2</sub> have been measured at room temperature for different pressures (ranging from 20.00 mbar to 66.21 mbar) using a tunable diode laser spectrometer. These transitions with *J* values varying from 0 to 23 are located from 1275 to 1370 cm<sup>-1</sup>. The collisional broadening coefficients of these lines have been determined using the Voigt, the Rautian, the Galatry and the quadratic Speed Dependent Voigt profiles. The obtained results are then compared with data of some previous studies realized for other bands of acetylene.

This paper is organized as follows: Section 2 describes the measurements. The used line-shape models are presented in Section 3 while the obtained results are presented and discussed in Section 4. Conclusion and future studies are subjects of Section 5.

## 2. Experimental details

The measurements have been performed using a high resolution diode laser spectrometer working on the infrared spectral region. Details of the experimental set-up can be found in previous publications from our group [42,43]. A confocal étalon with a free

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spectral range of  $0.007958 \text{ cm}^{-1}$  was used to determine the relative wavenumber scales of the spectra. In order to increase the signal-to-noise ratio, each recorded spectrum results from an average of 100 scans.

The samples of acetylene and oxygen were provided by *Air Liquide* with stated purities of 99.6% and 99.995%, respectively. The gas mixtures were contained in an absorption cell with an optical path length of 4.17 m. All measurements were realized at room temperature ( $297.0 \pm 1.0 \text{ K}$ ). The broadening spectra of each studied transition were recorded at four different pressures of oxygen ranging from 20.00 to 66.21 mbar. The partial pressure of the active gas was chosen depending on each transition and its values ranged from 0.01 to 0.16 mbar. Corrections were made to take into account the small contributions due to self-broadening determined from the measurements of Lepère et al. [35].

For each studied transition, eight consecutive spectra were recorded: the broadened lines at four different pressures of the perturbing gas; the spectrum of the empty cell which represents the laser emission profile; the line at a very low pressure of pure  $\text{C}_2\text{H}_2$  allowing to determine the instrumental line-shape function; the pure  $\text{C}_2\text{H}_2$  saturated line which represents the 0% transmission level and the étalon fringe pattern used for the relative calibration in wavenumber. Example for the set of recorded spectra for the P(23) transition of  $\text{C}_2\text{H}_2$  at  $1275.512169 \text{ cm}^{-1}$  is shown in Fig. 1.

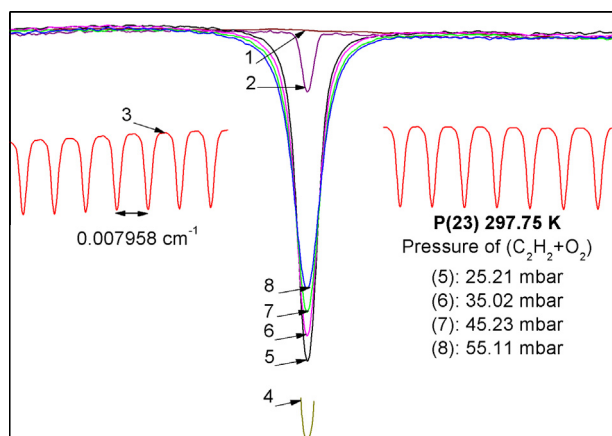
### 3. Line-shape profiles and data analysis

The experimental absorbance  $\alpha(\sigma)$  can be obtained for each recorded transition using the Beer–Lambert law as

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

where  $I_0(\sigma)$  and  $I_t(\sigma)$  are respectively intensities of the radiation source before and after transmittance through the gas sample at wavenumber  $\sigma$  ( $\text{cm}^{-1}$ ). By fitting a theoretical line-shape to the measured absorbance, the line parameters can be retrieved.

To achieve an accurate modelling of the experimental spectrum, different physical effects such as the Doppler broadening, collisional broadening, confinement narrowing and speed dependence effects must be considered. The Voigt profile [44,45] (VP) is the most widely-used line profile to model absorption spectra for the determination of spectroscopic parameters. This profile is a



**Fig. 1.** Example of spectra recorded for the P(23) line in the  $\nu_4 + \nu_5$  band of  $\text{C}_2\text{H}_2$  at room temperature: (1) the diode laser emission profile; (2) the spectrum of the line recorded at very low pressure of pure  $\text{C}_2\text{H}_2$  (0.0046 mbar); (3) the confocal étalon fringes pattern used for the relative calibration in wavenumber; (4) the saturated line giving the 0% transmission level; (5–8) the broadened lines recorded at different pressures of  $\text{O}_2$ .

convolution of a Gauss function (Doppler effect) and a Lorentz function (collisional effect). It can be expressed as

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

The  $W(x, y)$  function and parameters  $x, y$  and  $A$  are defined by following equations

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

$$A = \frac{S\sqrt{\ln 2}}{\Gamma_D \sqrt{\pi}}; y\sqrt{\ln 2} \frac{\Gamma}{\Gamma_D}; x = \sqrt{\ln 2} \frac{\sigma - \sigma_0 - \Delta}{\Gamma_D} \quad (4)$$

Here  $S$  is the integrated line intensity,  $\sigma_0$  (in  $\text{cm}^{-1}$ ) is the zero pressure line wavenumber,  $\Gamma_D$  (in  $\text{cm}^{-1}$ ) is the total collisional half-width at half maximum of the gas mixture,  $\Delta$  (in  $\text{cm}^{-1}$ ) is the collisional line shift and  $\Gamma$  is the theoretical Doppler half-width calculated by the following equation

$$\Gamma_D = 3.581163 \times 10^{-7} \sigma_0 \sqrt{\frac{T}{M}} \quad (5)$$

where  $T$  is the temperature in Kelvin and  $M$  is the absorber molecular mass in atomic mass unit.

The Voigt profile is only an approximation because the confinement narrowing effect which arises from velocity-changing collisions, also known as the Dicke effect [46], is neglected in this profile. Here, we use two more accurate models developed by Rautian and Sobel'man [47] and Galatry [48] taking this effect into account. The model of Rautian and Sobel'man (RP) is also called the hard collision model because it considers that the velocity memory of the absorber is lost after each collision. This profile can be described as

$$\alpha_R(A, x, y, z) = A \text{Re} \left[ \frac{W(x, y+z)}{1 - \sqrt{\pi} z W(x, y+z)} \right], \quad (6)$$

where the parameters  $A, x$  and  $y$  have the same definitions as in Eq. (4) and

$$z = \sqrt{\ln 2} \frac{B}{\Gamma_D}, \quad (7)$$

with  $B$  (in  $\text{cm}^{-1}$ ) representing the collisional narrowing due to the molecular confinement. In contrast to the RP, the Galatry model (GP) assumes that the velocity of the absorber does not significantly modify after each collision, so-called the soft collision model. It can be defined by Eq. (8) with the same definitions of parameters as for the RP.

$$\alpha_G(A, x, y, z) = \frac{A}{\sqrt{\pi}} \text{Re} \left\{ \int_{-\infty}^{+\infty} \exp \left[ -(ix+y)t + \frac{1}{2z^2} (1-zt - e^{-zt}) \right] dt \right\}, \quad (8)$$

The  $\beta_0$  collisional narrowing coefficient,  $\beta_0 = B/P$  with  $P$  being the pressure of perturber, can be compared to the dynamical friction parameter  $\beta_{\text{Diff}}$  (in  $\text{cm}^{-1} \text{ atm}^{-1}$ ), given in Ref. [49] and defined as

$$\beta_{\text{Diff}} = \frac{k_B T}{2\pi c M D}, \quad (9)$$

where  $k_B$  is the Boltzmann constant,  $c$  (in m/s) is the speed of light and  $D$  (in  $\text{cm}^2 \text{ s}^{-1}$ ) is the mass diffusion coefficient for the studied gas mixture which can be calculated through Lennard–Jones potential parameters [49], for instance.

The last profile used in this work is the Speed Dependent Voigt profile [50] which generalizes the Voigt profile by including the speed dependences of the collisional width and shift. The quadratic

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