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Diode-laser spectroscopy: Pressure dependence of N_2-broadening coefficients of lines in the $\nu_4 + \nu_5$ band of C_2H_2

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ABSTRACT

In this work, we have measured the N_2-broadening coefficients of 12 absorption lines in the $\nu_4 + \nu_5$ band of acetylene at room temperature, using a tunable diode-laser spectrometer. For each line under study, we have recorded spectra at 4–16 pressures of nitrogen ranging from 4.03 to 179.5 mbar. The line profiles were individually fitted, at each pressure, with different line shape models including fine effects as Dicke narrowing or/and speed dependence effect. From these fits, we have obtained the collisional half-widths at each pressure and then determined accurately the N_2-broadening coefficients of 12 lines. After that, we have studied the pressure dependence of the collisional broadening and narrowing coefficients following the considered line profile model. Finally, our results are compared with the previous studies realized in various absorption bands.

1. Introduction

Acetylene is a minor constituent of our atmosphere [1] as well as in the atmospheres of Saturn, Jupiter [2] and Titan [3]. The measurements of self and foreign-gas broadening coefficients provide important information for the analysis of atmospheric spectra and on intermolecular potentials via theoretical calculations. To obtain such line parameters as precise as possible, it is essential to fit the experimental profile with a theoretical line shape taking into account the different physical effects affecting the broadening of line.

In this work, we have measured N_2-broadening coefficients of $^{12}C_2H_2$ at room temperature for 12 lines belonging to the R-branch of the $\nu_4 + \nu_5$ band in the spectral range 1275–1394 cm^{-1} at a high-resolution using a diode-laser spectrometer. For each line under study, we have recorded spectra at 4–16 pressures of nitrogen ranging between 4.03 and 179.5 mbar. We retrieved the collisional line widths fitting the experimental profiles by the Voigt, Rautian, Galatry lineshape models and for the high pressures (>100 mbar) by a model taking into account simultaneously the Dicke narrowing and the speed dependence effect. The large range of pressures allowed an accurate collisional broadening coefficient determination. We also studied the dependence of collisional broadening as a function of pressure to determine the best experimental conditions and the most suited theoretical line shape model. The collisional broadening coefficients derived from our measurements are compared with values available in the literature [4–8].

Podolske et al. [4] have reported a line strength study in the $\nu_4 + \nu_5$ band and, they have measured collisional broadenings for 3 lines of C_2H_2 perturbed by N_2 and H_2 for $\nu_4 + \nu_5$ band. Devi et al. [5] have measured the N_2- and air-broadening coefficients for 29 lines in the same band. Later, Bouanich et al. [6] and Lambot et al. [7] have realized respectively theoretical and experimental studies, for several lines in the ν_5 band of C_2H_2 perturbed by N_2 and O_2. The more recent study, reported by Pine [8] in 1993, was devoted to the measurement of the line mixing and the self, N_2-, Ar-broadenings and line mixing were measured in the $\nu_1 + \nu_5$ band.

In this work, we have also studied the pressure dependence of the collisional narrowing coefficients following each theoretical line shape model. These experimental results have been compared with the calculated values using the theory of diffusion.

2. Experimental details

The spectra of C_2H_2–N_2 mixtures were recorded with an improved Laser Analytics (LS3 model) tunable diode-laser spectrometer previously detailed in Ref. [9]. The spectra resulted from an average of 100 scans in order to increase the signal-to-noise ratio. The relative calibration was obtained by introducing in the laser beam a confocal étalon with a free spectral range of 0.007958 cm^{-1}. Nitrogen was supplied by *Air Liquide company* with a purity of 99.9%, while acetylene was provided by *Air Liquide company* with a purity of 99.6%. The gas mixtures were contained in a White-type cell with one meter-distance between mirrors and

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with KBr windows. The pressures of C_2H_2 in the absorption cell were always chosen to be small (ranging from 0.0067 to 0.4463 mbar). Nevertheless, the C_2H_2 pressure was considered for all lines, and corrections were made to take into account the small contributions due to self-broadening were determined from the measurements of Lepère et al. [10]. The pressures of pure C_2H_2 and $C_2H_2 + N_2$ mixture were measured using three MKS Baratron gauges with full scale readings of 1.2, 120 and 1200 mbar. All data were recorded at the room temperature (i.e., 24.5 ± 1.5 °C). To obtain a good homogeneity in the mixtures, we waited 15 min before each spectrum record.

An example of the spectra obtained for the R(11) line of C_2H_2 at 1356.8555 cm^{-1} [11] is shown in Fig. 1. For each line under study, we have recorded the following consecutive spectra: (1) laser emission profile through the empty cell, (2) the record of the line at very low gas pressure of pure C_2H_2 and very small absorption, allowing the determination of the instrumental function, (3–6) the N_2-broadened spectra at four different nitrogen pressures, (7) the record of the étalon fringe pattern allowing relative calibration in wavenumber, (8) the pure C_2H_2 saturated line which represents the 0% transmission level.

3. Data reduction

The experimental absorbance $\alpha(\nu)$ can be deduced for each perturber pressure using the Beer–Lambert's law as

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

where $I_t(\nu)$ and $I_0(\nu)$ are respectively the transmitted through the gas sample and incident intensities at wavenumber ν (cm^{-1}). The line parameters were obtained by fitting a theoretical lineshape to the measured absorbance. First, we used the Voigt profile [12] which has three adjustable parameters. This profile is simply the convolution between a Gauss function (Doppler effect) and a Lorentz function (collisional effect), assuming that both effects are independent. It can be defined as [13]

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

with

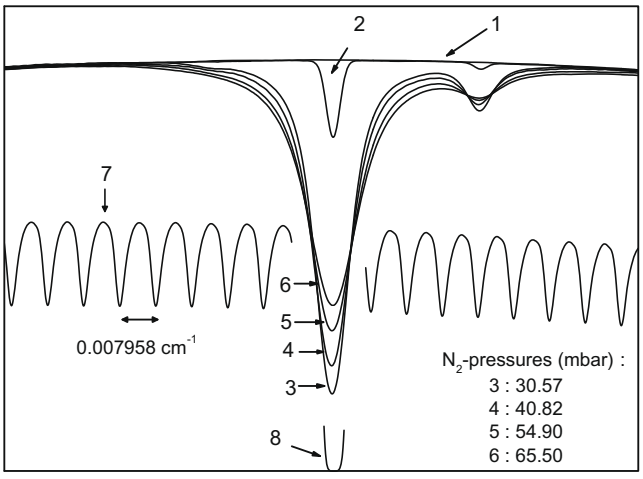

Fig. 1. Example of spectra recorded for the R(11) line at 1356.8555 cm^{-1} in the $\nu_4 + \nu_5$ band of C_2H_2 perturbed by N_2. (1) The diode-laser emission profile, (2) the spectrum of the line at very low pressure of pure C_2H_2 and very small absorption, (3–6) the broadened line recorded at different pressures of N_2, (7) the confocal étalon fringe pattern used for the relation calibration in wavenumber, (8) the saturated line giving the 0% transmission level.

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

and

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

Here $S = S_0\,p_1$, with S_0 (in $cm^{-2}\,atm^{-1}$) the line intensity and p_1 (in atm) the absorber pressure; ν_0 (in cm^{-1}) is the position of the line center (the eventual pressure shifts are very weak at such pressure and are not considered in this study); γ_D (in cm^{-1}) is the theoretical Doppler half-width that we calculate; γ_c (in cm^{-1}) is the collisional half-width and is equal to $\gamma_0\,p_2 + \gamma_{self}\,p_1$ where γ_0 (in $cm^{-1}\,atm^{-1}$) is the collisional broadening coefficient of C_2H_2 diluted in N_2, γ_{self} (in $cm^{-1}\,atm^{-1}$) is the self-broadening coefficient, p_1 and p_2 (in atm) are the partial pressures of the absorbing molecule and the perturber, respectively.

In reality, Doppler and collisional effects are not independent and intermolecular collisions perturb Doppler effect. The mean translation motion of the active molecules is reduced and the free streaming motion of the molecules becomes diffuse. This is well known as the Dicke effect [14]. We also fit the experimental profiles the Rautian and Sobel'man [15] and Galatry [16] models taking into account the Dicke effect and provide an additional parameter β_c which represents the collisional narrowing effect due to the molecular confinement.

The Rautian and Sobel'man model is also called hard collision model because it assumes that the velocity of the active molecule after the collision is independent of its velocity before the collision. This model is best suited when the perturber mass is larger than the mass of the active molecule. This profile may be described as [15]:

$$\alpha_R(A,x,y,z) = A\;Re\left[\frac{W(x,y+z)}{1-\sqrt{\pi}zW(x,y+z)}\right] \tag{5}$$

where the parameters A, x and y are the same as defined in Eq. (4) and

$$z = \sqrt{\ln 2}\,\frac{\beta_c}{\gamma_D} \tag{6}$$

with β_c (in cm^{-1}) representing the average effect of collisions on Doppler broadening. Here, $\beta_c = \beta_0\,p_2$ where β_0 (in $cm^{-1}\,atm^{-1}$) is the collisional narrowing coefficient.

The Galatry model is also called soft collision model because it assumes that the duration of each collision is short and does not modify significantly the velocity of the active molecule. This second model is best suited when the active molecule mass is larger than the perturber one. It can be defined by [16]:

$$\alpha_G(A,x,y,z) = \frac{A}{\sqrt{\pi}}Re\left[\int_{-\infty}^{+\infty}\exp\left(-ixt-yt-\frac{zt-1+e^{-zt}}{2z^2}\right)dt\right] \tag{7}$$

with the same definition of the parameters.

The collisional narrowing coefficient β_0 may be compared to the dynamical friction parameter β^0_{diff} (in $cm^{-1}\,atm^{-1}$) of the Brownian motion, expressed as [17]:

$$\beta^0_{diff} = \frac{k_B T}{2\pi c m D}, \tag{8}$$

where k_B is the Boltzmann constant, T (in K) is the temperature, c (in m/s) is the light velocity, m (in a.m.u.) is the absorber molecular mass and D (in $cm^{-2}\,s^{-1}$) is the mass diffusion coefficient for the $C_2H_2 + N_2$ system, calculated following [17].

At low pressures (below 100 mbar), the collisional widths were several times smaller than the Doppler widths and we have considered the Voigt profile as well as the Rautian and the Galatry models.