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Self- and foreign-broadening and shift coefficients for C_2H_2 lines at 1.54 μm

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Abstract. In this article we present experimental data for line parameters measurements of several transition lines of overtone bands of C_2H_2 at 1540 nm. The measurements were done with a spectrometer based on a semiconductor diode laser and a direct absorption spectroscopy scheme. Broadening and shift coefficients have been measured for the pure gas or in mixtures with N_2, O_2 and CO_2 as perturbing gas.

PACS. 33.70.-w Intensities and shapes of molecular spectral lines and bands – 33.70.Jg Line and band widths, shapes, and shifts

1 Introduction

Acetylene (C_2H_2) is a four-atoms, linear light molecule with a rotationally well resolved spectra. It is symmetric, without hindered degrees of freedom. For this reason it has been a test case for different theoretical molecular models and has been extensively studied in the past years. A large number of spectroscopic data contribute to well characterize this molecule: thousands of rovibrational transitions have been analysed and assigned between 600 cm^{-1} up to 20 000 cm^{-1} and beyond. Complete sets of vibrational and rotational constants have been determined for the different vibrational bands of several isotopic species [1]. The vibrational spectral features of acetylene have been used as a test for anharmonic models, such as the cluster model [2]. Particularly for the region around 1.5 μm detailed investigations were carried on in the last years [3,4], which calibrate the frequency of the recorded lines with respect to the second overtone rovibrational of CO, and assign new bands in this region. In the recent years C_2H_2 is also suited as a frequency reference standard in the near IR [5–7]. Different techniques have been adopted for investigate visible and infrared spectra, as Fourier Transform (FT) interferometry, photo-acoustic spectroscopy, diode laser spectroscopy, often along with high sensitivity frequency modulation detection schemes [8–21]. Several studies were addressed to the measurements of pressure broadening and shift for ν_5 [10–14], $\nu_1+\nu_5$ [15], $\nu_4+\nu_5$ [16,17] and $\nu_1+3\nu_3$ bands [18–21].

Semiconductor diode lasers received in the last decade an increasing interest as spectroscopical sources, due to the relatively narrow bandwidth and to the possibility of being continuously tuned over intervals of several tens of GHz, which make them particularly suited for spectroscopical investigation, specially for lineshape measurements [8,9,12–14,16–18,21]. In reference [6] several line of the $\nu_1+\nu_3$ band of $^{13}C_2H_2$ were investigated by saturation spectroscopy, using an extended cavity laser diode and a fiber amplifier.

From a practical point of view acetylene is one of the most abundant species produced during hydrocarbons combustion, and monitoring of its concentration during a combustion process is of great help in order to characterising it. There has been a considerable body of experimental work aimed at characterising combustion systems. Most of these measurements have utilised laser diagnostics such as Laser Induced Fluorescence (LIF), Raman spectroscopy, Resonance Enhanced Multiphoton Ionization (REMPI) or CARS (Coherent Anti-stokes Raman Spectroscopy) and Degenerate Four Wave Mixing (DFWM). The application of diode lasers to sensing of combustion-generated pollutant emissions began shortly after the developments in semiconductor diode laser technology [22]. Diode lasers found also applications to *in situ* measurements of combustion gases [23]. Recently, advances in room-temperature, near IR and visible diode laser sources are enabling a new generation of combustion sensors based on laser absorption spectroscopy. Absorption-based sensors have the highest sensitivity and selectivity when a spectrally narrow source is used to probe a spectrally narrow feature since it is possible to distinguish from background absorption, scattering, or extinction effects. Tunable Diode Laser Absorption Spectroscopy (TDLAS) has been demonstrated to be a valuable probe for species concentrations and temperature even when the local soot level

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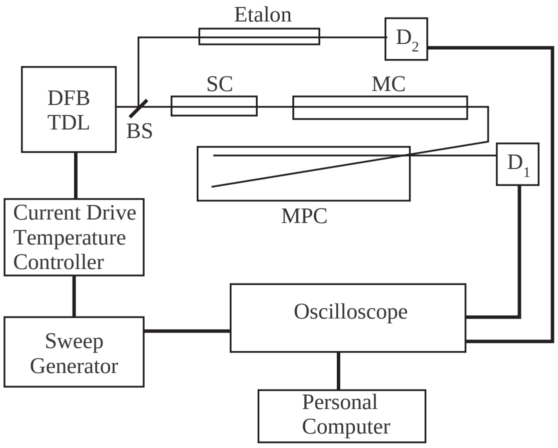

Fig. 1. Experimental setup. DFB TDL: distributed feedback tunable diode laser; BS: beam splitter; SC: short cell; MC: medium cell; MPC: multi pass cell; D_x: detector.

is high [24,25]. Nevertheless, *in situ* measurements of combustion species with room temperature diode lasers are only beginning to appear in the literature.

For these reason the spectral region around 1540 nm has a particular interest in order to realize a sensor for trace detection of C_2H_2, since the overtone bands occurring in this region are the strongest ones for which it is possible to have, to date, room temperature operating diode lasers.

In this article we present line parameters measurements of several transition lines belonging to different overtone bands of C_2H_2 around 1540 nm. We measured the pressure induced broadening and shift of lineshape for self and foreign perturbations (where N_2, O_2 and CO_2 are the perturbing gases). The measurements here described were made with a direct absorption spectroscopy scheme. The same spectrometer, equipped with a two tone frequency modulation detection electronics, is presently working as a sensor for combustion diagnostics.

2 Experimental

The experimental apparatus is a spectrometer based on a distributed feed-back (DFB) diode laser. The diode laser is temperature stabilized, within 1 mK, and driven with a low noise current generator. The emitted frequency, with a bandwidth of about 30 MHz, was coarsely tuned by varying the temperature in a range between 5 and 35 °C and then finely adjusted by changing the injection current. A slow (10 Hz) current ramp is added to the injection current, in order to sweep a frequency interval of few GHz across the transition(s). A schematical drawing of the apparatus is shown in Figure 1. The laser beam is divided by a beam splitter into two beams: the reference beam is sent into a Fabry-Perot interferometer (FPI), whose Free Spectral Range is $FSR = 298{\pm}2$ MHz). The main beam passes through three cells. One cell is 20 cm long, the second one is 50 cm long, the third one is a multipass Herriott cell (SIT Mod. MPC-283) with 28.3 m of effective length. In order to measure broadening coefficients one sample cell is filled with gas(es) at different pressures. When shifts are to be measured, a frequency origin is required, and in our case this is obtained by filling a second reference cell with pure C_2H_2 at low pressure (1–5 torr). The three cells have been used alternatively as reference or sample cells depending on the kind of measurement to be performed, and on the intensity of the line(s) involved. For the relatively stronger lines of the $\nu_1 + \nu_3$ band of $^{12}C_2H_2$ the multipass cell provided the reference absorption peak, while the 20 cm cell was used as sample cell. When measuring the foreign gases effects the multipass cell was the sample one, while one or both the other cells were used as reference. For normalization of the absorbed intensity a signal with empty cells was acquired before and after each series (few minutes). We periodically made a check on the single mode emission of our laser, and as a consequence on the real zero transmission level.

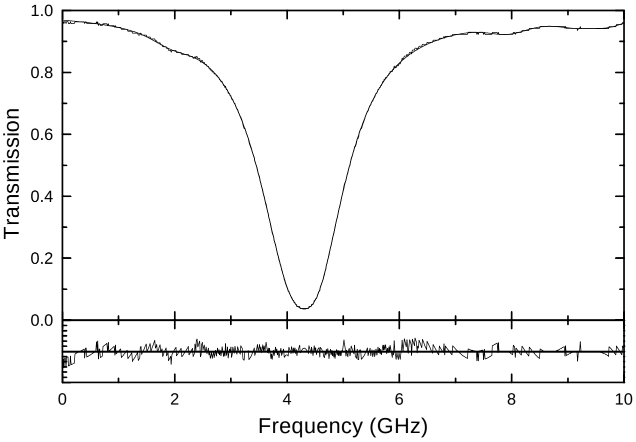

Fig. 2. Result of the fit procedure for P(24) line of $\nu_1+\nu_3$ band of $^{12}C_2H_2$, at 100 torr. The profile is due to absorption from both sample and reference cell; some weaker lines are visible in the wings and they have been included in the fit. In the lower part, the residual between experimental data and fitted lineshape is plotted magnified by 5.

The pressure range for self measurements was 50–110 torr, while for foreign measurements the perturbing gas pressure was in the range 150–450 torr. Two Ge photodetectors (EG&G J16-5SP-R03M) collected the transmitted radiation from the FPI and from the cells, and the signals where displayed by a digital oscilloscope (Tektronix TDS420A) and stored on a PC. The pressure was monitored by two capacitive vacuum gauge (Varian), with respectively 10 torr and 1 000 torr full scale. The direct absorption signals were analysed by means of the Linefit software package [27]: the transmission from the FPI provided a relative frequency scale; the absorption signal is normalized with respect to the transmitted intensity with empty cells and finally fitted according to the Beer–Lambert law and with Voigt lineshapes. The Voigt curve approximation used by Linefit is the four-Lorentzian one by Puerta-Martin [28]. In Figure 2 the results of the fit procedure for the P(24) line are shown. The residual has been multiplied by 5 for clarity. As the reference cell was kept at a

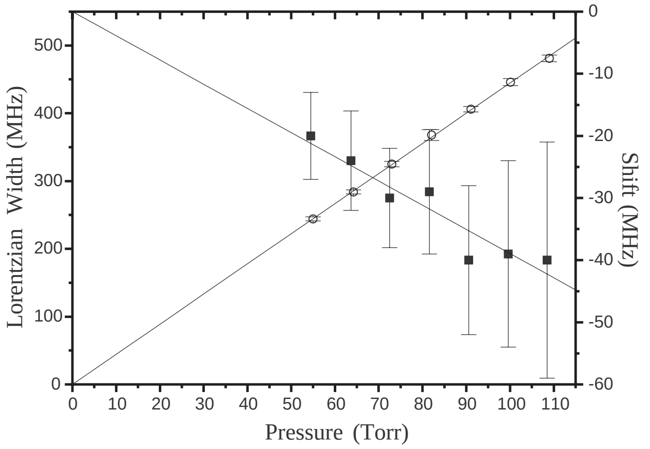

Fig. 3. Self-width (○) and shift (■) *versus* pressure for the P(24) line of $\nu_1 + \nu_3$ band of $^{12}C_2H_2$.

constant pressure during the shift measurements, the absorption signals are the superposition of the sharp reference peak and a broad profile. In the fit these two profiles are treated as two different lines and the shift is given by the difference of the frequencies of the two lines as resulting from the fit. For each line, the Doppler width has been measured at the lowest possible pressure. This value has been used in all the measurements for that line. At the end of each fit procedure, we have slightly changed the value of Doppler width in order to verify, by the examination of the χ^2, that no physical change occurred. We assumed a conservative error of 10 MHz for a single measurement of width or shift, even though we took the error coming from the fit procedure when larger than 10 MHz. Figure 3 shows how the broadening and shift coefficients are retrieved from the measurements at the various pressures. For the shifts the pressure of the gas in the reference cell has been subtracted from the pressure in the sample cell. Experimental data are fitted with a line crossing the axes origin, according to the law of pressure broadening and shift. Yet, for broadening only, data have been fitted also with a generic straight line, in order to verify *a posteriori* the correctness of the measurements. The uncertainty for broadening and shift coefficient reported in the Tables are twice the standard deviation coming from the linear fit.

3 Results

For the identification and assignment of the line we observed, first we made a comparison between a complete scan, by varying the temperature, of the tunability range of our diode laser, and the FT spectra of C_2H_2 collected in reference [29], where the measured frequencies of most of the recorded lines are reported, although the lines are not assigned. By comparing the relative spacing and intensity ratio between lines we were able to reasonably identify all the line we investigated. Then, we assigned all the observed lines according to the list of lines given in reference [3].

Table 1. Experimental self broadening a_s and self shift b_s coefficients for the 16 observed lines. They are all P-branch line of $^{12}C_2H_2$ bands, except where explicitly indicated. The listed wavenumbers ν are taken from reference [3].

ν	J	a_s	b_s
		10^{-3} cm^{-1}/atm	
$\nu_1 + \nu_3$			
6 487.0374	26	105 ± 1	−10.1 ± 0.3
6 490.0202	25	109 ± 1	−8.1 ± 0.8
6 492.9783	24	112 ± 1	−9.8 ± 0.3
6 495.9118	23	120 ± 1	−6.1 ± 1.0
6 498.8206	22	124 ± 1	−7.4 ± 0.5
$\nu_1 + \nu_3$ ($H^{13}C^{12}CH$)			
6 492.3787	20	130 ± 2	−6.2 ± 0.3
6 495.1300	19	137 ± 3	−9.6 ± 0.5
6 497.8573	18	135 ± 2	−9.1 ± 0.5
$\nu_1 + \nu_3 + \nu_4^1 - \nu_4^1$			
6 489.0746	16f	146 ± 1	−8.1 ± 0.8
6 489.1884	16e	139 ± 1	−7.4 ± 0.3
6 491.8037	15f	153 ± 2	−7.1 ± 0.5
6 491.9140	15e	146 ± 1	−6.0 ± 0.2
6 494.5090	14f	154 ± 1	−6.2 ± 0.2
6 494.6145	14e	148 ± 1	−8.3 ± 0.3
6 497.1894	13f	152 ± 2	−7.8 ± 0.3
6 497.2907	13e	163 ± 4	–
$\nu_1 + \nu_3 + \nu_5^1 - \nu_5^1$			
6 488.3709	18f	123 ± 2	−12.9 ± 0.5
6 488.4796	18e	131 ± 2	−8.6 ± 0.8
6 496.6637	15f	146 ± 2	−6.8 ± 0.2
6 496.7629	15e	147 ± 2	−7.8 ± 0.8

We have measured the self broadening and shift coefficients for the P(22–26) lines of the $\nu_1 + \nu_3$ band of C_2H_2, the P(18–20) lines of the $\nu_1 + \nu_3$ band of $H^{13}C^{12}CH$, and several l-splitted doublets belonging to the hot combination bands $\nu_1 + \nu_3 + \nu_4^1 - \nu_4^1$ and $\nu_1 + \nu_3 + \nu_5^1 - \nu_5^1$ of C_2H_2. The lines of each l-doublet are identified by the total angular momentum J and by the letters e and f, which refer to the different value of the angular momentum about the molecular axis. Foreign gas effects have been measured only for the P(22–26) lines of the $\nu_1 + \nu_3$ band of $^{12}C_2H_2$ due the the weakness of the other lines. The gas used as perturbers have been N_2, O_2 and CO_2.

It has been impossible to analyse the data for CO_2 effect on the P(25) line, because of the presence of a CO_2 line at 6 490.06078 cm^{-1} [30]. The problem does not arise from the impossibility of resolving two overlapping lines, but because our analysis software cannot assign a separate value for Gaussian width to each line in the spectrum.

The results are summarized for each band in Table 1 for self effects and in Tables 2 and 3 for foreign perturbers. Data are plotted *versus* J for self broadening, Figure 4, and for foreign effects in Figure 5. No specific comparison can be made with existing data.

A general comparison can be made with previous results for different bands. The values are in good agreement

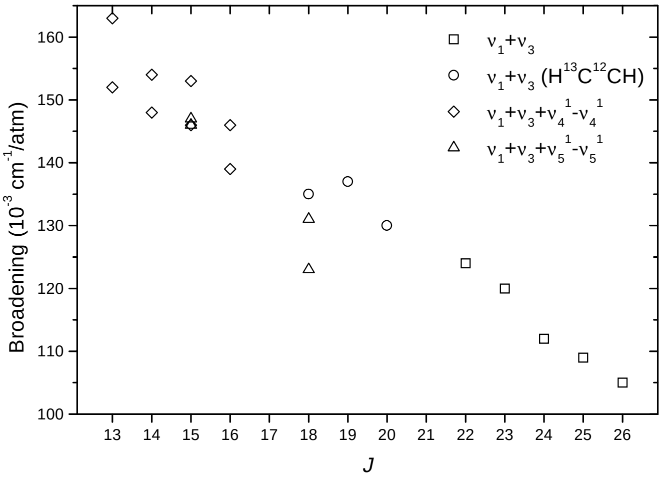

Fig. 4. Self broadening coefficients for all the investigated lines. Error bars and parity labels for *l*-doublets have been omitted for clarity (see Tab. 1 for details).

Table 2. Foreign broadening coefficients for the P(22–26) lines of the $\nu_1 + \nu_3$ band.

J	N_2	O_2	CO_2
		10^{-3} cm^{-1}/atm	
26	63.3 ± 0.8	47.4 ± 0.3	71.4 ± 0.5
25	66.1 ± 1.3	49.4 ± 0.8	–
24	63.6 ± 0.5	51.9 ± 0.3	70 ± 1
23	69.7 ± 0.8	53.7 ± 0.5	70.2 ± 0.5
22	65 ± 1	53.2 ± 0.3	71.7 ± 1.3

Table 3. Foreign shift coefficients for the P(22–26) lines of the $\nu_1 + \nu_3$ band.

J	N_2	O_2	CO_2
		10^{-3} cm^{-1}/atm	
26	−7.8 ± 0.5	−10.6 ± 0.3	−14.0 ± 0.2
25	−8.1 ± 0.8	−10.7 ± 0.2	–
24	−9.1 ± 0.1	−11.9 ± 0.3	−10.7 ± 0.2
23	−9.0 ± 0.2	−10.6 ± 0.5	−9.4 ± 0.2
22	−8.2 ± 0.2	−10.1 ± 0.5	−9.8 ± 0.2

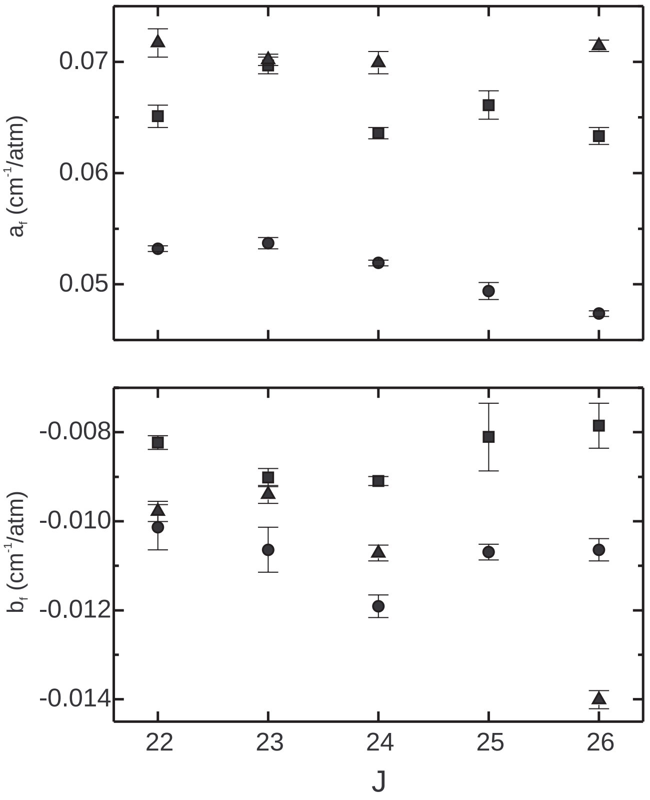

Fig. 5. Foreign broadening *a* and shift *b* coefficients for the P(22–26) lines of $^{12}C_2H_2$. The effects of CO_2 for the P(25) have not been measured, as explained in the text. (■) N_2, (●) O_2, (▲) CO_2.

with those measured at the same values of *J* for different vibrational bands, varying from 163 to 105 $\times 10^{-3}$ cm^{-1}. The *J* dependence of the self-broadening coefficient shows a well define decreasing behaviour of a_s with *J*. This behavior agrees with previous results [9,11,13,15], except for the results presented by Herregodts *et al.* [19], where, at least in the same range of *J* we investigated (J = 13–26), the broadening coefficients show a pretty flat behaviour. Moreover, in the same article a pressure dependence of the self-broadening coefficient has been reported, which was not observed before. These authors have observed that in the pressure range 0–150 torr the self-broadening coefficient increases with pressure, while above 150 torr it remains constant. They claim that the responsible for this behaviour is the so called Dicke narrowing. As the vibrational quantum numbers dependence of the self-broadening coefficients is expected to be small, we should have found the same effect, as our measurements have been carried out in the pressure range in which the variation should be the largest one. On the contrary, as can be seen in Figure 3 the linearity of width with respect to pressure is evident. All our experimental points lie on a straight line crossing the axes origin. This linear trend has been clearly shown in reference [13] as well. Often observation of effects similar to a Dicke narrowing can be induced from systematic errors in the normalization of the experimental spectra. The checks we made on the procedure of normalization and the high accuracy of the approximation we used for the Voigt profile lead us to exclude the presence of a narrowing effect as large as observed by Herregodts *et al.*

No data for shift coefficients are available in literature at this wavelength. Nevertheless, the comparison with data reported in reference [20], and references therein, for other bands shows how the vibrational dependence of shifts is not negligible. Our results do not exhibit a well defined trend with *J*, and the absolute values are a factor of about 2 lower than those in [20].

4 Conclusions

We have measured the self and foreign broadening and shift coefficients for several lines belonging to different combination bands of $^{12}C_2H_2$ and $H^{13}C^{12}CH$, for pure gas or in mixtures with N_2, O_2 and CO_2 as perturbing gas. A direct comparison with other data is not possible, while the band dependence of the coefficients has been examined. The apparatus used in this work, without the "etalon arm" and equipped with a Two-Tone Frequency Modulation detection electronics, is presently being used for combustion diagnostics.

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