Measurements of linestrengths, N₂-, Ar-, He- and self- broadening coefficients of acetylene in the $\nu_4+\nu_5$ combination band using a cw quantum cascade laser

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Abstract

Linestrengths, N₂-, Ar-, He- and self- broadening coefficients of acetylene have been measured at 296 K in the *P* branch of the $\nu_4+\nu_5$ combination band for 25 rotational transitions. The effect of gas temperature is studied over 296 – 683 K for five transitions to allow the determination of the temperature dependent exponent *n* for N₂- and Ar- broadening coefficients. These measurements were performed using a continuous-wave quantum cascade laser (cw-QCL) operating over 1253 – 1310 cm⁻¹. Spectroscopic parameters were obtained by fitting absorption spectra using Voigt, Galatry and Rautian profiles. Linestrength and broadening results are compared with previous studies available in literature for the $\nu_4+\nu_5$ combination band and other vibrational bands of acetylene.

Keywords: Acetylene; Linestrength; Collisional broadening; Infrared spectroscopy; Quantum cascade lasers.

1. Introduction

Acetylene (C_2H_2) has been identified as an important species in a variety of applications. In combustion, acetylene is produced during the oxidation of hydrocarbon fuels and acts as a precursor for soot formation which has carcinogenic effects on human health [1, 2]. Quantitative measurements of acetylene in combustion processes are critical in evaluating the environmental impact of different fuels [3]. Acetylene is also present in earth's atmosphere in trace quantities as it is formed by the burning of fossil fuels [4]. Furthermore, acetylene concentration in human breath has been identified as a biomarker for smoking [5]. Acetylene has been found as a trace constituent of the Titan atmosphere and in outer planetary atmospheres of Jupiter and Saturn [6, 7]. Accurate measurements of important spectroscopic parameters such as linestrengths, collisional broadening coefficients and their temperature dependencies are crucial for precise measurements of acetylene concentration in a variety of environments.

Acetylene is a linear symmetric molecule and has five vibrational modes. Unlike other bands in near infra-red region, the $\nu_4+\nu_5$ combination band, located in mid infra-red region, is fairly strong [8]. Rotational transitions in this combination band are separated sufficiently to be identified easily for the determination of individual spectroscopic parameters. A number of studies have been performed in the past to determine linestrengths and collisional broadening coefficients for the acetylene spectral region $1240 - 1390\text{ cm}^{-1}$. Podolske et al. [9] used a diode laser spectrometer to measure linestrengths for 17 transitions in the R - branch of the $\nu_4+\nu_5$ combination band. In the same study, collisional broadening coefficients of acetylene perturbed by H_2 and N_2 were reported for three lines. From measurements made with tunable diode lasers, Devi et al. [10] derived N_2 - and air- broadening coefficients for a total of 29 lines between 1250 and 1380 cm^{-1} in the P and R branches. Individual line intensities of

acetylene in the *P* and *R* branches of the $\nu_4 + \nu_5$ combination band have been measured at room temperature using Fourier Transform Infrared (FTIR) Spectroscopy in a number of studies [11-14]. Among recent measurements of spectroscopic parameters of acetylene in the $\nu_4 + \nu_5$ combination band, one should note the studies performed by Lepère's group [15-20]. Room temperature linestrengths and self-broadening coefficients have been measured for 30 lines in *P* and *R* branches over 1275 – 1390 cm^{-1} spectral region using a tunable diode laser spectrometer [15]. Temperature dependent exponents of self-broadening coefficients of 7 transitions was measured in the temperature range of 173 – 273 K [18]. Room temperature N_2 -broadening coefficients were measured for 12 transitions in the *R* branch of $\nu_4 + \nu_5$ band [19]. A similar study was carried out for 15 transitions in the temperature range of 173 – 273 K to determine temperature dependent exponents of N_2 -broadening coefficients [16, 17]. Room temperature CO_2 -broadening coefficients have also been reported for 24 transitions in the spectral range of 1270 – 1400 cm^{-1} [20].

Voigt profile is the most extensively used line profile to simulate absorption spectra for the determination of spectroscopic parameters. This profile is a convolution of Doppler broadening (Gaussian) and pressure broadening (Lorentzian). However, Voigt profile does not take into account collisional narrowing effect which arises from velocity-changing collisions. Hence, spectroscopic parameters derived from the Voigt profile can result in systematic errors of several percent when Doppler broadening is important [21-23]. More elaborate line-fitting profiles, i.e. Galatry [24] and Rautian [25] have been established which include the effect of collisional narrowing. These lineshape profiles account for the reduction in Doppler broadening due to velocity-changing collisions and resulting lineshape profile is narrower than the one modeled by Voigt profile [26]. Collisional narrowing effect can be modeled on the basis of either hard collision or soft collision theory. Soft collision model assumes that velocity after collision is strongly dependent on the velocity before collision,

while hard collision model presumes that velocity after collision is unrelated to the velocity before collision. Hard collision model simulated by Rautian and Sobel'man [25] profile is generally believed to be applicable in the limit when $M_1 \ll M_2$, while soft collision model simulated by Galatry profile [24] holds when $M_1 \gg M_2$, where M_1 and M_2 are molecular weights of absorber and perturber, respectively. In both hard and soft collisional models, a narrowing parameter (β) based on frequency of velocity-changing collisions is introduced to account for reduction in Doppler broadening [22]. Furthermore, the soft collision model can be applied in more general cases when M_1 and M_2 are not very different. This is because of the fact that small change in velocity can also result from small angle scattering of the long-range part of the intermolecular potential [22]. However, hard collision model is more difficult to apply in general situations as it explicitly assumes velocities after collision are unrelated to velocities before collisions [26]. Recently, more general line-fitting profiles taking into account velocity changes due to intermolecular collisions and speed dependence of collisional width have been developed for both soft collisional [27-29] and hard collisional models [30, 31]. These speed dependent line profiles incorporate in-depth treatment of underlying physical phenomena and show better agreement with experimentally measured line profiles than soft and hard collisional models which do not account for speed dependence of broadening coefficients [32, 33]. Ciurylo et al. [33] have also shown that the hard collisional model is not strictly valid in the limit $M_1 \ll M_2$.

The primary emphasis of the present study is to obtain precise linestrengths, N₂-, Ar-, He- and self- broadening coefficients of C₂H₂ for a total of 25 lines, $P(8) - P(33)$, in the $\nu_4 + \nu_5$ combination band. To our knowledge, the current study provides first measurement of Ar- and He- broadening coefficients for the selected transitions. In addition, we report measurements of the influence of gas temperature on N₂- and Ar- broadening coefficients in the temperature range of 296 - 683 K for five transitions. Studies were performed using

continuous-wave external cavity quantum cascade laser (cw EC-QCL) operating over 1253 – 1310 cm^{-1} to cover the target transitions. Spectroscopic parameters are derived by fitting measured absorption spectra using Voigt, Galatry and Rautian profiles.

2. Experimental Setup

A cw EC-QCL manufactured by Daylight solutions (model: 21077 MHF) has been used in this study as the tunable mid-IR light source. The laser has a tunable range of 1217 – 1328 cm^{-1} and covers the entire P branch of the $\nu_4+\nu_5$ combination band of acetylene. The laser head is connected to a control box which displays centerline frequency and allows operating the laser under different settings. The laser frequency, temperature and injection current can be set using the laser control box. The highly collimated laser light can reach an energy output of 120 mW. The laser is expected to have a line-width of less than 0.001 cm^{-1} . The laser chip was maintained at 16 $^{\circ}\text{C}$ with the help of thermoelectric cooling and recirculating chiller. Depending on the nature of the application, the laser can be operated in three different frequency modes. These include fixed wavelength, coarse modulation and fast modulation modes [34]. Fast modulation can provide a fine tuning range of approximately 0.1 cm^{-1} with a sinusoidal repetition rate of 10 kHz – 2 MHz, while coarse modulation provides wider tuning range of nearly 1 cm^{-1} at a maximum sinusoidal repetition rate of 100 Hz. In the current study, we have used the coarse modulation mode which provides sufficient tuning range to scan over an individual acetylene transition at the target temperature and pressure conditions. Coarse modulation is achieved by using a piezoelectric transducer (PZT) which mechanically modulates the external cavity grating. The laser PZT is driven by an external piezo-driver (Thorlabs MDT694A) which receives sinusoidal wave (100 Hz and 0 – 10V_{DC}) from a standard function generator (Stanford Research Systems DS 345).

Fig. 1: Schematic diagram of the experimental setup

Fig. 1 shows the experimental setup used in the present work. The stainless steel gas cell (Reflex Inc.), mounted with parallel ZnSe windows, has a path length of 10 cm and is designed to operate at relatively high pressure and temperature, up to 20 bar and 770 K, respectively. Temperature of the static gas cell was measured by recording the temperature distribution along the cell by using five equally positioned K-type thermocouples. Gas pressure was measured by using two MKS 627D capacitance manometers with full scale pressure ranges of 100 Torr and 1000 Torr. Prior to each set of measurements, the cell was evacuated to less than 10^{-3} Torr and the overall leak rate in the setup was measured to be less than 0.1 Torr/min. Acetylene gas with a purity of 99.99 % was provided by AHG gas-supplier. Gas mixtures of 0.95% C_2H_2/Ar , 0.96% C_2H_2/N_2 and 0.59% C_2H_2/He , prepared in a magnetically-stirred mixing tank, were used for measurements at 296 K. To obtain sufficient absorption, the compositions of the gas mixtures used for high-temperature measurements were 2.98% C_2H_2/N_2 and 3.1% C_2H_2/Ar .

The highly collimated beam produced by the laser was split into two paths by using a ZnSe beam-splitter. One beam was directed through the gas sample present in static cell while other beam was passed through a solid Germanium etalon. Both beams were then directed to two separate thermoelectrically-cooled infrared photovoltaic detectors (Vigo PVI 3TE-10.6). Neutral density (ND) filters were placed before both detectors to avoid signal saturation of detectors and to ensure that their operation was within the dynamic range. The laser was scanned over the entire absorption feature of the transition being investigated. Transmitted intensities were recorded with a 2.5 MS/s data acquisition system (NI PCI-6133). To increase the accuracy of the retrieved spectroscopic parameters, typically 9 – 11 measurements were conducted over a range of pressures (15 – 150 Torr) for each transition. At each pressure, 10 scans were recorded over the target absorption transition and the resulting spectroscopic parameters of each scan were averaged. The Germanium etalon was used to determine the relative laser frequency. The etalon has a length of 7.635 cm and a refractive index of 4.0069 near 7.83 μm which corresponds to a free spectral range (FSR) of 0.0163 cm^{-1} . We used the HITRAN 2012 database [8] to identify C_2H_2 transitions and their absolute frequencies.

3. Data Analysis

Experimentally measured absorption features are simulated using Voigt, Galatry and Rautian profiles to obtain integrated area and collisional width. These parameters are then used to calculate linestrength and collisional broadening coefficient, respectively. A Labview-based in-house peak fitting program was employed for the determination of spectroscopic parameters. The absorbance was calculated using Beer-Lambert law by taking the logarithmic of the ratio of the absorption signal (with sample) and background (under vacuum) signal. The peak fitting program simulates the absorption data with one of the three profiles (Voigt, Galatry, Rautian) using a Levenberg-Marquardt nonlinear least square algorithm. In the case of Voigt profile, value of Gaussian width was fixed to the calculated value of Doppler width.

The retrieval program then adjusts the peak absorbance, line center and collisional width to minimize the residual between the measured and simulated absorbance profiles. A floating value of collisional narrowing parameter (β) was used as input for the Galatry profile, while a fixed value of collisional narrowing parameter has been used for Rautian profile [35]. For the latter, β parameter is approximated from dynamic friction coefficient (β_{Diff}) inferred from diffusion coefficient D_{12} [36, 37]. We found good agreement between the theoretical dynamic friction and beta parameter obtained from Galatry profile. With Rautian profile, fixed value of beta results in lesser computational cost and more robust fitting. Bouanich et al. [35] showed that for Rautian profile, the broadening coefficients obtained with fixed beta and floating beta were within their uncertainty limits. Hence, we believe that results obtained with fixed-beta methodology will be similar to results obtained when beta is kept floating in Rautian simulations.

For each transition, the retrieval program outputs integrated absorbance, collisional half-width and narrowing parameter (β) in case of Galatry profile.

The integrated absorbance, $A [cm^{-1}]$, for an isolated line transition is defined as:

$$A = \int_{-\infty}^{\infty} \alpha_{\nu} d\nu = PL \chi_{abs} S(T) \quad (1)$$

where α_{ν} is the spectral absorbance, $P [atm]$ is the total gas pressure, $L [cm]$ is optical path length of the absorbing medium, χ_{abs} is the mole fraction of absorbing species and $S [cm^{-2} \cdot atm^{-1}]$ is the linestrength at temperature $T [K]$. Temperature dependence of the linestrength can be described by:

$$S(T) = S(T_0) \frac{Q(T_0)}{Q(T)} \left(\frac{T_0}{T}\right) \exp\left[-\frac{hcE''}{k} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \left[1 - \exp\left(-\frac{hcv_0}{kT}\right)\right] \left[1 - \exp\left(-\frac{hcv_0}{kT_0}\right)\right]^{-1} \quad (2)$$

In the above equation, T_0 is the reference temperature, $Q(T)$ is the partition function of absorbing molecule, $E'' [cm^{-1}]$ is the lower-state energy, $\nu_0 [cm^{-1}]$ is the line center frequency of transition, $h [J.s]$ is Plank's constant, $c [cm/s]$ is the speed of light and $k [J/K]$ is Boltzmann's constant.

Collisional broadening, $\Delta\nu_C$, is defined as:

$$\Delta\nu_C = P \sum_i 2\gamma_i \cdot \chi_i \quad (3)$$

where $\gamma_i [cm^{-1}.atm^{-1}]$ is the collisional broadening coefficient of absorbing species in the presence of i -perturber with χ_i mole fraction.

Temperature dependence of the collisional broadening coefficient is defined in terms of the temperature dependent exponent n , and is given by the power law:

$$\gamma_i(T) = \gamma_i(T_0) \left(\frac{T_0}{T}\right)^n \quad (4)$$

The narrowing parameter, $\beta [cm^{-1}.atm^{-1}]$, can be compared with dynamic friction coefficient $\beta_{Diff} [cm^{-1}.atm^{-1}]$, given by [22]:

$$\beta_{Diff} = \frac{kT}{2\pi c M_1 D_{12}} \quad (5)$$

where M_1 is the mass of absorbing molecule, c is the speed of light and D_{12} is the mass diffusion coefficient which can be calculated from Lennard-Jones potential parameters.

Major sources of uncertainties in our measurements include mixture composition, optical path length, pressure, temperature, line profile fitting uncertainty and standard deviation of the measurements as a function of pressure. We estimate the maximum uncertainty in the measurement of linestrength and collisional broadening coefficients to be less than 5 %.

4. Results and Discussion

Results for room temperature measurements (296 K) of linestrengths, N₂–, Ar–, He–, and self– broadening coefficients for acetylene in the $\nu_4+\nu_5$ band are successively presented. Moreover, a polynomial representation of $|m|$ (for *P*-branch, $m = -J$, where J is the rotational quantum number) which fits the measured collisional broadening coefficients is described and discussed. The derived temperature dependent exponents of the Ar– and N₂– broadening coefficients obtained from high-temperature absorption measurements between 296 and 683 K are reported for five transitions. The narrowing parameters are also presented and discussed.

4.1. Linestrength Measurements

Fig. 2 shows a representative measured absorption transition of C₂H₂. The *P* (19) line, centered at 1284.506 cm⁻¹, is fit with Voigt, Galatry and Rautian profiles. In this example, the gas mixture is 0.96% C₂H₂/N₂ at a total pressure of 19.52 Torr and the gas temperature is 296 K. The residuals between the measurement and simulated line profiles are shown at the bottom of the figure. The residual is typically around 1% near the peak when using Voigt profile. Galatry and Rautian profiles produce much better fits and the residual is near the noise level i.e. less than 0.1 %. This improvement in line fitting clearly demonstrates the importance of the collisional narrowing effect incorporated in Galatry and Rautian profiles. The effect of collisional narrowing is dominant at low pressures and high temperatures where Doppler broadening is important.

Fig. 2: Comparison of residual resulting from three different profiles. Residual from the Voigt fit shows characteristic gull-wing like shape around the peak of absorption feature. Galatry and Rautian profiles better model the measured lineshape. Conditions are: $P=19.52$ Torr, $T=296$ K, $L=10$ cm, 0.96% C_2H_2/N_2 , line-center is 1284.5062 cm^{-1}

Linestrength of each transition is obtained by plotting the integrated absorbance areas versus the total gas pressure; Fig. 3 shows an example of pressure dependence of the integrated area for $P(21)$ line centered at 1280.0093 cm^{-1} . As expected, the behavior is linear with zero-intercept and a high correlation coefficient of ~ 0.99 is obtained from the corresponding linear fit. The slope of

Fig. 3: Integrated area versus pressure for $P(21)$ line of $\nu_4+\nu_5$ band of C_2H_2 at 1280.0095 cm^{-1} . Linestrength is calculated from the slope of linear fit. Conditions are: $T = 296\text{ K}$, $L = 10\text{ cm}$, 0.96% C_2H_2 in N_2 .

the linear fit is used to determine the average value of the linestrength (S) at a particular temperature. In an analogous fashion, we have measured room-temperature (296 K) linestrengths for 25 lines, $8 \leq |m| \leq 33$, in the P -branch of $\nu_4+\nu_5$ combination band of acetylene. Results obtained by the three fitting methods are reported in the Table 1. The retrieved values from Galatry and Rautian profiles are larger by about 2% than those derived from Voigt profile. The present values are compared with values taken from previous measurements and agree well with Vander Auwera et al. [11] and Lepère et al. [15]. Both Voigt and Rautian profiles were used to obtain linestrength values by Lepère et al. [15]. Similar to our results, their linestrengths obtained by the Rautian profile are relatively larger

than those obtained from Voigt profile. We have also compared our measurements with the values listed in HITRAN 2012 database. Good agreement

Table 1: Linestrength values S [$\text{cm}^{-2} \text{ atm}^{-1}$] for P branch of $\nu_4+\nu_5$ band of C_2H_2 measured at 296 K and their comparison with measurements reported in literature.

		This work			HITRAN 2012	Vander Auwera et al. [11] T = 296 K	Lepère et al. [15] T = 297 K	
m	Line Position [cm^{-1}]	Voigt	Galatry	Rautian		Voigt	Voigt	Rautian
8	1309.459	1.0656	1.0695	1.0678	1.0201	1.009	0.9907	0.9939
9	1307.165	3.0663	3.0791	3.0797	3.105		3.1302	3.1511
10	1304.877	1.0316	1.0445	1.0437	1.0256	1.021	1.0032	1.0096
11	1302.595	2.988	2.9943	2.9982	2.9831		3.1138	3.1191
12	1300.319	0.9568	0.9604	0.9643	0.9454		0.931	0.9356
13	1298.049	2.603	2.6175	2.6132	2.6472		2.6923	2.7023
14	1295.783	0.7622	0.7763	0.77873	0.8088	0.8001	0.8133	0.8224
15	1293.521	2.1296	2.1401	2.1385	2.1879		2.2324	2.2366
16	1291.263	0.6089	0.6194	0.6123	0.6471		0.6466	0.6511
18	1286.756	0.4813	0.4918	0.4903	0.4862		0.4969	0.5065
19	1284.506	1.2316	1.2946	1.2788	1.2353		1.3288	1.3474
20	1282.258	0.3473	0.3586	0.3524	0.3441	0.3349	0.3393	0.3423
21	1280.009	0.8458	0.8549	0.8496	0.8497	0.8357	0.8648	0.8685
22	1277.761	0.2298	0.2364	0.2332	0.2299	0.2303	0.2254	0.2265
23	1275.512	0.5458	0.5498	0.5567	0.5518	0.5708		
24	1273.262	0.1463	0.1496	0.1485	0.1452			
25	1271.01	0.3379	0.3382	0.3382	0.3394	0.3359		
26	1268.755	0.0762	0.0774	0.0783	0.0869	0.0841		
27	1266.497	0.1967	0.1983	0.1994	0.1976	0.1996		
28	1264.235	0.0507	0.0517	0.0501	0.0493	0.0495		
29	1261.969	0.1062	0.1093	0.1081	0.1091	0.1053		
30	1259.699	0.0259	0.0268	0.0271	0.0265	0.0266		
31	1257.423	0.0579	0.0586	0.0581	0.0572	0.0558		
32	1255.142	0.0131	0.0142	0.0139	0.0135	0.0288		
33	1252.855	0.0281	0.0288	0.0282	0.0285	0.0282		

is found and no systematic difference is observed. It should be noted that linestrength values for these transitions exhibit alternating pattern of weaker and stronger lines for even and odd rotational quantum numbers, respectively.

4.2. Collisional Broadening Measurements

Collisional broadening coefficients for P -branch transitions of acetylene in the $\nu_4+\nu_5$ combination band are determined using the line profile analysis described in Section 3. Broadening coefficients are measured in the presence of different foreign gases (N_2 , Ar and He) and as well as for pure acetylene.

Fig. 4: Collisional width versus pressure for $P(21)$ line of $\nu_4+\nu_5$ band of C_2H_2 at 1280.0095 cm^{-1} . Broadening coefficient is calculated from the slope of linear fit. Conditions are: $T = 296\text{ K}$, $L = 10\text{ cm}$, 0.96% C_2H_2 in N_2 .

4.2.1. N₂-, Ar- and He- broadening coefficients

N₂-, Ar- and He- broadening coefficients of acetylene at 296 K have been measured over $8 \leq |m| \leq 33$ for the *P* branch of $\nu_4+\nu_5$ combination band. Fig. 4 shows an example of the linear dependence of the collisional width on the total gas pressure for the determination of N₂-broadening coefficient of *P* (21) line at 296 K. Tables 2, 3 and 4 list measured broadening coefficients ($2\gamma_{\text{C}_2\text{H}_2-\text{i}}$) at 296 K obtained using Voigt, Galatry, and Rautian profiles for the 17 transitions of C₂H₂ in the presence of N₂, Ar and He bath gases respectively. The self-broadening coefficients ($2\gamma_{\text{C}_2\text{H}_2-\text{C}_2\text{H}_2}$) used to deduce foreign broadening coefficients have been obtained from HITRAN 2012 database, as will be discussed in Section 4.2.2. Pressure broadening coefficients obtained from Galatry and Rautian profiles are larger by about 1 – 3% than those obtained from Voigt profile. This difference is observed for most of the transitions considered in this study and is independent of the bath gas.

In Table 2, nitrogen-broadening coefficients ($2\gamma_{\text{C}_2\text{H}_2-\text{N}_2}$) are compared with the experimental data of Dhyne et al. [17] who measured room temperature N₂-broadening coefficients in the $\nu_4+\nu_5$ vibrational band for a few *P*-branch transitions. Their data were also deduced from Voigt, Galatry and Rautian profiles. In all cases, our results agree well with Dhyne et al. [17] with a maximum difference of about 2%. We have also compared our results with Arteaga et al. [38] who reported N₂-broadening coefficients for $\nu_1+\nu_3$ band over the same rotational quantum numbers as our measurements in $\nu_4+\nu_5$ band. Arteaga et al. [38] measurements are also found to be in good agreement with our results.

Table 2: N_2 -broadening coefficients, $2\gamma_{C_2H_2-N_2}$ [$cm^{-1}atm^{-1}$], for P branch of $\nu_4+\nu_5$ band of C_2H_2 measured at 296 K and their comparison with previous studies.

m	This work			$2\gamma_{C_2H_2-Air}$ HITRAN 2012 [8]	Dhyne et al. [17] $\nu_4+\nu_5$ band T= 298 K			Arteaga et al. [38] $\nu_1+\nu_3$ band T=295 K
	Voigt	Galatry	Rautian		Voigt	Rautian	Galatry	Voigt
8	0.1740	0.1771	0.1758	0.1668	0.1698	0.1714	0.1714	0.1723
9	0.1675	0.1707	0.1696	0.1640				0.1646
10	0.1625	0.1660	0.1673	0.1616	0.1644	0.1674	0.1676	0.1682
11	0.1645	0.1687	0.1659	0.1592				0.1610
12	0.1604	0.1624	0.1653	0.1574	0.1582	0.1612	0.1612	0.1648
13	0.1591	0.1616	0.1627	0.1554				0.1578
14	0.1540	0.1555	0.1571	0.1536	0.1598	0.1668	0.1674	0.1591
15	0.1565	0.1586	0.1586	0.1512				0.1531
16	0.1533	0.1556	0.1561	0.1492	0.1564	0.1614	0.1616	0.1613
18	0.1511	0.1529	0.1537	0.1438				0.1509
19	0.1474	0.1500	0.1508	0.1408				0.1477
20	0.1408	0.1438	0.1426	0.1376				0.1506
21	0.1376	0.1401	0.1392	0.1342	0.1370	0.1390	0.1390	0.1431
22	0.1371	0.1389	0.1384	0.1306				0.1425
23	0.1285	0.1299	0.1294	0.1270	0.1280	0.1332	0.1336	0.1343
24	0.1291	0.1306	0.1298	0.1232				0.1362
25	0.1191	0.1209	0.1202	0.1194				0.1292

Table 3: Ar–broadening coefficients, $2\gamma_{C_2H_2-Ar}$ [$cm^{-1}atm^{-1}$], for *P* branch of $\nu_4+\nu_5$ band of C_2H_2 measured at 296 K and their comparison with previous studies for other bands of C_2H_2 .

m	This work			Bouanich et al. [35] ν_5 band, T=297 K			Arteaga et al. [38] $\nu_1+\nu_3$ band, T=295 K
	Voigt	Galatry	Rautian	Voigt	Rautian	Calculation	Voigt
8	0.1138	0.1183	0.1187	0.1178	0.1200	0.1132	0.1144
9	0.1090	0.1134	0.1128	0.1138	0.1150	0.1128	0.1098
10	0.1075	0.1116	0.1106				0.1076
11	0.1072	0.1117	0.1101	0.1132	0.1154	0.1122	0.1038
12	0.1035	0.1070	0.1074	0.1078	0.1092	0.1114	0.1025
13	0.1034	0.1068	0.1072				0.1004
14	0.0978	0.1018	0.1023	0.1038	0.1064	0.1092	0.0990
15	0.0980	0.1019	0.1015	0.1014	0.1084	0.1078	0.0993
16	0.0971	0.1001	0.1004				0.0945
18	0.0930	0.0967	0.0967			0.1040	0.0913
19	0.0917	0.0955	0.0947	0.0936	0.0956	0.1020	0.0859
20	0.0889	0.0925	0.0926				0.0879
21	0.0872	0.0906	0.0908	0.0876	0.0900	0.0950	0.0842
22	0.0847	0.0881	0.0884	0.0874	0.0896	0.0926	0.0812
23	0.0808	0.0839	0.0836	0.0836	0.0868	0.0900	0.0817
24	0.0793	0.0821	0.0816				0.0737
25	0.0775	0.0804	0.0796	0.0768	0.079	0.0848	0.0733

In Table 3, we report measurements of Ar–broadening coefficients ($2\gamma_{C_2H_2-Ar}$) in the $\nu_4+\nu_5$ band at room temperature (296 K) deduced from Voigt, Galatry and Rautian profiles. To our knowledge, this study reports the first measurements of Ar–broadening coefficients for $\nu_4+\nu_5$ band of acetylene. Previous Ar-broadening studies performed in other spectral regions of acetylene include Bouanich et al. [35] for ν_5 band and Arteaga et al. [38] for $\nu_1+\nu_3$ band. These data are also presented in Table 3 for comparison with our data. We find a good agreement confirming the weak vibrational dependence of the Ar–broadening coefficients.

Table 4: He-broadening coefficients, $2\gamma_{C_2H_2-He}$ [$cm^{-1}atm^{-1}$], for P branch of $\nu_4+\nu_5$ band of C_2H_2 measured at 296 K and their comparison with published literature data.

m	This work			Arteaga et al. [38] $\nu_1+\nu_3$ band, T=295 K	Thibault [39] Calculations, T=296 K
	Voigt	Galatry	Rautian	Voigt	Calculations
9	0.0873	0.0907	0.0904	0.0867	0.0882
10	0.0871	0.0902	0.0903	0.0866	0.0882
11	0.0868	0.0901	0.0900	0.0869	0.0883
12	0.0866	0.0900	0.0901	0.0873	0.0884
13	0.0872	0.0903	0.0902	0.0873	0.0884
14	0.0868	0.0902	0.0901	0.0880	0.0884
15	0.0870	0.0899	0.0900	0.0877	0.0883
16	0.0861	0.0895	0.0896	0.0883	0.0881
18	0.0859	0.0894	0.0895	0.0859	0.0874
19	0.0874	0.0905	0.0904	0.0874	0.0871
20	0.0861	0.0895	0.0895	0.0881	0.0868
21	0.0867	0.0902	0.0901	0.0863	0.0865
22	0.0864	0.0897	0.0898	0.0868	
23	0.0863	0.0898	0.0898	0.0862	
24	0.0857	0.0892	0.0893	0.0881	
25	0.0850	0.0884	0.0883	0.0865	

Helium-broadening coefficients ($2\gamma_{C_2H_2-He}$) measured at 296 K for the $\nu_4+\nu_5$ band are listed in Table 4. Again, this work reports, to our knowledge, first measurements of He-broadening coefficients measured in the $\nu_4+\nu_5$ band. Values obtained using Galatry and Rautian profiles are larger than the corresponding ones resulting from the Voigt profile by about 4%. Our measurements are compared in Table 4 with Arteaga et al. [38] data for $\nu_1+\nu_3$ band and the calculations performed by Thibault [39] for the R -branches of acetylene. Excellent agreement is seen among our measurements, Arteaga et al. [38] data and Thibault [39] calculations with a maximum difference of about 1.5%.

4.2.2. Self– broadening coefficients

Self–broadening coefficients of acetylene are measured for $|m|$ values between 26 and 33 for the P –branch of $\nu_4+\nu_5$ combination band at 296 K. The use of 100% acetylene sample saturated the signal for transitions with lower quantum numbers ($|m| < 26$). Thus self–broadening coefficients are not measured for these transitions. Measured self–broadening parameters are presented and compared with previously reported measurements and calculations in Table 5. Our measured values using Voigt profile differ from Galatry and Rautian profiles by less than 4%, while the Galatry and Rautian profiles agree with each other within 1%. We have compared our measured results with the listed self–broadening coefficients in HITRAN 2012 database [8], measurements of Jacquemart et al. [12] and theoretical calculations of Lepère et al. [15] The current data obtained by both Galatry and Rautian profiles generally agree very well with HITRAN 2012 [8] values and the difference is less than 2%. Our results differ by as much as 7% from Jacquemart et al. [12] for the $|m| = 26$ transition but are in better agreement for other ($|m| > 26$) transitions. Lepère et al. [15] calculated self–broadening coefficients by two different assumptions in the framework of a semi–classical formalism. Our experimental results are within the two limits defined by their theoretical calculations.

Table 5: Self- broadening coefficients, $2\gamma_{C_2H_2-C_2H_2}$ [$cm^{-1}atm^{-1}$], for P branch of $\nu_4+\nu_5$ band of C_2H_2 measured at 296 K and its comparison with literature data.

m	This work			HITRAN 2012 [8]	Lepère et al. [15]		Jacquemart et al. [12]
	Voigt	Galatry	Rautian		Calc-I	Calc-II	Voigt
26	0.2210	0.2145	0.2139	0.2140	0.2040	0.2200	0.2055
27	0.2100	0.2084	0.2073	0.2080	0.1974	0.2148	0.2026
28	0.1981	0.2022	0.2035	0.2018	0.1901	0.2100	0.1949
29	0.1983	0.1958	0.1979	0.1954	0.1846	0.2052	0.1911
30	0.1859	0.1809	0.1887	0.1886	0.1784	0.2006	0.1852
31	0.1868	0.1817	0.1812	0.1814			0.1791
32	0.1747	0.1743	0.1741	0.1740			0.1731
33	0.1708	0.1665	0.1671	0.1662			0.1693

4.2.3. Empirical representations of broadening coefficients

Our measurements of collisional broadening coefficients of acetylene cover a large number of transitions ($8 \leq |m| \leq 25$). We used cubic polynomial to fit measured pressure broadening coefficients [40] and then interpolated the empirical fitting expression to predict broadening coefficients for transitions not covered in the current study.

$$(2\gamma_{\text{C}_2\text{H}_2-i}) = a_0 + a_1 |m| + a_2 |m|^2 + a_3 |m|^3 \quad (6)$$

where a_i are the constants obtained by the empirical fitting. The measured N_2 - and Ar -broadening coefficients are plotted in Fig. 5 along with the empirical representation. The above expression, Eq. (6), is also used to fit the data of Arteaga et al. [38] in the $\nu_1 + \nu_3$ band. The corresponding a_0 , a_1 , a_2 and a_3 constants are shown in Tables 6 and 7. It should be noted that the constant a_0 corresponding to $|m| = 0$ (offset) is deduced from the fitting of Arteaga et al. [38] data. The cubic polynomial expressions fit our measured data within 2%. In comparison with N_2 -broadening coefficients of Arteaga et al. [38] the empirical polynomial function of the current work begins to deviate at higher $|m|$ values (> 25). Therefore, we recommend using Eq. (6) and the polynomial coefficients of the current study over $1 \leq |m| \leq 35$ and $1 \leq |m| \leq 25$ for Ar - and N_2 -broadening coefficients, respectively. The measured He -broadening coefficients do not systemically decrease with increasing $|m|$, and thus an empirical representation is not proposed here for He -broadening coefficients.

Fig. 5. Empirical representation of (a) Ar- and (b) N_2 - broadening coefficients of acetylene for $1 \leq |m| \leq 35$.

Table 6. Polynomial coefficients of Eq. (6) to represent Ar–broadening coefficients over $1 \leq |m| \leq 35$.

	a_0	a_1	a_2	a_3
This work (Voigt)	0.178	-0.01224	6.56 E-4	-1.32 E-5
Arteaga et al. [38]	0.178	-0.0117	5.80 E-4	-1.11 E-5

Table 7. Polynomial coefficients of Eq. (6) to represent N₂–broadening coefficients over $1 \leq |m| \leq 35$.

	a_0	a_1	a_2	a_3
This work (Voigt)	0.235	-0.01259	7.27 E-4	-1.63 E-5
Arteaga et al. [38]	0.235	-0.01156	5.69 E-4	-1.06 E-5

4.2.4. Temperature dependence of N₂– and Ar– broadening coefficients

The temperature dependence of N₂– and Ar–broadened lines for different vibrational bands of acetylene has been reported by several researchers. All of those measurements were carried out for $T < 298$ K, which depict the temperature range for atmospheric and astrophysical applications of acetylene. In the present study, we report the first measurements of broadening coefficients of acetylene at temperatures higher than room temperature. The temperature dependence of N₂– and Ar– broadening coefficients is reported for five transitions, $P(8)$ to $P(12)$, in the $\nu_4 + \nu_5$ band. The measurements have been performed in over 296 – 683 K. N₂- and Ar- broadening coefficients, obtained from Voigt, Galatry and Rautian profiles, are listed in Table 8. As expected, broadening coefficients decrease with increasing temperature since they scale in a manner similar to number density.

Fig. 6: N_2 -broadening coefficients as function of temperature for $P(8)$ line in the $\nu_4+\nu_5$ band of C_2H_2 . The temperature dependent exponent n of the broadening coefficient is obtained from the slope of the best-fit line on log-log scale.

Temperature dependent exponent, n , is determined from the linear dependence of broadening coefficients versus gas temperature on a logarithmic plot; a representative case is shown in Fig. 6 for N_2 - broadening coefficients. It is worth noting that the correlation, Eq. (4), is based on the assumption that the parameter n remains independent of the temperature. However, this assumption may not be correct under all conditions and care must be exercised in extrapolating the temperature dependent exponent n outside the temperature range where it is measured.

The obtained values of temperature dependent exponent n are plotted in Fig. 7 (a-b) for Ar- and N_2 - broadening coefficients, respectively. For Ar-broadening, the value of n varies between 0.77 and 0.86 for $8 \leq |m| \leq 12$. The values of n are between 0.70 and 0.80 for the case of N_2 -broadening. It is apparent that for all transitions, the value of n obtained from Voigt and Rautian/Galatry profiles are very close and no systematic pattern is observed. Our

measured Ar-broadening temperature dependent exponents are compared with Bouanich et al. [35] who reported values of n for Ar-broadening in ν_5 band over 173.2 – 297 K. Nitrogen-broadening temperature dependent exponents are compared with Bouanich et al. [41] who reported values of n for N₂-broadening in ν_5 band over 173.2 – 297 K and with Dhyne et al. [18] who measured n values for N₂-broadening in the R branch of $\nu_4+\nu_5$ band over 173.2 – 298.2 K. Our Ar-broadening coefficients result in slightly larger values of n compared to earlier studies. This is probably due to the different temperature ranges used in our and previous studies.

Table 8: Measurements of $2\gamma_{C_2H_2-N_2}$ and $2\gamma_{C_2H_2-Ar}$ [$cm^{-1}atm^{-1}$] as a function of temperature.

m	Temp [K]	$2\gamma_{C_2H_2-N_2}$				$2\gamma_{C_2H_2-Ar}$		
		Voigt	Galatry	Rautian		Voigt	Galatry	Rautian
8	296	0.1740	0.1771	0.1758		0.1138	0.1183	0.1187
	364	0.1463	0.1508	0.1498		0.0984	0.1031	0.1033
	455	0.1157	0.1197	0.1191		0.0796	0.0834	0.0835
	546	0.1006	0.1045	0.1037		0.0678	0.0714	0.0712
	683	0.0859	0.0899	0.0891		0.0603	0.0640	0.0642
9	296	0.1675	0.1707	0.1696		0.1090	0.1133	0.1128
	364	0.1374	0.1411	0.1417		0.0903	0.0947	0.0944
	455	0.1132	0.1167	0.1159		0.0792	0.0839	0.0837
	546	0.1001	0.1040	0.1047		0.0647	0.0693	0.0691
	683	0.0874	0.0917	0.0912		0.0584	0.0624	0.0622
10	296	0.1625	0.1660	0.1673		0.1075	0.1117	0.1106
	364	0.1406	0.1433	0.1438		0.0888	0.0935	0.0928
	455	0.1171	0.1204	0.1208		0.0746	0.078	0.0782
	546	0.0975	0.1009	0.0996		0.0634	0.0673	0.0677
	683	0.0863	0.0902	0.0905		0.0559	0.0592	0.0594
11	296	0.1645	0.1687	0.1659		0.1072	0.1116	0.1101
	364	0.1363	0.1405	0.1388		0.0926	0.0969	0.0962
	455	0.1186	0.1215	0.1216		0.0796	0.0846	0.0841
	546	0.0999	0.1047	0.1047		0.0672	0.0721	0.0720
	683	0.0806	0.0839	0.0842		0.0555	0.0591	0.0588
12	296	0.1604	0.1624	0.1653		0.1035	0.1067	0.1074
	364	0.1325	0.1350	0.1345		0.0894	0.0929	0.0933
	455	0.1151	0.1183	0.1191		0.0720	0.0756	0.0758
	546	0.0959	0.1001	0.1013		0.0610	0.0648	0.0652
	683	0.0785	0.0811	0.0807		0.0546	0.0585	0.0589

Fig. 7. Variation of temperature dependent exponent n with rotational quantum number m for (a) Ar- (b) N₂- broadening coefficients of C₂H₂ in the P branch of $\nu_4+\nu_5$ band. Bouanich et al. [35] reported values of n for Ar-broadening in ν_5 band for the temperature range of 173.2 – 297 K. Bouanich et al. [41] reported values of n for N₂-broadening in ν_5 band over 173.2 – 297 K. Dhyne et al. [17] determined n for N₂-broadening in the R branch of $\nu_4+\nu_5$ band over 173.2 – 298.2 K.

4.2.5. Collisional narrowing parameters

Collisional narrowing effect is incorporated in Galatry and Rautian profiles by introducing collisional narrowing parameter. However, this parameter is very sensitive to baseline uncertainties and is, therefore, very difficult to measure accurately. We have determined the average value of collisional narrowing parameter and compared it with dynamic friction coefficient for different gas mixtures used in this study. The results are listed in Table 9. It

can be observed that pure acetylene gas has the largest values of collisional narrowing coefficient ($0.056 \text{ cm}^{-1}\text{atm}^{-1}$), while $\text{C}_2\text{H}_2\text{-He}$ measurements result in smallest value of β ($0.026 \text{ cm}^{-1}\text{atm}^{-1}$). Collisional narrowing parameter and dynamic friction coefficient decrease with increase in temperature for both Ar- and N_2 - broadening cases; these values are summarized in Table 10. Collisional narrowing coefficients of $\text{C}_2\text{H}_2\text{-N}_2$ and $\text{C}_2\text{H}_2\text{-Ar}$ mixtures are not too different from each other. This can be attributed to the relatively large uncertainty ($\sim 20\%$) in measuring collisional narrowing which does not allow deducing small differences in collisional narrowing coefficients. Furthermore, it should be noted that our present work is based on Galatry and Rautian line profiles, which do not account for speed dependent effects. It has been shown in some earlier studies that speed dependent effects are important and their inclusion in simulated line profiles results in better agreement with experimental measurements [42-44]. Therefore, we believe that the application of speed dependent soft and hard collisional models can help in more accurate determination of collisional narrowing parameters.

Table 9: Average values of collisional narrowing coefficient (retrieved using Galatry profile) and theoretical values of dynamic friction coefficient for different gas mixture. $T = 296 \text{ K}$.

Mixture	$\beta [\text{cm}^{-1} \text{atm}^{-1}]$	$\beta_{\text{Diff}} [\text{cm}^{-1} \text{atm}^{-1}]$
$\text{C}_2\text{H}_2\text{-Ar}$	0.039	0.035
$\text{C}_2\text{H}_2\text{-N}_2$	0.045	0.036
$\text{C}_2\text{H}_2\text{-He}$	0.026	0.020
$\text{C}_2\text{H}_2\text{-C}_2\text{H}_2$	0.056	0.048

Table 10: Average values of collisional narrowing coefficient (retrieved using Galatry profile) and theoretical values of dynamic friction coefficient as a function of temperature for $C_2H_2-N_2$ and C_2H_2-Ar mixtures.

T [K]	$C_2H_2-N_2$ mixture		C_2H_2-Ar mixture	
	β [$cm^{-1} atm^{-1}$]	β_{Diff} [$cm^{-1} atm^{-1}$]	β [$cm^{-1} atm^{-1}$]	β_{Diff} [$cm^{-1} atm^{-1}$]
296	0.042	0.036	0.041	0.035
364	0.034	0.032	0.035	0.032
455	0.031	0.029	0.031	0.028
546	0.026	0.026	0.024	0.026
683	0.023	0.024	0.021	0.023

5. Conclusions

Linestrengths, N_2 -, Ar -, He - and self- broadening coefficients are measured for P -branch transitions of the $\nu_4+\nu_5$ combination band of acetylene. Line parameters are obtained using Voigt, Galatry and Rautian profiles. Experimental line shapes are better modeled by Galatry and Rautian profiles which account for collisional narrowing effects. Measured data are compared with published literature for $\nu_4+\nu_5$ band as well as for other bands of acetylene. Broadening coefficients show very weak vibrational dependence and compare quite well for different vibrational bands. Nitrogen- and argon- broadening coefficients decrease with increasing rotational quantum number, while helium- broadening coefficients exhibit slight dependence on rotational quantum numbers. Temperature dependent exponents are also measured in the temperature range of 296 K – 683 K for N_2 - and Ar - broadening of five lines. Measured temperature dependent exponent values in the current work compare quite well with those measured at temperatures lower than room temperature. Finally, collisional narrowing parameters are found to have similar magnitude as the calculated values of dynamic friction coefficients.

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