Intensities, broadening and narrowing parameters in the ν_3 band of methane

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Abstract

The P- branch of methane's ν_3 band is probed to carry out an extensive study of the 2905 – 2908 cm^{-1} infrared spectral region. Absolute line intensities as well as N_2 -, O_2 -, H_2 -, He -, Ar - and CO_2 - broadening coefficients are determined for nine transitions at room temperature. Narrowing parameters due to Dicke effect have also been investigated. A narrow emission line-width ($\sim 0.0001 \text{ cm}^{-1}$) difference-frequency-generation (DFG) laser system is used as the tunable light source. To retrieve the CH_4 spectroscopic parameters, Voigt and Galatry profiles were used to simulate the measured line shape of the individual transitions.

Keywords: Methane; line intensities; collisional broadening; collisional narrowing; difference-frequency-generation laser

1. Introduction

The 3–4 μm spectral region, the location of the fundamental C–H stretching mode for many hydrocarbons and atmospheric trace molecules, is one of the most important spectral region for C–H containing compounds. Since Raman and Rayleigh scattering contributions are limited, this spectral region presents significant advantages for reliable quantitative interpretation of theoretical and/or observational atmospheric and astrophysical data. Methane (CH_4), which is an important atmospheric constituent in many planetary systems, has dense transition lines with strong absorption near 3–4 μm [1-2]. Identification and quantification of these lines in the spectrum are of considerable interest for the retrieval of CH_4 abundance in planetary atmosphere. Methane is the second most important greenhouse gas in Earth's atmosphere after CO_2 [3] and its abundance with the altitude in our atmosphere, monitored near 3.4 μm , has been recently reported in [4-6]. Methane is one of the important constituents detected in the atmosphere of Saturn [7-9], Titan [10-16], Jupiter [17-18], Uranus [19-20], Mars [21-22] and Pluto [23]. Accurate knowledge of the spectroscopic parameters of CH_4 is needed for monitoring its abundance in Earth's atmosphere and for the retrieval of methane abundances in various planetary atmospheres.

Methane has four fundamental vibrational modes [1]: symmetric stretch ν_1 (2917 cm^{-1}), symmetric bend ν_2 (1534 cm^{-1}), asymmetric stretch ν_3 (3019 cm^{-1}) and the asymmetric bend ν_4 (1311 cm^{-1}). Due to its strong IR absorption, the ν_3 band near 3.4 μm has been studied by a number of spectroscopic methods and theoretical approaches. The self-broadening parameters and line intensities of CH_4 in the P– branch of the $\nu_2+\nu_4$ combination band were studied experimentally by Hubbert et al. [24]. Subsequently, spectral region between 3036 and 3185 cm^{-1} of CH_4 was studied extensively using absorption spectroscopy by Varanasi [25]. In this work, self– and pressure– broadening coefficients of CH_4 with H_2 , He, N_2 , O_2 and air were measured for 10 transitions in the ν_3 and $2\nu_3$ bands at spectral resolutions of 0.1 cm^{-1} and 0.5 cm^{-1} , respectively. The retrieved spectroscopic parameters for the R– branch transitions were obtained by modeling spectra using a Lorentzian profile. Intensities, self– and N_2 – broadening coefficients were measured for several transitions by Devi et al. [26] in the spectral range from 2870 to 2883 cm^{-1} (including the ν_3 and $\nu_2+\nu_4$ bands). Devi et al. [26] used a tunable diode laser spectrometer to study five transitions for temperatures between 215 and 297 K to deduce the temperature coefficients, n . Later, Devi et al. [27] reported measurements using Fourier Transform Infrared (FTIR) spectroscopy at 0.01 cm^{-1} resolution for 75 individual vibration–rotation transitions of the P– and R– branches in the ν_3 fundamental band of CH_4 in the 2873 – 3077 cm^{-1} range. They used a nonlinear least–squares curve fitting technique, assuming a Voigt line shape, to determine air–, N_2 – and O_2 –

broadening parameters and line shifts at 298 K. An extensive study of sixty six CH_4 transitions of the Q- branch of the ν_3 band in the $3012 - 3018 \text{ cm}^{-1}$ domain was reported by Pine [28]. He determined intensities, self-, foreign shift- and broadening- coefficients with numerous partner gases such as N_2 , O_2 , H_2 , Ar and He. In this study, measurements were performed at room temperature using a difference-frequency spectrometer and spectra were fitted by Rautian profiles to retrieve the spectroscopic parameters. Benner et al. [29] used a FTIR instrument at 0.01 cm^{-1} spectral resolution to measure N_2 -, O_2 -, air- broadening and line-shifting parameters for 450 weak methane transitions belonging to the ν_3 , $\nu_2+\nu_4$, $2\nu_2^2$ and $2\nu_4^2$ bands located in the $2650 - 3200 \text{ cm}^{-1}$ spectral range. These measurements were carried out at 296 K. Using a tunable diode laser spectrometer Pine [30] examined 102 transitions between 2916 and 3123 cm^{-1} of the P- and R- branches of the ν_3 band to measure intensities, N_2 - and Ar- broadening and shift coefficients at room temperature. Pine used an improved lineshape model, based on the Rautian model, that accounts for Dicke narrowing and line mixing effects [30]. Mondelain et al. [31] studied 4 transitions, between 2914 and 2922 cm^{-1} , belonging to the $\nu_2+\nu_4$ combination band using a tunable diode laser spectrometer. In their work [31], intensities, self-, N_2 - and O_2 - broadening and shifting parameters were obtained from spectra simulation using the Voigt profile as well as the Rautian (hard-collision) and Galatry (soft-collision) models. Because of the molecular confinement, the two latter models were also used to deduce the collisional narrowing of CH_4 in N_2 and O_2 bath gases. In another experimental study, Mondelain et al. [4] used Voigt profile and hard-collision model to retrieve the N_2 - collisional broadening, collisional narrowing and line-mixing coefficients for 4 isolated lines near 2927 cm^{-1} in the P branch of the ν_3 band of CH_4 . These measurements were conducted at for atmospheric applications over a large temperature range ($90 - 296 \text{ K}$). More recently, Ghysels et al. [6] revised the R(6) manifold transitions of the ν_3 band of CH_4 using a difference-frequency-generation (DFG) laser near 3086 cm^{-1} with the purpose to monitor in-situ CH_4 in the middle atmosphere using the PicoSDLA- CH_4 spectrometer. The spectroscopic parameters of air-broadening, air-narrowing and line-mixing were measured for six lines of CH_4 at gas temperature between 213.5 and 296 K [6]. A few other studies used difference-frequency-generation (DFG) techniques to report the detection of absorption lines in ambient air and spectroscopic parameters of CH_4 in the ν_3 band around $3.4 \mu\text{m}$ [32-35].

There have been a large number of theoretical approaches to determine the spectroscopic parameters of CH_4 in the $3-4 \mu\text{m}$ spectral region. Pieroni et al. [36] proposed a detailed model based on state-to-state collisional transfer rate to study line-mixing effects in the ν_3 band of CH_4 perturbed by N_2 at room temperature. In their study, the measured spectra were computed to computed ones to prove the quality of the proposed theoretical approach to

obtain the absorption coefficients of CH₄ in the 2800 – 3200 cm⁻¹ spectral range over a wide range of pressures (0.25 – 80 atm). Féjard et al. [37] built an effective transition moment model in tensorial form to revise the line intensities of CH₄ from 3 to 5 μm on the basis of new absorption measurements from an FTIR instrument. Pine and Gabard [38] combined calculation with spectroscopic measurements to report a CH₄ speed-dependent first-order line-mixing model and a speed-independent full relaxation matrix model to retrieve N₂- and Ar- broadening coefficients as well as the collisional shifts. They studied 102 lines in the P- and R- branches located between 2917 and 3028 cm⁻¹ in the ν₃ band [38]. A similar approach was used by Pine and Gabard [39] to determine the CH₄- broadening, shifting, Dicke narrowing and line-mixing parameters in the Q branch of the ν₃ band using pure CH₄ and with H₂, He, N₂, O₂, Ar as perturber gases. Semi-classical line broadening calculations based on the Hamiltonian model for CH₄ perturbed by Ar [40] and He [41-42] were reported to simulate many transitions in the ν₃ vibrational band. Line-mixing effects were studied extensively from low to high pressures for CH₄/He mixtures by combining measurements and calculations in the framework of the Robert and Bonamy semi-classical approach [43]. Antony et al. [44] used a similar formalism to calculate the pressure-broadened temperature coefficients and line-shifts to provide data for 524 transitions in the ν₃ band of methane. This work reported broadening parameters for methane with N₂, O₂ and air as collision partners in the spectral range from 2726 to 3200 cm⁻¹ and relatively low temperatures (225 – 296 K). Also, semi-classical line broadening calculations for methane perturbed by N₂ have been reported by Gabard and Boudon [45].

In view of the available literature mentioned above for spectroscopic parameters of CH₄ near 3–4 μm, we note that the 2905– 2908 cm⁻¹ IR spectral region of the P branch of methane's ν₃ band has not received much attention. To our knowledge, only the two works of Devi et al. [27] and Benner et al. [29] examined few lines in this region to retrieve the half-widths of CH₄ broadened by N₂, O₂ and air using FTIR spectroscopy at relatively low resolution (0.01 cm⁻¹). Indeed, no experimental information concerning pressure broadening coefficients with H₂, CO₂ and He bath gases is currently available in the literature. Absolute line intensities and foreign- broadening coefficients of CH₄ are difficult to measure accurately in the 2905 – 2908 cm⁻¹ region due to the high density of transitions as well as overlap among neighboring lines. Experimental studies require high spectral resolution measurements as well as relatively low pressures to minimize overlapping of the spectral transitions. Absorption spectroscopy with an FTIR spectrometer or difference-frequency-generation (DFG) laser systems are two general approaches that can be used to obtain detailed information on line intensities, broadening and narrowing coefficients of CH₄ with different perturber gases. DFG

spectroscopy is advantageous compared to FTIR spectroscopy due to a narrow emission line-width and faster time response.

As part of the various efforts that are done to provide spectroscopic parameters of CH₄, we report here absolute line intensities and N₂–, O₂–, H₂–, He–, Ar– and CO₂– broadening coefficients for 9 transitions in the ν_3 fundamental band over the 2905 – 2908 cm^{–1} spectral region. To our knowledge, this is the first determination of H₂–, Ar–, and CO₂– broadening coefficients in the P(11) manifold of the ν_3 band of methane. Air– broadening coefficients were deduced from the O₂ and N₂ measurements. Narrowing parameters of CH₄ with N₂, O₂, Ar and CO₂ perturbors were measured. Measurements were performed using narrow emission line-width (~ 0.0001 cm^{–1}) DFG laser system. The spectroscopic parameters were retrieved by modeling the line shape of the measured spectra using Voigt and Galatry profiles. Relatively low pressures (i.e. ≤ 101 Torr) were chosen for measurements to minimize the interference from neighboring lines. The obtained data have been compared, when possible, with previous experimental values available in the literature.

2. Experimental setup

In the present study, a tunable mid-IR Difference-Frequency-Generation (DFG) laser system (Nova-wave IRIS 1000) [46], having an instrumental line width of 3 MHz, was used to measure the spectroscopic parameters of methane. The experimental setup comprises the DFG system to generate wavelengths near 3.44 μ m, an optical absorption cell and a fast IR-detector combined with an oscilloscope. The DFG system has been described in detail elsewhere [47]. To produce mid-IR light, a pump laser operating at 1074 nm was combined with near-IR distributed feedback (DFB) diode lasers in a Periodically Poled Lithium Niobate (PPLN) crystal. Many replaceable DFB laser diodes can be used to access a range of frequencies. The temperature of the PPLN crystal and the temperature/current of the DFB laser were chosen appropriately to satisfy the phase-matching condition and hence to get the desired wavelength with a maximum output power. In our case, the temperature of the PPLN crystal was 73 °C, whereas the DFB laser (operating near 1560.6 nm region) was operated at 38 °C and 320 mA. To achieve frequency modulation, a linear ramp of voltage (0.8 V peak-to-peak) was applied to the DFB laser from a function generator. The applied ramp was limited to select the desired wavelength-scanning window (2905 – 2909 cm^{–1}).

The schematic of the experimental setup is shown in Fig. 1. The laser output was separated into two beams with a beam-splitter. One beam was sent to a spectrum analyzer (Bristol Instruments 721B) [48] to monitor the frequency and stability of the laser. The second beam was directed through the test gas contained inside an optical cell. The optical cell had CaF₂

windows and an optical path length of 52 cm. To reduce line mixing effects, measurements were conducted at pressures less than 100 Torr. All experiments were performed under controlled room-temperature conditions (297 ± 1 K).

Prior to each set of measurements, the absorption cell was evacuated to less than 10^{-4} mbar. Three MKS Baratron capacitance manometers (20, 100 and 1000 Torr range) were used to measure the gas pressure. The transmitted signal with and without the sample was monitored with an IR photo-detector supplied by Vigo Systems (PVMI – 3TE –10.6, S= 4 mm² active area), and acquired with a 1 GHz oscilloscope (Lecroy). Frequency drift of the DFG laser was checked in the fixed-wavelength mode with the high-resolution (0.002 cm^{-1}) spectrum analyzer. The output of the DFG laser was very stable and frequency drift was measured to be less than 0.008 cm^{-1} over 30 minutes. The absolute line positions of CH₄ during the modulation of the laser system were determined by using peak positions of each transition from HITRAN 2012 database (see Table 1) and a solid Germanium etalon with a free spectral range (FSR) of 0.0163 cm^{-1} .

Typical raw data traces for room-temperature measurement of 1% CH₄ in N₂ at a total pressure of 80 Torr are shown in Fig. 2. The frequency of the laser was scanned over 3 cm^{-1} to cover all ro-vibrational transitions in the $2905 - 2908 \text{ cm}^{-1}$ spectral range. In Fig. 2, the measured transmission is divided into three regions for clarity. As shown in the Fig. 2c, our laser system can resolve and separate lines for which line-center wavenumbers differ by only 0.015 cm^{-1} . We used the HITRAN 2012 database to identify the ro-vibrational transitions and absolute frequencies [1]. The 9 strong transitions of the P(1)1 manifold can be seen in Fig. 2. In addition, there are five lines of P(10) manifold and two lines of P(6) manifold allowed by ro-vibrational coupling/perturbation in this wavenumber region (i.e. $2905 - 2908 \text{ cm}^{-1}$). However, those lines are very weak and not studied in this work. All assignments in the $2905 - 2908 \text{ cm}^{-1}$ spectral range are listed in Table 1 along with their line positions.

3. Data analysis

Data analysis was carried out following the fitting procedure used previously to determine the spectroscopic parameters of ammonia [50] and acetylene [51]. The line intensities and broadening coefficients were derived from Voigt and Galatry profiles by fitting the absorption line shape measurements at various pressures. Integrated absorbance and half-width of the absorption lines are then retrieved to calculate the absolute line intensity and broadening coefficients, respectively. The Voigt profile combines contributions of Lorentzian (pressure-broadening) and Gaussian (Doppler-broadening) profiles. In Voigt profile, Doppler width was

used as an input parameter and the retrieval program adjusts the peak absorbance, baseline, line center and collisional width to minimize the residual between the measured and calculated spectrum. The line positions of CH₄ in 2905 – 2908 cm⁻¹ spectral region were taken from the HITRAN 2012 database [1]. The Voigt profile is calculated using the following equation:

$$V(x, y) = \frac{1}{\sqrt{\pi}} \operatorname{Re} \left[\frac{i}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{x-t+iy} dt \right] \quad (1)$$

where the normalized frequency x and collisional coefficient y are given by:

$$x = \frac{\nu - \nu_0}{\gamma_D}, \quad (2)$$

$$y = P \frac{\gamma_C}{\gamma_D}, \quad (3)$$

The quantity $\nu - \nu_0$ (cm⁻¹) is the detuning from the line-center frequency, ν_0 (cm⁻¹). The parameter γ_D (cm⁻¹) is defined as 1/e Doppler half-width at half-maximum (HWHM). P is the total pressure of the gas mixture. The Doppler FWHM, $\Delta\nu_D$ (cm⁻¹), is related to γ_D by:

$$\Delta\nu_D = 2\sqrt{\ln 2} \gamma_D = 7.162 \times 10^{-7} \nu_0 \sqrt{T/M} \quad (4)$$

where T ($= 297 \pm 1$ K) is the gas temperature and M ($= 16$ g/mol) is molecular weight of the absorbing species of CH₄. The parameter $P\gamma_C$ (cm⁻¹) is the collisional width, and $P\gamma_C = \Gamma_C$.

However, the effect of Dicke line narrowing is not incorporated in the Voigt profile and can lead to systematic errors of few percent near the line center at relatively low pressure when Doppler broadening is dominant [49- 52-53]. In such situations, Galatry profile, that includes line narrowing, can be used to model the measured spectra. The Galatry line shape function is given by the following expression:

$$G(x, y, z) = \frac{1}{\sqrt{\pi}} \operatorname{Re} \left(\int_0^\infty \exp \left\{ -ixt - yt + \frac{1}{2z^2} [1 - zt - \exp(-zt)] \right\} dt \right) \quad (5)$$

where z is a normalized parameter related to the collisional narrowing coefficient β (cm⁻¹. atm⁻¹) by:

$$z = P\beta/\gamma_D \quad (6)$$

When the normalized parameter $z = 0$, Galatry profile is reduced to Voigt profile. To analyze the experimental line shape using Galatry profile, the retrieval program adjusts the collisional

width, collisional narrowing, line center and integrated area while Doppler width is an input parameter. During the fitting process, the program is initially provided with guess values of the line center frequency, line intensity and collisional-width obtained from the HITRAN 2012 database [1].

After fitting the measured line shape with either Voigt or Galatry profile, the retrieved values of the line intensity S and collisional broadening coefficient γ_i are calculated using the following equations:

$$A = PLX_{CH_4}S \quad (7)$$

$$\Gamma_C = P[\gamma_{self} \cdot X_{CH_4} + (1 - X_{CH_4})\gamma_i] \quad (8)$$

where A is the integrated absorbance, $P(atm)$ is the total gas pressure, $L(cm)$ is the optical path length of the absorbing medium, X_{CH_4} is the methane mole fraction, $\gamma_{self} (cm^{-1} \cdot atm^{-1})$ is the self- broadening coefficient ($CH_4 - CH_4$) and $\gamma_i (cm^{-1} \cdot atm^{-1})$ is the collisional broadening coefficient of CH_4 in the presence of the perturbing gas i ($i = N_2, O_2, H_2, He, Ar$ or CO_2).

The rough estimate of an overall standard deviation Δ_{sp} in spectroscopic measurement of line intensities, collisional- broadening coefficients and narrowing parameters are obtained by taking into account the major sources of uncertainty:

$$\frac{\Delta_{sp}}{sp} = \sqrt{(\Delta_A)^2 + (\Delta_{X_i})^2 + (\Delta_P)^2 + (\Delta_L)^2 + (\Delta_T)^2 + (\Delta_S)^2} \quad (9)$$

where sp and Δ_{sp} stand for a given spectroscopic parameter and its associated standard deviation. The error on the absorbance Δ_A ranged from 1 to 2 %. Each binary mixture was prepared in a mixing tank and the uncertainty Δ_{X_i} on X_i is less than 1%. The measured pressure has an uncertainty of 0.12 % resulting from the Baratron measurements. The uncertainty on the optical path-length Δ_L is less than 0.5% determined by comparing the present data, using an absorption cell of 52 cm, with measurements performed in another optical cell with a known optical path-length of 10 cm. The uncertainty in temperature Δ_T is about 0.3 %. During the fitting process, small adjustments were made to the baseline using a second-order polynomial function. Baseline uncertainties remain the dominant source of errors, mainly for the determination of the narrowing parameters β . The systematic error in the fitting process Δ_S ranged from 1 to 4 % arising mainly from the uncertainty in the baseline

of the absorption line shape. Finally, some uncertainty is also caused by the merged line transitions P(11) F2 1 and P(11) F1 1) at 2907.321273 and 2907.336088 cm^{-1} , respectively. Accounting for all sources of error, the overall uncertainty on the measured parameters comes out to be 3 %.

4. Results and discussion

4.1. Line intensities

Fig. 3a shows an example of typical measured spectra for P (11) F1 2 line at 2906.282 cm^{-1} . Voigt as well as Galatry profiles and their corresponding residuals are also shown. The absorbance is retrieved from the Beer-Lambert law and is presented as a function of the absolute wavenumber by using the etalon signal and the peak position taken from [1]. Examination of the residuals between the experimental data and the two fitting models clearly shows a relatively large systematic difference between measured and simulated spectra in the case of Voigt profile, whereas the residuals for the Galatry profile are lower by a factor of 2. This is because of the fact that Galatry profile adequately computes the measured absorption taking into account the Dicke narrowing effect. Line narrowing effects are mainly observed near the line center at relatively low pressures when Doppler broadening is dominant [49- 52- 53]. Line-mixing effects are not included in either Voigt or Galatry profiles and thus small structures appear even when using Galatry profile to simulate the measured spectra. This was mainly observed for the two merged transitions P (11) F2 1 and P (11) F1 1 at 2907.321273 and 2907.336088 cm^{-1} , respectively.

According to Eq. (7) above, the integrated absorbance is a linear function of the product $(P.L.X_{CH_4})$. The absolute line intensity S can be directly derived from the linear fit. Fig. 4 plots integrated absorbance for all the P(11) transitions in the case of a 1% CH_4/H_2 mixture. For each foreign gas, the CH_4 mole fraction is kept constant at 1% and the total gas pressure was changed from 5 to 100 Torr. Examination of Fig. 4 demonstrates the importance of determining absolute line intensities with high accuracy from the linear dependence of the integrated area versus gas pressure, rather than from a single measurement. As expected, the behavior is linear with zero-intercept for all transitions. High correlation coefficients of ≈ 0.99 were obtained for each linear fit and for all gas mixtures considered in the current study. To increase the accuracy of the obtained line intensities, measurements were conducted at relatively low pressures to minimize line-mixing effects.

The line intensities obtained from each binary mixture are shown in Fig. 5a. As expected, lines intensities are not sensitive to the bath gas used for experiments and we get same values

for the six mixtures used here. A maximum deviation of 2% results for the two P (11) F2 1 and P (11) F1 1 neighboring lines. Line intensities resulting from the Voigt fit are about 1- 6 % less than those obtained from the Galatry model due to line narrowing effects.

Measured CH₄ line intensities of the six gas mixtures have been averaged for each rotational transition and compared with literature values, HITRAN 2012 [1] and Féjard et al. [37], in Fig. 5b. These data are also listed in Table 2. The last three columns of Table 2 report the percentage difference between retrieved values using the Voigt profile and the Galatry profile (column χ), between values obtained by Galatry profile and data taken from the HITRAN 2012 [1] (column δ), and between values obtained by Galatry profile and data of Féjard et al. [37] (column ϵ). In all cases, Galatry model gives higher values compared to Voigt one. A maximum difference of about 4 % and 3.4 % is obtained when comparing our data with Rothman et al. [1] and Féjard et al. [37], respectively.

4.2. CH₄ collisional-broadening coefficients

Collisional-broadening coefficients were obtained from Voigt and Galatry fits of the measured absorption line shapes. According to Eq. (8), collisional width Γ_C is linear function of the gas pressure and thus the collisional-broadening parameters g_i ($i = \text{N}_2, \text{O}_2, \text{H}_2, \text{He}, \text{Ar}$ and CO_2) can be retrieved from the linear fits. The total collisional width has a small contribution from g_{self} (1% CH₄), which values are taken from the HITRAN 2012 database. In Fig. 6, collisional widths of the nine P(11) transitions are plotted for a 1% CH₄/H₂ mixture. A good linearity with a correlation factor of ~ 0.99 is obtained for all bath gases used here.

4.2.1. He, N₂, and O₂ bath gases

Retrieved values of γ_i where $i = \text{He}, \text{N}_2, \text{O}_2$ are listed in Tables 3, 4 and 5, respectively. In most cases, Galatry profile gives relatively larger values compared to the Voigt function. It can be observed that γ_{He} is much lower than γ_{N_2} and γ_{O_2} . O₂-broadening values are a few percent smaller than nitrogen-broadening. The short range interaction of helium, a light inert gas, with methane is relatively weak. Thus, the line broadenings are small, compared to the case of nitrogen or oxygen.

The measured values of broadening coefficients are compared with available data in the literature. Broadening coefficients are not available in the literature for P (11) F2 1 and P (11) F1 1 neighboring transitions and this work reports the values for the first time. In the case of γ_{He} (Table 3), the Galatry values differ by about 3 – 17 % from the values taken from

Grigoriev et al. [41]. As mentioned earlier, Grigoriev et al. [41] determined γ_{He} by combining measurements and semi- classical calculations. In Tables 4 and 5, measured values of γ_{N_2} and γ_{O_2} are compared against the FTIR study of Benner et al. [29]; the present data differ by about 3 – 13% and 2 – 23%, respectively. Benner et al. [29] determined spectroscopic parameters by means of an interactive nonlinear least-squares spectrum fitting technique by assuming Voigt line shapes of the absorption transitions.

Since N_2 and O_2 are the major constituents of the Earth's atmosphere, it is possible to determine γ_{air} by using $\gamma_{\text{air}} = 0.79 \gamma_{\text{N}_2} + 0.21 \gamma_{\text{O}_2}$. In general, we observed that values of γ_{air} and γ_{N_2} are nearly equal. The deduced γ_{air} are listed in Table 6 and compared against literature values of Rothman et al. [1] and Benner et al. [29]. The differences between our measurements and the data from Rothman et al. [1] can reach 20%. Relatively large differences (up to 15%) are observed between our values and Benner et al. [29].

4.2.2. H_2 , Ar, and CO_2 bath gases

The first measurements of γ_{H_2} , γ_{Ar} and γ_{CO_2} of methane's P(11) manifold, near the 2905 – 2908 cm^{-1} spectral range, are reported in Fig. 7. For all three perturbers, Galatry profile gives values 2 – 5 % larger compared with Voigt profile. As observed earlier for He, argon's interaction with CH_4 is weak which results in relatively small values of the broadening coefficients. The values of γ_{Ar} are smaller by about 41 – 66 % compared with γ_{H_2} and γ_{CO_2} values.

4.2.3. Transition-averaged ratios

Ratios of broadening coefficients are used readily for atmospheric and astrophysical interpretations of acquired spectra when measured values are not available for a specific purterber [9, 54-55]. Table 7 lists the transition-averaged ratios γ_{ratio} of the collisional-broadening coefficients for various pairs of partner gases. The broadening coefficients are averaged over the nine rotational transitions of the P(11) manifold measured here. The first two rows of Table 7 present ratios obtained by using the values measured in this work with Voigt and Galatry profiles, respectively. We can see that the two profiles give a nearly constant γ_{ratio} for each pairs where the variations are < 2% for most of the pairs, except Ar/ N_2 and He/Ar where the Galatry and Voigt based ratios differ by 5 and 7 %, respectively.

Our data are compared with published values available in the literature obtained by Pine [28], Benner et al. [29]; Pine and Gabard [39], and Tran et al. [9]. Our γ_{ratio} for (CH₄/N₂) is larger by about 11% compared to the value determined in [28]. Relatively small differences (< 3%) were observed for γ_{ratio} (O₂/N₂, He/H₂) between our work and other literature data. In the case of H₂/N₂, the obtained γ_{ratio} is larger by about 10 % in comparison with Pine and Gabard [39] and Pine [28]. In case of Ar/N₂ and He/Ar, the comparison is less consistent. Our γ_{ratio} value is larger by about 18 % compared to the values obtained by Pine and Gabard [39] and Pine [28]. Thus, it is not surprising to find large differences when comparing ratios of average data. In references [28,39], the γ_{ratio} corresponds to sixty six CH₄ transitions of the Q branch of the ν_3 band covering the 3012 – 3018 cm⁻¹ spectral region. The O₂/N₂ γ_{ratio} of Benner et al. [29] is calculated for 7 CH₄ lines in the P(11) manifold excluding the two P (11) F2 1 and P (11) F1 1 neighboring transitions. The He/H₂ γ_{ratio} obtained by Tran et al. [9] covers a large spectral domain from 2800 to 3200 cm⁻¹.

5. Collisional narrowing parameters

Since Galatry model incorporates the Dicke narrowing effect to simulate the measured line shape, we have determined narrowing parameters β for different combinations of CH₄/bath gas. For high accuracy measurements, studies were conducted at various pressures for most of transitions of the P(11) manifold in the ν_3 band. For the relatively small-mass colliders (H₂ and He), the corresponding β values are too small (see reference [28]). Under our experimental conditions, we observed a convergence of the Galatry fit to the negative collisional narrowing values in case of H₂ and He partners. This is probably because of the fact that β parameters are masked by the contribution of Lorentzian broadening. It is interesting to mention that the narrowing effects dominate at intermediate pressures since Doppler broadening dominates at low pressures and Lorentzian broadening dominates at higher pressures.

Collisional narrowing parameters β of CH₄ with N₂, O₂, Ar and CO₂ perturbors were deduced by plotting the measured z parameter as a function of gas pressure (see Eq. (6)). This procedure resulted in relatively small systematic error. Fig. 8a shows an example of the measured z parameter as a function of pressure for the P (11) F1 3 and P (11) E 2 transitions in a CH₄/N₂ mixture. The corresponding β coefficients are shown in Fig. 8b. The obtained Dicke narrowing parameters for various gas mixtures are listed in Table 8 for seven transitions of the P(11) manifold. The uncertainties of the reported β coefficients are about 20%, mainly due to the fluctuation of the baseline and the relatively small values of narrowing coefficients. The narrowing parameters are not reported for P (11) F2 1 and P (11)

F1 1 neighboring transitions since the two lines are not well-isolated which makes the determination of β coefficients very difficult.

Narrowing parameters are not available in literature for the transitions studied in this work. We compared our transition-averaged β values with narrowing measurements carried out in other wavenumber regions. Pine [28] determined β parameters in the ν_3 band over 3012 – 3020 cm^{-1} region using the Rautian model. Mondelin et al. [31] measured β coefficients using Rautian and Galatry profiles to simulate two transitions at 2914.4986 and 2921.3385 cm^{-1} in the $\nu_2+\nu_4$ combination band of methane. These data are listed in Table 9 where a reasonable agreement is seen between narrowing parameters measured in different wavenumber regions. Additionally, the β coefficients retrieved using Galatry profile are quite close to those obtained from Rautian profile.

6. Conclusions

In this work, we have presented accurate measurements of absolute line intensities, pressure broadening coefficients and narrowing coefficients for nine transitions of the P(11) manifold in the ν_3 band of CH_4 over 2905 – 2907 cm^{-1} spectral region. Measurements were conducted at 297 ± 1 K in binary mixtures with 1% CH_4 / N_2 , O_2 , H_2 , He , Ar and CO_2 using a narrow emission line-width (~ 0.0001 cm^{-1}) Difference–Frequency–Generation (DFG) laser system. To retrieve the CH_4 spectroscopic data, Voigt and Galatry profiles were used to compute the measured line shape of each individual transition at various gas pressures. Since Galatry profile incorporates Dicke narrowing effect, the line intensities determined using Galatry profile are higher by about 2 – 5 % compared with values obtained from Voigt fitting. The line intensities are not sensitive to the bath gas and a variation of less than 1 % was observed. The resulting values of the line intensities are compared, where possible, with previous experimental data available in the literature. Our measured line intensities are within 2 – 5% of the literature values.

Broadening coefficients of CH_4 with N_2 , O_2 and He were measured and compared with previous studies. Broadening parameters are highest for N_2 , followed by O_2 and He . Air–broadening parameters were also compared with data in the literature. Further, the present work is the first known determination of H_2 , Ar and CO_2 broadening coefficients of CH_4 for the P(11) manifold of the ν_3 band. Narrowing parameters of CH_4 in the presence of N_2 , O_2 , Ar and CO_2 are measured and compared with literature data.

The present spectroscopic data may have significant implications for the interpretation of atmospheric and astrophysical data of CH₄ interacting with N₂, O₂, Air, H₂, He, Ar and CO₂. Nitrogen and oxygen are the primary constituents of earth's atmosphere whereas Nitrogen is the main compound in Titan's atmosphere. Argon is also a constituent of the Titan's atmosphere. H₂ and He are the main constituent of the atmosphere of the giant planet Jupiter. Carbon dioxide is found mostly in the atmosphere of Venus and Mars. Hence the measured CH₄ spectroscopic parameters are important for knowing the atmospheres of these planets and satellites in the outer Solar System. Our data may also help in the compilation and validation of the HITRAN database.

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Tables

Table 1. The identified line transitions of vibration–rotation in the P(11)– manifold region of the ν_3 band of CH_4 studied in this work.

* Line positions and their corresponding assignments are taken from the HITRAN 2012 database [1]. J' , C' , N' (respectively, J'' , C'' , N'') are the upper (respectively, lower) state labels; J : rotational quantum number, C : symmetry label, N : order index [49].

<i>Line position*, cm^{-1}</i>	<i>assignment</i>					
	J'	C'	N'	J''	C''	N''
2905.633661	10	F2	41	11	F1	3
2905.697533	10	E	27	11	E	2
2905.813742	10	F1	39	11	F2	3
2906.094436	9	A2	14	10	A1	1
2906.282471	10	F2	42	11	F1	2
2906.588832	10	E	28	11	E	1
2906.647628	10	F1	40	11	F2	2
2906.734957	10	A1	15	11	A2	1
2906.842536	9	A1	12	10	A2	1
2906.863001	9	F1	39	10	F2	1
2907.321273	10	F1	41	11	F2	1
2907.336088	10	F2	43	11	F1	1
2908.331351	7	A1	5	6	A2	1
2908.764164	9	A1	25	10	A2	2
2909.243959	9	F2	33	10	F1	1
2909.270745	7	F1	18	6	F2	2

Table 2. Absolute line intensities S together with their uncertainties, in the units of ($\text{cm}^{-2} \cdot \text{atm}^{-1}$), of the P(11) manifold of the ν_3 band of CH_4 measured at 297 ± 1 K using Voigt and Galatry models. The last three columns present the percentage differences: $\chi = (S_{\text{Galatry}} - S_{\text{Voigt}}) \times 100 / S_{\text{Galatry}}$, $\delta = (S_{\text{Galatry}} - S_{\text{Rothman et al.}}) \times 100 / S_{\text{Galatry}}$ and $\epsilon = (S_{\text{Galatry}} - S_{\text{Féjard et al.}}) \times 100 / S_{\text{Galatry}}$

* Line positions are taken from the HITRAN 2012 [1]

<i>position*</i> , cm^{-1}	assignment			<i>Line intensities (S), $10^{-2} (\text{cm}^{-2} \cdot \text{atm}^{-1})$</i>				<i>Difference</i>		
	<i>J''</i>	<i>C''</i>	<i>N''</i>	This work (<i>Voigt</i>)	This work (<i>Galatry</i>)	Rothman et al. [1]	Féjard et al. [37]	χ , %	δ , %	ϵ , %
2905.633661	11	F1	3	27.598±0.212	28.030±0.210	28.055	28.0	+3.9	-0.1	+0.1
2905.697533	11	E	2	17.936±0.302	19.043±0.261	18.553	18.5	+1.5	+2.6	+2.8
2905.813742	11	F2	3	27.467±0.342	28.270±0.604	27.7807	27.8	+8.6	+1.6	+1.7
2906.282471	11	F1	2	27.275±0.243	27.385±0.352	27.411	27.3	+2.7	-0.1	+0.3
2906.588832	11	E	1	17.849±0.10	18.530±0.230	18.313	18.2	-6.5	+1.2	+1.8
2906.647628	11	F2	2	26.728±0.303	26.857±0.278	27.510	27.4	+4.7	-2.4	-2.0
2906.734957	11	A2	1	45.353±0.433	46.005±0.334	45.8073	45.9	+5.7	-0.1	+0.2
2907.321273	11	F2	1	27.00±0.361	27.168±0.335	28.278	28.1	+ 3.0	-4.1	-3.4
2907.336088	11	F1	1	28.507±0.332	28.705±0.320	28.278	28.1	+ 2.0	-1.5	+ 2.1

Table 3. Collisional-broadening coefficients of CH₄ with He (γ_{He}) at 297 ± 1 K. Measurements are compared against Grigoriev et al. [41]. Last two columns present the percentage differences; $\chi = (\gamma_{\text{Galatry}} - \gamma_{\text{Voigt}}) \times 100 / \gamma_{\text{Galatry}}$ and $\delta = (\gamma_{\text{Galatry}} - \gamma_{\text{Grigoriev et al.}}) \times 100 / \gamma_{\text{Galatry}}$

* Line positions are taken from the HITRAN 2012 [1]

<i>position</i> *, cm^{-1}	<i>assignment</i>			<i>Broadening coefficients</i> (γ_{He}), $10^{-3} (\text{cm}^{-1} \cdot \text{atm}^{-1})$			<i>Difference</i>	
	<i>J''</i>	<i>C''</i>	<i>N''</i>	This work (<i>Voigt</i>)	This work (<i>Galatry</i>)	Grigoriev et al. [41]	χ , %	δ , %
2905.633661	11	F1	3	32.63±0.158	33.94±0.134	38.3 (2)	+3.9	-12.8
2905.697533	11	E	2	22.13±0.221	22.47±0.465	24.8 (2)	+1.5	-10.4
2905.813742	11	F2	3	36.96±0.310	40.43±0.185	36.6 (5)	+8.6	+9.5
2906.282471	11	F1	2	35.3±0.124	36.29±0.083	37.3 (2)	+2.7	-2.8
2906.588832	11	E	1	30.48±0.044	28.61±0.241	33.4 (4)	-6.5	-16.7
2906.647628	11	F2	2	34.03±0.114	35.73±0.287	37.0 (7)	+4.7	-3.5
2906.734957	11	A2	1	34.48±0.064	36.57±0.339	34.8 (3)	+5.7	+4.8
2907.321273	11	F2	1	33.17±0.094	34.20±0.339	---	+3.0	---
2907.336088	11	F1	1	31.49±0.371	32.15±0.339	---	+2.0	---

Table 4. Collisional-broadening coefficients of CH₄ with N₂(γ_{N_2}) at 297 ± 1 K. Measurements are compared against Benner et al. [29]. Last two columns present the percentage differences; $\chi=(\gamma_{Galatry} - \gamma_{Voigt}) \times 100/\gamma_{Galatry}$ and $\delta=(\gamma_{Galatry} - \gamma_{Benner \text{ et al.}}) \times 100/\gamma_{Galatry}$

* Line positions are taken from the HITRAN 2012 [1]

<i>position*</i> , cm^{-1}	assignment			<i>Broadening coefficients</i> (γ_{N_2}), $10^{-3} (cm^{-1}.atm^{-1})$			<i>Difference</i>	
	<i>J''</i>	<i>C''</i>	<i>N''</i>	This work (<i>Voigt</i>)	This work (<i>Galatry</i>)	Benner et al. [29]	χ , %	δ , %
2905.633661	11	F1	3	52.88 $\pm$ 0.116	57.39 $\pm$ 0.74	50.4 (9)	+7.8	+12.2
2905.697533	11	E	2	32.27 $\pm$ 0.069	37.68 $\pm$ 0.54	42.4 (3)	+14.3	-12.5
2905.813742	11	F2	3	54.92 $\pm$ 0.069	58.93 $\pm$ 0.456	51.1 (11)	+6.8	+13.3
2906.282471	11	F1	2	50.70 $\pm$ 0.074	53.33 $\pm$ 0.128	55.2 (6)	+4.9	-3.5
2906.588832	11	E	1	50.47 $\pm$ 0.172	48.85 $\pm$ 0.112	52.5 (5)	- 3.3	-7.5
2906.647628	11	F2	2	48.49 $\pm$ 0.470	47.16 $\pm$ 0.236	53.5 (7)	-2.8	-13.4
2906.734957	11	A2	1	42.35 $\pm$ 0.153	45.38 $\pm$ 0.215	47.2 (5)	+6.7	-4.0
2907.321273	11	F2	1	41.15 $\pm$ 0.569	43.15 $\pm$ 0.325	---	+4.6	---
2907.336088	11	F1	1	41.33 $\pm$ 0.876	42.64 $\pm$ 0.236	---	+3.1	---

Table 5. Collisional-broadening coefficients of CH₄ with O₂ (γ_{O_2}) at 297 ± 1 K. Measurements are compared against Benner et al. [29]. Last two columns present the percentage differences; $\chi=(\gamma_{Galatry} - \gamma_{Voigt}) \times 100/\gamma_{Galatry}$ and $\delta=(\gamma_{Galatry} - \gamma_{Benner et al.}) \times 100/\gamma_{Galatry}$

* Line positions are taken from the HITRAN 2012 [1]

<i>position*</i> , cm^{-1}	assignment			<i>Broadening coefficients</i> (γ_{O_2}), 10^{-3} ($cm^{-1}.atm^{-1}$)			<i>Difference</i>	
	<i>J''</i>	<i>C''</i>	<i>N''</i>	This work (<i>Voigt</i>)	This work (<i>Galatry</i>)	Benner et al. [29]	χ , %	δ , %
2905.633661	11	F1	3	49.29±0.163	50.05±0.220	50.4 (7)	+1.5	+2.2
2905.697533	11	E	2	32.21±0.054	34.48±0.231	42.0 (2)	+6.6	+23.3
2905.813742	11	F2	3	50.81±0.257	58.01±0.080	54.2 (2)	+12.4	+6.2
2906.282471	11	F1	2	49.26±0.074	51.12±0.023	53.7 (2)	+3.6	+8.3
2906.588832	11	E	1	47.09±0.384	41.01±0.032	50.2 (4)	-14.8	+6.2
2906.647628	11	F2	2	45.87±0.242	48.27±0.287	51.8 (4)	+5.0	+11.4
2906.734957	11	A2	1	41.31±0.030	44.37±0.067	46.8 (1)	+6.9	+11.7
2907.321273	11	F2	1	39.46±0.134	42.11±0.145	---	+6.3	---
2907.336088	11	F1	1	39.16±0.059	41.58±0.215	---	+5.8	---

Table 6. Collisional-broadening coefficients of CH₄ with air (γ_{air}) at 297 ± 1 K. Air-broadening is obtained by $\gamma_{\text{air}}=0.79\gamma_{\text{N}_2} + 0.21\gamma_{\text{O}_2}$. Measurements are compared against HITRAN 2012 [1] and Benner et al. [29]. Last three columns present the percentage differences; $\chi=(\gamma_{\text{Galatry}} - \gamma_{\text{Voigt}})\times 100/\gamma_{\text{Galatry}}$, $\delta=(\gamma_{\text{Galatry}} - \gamma_{\text{Rothman et al.}})\times 100/\gamma_{\text{Galatry}}$ and finally $\epsilon=(\gamma_{\text{Galatry}} - \gamma_{\text{Benner et al.}})\times 100/\gamma_{\text{Galatry}}$

* Line positions are taken from the HITRAN 2012 [1]

<i>position</i> *, <i>cm</i> ⁻¹	assignment			<i>Broadening coefficients</i> (γ_{air}), <i>10</i> ⁻³ (<i>cm</i> ⁻¹ . <i>atm</i> ⁻¹)				<i>Difference</i>		
	<i>J</i> ''	<i>C</i> ''	<i>N</i> ''	This work (<i>Voigt</i>)	This work (<i>Galatry</i>)	Rothman et al. [1]	Benner et al. [29]	χ , %	δ , %	ϵ , %
2905.633661	11	F1	3	51.12±0.126	55.85±0.631	50.00	50.5 (10)	+8.5	+10.5	+9.6
2905.697533	11	E	2	32.26±0.066	37.01±0.475	41.20	41.2 (4)	+12.8	-11.3	-11.3
2905.813742	11	F2	3	54.06±0.108	58.74±0.377	50.00	49.9 (11)	+8.0	+14.9	+15.0
2906.282471	11	F1	2	50.40±0.074	52.86±0.106	54.10	54.1 (6)	+4.6	-2.3	-2.3
2906.588832	11	E	1	49.76±0.216	47.20±0.095	51.60	51.6 (4)	-5.4	-9.3	-9.3
2906.647628	11	F2	2	47.94±0.422	47.39±0.247	53.60	53.6 (4)	-1.2	-13.1	-13.1
2906.734957	11	A2	1	42.13±0.127	45.17±0.184	53.80	46.9 (4)	+6.7	-19.1	-3.8
2907.321273	11	F2	1	40.79±0.477	42.93±0.287	50.20	---	+5.0	-16.9	---
2907.336088	11	F1	1	40.87±0.704	42.42±0.232	49.80	---	+3.6	-17.4	---

Table 7. Ratios (γ_{ratio}) of collisional-broadening coefficients averaged over the nine transitions of the P(11) manifold of the ν_3 band of CH_4 . Literature data are taken from Pine and Gabard 2003 [39]; Pine [28]; Tran et al. [9] and Benner et al. [29].

^s Self-broadening data of CH_4 are taken from the HITRAN 2012 [1] to calculate $\gamma_{\text{ratio}}(\text{CH}_4/\text{N}_2)$

γ_{ratio}	CH_4/N_2	O_2/N_2	H_2/N_2	Ar/N_2	CO_2/N_2	He/H_2	He/Ar	He/CO_2
Voigt (this work) ^s	1.476±0.030	0.954±0.024	1.136±0.117	0.757±0.098	1.308±0.107	0.623±0.033	0.944±0.133	0.540±0.029
Galatry (this work) ^s	1.408±0.024	0.947±0.059	1.114±0.109	0.798±0.086	1.312±0.109	0.624±0.056	0.877±0.130	0.531±0.063
Pine and Gabard [39]	1.261 (038)	0.943(013)	1.017 (039)	0.881 (013)	---	0.633(011)	0.732(025)	
Pine [25]	1.249 (036)	0.937(015)	1.013 (040)	0.878 (011)	---	0.631(015)	0.725(026)	
Tran et al. [9]	---	---	---	---	---	0.63	---	
Benner et al. [29]	---	0.99143	---	---	---	---	---	

Table 8. Narrowing parameters β measured at 297 ± 1 K for CH₄ perturbed by N₂, O₂, Ar and CO₂ for the P(11) manifold. Retrieved β values are obtained by simulating the measured line shape with Galatry profile

<i>Line position,</i> <i>cm⁻¹</i>	assignment			<i>Narrowing coefficients (β), 10⁻³ (cm⁻¹.atm⁻¹)</i>			
	<i>J''</i>	<i>C''</i>	<i>N''</i>	$\beta_{\text{CH}_4-\text{N}_2}$	$\beta_{\text{CH}_4-\text{O}_2}$	$\beta_{\text{CH}_4-\text{Ar}}$	$\beta_{\text{CH}_4-\text{CO}_2}$
2905.633661	11	F1	3	25.01±1.42		18.03±4.0	23.01±2.3
2905.697533	11	E	2	29.04±2.69	18.32±1.16	25.86±2.34	23.80±3.3
2905.813742	11	F2	3	26.79±2.90	25.27±5.0	24.32±4.0	26.20±3.5
2906.282374	11	F1	2	17.90±2.30	11.0±3.3	15.08±2.90	20.93±4.0
2906.588591	11	E	1	23.97±3.55	15.74±3.0	26.43±4.29	
2906.647660	11	F2	2	14.70±2.0	22.17±7.35	25.19±2.04	
2906.734832	11	A2	1	36.95±2.66	25.29±1.4	27.44±2.34	42.27±8.3

Table 9. Averaged narrowing parameters β at 297 ± 1 K for CH_4 perturbed by N_2 , O_2 , Ar and CO_2 . Data are compared with measurements of Pine [28] and Mondelain et al. [31].

*Since the β measurements for the two transitions at 2914.49860 and $2921.33185 \text{ cm}^{-1}$ of CH_4 in the $\nu_2+\nu_4$ combination band are very close, these two β values are averaged to obtain one value for comparison

<i>Transition averaged narrowing coefficients (β), $10^{-3} (\text{cm}^{-1}.\text{atm}^{-1})$</i>				
	$\beta_{\text{CH}_4-\text{N}_2}$	$\beta_{\text{CH}_4-\text{O}_2}$	$\beta_{\text{CH}_4-\text{Ar}}$	$\beta_{\text{CH}_4-\text{CO}_2}$
This work (Galatry)	24.91$\pm$2.50	19.63$\pm$3.53	23.19$\pm$3.13	27.24$\pm$4.28
Pine [28] (Rautian)	20.50 (15)	18.46 (13)	21.25 (16)	----
Mondelain et al. [31] (Galatry)*	27.4 (10.5)	24.95 (10.5)	----	----
Mondelain et al. [31] (Rautian)*	20.65 (8)	18.90 (2.7)		----

Figures

Fig. 1. Experimental setup

Fig. 2. An example of the measured raw data traces of the transmission (red lines), background (black lines) and etalon (blue lines). The measured spectrum is taken under experimental conditions of 1 % CH_4/N_2 at a total pressure of 80 Torr and gas temperature of 297 ± 1 K. The measured transmission is divided into three regions for clarity. The identification and frequency of all transitions are given in Table 1

Fig. 3. (a): Measured absorbance of P (11) F1 2 assignment in the ν_3 band of CH₄. Simulated Voigt and Galatry models are also shown. (b): The residuals in terms of the percentage difference between measured and simulated spectra. The measured spectrum is taken under experimental conditions of 1% CH₄/N₂ at a total pressure of 80 Torr and gas temperature of 297 ± 1 K

Fig. 4. The integrated absorbance area for the studied P(11) manifold of CH_4 for a 1% CH_4/H_2 mixture at gas temperature at 297 ± 1 K. Area is plotted as a function of the product of total pressure (P), optical path length (L) and the mole fraction of methane in the mixture X_{CH_4} . Line shapes are fitted using Voigt profile (full symbols; (a)) and Galatry profile (open symbols; (b)). Integrated absorbances of some transitions are quite similar and thus difficult to distinguish on the plot

Fig. 5. (a): Absolute line intensity (S), in the unit of ($\text{cm}^{-2} \cdot \text{atm}^{-1}$), at 297 ± 1 K for the P (11) manifold of the ν_3 band of CH_4 , measured using Voigt (full symbols) and Galatry (open symbols) profiles. (b): Averaged line intensities of the six mixtures are compared with HITRAN 2012 [1] and Féjard et al. [37]

Fig. 6. Collisional widths (Γ_C) for the studied P(11) manifold of CH_4 for a 1% CH_4/H_2 mixture at gas temperature at 297 ± 1 K. Line shapes are fitted using Voigt profile (full symbols; (a)) and Galatry profile (open symbols; (b)). Collisional widths of some transitions are quite similar and thus difficult to distinguish on the plot. The linear fits are used to retrieve the broadening coefficients γ_i , according to Eq. (8)

Fig. 7. Collisional-broadening coefficients of CH_4 for P(11) manifold of the ν_3 band in the presence of (a): H_2 partner (γ_{H_2}), (b): Ar partner (γ_{Ar}) and (c): CO_2 partner (γ_{CO_2}). Study is performed using both Voigt (full symbols) and Galatry (open symbols) profiles. Error bars are standard deviations of the measurements

Fig. 8. (a): Collisional narrowing z parameter as a function of pressure, (b): Collisional narrowing coefficient β as a function of pressure. Data are plotted for two CH₄ transitions [P(11) F1 3 and P(11) E 2] perturbed by N₂. Line shapes were simulated using Galatry profile