Intensities, broadening and narrowing parameters in the $\nu_3$ band of methane

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The P-branch of methane's $\nu_3$ 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 the Dicke effect have also been investigated. A narrow emission line-width ($\sim$0.0001 cm$^{-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.

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1. Introduction

The 3–4 $\mu$m 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 $\mu$m [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 $\mu$m, 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 $\nu_1$ (2917 cm$^{-1}$), symmetric bend $\nu_2$ (1534 cm$^{-1}$), asymmetric stretch $\nu_3$ (3019 cm$^{-1}$) and the asymmetric bend $\nu_4$ (1311 cm$^{-1}$). Due to its strong IR absorption, the $\nu_3$ band near 3.4 $\mu$m 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 $\nu_3+\nu_4$ 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 $\nu_3$ and
2ν3 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 N2- broadening coefficients were measured for several transitions by Devi et al. [26] in the spectral range from 2870 to 2883 cm⁻¹ (including the ν3 and ν2+ν4 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) spectrometer at 0.01 cm⁻¹ resolution for 75 individual vibration sphere using the PicoSDLA-CH4 spectrometer. The spectro-frequency-generation (DFG) laser near 3086 cm⁻¹ was used to monitor in-situ CH4 in the middle atmosphere using the Voigt profile as well as the Rautian (hard-shifting parameters were obtained from spectra simulations. In their work, these measurements were conducted for atmospheric applications over a large temperature range (90–296 K). 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 as collision partners in the spectral range from 2726 to 3200 cm⁻¹ and relatively low temperatures (225–296 K). 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 ν₃ 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 ν₃ band of methane. Air-broadening coefficients were deduced from the O₂ and N₂ measurements. Narrowing parameters of CH₄ with N₂, O₂, Ar and CO₂ perturbers 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 μm, 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 (0.8V 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 min. The absolute line positions of CH₄ during the modulation of the

![Fig. 1. Experimental setup.](image-url)
Table 1
The identified line transitions of vibration–rotation in the P(11)-manifold region of the ν3 band of CH4 studied in this work.

<table>
<thead>
<tr>
<th>Line position, cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>N</td>
</tr>
<tr>
<td>2905.63661</td>
<td>10</td>
</tr>
<tr>
<td>2905.69753</td>
<td>10</td>
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<tr>
<td>2905.81374</td>
<td>10</td>
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<tr>
<td>2906.09443</td>
<td>9</td>
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<tr>
<td>2906.28728</td>
<td>10</td>
</tr>
<tr>
<td>2906.34957</td>
<td>10</td>
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<tr>
<td>2906.84253</td>
<td>9</td>
</tr>
<tr>
<td>2907.33608</td>
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<tr>
<td>2908.76416</td>
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<tr>
<td>2907.33608</td>
<td>10</td>
</tr>
<tr>
<td>2908.76416</td>
<td>9</td>
</tr>
</tbody>
</table>

* Line positions and their corresponding 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].

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 cm⁻¹ spectral range. In Fig. 2, the measured transmission is divided into three regions for clarity. As shown in Fig. 2, 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(11) 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 cm⁻¹). However, those lines are very weak and not studied in this work. All assignments in the 2905–2908 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:

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

where the normalized frequency \( x \) and collisional coefficient \( y \) are given by

\[ x = \frac{\nu - \nu_0}{\gamma_D} \]

\[ y = \frac{\nu C}{\gamma_D} \]

The quantity \( \nu - \nu_0 \) (cm⁻¹) is the detuning from the line-center frequency, \( \nu_0 \) (cm⁻¹). The parameter \( \gamma_D \) (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 \( \gamma_D \) by

\[ \Delta\nu_D = 2\sqrt{\ln 2} \gamma_D = 7.162 \times 10^{-7} \nu_0 \sqrt{T/M} \]
where $T$ ($-297 \pm 1$ K) is the gas temperature and $M$ (=16 g/mol) is the molecular weight of the absorbing species of CH$_4$. The parameter $P_P$ (cm$^{-1}$) is the collisional width, and $P_P = \Gamma_c$.

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:

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

where $z$ is a normalized parameter related to the collisional narrowing coefficient $\beta$ (cm$^{-1}$ atm$^{-1}$) by

$$z = P\beta/\gamma_D$$  \hspace{1cm} (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 $\gamma_i$ are calculated using the following equations:

$$A = P_L X_{CH_4} S$$  \hspace{1cm} (7)

$$\Gamma_c = P_L \gamma_{self} X_{CH_4} + (1 - X_{CH_4}) \gamma_i$$  \hspace{1cm} (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$^{-1}$ atm$^{-1}$) is the self-broadening coefficient (CH$_4$→CH$_4$) and $\gamma_i$ (cm$^{-1}$ 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 $\sigma_{sp}$ in spectroscopic measurement of line intensities, collisional-broadening coefficients and narrowing parameters is obtained by taking into account the major sources of uncertainty:

$$\sigma_{sp} = \sqrt{(e_A)^2 + (e_X)^2 + (e_P)^2 + (e_\gamma)^2 + (e_T)^2 + (e_\beta)^2}$$  \hspace{1cm} (9)

where $sp$ and $\sigma_{sp}$ stand for a given spectroscopic parameter and its associated standard deviation respectively. The error on the absorbance $e_A$ ranged from 1% to 2%. Each binary mixture was prepared in a mixing tank and the uncertainty $e_X$ 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 $e_L$ 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 $e_T$ 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 $\beta$. The systematic error in the fitting process $e_\beta$ 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 2907.3360088 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% CH₄/H₂ mixture. For each foreign gas, the CH₄ 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 \( \approx 0.99 \) 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, line 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 in Table 2 report the percentage difference between retrieved values using the Voigt profile and the Galatry profile (column \( \chi \)), between values obtained by Galatry profile and data taken from the HITRAN 2012 [1] (column \( \delta \)), and between values obtained by Galatry profile and data of Féjard et al. [37] (column \( \epsilon \)). 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 \( \Gamma_c \) is a linear function of the gas pressure and thus the collisional-broadening parameters \( \gamma_i \) (\( i = \text{N}_2, \text{O}_2, \text{H}_2, \text{He}, \text{Ar} \) and \( \text{CO}_2 \)) can be retrieved from the linear fits. The total collisional width has a small contribution from \( \gamma_{self} \) (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
Table 2

Absolute line intensities $S$ together with their uncertainties, in the units of (cm$^{-2}$ atm$^{-1}$), of the P(11)-manifold of the $v_2$ band of CH$_4$ measured at 297 ± 1 K using Voigt and Galatry models. The last three columns present the percentage differences: $\gamma = (S_{\text{Galatry}} - S_{\text{Voigt}}) \times 100/S_{\text{Galatry}}$, $\delta = (S_{\text{Galatry}} - S_{\text{Rothman et al.}}) \times 100/S_{\text{Galatry}}$ and $\epsilon = (S_{\text{Galatry}} - S_{\text{Féjard et al.}}) \times 100/S_{\text{Galatry}}$.

<table>
<thead>
<tr>
<th>Position*, cm$^{-1}$</th>
<th>Assignment</th>
<th>Line intensities ($S$), 10$^{-2}$ (cm$^{-2}$ atm$^{-1}$)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J^*$</td>
<td>$C^*$</td>
<td>$N^*$</td>
</tr>
<tr>
<td>2905.633661</td>
<td>11 F1</td>
<td>3</td>
<td>27.598 ± 0.212 28.030 ± 0.210 28.055</td>
</tr>
<tr>
<td>2905.697533</td>
<td>11 E</td>
<td>2</td>
<td>19.796 ± 0.302 19.043 ± 0.261 18.553</td>
</tr>
<tr>
<td>2905.813742</td>
<td>11 F2</td>
<td>3</td>
<td>27.467 ± 0.342 28.270 ± 0.604 27.7807</td>
</tr>
<tr>
<td>2906.282471</td>
<td>11 F1</td>
<td>2</td>
<td>27.275 ± 0.243 27.385 ± 0.352 27.411</td>
</tr>
<tr>
<td>2906.588332</td>
<td>11 E</td>
<td>1</td>
<td>17.849 ± 0.10 18.530 ± 0.230 18.313</td>
</tr>
<tr>
<td>2906.647628</td>
<td>11 F2</td>
<td>2</td>
<td>26.728 ± 0.303 26.857 ± 0.278 27.510</td>
</tr>
<tr>
<td>2907.321273</td>
<td>11 F2</td>
<td>1</td>
<td>45.353 ± 0.433 46.005 ± 0.334 45.8073</td>
</tr>
<tr>
<td>2907.336088</td>
<td>11 F1</td>
<td>1</td>
<td>27.00 ± 0.361 27.168 ± 0.335 28.278</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>28.507 ± 0.332 28.705 ± 0.320 28.278</td>
</tr>
</tbody>
</table>

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

4.21. He, N$_2$, and O$_2$ bath gases

Retrieved values of $\gamma_i$ where $i=\text{He, N}_2$, 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 $\gamma_{\text{He}}$ is much lower than $\gamma_{\text{N}}$ and $\gamma_{\text{O}_2}$. O$_2$-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 $\gamma_{\text{He}}$ (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 $\gamma_{\text{He}}$ by combining measurements and semi-classical calculations. In Tables 4 and 5, measured values of $\gamma_{\text{N}}$ and $\gamma_{\text{O}_2}$ 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 $\gamma_{\text{air}}$ by using $\gamma_{\text{air}} = 0.79\gamma_{\text{N}} + 0.21\gamma_{\text{O}_2}$. In general, we observed that values of $\gamma_{\text{air}}$ and $\gamma_{\text{N}}$ are nearly equal. The deduced $\gamma_{\text{air}}$ 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. H₂, Ar, and CO₂ bath gases

The first measurements of \( \gamma_{\text{H}_2} \), \( \gamma_{\text{Ar}} \), and \( \gamma_{\text{CO}_2} \) 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 \( \gamma_{\text{Ar}} \) are smaller by about 41–66% compared with \( \gamma_{\text{H}_2} \) and \( \gamma_{\text{CO}_2} \) values.

4.2.3. Transition-averaged ratios

Ratios of broadening coefficients are used readily for atmospheric and astrophysical interpretations of acquired...
Collisional-broadening coefficients of CH4 with air ($\gamma_{air}$) at 297 ± 1 K. Air-broadening is obtained by $\gamma_{air} = 0.79 n_{Ar} + 0.21 n_{O2}$. Measurements are compared against HITRAN 2012 [1] and Benner et al. [29]. Last three columns present the percentage differences: $\chi = (\gamma_{Galatry} - \gamma_{Voigt}) \times 100/\gamma_{Galatry}$, $\delta = (\gamma_{Galatry} - \gamma_{Rothman et al.}) \times 100/\gamma_{Galatry}$ and finally $\epsilon = (\gamma_{Galatry} - \gamma_{Benner et al.}) \times 100/\gamma_{Galatry}$.

<table>
<thead>
<tr>
<th>Position*, cm⁻¹</th>
<th>Assignment</th>
<th>Breathing coefficients ($\gamma_{ratio}$) × 10⁻³ (cm⁻¹ atm⁻¹)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J^\prime$</td>
<td>$C^\prime$</td>
<td>This work (Voigt)</td>
</tr>
<tr>
<td>2905.633661</td>
<td>11 F1</td>
<td>1</td>
<td>51.12 ± 0.126</td>
</tr>
<tr>
<td>2905.697533</td>
<td>11 E</td>
<td>2</td>
<td>32.26 ± 0.066</td>
</tr>
<tr>
<td>2905.813742</td>
<td>11 F2</td>
<td>3</td>
<td>54.06 ± 0.108</td>
</tr>
<tr>
<td>2906.282271</td>
<td>11 F1</td>
<td>2</td>
<td>50.40 ± 0.074</td>
</tr>
<tr>
<td>2906.588382</td>
<td>11 E</td>
<td>1</td>
<td>49.76 ± 0.216</td>
</tr>
<tr>
<td>2906.647628</td>
<td>11 F2</td>
<td>2</td>
<td>47.94 ± 0.422</td>
</tr>
<tr>
<td>2906.734957</td>
<td>11 A2</td>
<td>1</td>
<td>42.13 ± 0.127</td>
</tr>
<tr>
<td>2907.321273</td>
<td>11 F2</td>
<td>1</td>
<td>40.79 ± 0.477</td>
</tr>
<tr>
<td>2907.336088</td>
<td>11 F1</td>
<td>1</td>
<td>40.87 ± 0.704</td>
</tr>
</tbody>
</table>

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

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 $\gamma_{ratio}$ for (CH4/N2) is larger by about 1% compared to the value determined in [28]. Relatively small differences (< 3%) were observed for $\gamma_{ratio}$ (O2/N2, He/He) between our work and other literature data. In the case of H2/N2, the obtained $\gamma_{ratio}$ 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 $\gamma_{ratio}$ 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 $\gamma_{ratio}$ corresponds to sixty-six CH4 transitions of the Q branch of the $\nu_3$ band covering the 3012–3018 cm⁻¹ spectral region. The O2/N2 $\gamma_{ratio}$ 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/He $\gamma_{ratio}$ 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 $\beta$ for different combinations of CH4/bath gas. For high accuracy measurements, studies were conducted at various pressures for most of the transitions of the P(11) manifold in the $\nu_3$ band. For the relatively small-mass colliders (H2 and He), the corresponding $\beta$ 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 $\beta$ 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.
Table 7
Ratios ($\gamma$) of collisional-broadening coefficients averaged over the nine transitions of the $P(11)$ manifold of the $\nu_3$ 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].

|Transition| 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$_2$
<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Voigt (this work)*</td>
<td>1.476 ± 0.030</td>
<td>0.954 ± 0.024</td>
<td>1.136 ± 0.117</td>
<td>0.757 ± 0.098</td>
<td>1.308 ± 0.107</td>
<td>0.623 ± 0.033</td>
<td>0.944 ± 0.133</td>
<td>0.540 ± 0.029</td>
</tr>
<tr>
<td>Galatry (this work)*</td>
<td>1.408 ± 0.024</td>
<td>0.947 ± 0.059</td>
<td>1.114 ± 0.109</td>
<td>0.798 ± 0.086</td>
<td>1.312 ± 0.109</td>
<td>0.624 ± 0.056</td>
<td>0.877 ± 0.130</td>
<td>0.531 ± 0.063</td>
</tr>
<tr>
<td>Pine and Gabard [39]</td>
<td>1.261 (038)</td>
<td>0.943(013)</td>
<td>1.017 (039)</td>
<td>0.881 (013)</td>
<td>–</td>
<td>0.636(011)</td>
<td>0.749(025)</td>
<td>–</td>
</tr>
<tr>
<td>Pine [25]</td>
<td>1.249 (036)</td>
<td>0.937(015)</td>
<td>1.013 (040)</td>
<td>0.878 (011)</td>
<td>–</td>
<td>0.631(015)</td>
<td>0.725(026)</td>
<td>–</td>
</tr>
<tr>
<td>Tran et al. [9]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.63</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Benner et al. [29]</td>
<td>–</td>
<td>0.99143</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

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

 Collisional narrowing parameters $\beta$ of CH$_4$ with N$_2$, O$_2$, Ar and CO$_2$ perturbers were deduced by fitting 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 gas pressure for the $P(11)$ F1 3 and $P(11)$ E 2 transitions in a CH$_4$/N$_2$ mixture. The corresponding $\beta$ 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 $\beta$ 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 $\beta$ coefficients very difficult.

Narrowing parameters are not available in literature for the transitions studied in this work. We compared our transition-averaged $\beta$ values with narrowing measurements carried out in other wavenumber regions. Pine [28] determined $\beta$ parameters in the $\nu_3$ band over 3012–3020 cm$^{-1}$ region using the Rautian model. Mondelain et al. [31] measured $\beta$ 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 $\beta$ 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 of CH$_4$ over 2905–2907 cm$^{-1}$ spectral region. Measurements were conducted at $297 \pm 1$ K in binary mixtures with 1% CH$_4$/N$_2$, CH$_4$/O$_2$, CH$_4$/He, CH$_4$/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 the 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 $\nu_3$ 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 CH$_4$ interacting with N$_2$, O$_2$, Ar, H$_2$, He, Ar and CO$_2$. 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. H$_2$ and He are the main constituents 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.

Acknowledgments

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