H₂-Induced Pressure Broadening and Pressure Shift in the $P$-Branch of the $ν₃$ Band of CH₄ from 300 to 700 K

Ehsan Gharib-Nezhad¹, Alan N. Heays²,³, Hans A. Bechtel⁴, James R. Lyons²

¹School of Molecular Sciences, Arizona State University, Tempe, AZ. 85287, USA.
²School of Earth and Space Exploration, Arizona State University, Tempe, AZ. 85287, USA.
³NASA Astrobiology Institute, NASA Ames Research Center, Moffett Field, CA., USA.
⁴Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA. 94720, USA.

Abstract

For accurate modelling of observations of exoplanet atmospheres, quantification of the pressure broadening of infrared absorption lines for and by a variety of gases at elevated temperatures is needed. High-resolution high-temperature H₂-pressure-broadened spectra are recorded for the CH₄ $ν₃$-band $P$-branch. Measured linewidths for 116 transitions between 2840 and 3000 cm⁻¹ with temperature and pressures ranging between 300 and 700 K, and 10 and 933 Torr, respectively, were used to find rotation- and tetrahedral-symmetry-dependent coefficients for pressure and temperature broadening and pressure-induced lineshfts. The new pressure-broadening data will be useful in radiative-transfer models for retrieving the properties of observed exoplanet atmospheres.

Keywords: Methane (CH₄), High-Temperature FTIR Spectroscopy, High-Temperature Pressure-induced collisional broadening and shift, Lorentzian linewidth coefficients, exoplanetary atmospheres, hydrogen-dominant atmospheres

1. Introduction

Methane (CH₄) has been observed in the infrared spectra of different solar-system atmospheres including those of terrestrial planets (e.g., on the surface of Mars [1, 2]), Jovian planets (e.g., Jupiter, Saturn, Uranus [3, 4]), and Titan [5, 6]. The abundance of CH₄ is also important in constraint understanding the C/O ratio in the atmospheres of brown dwarfs and exoplanets, as well as understanding their formation history [7, 8]. Because the thermochemically dominant carbon-bearing molecule at T>1200 K is CO and at T<800 K is CH₄ [6], their mixing ratios with CO₂ are used as a temperature probe and to determine super-Earths/sub-Neptune metallicities [9, 10]. Moreover, CH₄ near-infrared (NIR) spectra are an important tool for classifying brown dwarf types (e.g., T-dwarfs [11]). Despite extensive endeavors to model the chemical composition of exoplanetary atmospheres by means of radiative transfer modeling (i.e., transmission and emission exoplanetary spectra [12, 14]), a proposed detection of CH₄ is still under debate [15]. Additionally, high-resolution Earth-based searches of methane through the cross-correlation technique have been unsuccessful [16]. However, it has been argued thermochemically that CH₄ is one of the main absorbers in super-Earth to sub-Neptune atmospheres [17]. H₂ is the major broadening molecule (or perturber) in these exoplanetary atmospheres, and therefore, the accuracy of radiative transfer modeling, particularly for the cross-correlation technique (see section 3.5 in [18]), relies strongly upon the accuracy and completeness of CH₄ spectroscopic data including rovibrational transitions and pressure-broadening coefficients appropriate for high-temperature and H₂-dominated atmospheres [19, 20]. Accurate quantification...
of pressure-broadening coefficients at room- and high-temperature is fundamental because they influence the absorption cross-section data and, therefore, the modeled exoplanet atmospheric spectra \[20, 21\].

Methane is a tetrahedral molecule with five symmetry species: \(A_1, A_2, E, F_1, \) and \(F_2\). The \(v_3\) fundamental band arises from asymmetric C–H stretching (see chapter 7 in \[22\]). Given the relevance of CH\(_4\) infrared (IR) absorption and emission in the study of brown dwarfs and planetary/exoplanetary atmospheres, many experimental and theoretical studies recorded or computed the relevant rovibrational transitions. High-resolution IR spectra of CH\(_4\) have been recorded at both room \[23, 24\] and high temperatures \[25–30\]. Additionally, several ab-initio studies have computed the CH\(_4\) rovibrational transitions \[25, 31–34\].

Since the 1980s, several laboratory measurements of the pressure-broadening of CH\(_4\) by various broadeners (hereafter referred to as absorber[@broadener], e.g., CH\(_4@\)\([\text{H}_2]\)) at room temperature have been made. Non-Voigt pressure-broadening coefficients of the CH\(_4@\)\([\text{H}_2, \text{N}_2, \text{Ar, or He}]\) \(v_3\) band \(Q\) branch were analyzed using a laser spectrometer at high resolution \[35–36\] and showed a strong dependency of linewidths on broadener and total angular-momentum quantum number, \(J\). In addition, the measured linewidths are dependent on the tetrahedral symmetry species (i.e., \(A_1, A_2, E, F_1, F_2\)). The \(R\)-branch of the \(3v_3\) overtone (\(\sim 9000\) cm\(^{-1}\)) of CH\(_4@\)\([\text{H}_2]\) was measured up to \(J_{\text{low}} = J'' = 6\) by Fourier transform spectroscopy with 0.01 cm\(^{-1}\) spectral resolution \[37, 38\].

Several studies have used quantum or semi-classical approaches to calculate, predict, and explain pressure broadening of CH\(_4\) in different broadeners (or perturbers) \[39\]. Anderson theory, for instance, utilizes a perturbation approach to compute the line broadening and their temperature-dependence coefficients through electrostatic interactions \[40, 42\]. However, it was shown later that electrostatic forces are not able to explain the broadening for some perturbers such as O\(_2\) and N\(_2\) \[43\]. In comparison, Robert-Bonamy theory \[44\] was used to show the atom-atom potential energy is the main cause of collisional broadening for these species \[45\].

To the best of our knowledge, there are no measurements of CH\(_4@\)\([\text{H}_2]\) (or any other broadeners) at \(T > 315\) K. Measurements for temperatures between 200 and 300 K show the temperature-dependence coefficient \(n_\gamma\), see section \[4, 4\] of the \(v_3\) band of CH\(_4@\)\([\text{Air}]\) and CH\(_4@\)\([\text{N}_2]\) is 0.6 – 1.0 \[46\] and 0.94–0.97 \[43\], respectively. For the \(v_3\) band of CH\(_4@\)\([\text{Air}]\) and CH\(_4@\)\([\text{N}_2]\), \(n_\gamma\) is 0.5 – 0.8 \[47\]. A complete list of literature regarding measurement of temperature-dependence coefficients is reported in Table \[5\].

For this study, we used Fourier-transform infrared spectroscopy (FTIR) to record rovibrational lines of CH\(_4@\)\([\text{H}_2]\) in the \(P\) branch of the \(v_3\) band over the temperature range 300–700 K (Sec. \[2\]). Then, using a least-squares fitting analysis, the Lorentzian linewidth \(\gamma_L\) and temperature-dependence coefficients \(n_\gamma\) are determined for \(J'' = 2 – 17\) (Sec. \[3\]). The dependency of the Lorentzian coefficients on total quantum number \(J''\) and the tetrahedral symmetry species is discussed in Sec. \[4\].

2. Experimental details

2.1. Instrumental setup

All spectra in this study were recorded with a Bruker 125HR infrared Fourier-transform spectrometer located at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL). As shown in Fig. \[1\], the evacuated sample chamber in this model of spectrometer is located between the beam splitter and detector. In this case, the thermal IR emission from the heated sample gas cells does not contribute to the recorded interferogram, and no post-analysis correction for the cell emission is required in comparison with other studies in which the heated cell was placed at the entrance to the spectrometer (e.g., Ref. \[26\]). For measurements at high temperature, we designed a sealed monolithic gas cell. Due to its high transmittance over a spectral range of 2750–3250 cm\(^{-1}\) and high melting point, the whole gas cell and spectral windows are fabricated from fused quartz.

2.2. Recorded Spectra

We recorded spectra for temperatures 300, 500 and 700 K and over a pressure range of \(\sim 0.8 – 7.0\) Torr for CH\(_4\) gas and \(\sim 10 – 933\) Torr (0.013–1.2 atm) of H\(_2\) broadening gas. In total, four quartz gas cells with a path length of 10±0.2 cm were used in these measurements. Different amounts of CH\(_4\) and H\(_2\) gases were inserted in each tube at room temperature and then the port was
Figure 1: Schematic view of the Bruker 125HR IFS spectrometer: both the sample gas cell and the heat tape are located inside the evacuated sample compartment. The infrared emission from the gas cell does not contribute to the interferogram, and the AC-coupled detector also automatically eliminates infrared emission of the gas cell. Additionally, fused silica and Ge filters were used between sample and detector to prevent detector saturation.

sealed. After sealing the gas cell at room temperature with known number densities of CH₄ and H₂, FTIR transmittance spectra of each tube were recorded at three different temperatures: 300, 500, 700 K. Table 1 reports the experimental conditions in detail.

Overall, 12 different spectra of CH₄ were recorded at various resolutions. Figure 2 represents an overview of spectrum #4 (i.e., P(CH₄)=1.1 Torr and P(H₂)=100.0 Torr), which encompasses P, Q, and R branches up to J”=17. In addition, each J’’ consists of a cluster of transitions with various symmetry species and N quantum index. Figure 3 illustrates the modeled spectra for P(7) transitions. The elevated temperature gas pressures, P(CH₄) and P(H₂), were then calculated using the ideal gas law. Table 2 lists the resolution, number of scans, and the P(CH₄) and P(H₂) values for all measurements. Spectrum #1 was used to measure the unbrodened Doppler-width and intensity of each line.

The decomposition of CH₄ is an important issue for high-temperature measurements. To decrease the potential for loss of CH₄, we added 10 Torr of H₂ into the first gas cell at room temperature. The main product of CH₄ + CH₄ bimolecular dissociation in the absence of H₂ is CH₃, but in the presence of H₂ gas as a third-body component, CH₄ will reform. In other words, H₂ gas will decrease the amount of decomposition by increasing the back reaction. Additionally, 10 Torr of H₂ has a negligible pressure-broadening effect. The volume mixing ratios of these gases can be calculated through minimizing Gibbs free energy which is dependent on the temperature, pressure, and gas concentrations. Therefore, we used the online thermodynamical simulator to calculate the fraction of decomposition of pure CH₄ at different temperatures and pressures. Table 3 (case 1) represents the thermodynamic mixing ratios of 0.8 Torr of pure CH₄. Note that these calculations are done up to 900 K while the maximum laboratory temperature in this work is 700 K. Thermal decomposition of pure CH₄ is predicted to occur for temperatures 700 K and above but is suppressed by the mixture of a small amount of H₂. Ultimately, no significant decrease of the CH₄ column density was noted even at 700 K. In this study, the line assignments and the line positions of CH₄ were adopted from HITRAN2016.

The CH₄ and H₂ gases were 99.99% and obtained from Matheson. The gas pressure while filling the sample

Table 1: Experimental conditions and characteristics of the spectra.

| Parameter                          | Value                      |
|-----------------------------------|----------------------------|
| Spectral coverage                 | 2800 – 3200 cm⁻¹           |
| Temperature range                  | 300 – 700 K                |
| CH₄ pressure                       | 0.8 – 7.0 Torr             |
| H₂ pressure                        | 10.0 – 933.3 Torr          |
| Cells path length                  | 10.0±0.2 cm                |
| Number of averaged scans           | 100 – 400                  |
| Gas cell material/windows          | Quartz (SiO₂)              |
| Gas cell transmission range        | 2750 – 3250 cm⁻¹           |
| Light source                       | SiC Globar                 |
| Beam splitter                      | KBr                        |
| Detector                           | MCT LN₂                     |
| Filter                             | fused silica and Ge        |
| Spectral resolution (cm⁻¹)         | 0.01 – 0.005               |
| Apodization function               | Box-car                     |

1 The CH₄ energy levels are labelled by different quantum numbers such as J and C (tetrahedral symmetry), and N (quantum index) defined in Brown et al. [48].

2http://navier.engr.colostate.edu/code/code-4/index.html
Figure 2: The measured spectrum of the CH$_4$ $\nu_3$ band: $P_{CH4}=1.1$ Torr and $P_{H2}=100.0$ Torr. The strong lines ($J''=0$–17) belong to the $\nu_3$ band consisting of $P$, $Q$, and $R$ branches. Weak lines belong to $\nu_3+\nu_4-\nu_4$ and $\nu_2+\nu_3+\nu_2$ combination bands.

Table 2: Summary of the experimental conditions

| # | Tube | $T$ [K] | $R$ [cm$^{-1}$] | Scan$^\dagger$ | $P_{CH4}$ [Torr] | $P_{H2}$ [Torr] |
|---|------|--------|-----------------|------------|-----------------|-----------------|
| 1 | 1    | 300    | 0.005           | 400        | 0.8             | 10.0            |
| 2 | 1    | 500    | 0.005           | 200        | 1.3             | 16.7            |
| 3 | 1    | 700    | 0.005           | 200        | 1.9             | 23.3            |
| 4 | 2    | 300    | 0.01            | 150        | 1.1             | 100.0           |
| 5 | 2    | 500    | 0.01            | 100        | 1.8             | 166.7           |
| 6 | 2    | 700    | 0.01            | 100        | 2.6             | 233.3           |
| 7 | 3    | 300    | 0.01            | 200        | 2.2             | 200.0           |
| 8 | 3    | 500    | 0.01            | 200        | 3.7             | 333.3           |
| 9 | 3    | 700    | 0.01            | 200        | 5.1             | 466.7           |
| 10| 4    | 300    | 0.02            | 100        | 3.0             | 400.0           |
| 11| 4    | 500    | 0.02            | 100        | 5.0             | 666.7           |
| 12| 4    | 700    | 0.02            | 100        | 7.0             | 933.3           |

Table 3: Predicted thermodynamic CH$_4$ volume mixing ratios$^\ddagger$

| $T$ [K] | CH$_4$ (%) | H$_2$ (%) | C$_2$H$_2$ (%) | C$_2$H$_4$ (%) |
|---------|------------|-----------|----------------|---------------|
| Case 1: pure (100%) | 0.8 Torr of CH$_4$ at 300 K$^\ddagger$ | | | |
| 300 | 100 | 0.0 | 0.0 | 0.0 |
| 500 | 99.9 | 0.01 | 0.0 | 0.0 |
| 700 | 98.6 | 0.9 | 0.0 | 0.5 |
| 900 | 81.2 | 13.1 | 1.7 | 4.0 |
| Case 2: 0.8 (7.4%) CH$_4$ in 10.0 Torr (92.6%) H$_2$ at 300 K$^\ddagger$ | | | | |
| 300 | 7.4 | 92.6 | 0.0 | 0.0 |
| 500 | 7.4 | 92.6 | 0.0 | 0.0 |
| 700 | 7.4 | 92.6 | 0.0 | 0.0 |
| 900 | 7.4 | 92.6 | 0.0 | 0.0 |

$^\dagger$These mixing ratios are calculated by minimizing the Gibbs free energy of an ideal gas mixture.

$^\ddagger$The reported pressure in each case is for 300 K. $P_{H2}$ and $P_{CH4}$ at high temperatures are calculated using ideal gas law.

$^\ddagger$In this study, 10 Torr of H$_2$ gas added in order to suppress the CH$_4$ decomposition.

Tube lengths are 10.3, 9.8, 10.2, and 9.9 cm, respectively.

$^\dagger$Spectral resolution.

$^\ddagger$Number of scans averaged.

The measured spectrum of the CH$_4$ $\nu_3$ band was measured using two different MKS Baratron pressure gauges (maximum range 100 and 1000 Torr). For controlling the temperature, heat tapes from BriskHeat company (Type BW0) were used. A thermocouple connected to each gas cell was used in a feedback loop with the heat-tape controller to maintain a constant temperature. Omega company states typical uncertainties as 0.1% of the displayed reading for their digital readers. The uncertainty for type K probes is estimated to be 0.75% (2 K at 300 K). Therefore, the overall uncertainty is due to the probe, not the reader, and T is good to within $\pm 2$ K at the location of the junction. There is a possibility of temperature nonuniformity in our gas cell. We expect this effect to be small given the high heating-element coverage of the cell excluding the transmitting windows but including its support structure, the small size of the cell, and Omega company's typical uncertainties for their digital readers.
3. Data Analysis

Our main goal is to extract pressure-induced broadening coefficients by modeling all lines with Voigt line profiles. Lorentzian and temperature-dependence coefficients for each rovibrational line are determined from linewidths extracted from spectra #1–12 using a least-squares fitting method. The signal-to-noise ratio (S/N) is insufficiently high to justify modeling the spectra with non-Voigt profiles.

The negligibly pressure-broadened sample tube #1 was analyzed first to determine the correct CH4 line assignments, wavenumber calibration, and the presence of other CH4 bands and other contaminant species. Line strengths were determined separately at each measured temperature. The highly-blended pressure-broadened spectra were analyzed with line strengths fixed to their unbroadened values for our various measurements are in the range 0.004–0.007 cm⁻¹, which is fully negligible when fitting the spectra.

3.1. Continuum / baseline fitting

All CH4 spectra were converted from their interferograms with a Boxcar apodization using the OPUS software. The effect of instrumental broadening was modeled using a custom fitting code as a sinc function. The background continuum is also modeled using cubic splines optimized during the least-squares fitting procedure. Additionally, interference between the two cell windows that affects the recorded spectra by introducing sinusoidal behavior into the spectral continuum. We modeled this interference effect by employing two sine functions scaling the modeled spectrum.

3.2. Line position corrections

Line assignments are determined from the recent version of HITRAN. All corresponding line positions from HITRAN were input into the fitting code, and a global fit was made to calculate a single global shift induced by any slight miscalibration of the spectrometer. Afterward, the calculated shift was applied to our low pressure spectra (i.e., spectra #1–3 in Table). Later, the corrected/shifted line positions from the low pressure spectra were used to fit high pressure spectra (i.e., spectra #4–12 in Table), where pressure-induced lineshifting were also evident.

\[
\begin{align*}
  f_G(v - v_{ij}, \Gamma_D) &= \sqrt{\frac{\ln(2)}{\pi \Gamma_D^2}} \exp \left( -\frac{\ln(2)(v - v_{ij})^2}{\Gamma_D^2} \right) \\
  \Gamma_D(T) &= \frac{v_{ij}}{c} \sqrt{\frac{2 \ln(2) N_A k_b T}{M}} \\
  f_L(v; v_{ij}, \Gamma_L, \Delta_L) &= \frac{1}{\pi} \frac{\Gamma_L(p, T)}{[\Gamma_L(p, T)]^2 + [v - (v_{ij} + \Delta_L)]^2}
\end{align*}
\]

where \(M\) is the molar mass of the absorber molecule in grams, \(N_A\) is the Avogadro constant, \(k_b\) is the Boltzmann constant, and \(v_{ij}\) is the line position or the energy gap between quantum levels \(i\) and \(j\) in any arbitrary energy unit (e.g., cm⁻¹). \(\Gamma_D\) values for our various measurements are in the range 0.004 – 0.007 cm⁻¹ given the dependence of \(\Gamma_D\) on the temperature and wavenumber. The natural radiative linewidth of the CH4 \(\nu_3\) band is \(\sim 10^{-9}\) cm⁻¹ (i.e., in the range of 10–100 Hz), which is fully negligible when fitting the spectra.

Since the intensity of each line is distributed as a result of pressure-broadening, we increased the column density of CH4 when a high \(H_2\) pressure is present in order to obtain optimal S/N ratios without saturating any lines. As a result of this change, the modeled CH4 optical depth of high-pressure spectra (i.e., spectrum #4–12) were scaled up uniformly.

The Lorentzian HWHM linewidth \(\Gamma_L\) and lineshift \(\Gamma_L\) were fitted individually for each line using the Lorentzian line profile \(f_L\):

\[
f_L(v; v_{ij}, \Gamma_L, \Delta_L) = \frac{\Gamma_L(p, T)}{\pi [\Gamma_L(p, T)]^2 + [v - (v_{ij} + \Delta_L)]^2}
\]
Figure 3: Examples of recorded spectra showing the P(7) cluster of the \( \nu_3 \) band of CH\(_4\) in a H\(_2\) bath gas: In this study, four quartz cells (I–IV) with different amounts of P\(_{CH_4}\) and P\(_{H_2}\) (i.e., P\(_{CH_4}\) (Torr) : P\(_{H_2}\) (Torr) = 0.8:10, 1.1:100, 2.2:200, 3.0:400) were used to record the FTIR transmittance spectra of CH\(_4\) in H\(_2\) at 300 K (blue), 500 K (black), and 700 K (red). Transitions with E symmetry are weaker than A\(_1\)/A\(_2\) and F\(_1\)/F\(_2\) symmetries for similar quantum number \( J \). The measured resolution for these 12 spectra varies from 0.005 cm\(^{-1}\) for the lowest pressure (panel I) to 0.02 cm\(^{-1}\) for the highest pressure (panel IV, 700 K). A least-squares fitting procedure with Voigt line profiles was employed to model the spectra. The residual (Res) subpanels represent difference between modeled and recorded spectra. In addition, we also find lines from other bands such as 2\( \nu_2 \) and \( \nu_2 + \nu_4 \) bands; however, their S/N is not strong enough for pressure-broadening analysis.
\[ \Gamma_L = \left( \frac{T}{T_0} \right)^{-n_T} \gamma_L P_{H_2} \]  
\[ \Delta_L = \left( \frac{T}{T_0} \right)^{-n_L} \delta_L P_{H_2} \]

in which \( \gamma_L \) (cm\(^{-1}\)/atm) and \( n_T \) are the Lorentzian linewidth and its temperature-dependence coefficient, respectively. \( \delta_L \) (cm\(^{-1}\)/atm) and \( n_L \) are the Lorentzian lineshift coefficient and its temperature-dependence coefficient, respectively. \( T_0 \) is a reference temperature, and it is set equal to 300 K. Note, all these coefficients are dependent on the total rotational quantum number \( J \), tetrahedral (T\(_4\)) symmetry species, and the broadeners. The code computes the Voigt profile as the Faddeeva function.

The Lorentzian coefficients \( \Gamma_L \), extracted from the recorded spectra result from the effect of \( P_{H_2} \) collisional-induced broadening. The pressure-broadening from CH\(_4\) self-broadening is negligible since \( P_{CH_4} \leq 1.1\% \times P_{H_2} \). Regarding Dicke narrowing, this effect becomes important at intermediate pressures or the Doppler–Lorentzian transition region because Doppler broadening at low pressures and Lorentzian broadening at high pressures mask the narrowing. For example, Pine [35] found the largest discrepancy between Voigt and Rautian at 50 Torr H\(_2\), and a corresponding 5% difference in the derived \( \gamma_L \) for the two cases. This difference will be reduced by about half at 100 Torr (the lowest pressure we use). Then our Lorentzian linewidths fitted at 100 Torr may be underestimated by up to 3% (in comparison with random fitting uncertainties of at 4% or more).

Other formulations for the temperature-dependence of Eq. 5 have been adopted elsewhere [47]. We use the most conventional single-parameter temperature dependence formula above given the limited temperature sampling of our data.

4. Results and Discussion

4.1. Pressure broadening coefficients: \( \gamma_L \) and \( n_T \)

After fitting all 12 spectra from 300 to 700 K, the Lorentzian HWHM (i.e., \( \Gamma_L \) in Eq. 4) is extracted for each tetrahedral rovibrational transition. Then, the \( \gamma_L \) and \( n_T \) coefficients are computed in three different ways: 1) for all lines individually including its own \( J \), symmetry and \( N \) numbers, 2) averaged over lines with the same \( J'' \) but different symmetry and \( N \) index (i.e., the multiplicity index), and 3) all lines with the same \( J'' \) and symmetry but different \( N \) index were fitted. As a sample fitting, Fig. 4 illustrates \( \Gamma_L \) versus (T/300 K)\(^{-n_L} \) \( P_{H_2} \) for \( J''=7 \) and different symmetry species (\( n_T \) is computed below). Figure 4 shows the fitted slope (i.e., \( \gamma_L \)) of transitions with \( A_1/A_2 \) and \( F_1/F_2 \) is higher than for the \( E \) symmetry lines.

Figure 5(II–III) illustrates the trend of \( \gamma_L \) and \( n_T \) with \( J'' \). Figure 5(II) represents \( \gamma_L \) and \( n_T \) fitted to all lines individually. At each \( J'' \) value, there is the scatter of both \( \gamma_L \) and \( n_T \) coefficients which arise from the difference between \( T_4 \) symmetries, \( N \) indexes, and random fitting errors. In the first analysis step, individual lines with the same \( J, \) symmetry, \( N \) from all spectra were fitted to extract the \( \gamma_L \) and \( n_T \) coefficients. From this we determine the Lorentzian linewidth of each individual line as a result of H\(_2\) collisional impact. Figures 4 and 5(II) as well as the supplementary Table (S1) represent these results. The error bars shown in these figures and the table uncertainties are due to the fitting uncertainties, noise, and the low signal-to-noise of some lines. These line-by-line coefficients are the main outcome of this study and they can be utilized in generating absorption cross-section (or opacity) data the standard HITRAN code [46] or the NASA Ames Freedman’s code [19, 57].

In contrast, if we average the coefficients for all lines with the same \( J'' \) value, then \( \gamma_L \) and \( n_T \) coefficients fall in the range of 0.07–0.03 and 0.65–0.25, respectively (see Fig. 5(II) and Table 4). In Table 4, the scatter of these coefficients are mostly due to the scattering of lines with the same \( J'' \) but different symmetries and \( N \) dependencies, as well as, the uncertainty in fitting the Lorentzian linewidths from the recorded spectra. Another motivation for this step is to provide data for opacity codes which input only \( J \)-dependent pressure-broadening val-

\footnote{\url{http://ab-initio.mit.edu/wiki/index.php/Faddeeva_Package}}
ues such as the current version of EXOCROSS code\[^{[58]}\]. Figure [5][III] shows that there is a clear dependency of the Lorentzian coefficient and its temperature-dependence with \(\gamma_L\) and \(n_\gamma\) on \(J\). This data are also presented in Table [4] and the range of scatter for each one is shown as a range of \(\gamma_{L\min} - \gamma_{L\max}\) and \(n_{\gamma\min} - n_{\gamma\max}\). According to the Anderson collisional theory \[^{[40]}\], the \(n_\gamma\) coefficient is expected to be 0.5; however, our analysis shows that \(n_\gamma\) coefficients deviate from this value by up to 30%. We also find that \(\gamma_L\) and \(n_\gamma\) decrease by 25% and 80%, respectively, between \(J''=2\) and 17 in agreement with the trend calculated by Neshyba et al. \[^{[45]}\] and Gabard \[^{[44]}\].

Next, we grouped the lines with similar symmetries, and extracted the Lorentzian coefficients from each group. Figure [5][III] shows the symmetry-dependence of \(\gamma_L\) and \(n_\gamma\). The bars shown in this figure are due to the uncertainty in fitting this data (similar to Fig. [5][III]) and also the scatter imposed by different values of the \(N\) quantum index. It should be noted that only some symmetry-\(J\) combinations have multiple \(N\) values. Therefore, two kinds of uncertainties are shown in Table [7] statistical fitting uncertainties for singular-\(N\) values, and the range of scatter for values averaged over multiple \(N\) transitions. In general, within each \(J\) manifold, \(E\)-lines are the weakest and also have the narrowest Lorentzian linewidth \(\Gamma_L\). In contrast, lines with \(A_1/A_2\) and \(F_1/F_2\) symmetries are generally the strongest, and have the broadest linewidth.

Following the complex Robert-Bonamy theory \[^{[59]}\], Neshyba et al. \[^{[45]}\] calculated the impact of electrostatic and atom-atom intermolecular potential on the line broadening and line shift of the CH\(_4@\) [N\(_2\)] system. They found that the atom–atom potential component is the main reason for the line broadening with a corresponding decrease with increasing total angular momentum, \(J\). In addition, the broadening effect is symmetry dependent and it was shown \[^{[44]}\][[47]][[60]\] that the total collisional cross-section for \(E\) symmetry is lower than for \(A_1/A_2\) and \(F_1/F_2\) at low \(J\), which results in smaller perturbation and collisional-broadening for the \(E\)-symmetry species, as we observed.

4.2. Lorentzian temperature-dependence coefficient: \(n_\gamma\)

According to early Anderson collisional theory \[^{[40]}\][[61]\], a broadened line has a Lorentzian profile (Eq. [5]), and the broadening linewidth is proportional to \(T^{-0.5}\) following Eqs. [6] and [7]:

\[
\Gamma_L = \frac{n \bar{v}_{th} \sigma_r}{2\pi} \tag{6}
\]

where \(n\) is the broadener column density (i.e., \(n=m_{H_2} = P_{H_2}/k_bT\)), \(\bar{v}_{th}\) is the mean thermal velocity from Maxwell-Boltzmann distribution (i.e., \(\bar{v}_{th} = \sqrt{8k_bT/\pi m}\) where \(m\) is the \(H_2\) mass), and \(\sigma_r\) is the real component of the collisional cross-section (see discussion in \[^{[62]}\]).

\[
\Gamma_L = \sqrt{\frac{2}{k_B m n \pi}} P_{H_2} T^{-0.5} \sigma_r \tag{7}
\]

Following Eqs. [6] & [7], the temperature-dependence coefficient, \(n_\gamma\) is 0.5. Note, there are different assumptions at play in Eq. [7] including the hard-sphere approximation, ideal gas law, and also a single thermal velocity \(\bar{v}_{th}\) for all broadeners. Therefore, this \(n_\gamma=0.5\) value should be considered as a gas kinetic value, and a more sophisticated picture is reviewed by Ganache and Vispoel \[^{[63]}\]. Our results show that \(n_\gamma\) strongly depends on \(J\), and it is in the range of \(~0.65–0.2\) (see Fig. [5][II]). No significant dependence of \(n_\gamma\) on the tetrahedral symmetry species is found.

Table [5] lists most previous temperature-dependence measurements of CH\(_4\) in different broadeners. In addition, the measurements are for different fundamental and...
Figure 5: Dependence of the Lorentzian coefficients $\gamma_L$ and $n_\gamma$ on quantum number $J''$. Panel I: All lines were fitted individually. The uncertainties are 1-$\sigma$ error in each individual line but the scatter arises primarily from the symmetry and $N$ index. Panel II: Average of all lines over symmetry and $N$ index. However this approach ignores the dependence of symmetry and $N$ dependency, and therefore, it disregards these important physical effects. Panel III: Average of all lines within a symmetry species. $\gamma_L$ and $n_\gamma$ are reported in Tables 4, 7, and in the Table S1 (supplementary file). Note that a few points are out of the fitted trend (dotted line), and therefore, the fitted coefficients are reported in these tables. In addition, weak lines with low S/N ratio and high-uncertainty are removed from the list in Table S1 (supplementary file). Where error bars are not visible, the uncertainty from fittings for the data is smaller than the symbol size itself.

Combination vibrational modes providing insight into the vibrational dependency of $n_\gamma$. The $n_\gamma$ of CH$_4$@[N$_2$] and CH$_4$@[Air] falls in the range of $\sim$0.55–1.0 and $\sim$0.4–0.9, respectively, which are roughly 30% larger than our results for CH$_4$@[H$_2$]. In comparison, CH$_4$@[He] is about half that of CH$_4$@[H$_2$]. Table 5 also illustrates the slight
4.3. Lorentzian line-shift coefficients: $\delta_L$ and $n_\delta$

The S/N ratio in the current study is insufficiently high to extract pressure shifts for all lines. Hence, a pressure-shift coefficient is calculated only for lines with $J''=2$–11, and falls in the range of $-0.004$ to $-0.002$ cm$^{-1}$/atm. We discern no significant dependence of the Lorentzian pressure-shift coefficients on the $J$ values (Fig. 6), and the mean value of $\delta_L$ and $n_\delta$ are $-0.0035$ cm$^{-1}$/atm and 1.24, respectively. The reported uncertainties for Lorentzian pressure-shift coefficients ($\delta_L$ and $n_\delta$) are due to the scatter of the symmetry- and $N$-dependence. Note that our $n_\delta$ is larger than $n_\gamma$, and this difference has been reported for water self-broadening as well [70].

The form of Eq. 5 is based on Eq. 4, which is derived from the ideal gas law and hard-sphere approximation. Some studies of other systems such as Frost [41] and Baldacchini et al. [21] have shown temperature-dependence has more complex form than our selected formula in Eq. 5. Additionally, Smith et al. [47] found both positive and negative $\delta_L$ and $n_\delta$ values for the CH$_4$ v4 band. However, we exclusively observed negative $\delta_L$ and positive $n_\delta$ values.

### Table 4: $J'$-dependent Lorentzian coefficients averaged over $\nu_3$ P branch line cluster of CH$_4$.

| $J''$ | $J'''$ | $\gamma_L$ | $\gamma_L^{\min} - \gamma_L^{\max}$ | $\delta_L$ | $n_\delta$ |
|-------|-------|------------|------------------------------------|------------|------------|
|       |       |            |                                    |            |            |
| 1     | 2     | 0.069      | 0.068–0.069                         | 0.65       | 0.59–0.66  |
| 2     | 3     | 0.067      | 0.066–0.068                         | 0.56       | 0.55–0.57  |
| 3     | 4     | 0.065      | 0.061–0.068                         | 0.56       | 0.51–0.60  |
| 4     | 5     | 0.066      | 0.063–0.067                         | 0.60       | 0.54–0.68  |
| 5     | 6     | 0.066      | 0.063–0.068                         | 0.58       | 0.55–0.63  |
| 6     | 7     | 0.064      | 0.054–0.067                         | 0.59       | 0.51–0.65  |
| 7     | 8     | 0.063      | 0.057–0.061                         | 0.55       | 0.54–0.57  |
| 8     | 9     | 0.063      | 0.062–0.063                         | 0.55       | 0.53–0.56  |
| 9     | 10    | 0.059      | 0.045–0.062                         | 0.52       | 0.44–0.54  |
| 10    | 11    | 0.058      | 0.049–0.060                         | 0.48       | 0.42–0.52  |
| 11    | 12    | 0.057      | 0.054–0.058                         | 0.46       | 0.41–0.47  |
| 12    | 13    | 0.053      | 0.035–0.057                         | 0.42       | 0.25–0.48  |
| 13    | 14    | 0.051      | 0.037–0.054                         | 0.36       | 0.20–0.54  |
| 14    | 15    | 0.046      | 0.041–0.051                         | 0.24       | 0.14–0.41  |
| 15    | 16    | 0.043†     |                                    | 0.26       |            |
| 16    | 17    | 0.041†     | 0.038–0.049                         | 0.20       | 0.14–0.65  |

Note:

* $\gamma_L^{\min}$ and $\gamma_L^{\max}$ represent the range of coefficients before averaging over symmetry and $N$. Only the lines with high S/N ratios are considered for extracting the Lorentzian pressure-shift coefficients ($\delta_L$ and $n_\delta$).

† The scattering in the pressure-shift coefficients arises from their dependencies into the symmetry and $N$.

‡ The extracted values of $\gamma_L$ and $n_\delta$ for $J''=16$ are 0.0324(51) and -0.2(1), which are out of the trend. Therefore, these values are replaced with the expected values from the polynomial equation due to the weakness of the lines.

4.4. Global equations for Lorentzian coefficients

In order to provide Lorentzian broadening coefficients ($\gamma_L$ and $n_\gamma$) for high-temperature H$_2$-dominated exoatmospheres (i.e., super-Earth or warm-Nepaltes with 400–900 K temperature), the dependency of these coefficients with $J''$ is presented by fitting the experimental results to a second-order polynomial $J''$-dependence (e.g., Eq. 8 [see the red-dashed line in Fig. 5(II)]. Additionally, due to the significant dependence of $\gamma_L$ on the symmetry species, the fitting coefficients are extracted from them separately (i.e., Eq. 9 [dashed lines in Fig. 5(II)]) conforming to:

$$X(J'') = m_1 + m_2 J'' + m_3 J''^2$$

(8)

$$X(J'', \text{sym}) = m_1 + m_2 J'' + m_3 J''^2$$

(9)

where $m_1$, $m_2$, and $m_3$ are the fitted constants, $X$ is the Lorentzian coefficient i.e., $\gamma_L$, $n_\gamma$, and “sym” can be $A_1/A_2$, $F_1/F_2$, or $E$ symmetry species. All the polynomial fitted constants are presented in Table 6.
In general our $n_r$ coefficients (i.e., CH$_4$@[H$_2$]) are smaller than both @[Air]-broadening for $ν_p$, and $ν$-branch data. In addition, this figure shows that the collisional effect of N$_2$ and Ar species on pressure shift is larger than H$_2$. The largest $δ_L$, however, would be due to the CH$_4$ self-broadening interactions, and it is $~2×$ higher than our results ($δ_L$(CH$_4$@[H$_2$])).

5. Summary & Conclusion

High-temperature Lorentzian broadening and shift coefficients of CH$_4$@[H$_2$] for more than 100 individual rovibrational transitions in $ν_3$ $P$ branch are obtained using high resolution (0.01–0.005 cm$^{-1}$) FTIR spectroscopy. We find that $γ_3$ falls in the range 0.03–0.07 cm$^{-1}$/atm, and is strongly dependent on molecular rotation and symmetry dependent. The temperature-dependence broadening coefficient, $n_r$, falls in the range 0.20–0.65. The averaged shift pressure and its temperature-dependence coefficient, $δ_L$, and $n_r$ are $~0.035$ cm$^{-1}$/atm and 1.24, respectively, and these are constant with $J$ as far as our data can determine.

All these coefficients were fitted to simple polynomial equations in terms of $J''$ and neglecting symmetry and $N$ quantum index for the benefit of the astrophysical/exoplanetary community. Table S1 lists the $γ_3$ and $n_r$ for all individual lines, showing the change in these coefficients with $J$, symmetry, and $N$ numbers, and is recommended to use these data where these details are important. The detection of CH$_4$ spectral features in hot-Jupiters to super-Earths needs these pressure-broadening data because of their high-temperature and H$_2$-dominant atmospheres.

Table 6: Fitted constants for global equations

| Case | $m_1$ | $m_2$ | $m_3$ |
|------|-------|-------|-------|
| $γ_L(J'')$ | 0.066 | 0.0008 | −0.00014 |
| $n_r(J'')$ | 0.520 | 0.0290 | −0.00290 |
| $γ_L(J''_1, F_1/F_2)$ | 0.0657 | 0.0012 | −0.00017 |
| $γ_L(J''_2, A_1/A_2)$ | 0.0650 | 0.0007 | −0.00011 |
| $γ_L(J'', E)$ | 0.0690 | −0.0010 | −0.00010 |

† Eqs. 8 and 9 are used to fit the $γ_L$ and $n_r$ results. Note: $γ_L$ and $n_r$ coefficients are reported in Table S1 for all $ν_3$ $P$-branch lines. The polynomial equations Eqs. 8 and 9 should be used to determine these coefficients for transitions in the range of $J''$=0–18.
These pressure-broadening and pressure-shift coefficients can be directly incorporated into current databases, such as HITRAN/HITEMP or EXOMOL.

6. Acknowledgment

We kindly thank Glenn Stark, David Wright, Adam Schneider, and the Arizona State University exoplanet group for many useful discussions. E.G.N. especially thanks Mike Line for invaluable numerous invaluable discussions during this work as well as Richard Freedman and Mark Marley invaluable discussions regarding the intricacies of opacity data. E.G.N. acknowledges funding from the GRSP research grant from the Arizona State University Graduate office program award XH51027. A.N.H.’s research was supported by an appointment to the NASA Postdoctoral Program at Arizona State University and the NASA Astrobiology Institute, administered by Universities Space Research Association under contract with NASA. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.
This Study

Figure 8: Comparison of our temperature-dependence coefficients (i.e., $\nu_3$ $P$-branch CH$_4@[H_2]$) at temperature range 300–700 K with $\nu_4$ $Q$-branch CH$_4@[N_2]$ Smith et al. [47] and $\nu_4$ $P$- and $R$-branch CH$_4@[Air]$ Smith et al. [74] at temperature range of 210–314 K.

Figure 9: Comparison of our $\gamma_L$ results with the literature data including $\nu_3$ $Q$-branch CH$_4@[He, N_2, and Self]$ [35]. Note that our results are averaged over $N$, however, the scatter of the literature data arises from the $N$ quantum index. Where error bars are not visible, the uncertainties are smaller than the symbol size.
Figure 10: The comparison of pressure-shift coefficient $\delta_L$ for different broadeners (i.e., H$_2$, N$_2$, Ar, and self-broadening), and different branches $Q$ and $P$ [35, 72, 75].
Table 5: Overview of previous measured temperature-dependence coefficients, $n_\gamma$, of CH$_4$ in various broadeners

| Broadener T[K] | Band | Lines | $n_\gamma$ | Ref. |
|---------------|------|-------|-----------|------|
| **H$_2$**     |      |       |           |      |
| 300 – 700    | $v_3$ | 116   | 0.2 – 0.68 | Fs   |
| 77 – 295     | $6v_1,5v_3$ | 2   | 0.45, 0.53 | 64   |
| 130 – 295    | $v_4$  | 6    | 0.46       | 65   |
| 161 – 295    | $v_4$  | 6    | 0.35       | 62   |
| **Air**      |      |       |           |      |
| 200 – 300    | $v_3$  | 3    | 0.62 – 1.0 | 46   |
| 211 – 314    | $v_4$  | 148  | 0.50       | 47   |
| 212 – 297    | $v_1 + v_4$ | 130 | 0.50       | 68   |
| 212 – 297    | $v_3 + v_4$ | 406 | 0.50       | 68   |
| 212 – 297    | $v_2 + v_3$ | 71  | 0.40       | 68   |
| **N$_2$**    | $v_3$  | 3    | 0.94       | 43   |
| 215 – 297    | $v_2 + v_4$ | 2   | 0.86, 0.92 | 43   |
| 77 – 295     | $6v_1,5v_3$ | 2   | 0.77, 0.97 | 64   |
| 130 – 295    | $v_4$  | 6    | 0.75       | 65   |
| 161 – 295    | $v_4$  | 6    | 0.71       | 67   |
| 211 – 314    | $v_4$  | 148  | 0.55       | 47   |
| 90 – 296     | $v_3$  | 4    | 0.84       | 69   |
| **Self**     |      |       |           |      |
| 77 – 295     | $6v_1,5v_3$ | 2  | 0.84, 0.93 | 64   |
| **He**       |      |       |           |      |
| 77 – 295     | $6v_1,5v_3$ | 2  | 0.37, 0.67 | 64   |
| 130 – 295    | $v_4$  | 6    | 0.28       | 65   |
| 161 – 295    | $v_4$  | 6    | 0.26       | 67   |
| **Ar**       |      |       |           |      |
| 130 – 295    | $v_4$  | 2    | 0.80       | 65   |
| 161 – 295    | $v_4$  | 6    | 0.72       | 67   |

† $n_\gamma$ coefficients are reported within a range due to their dependency on $J$ and vibrational quantum numbers. In this table, the reported $n_\gamma$ in some cases are extracted from a few transitions.

Table 7: Broadening coefficients averaged over $N$.

| $J^\prime$ | $J^\prime\prime$ | Sym | $T_L$ \text{[cm}^{-1}\text{/atm]} | $n_\gamma$ | $n_{\gamma-L}$ | $\gamma_L$ | $\gamma_L - \gamma_{L,max}$ |
|------------|-----------------|-----|-----------------|----------|---------------|---------|-------------------------|
| 1          | 2               | $E$ | 0.069(1)        | 0.59(4)  | 0.66(3)       | 0.55(3) |
| 2          | 3               | $F$ | 0.068(1)        | 0.60(3)  | 0.55(3)       | 0.53(2) |
| 3          | 3               | $A$ | 0.066(1)        | 0.60(3)  | 0.55(3)       | 0.53(2) |
| 4          | 2               | $F$ | 0.067(1)        | 0.57(2)  | 0.51(3)       | 0.51(3) |
| 4          | 3               | $A$ | 0.064(2)        | 0.51(3)  | 0.51(3)       | 0.51(3) |
| 5          | 3               | $E$ | 0.061(2)        | 0.56(4)  | 0.56(4)       | 0.56(4) |
| 6          | 3               | $F$ | 0.063(1)        | 0.55(3)  | 0.55(3)       | 0.55(3) |
| 6          | 4               | $F$ | 0.068           | 0.51(3)  | 0.51(3)       | 0.51(3) |
| 7          | 6               | $E$ | 0.067(1)        | 0.51(2)  | 0.51(2)       | 0.51(2) |
| 7          | 5               | $F$ | 0.062           | 0.57(2)  | 0.57(2)       | 0.57(2) |
| 8          | 5               | $A$ | 0.061(1)        | 0.56(2)  | 0.56(2)       | 0.56(2) |
| 9          | 8               | $E$ | 0.057           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 9          | 7               | $F$ | 0.065           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 10         | 7               | $A$ | 0.062           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 10         | 6               | $E$ | 0.063           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 11         | 6               | $E$ | 0.063           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 11         | 5               | $F$ | 0.062           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 12         | 5               | $A$ | 0.061           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 13         | 5               | $F$ | 0.064           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 13         | 4               | $A$ | 0.065           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 14         | 4               | $F$ | 0.066           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 14         | 3               | $A$ | 0.065           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 15         | 3               | $F$ | 0.062           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 15         | 2               | $A$ | 0.064           | 0.52(3)  | 0.52(3)       | 0.52(3) |
| 16         | 2               | $F$ | 0.065           | 0.52(3)  | 0.52(3)       | 0.52(3) |

Note:
- The uncertainties in parentheses (in units of the least-significant digit) are derived from the estimated uncertainty of fitted linewidths. These are not well-defined where lines of differing quantum index, $N$, have been averaged and instead the range of parameters for individual lines is given as $\gamma_L - \gamma_{L,max}$ and $\gamma_{L,max} - \gamma_{L,min}$.
- Extracted values of $\gamma_L$ and $n_\gamma$ for $J^\prime=16$ are $0.041(12)$ and $-0.00(27)$, which are out of the trend. Therefore, these values are replaced with the expected values from the polynomial equation due to the weakness of the lines.
- The extracted values of $\gamma_L$ and $n_\gamma$ for $J^\prime=16$ are $0.008(6)$ and $-1.50(66)$, which are out of the trend. Therefore, these values are replaced with the expected values from the polynomial equation due to the weakness of the lines.

\[ n_{\gamma-L} = \gamma_L - \gamma_{L,max} \]
7. Reference

References

[1] V. A. Krasnopolsky, J. P. Maillard, T. C. Owen, Detection of methane in the martian atmosphere: evidence for life?, Icarus 172 (2) (2004) 537–547, ISSN 0019-1035.

[2] J. R. Lyons, C. Manning, F. Nimmo, Formation of methane on Mars by fluid-rock interaction in the crust, GRL 32 L13201.

[3] G. S. Orton, J. I. Moses, L. N. Fletcher, A. K. Mainzer, D. Hines, H. B. Hammel, J. Martin-Torres, M. Burgdorf, C. Merlet, M. R. Line, Mid-infrared spectroscopy of Uranus from the Spitzer infrared spectrometer: 2. Determination of the mean composition of the upper troposphere and stratosphere, Icarus 243 (2014) 471–493, ISSN 0019-1035.

[4] G. S. Orton, L. N. Fletcher, J. I. Moses, A. K. Mainzer, D. Hines, H. B. Hammel, F. J. Martin-Torres, M. Burgdorf, C. Merlet, M. R. Line, Mid-infrared spectroscopy of Uranus from the Spitzer Infrared Spectrometer: 1. Determination of the mean temperature structure of the upper troposphere and stratosphere, Icarus 243 (2014) 494–513, ISSN 0019-1035.

[5] S. K. Atreya, P. R. Mahaffy, H. B. Niemann, M. H. Wong, T. C. Owen, Composition and origin of the atmosphere of Jupiter - An update, and implications for the extrasolar giant planets, Planetary and Space Science 51 (2) (2003) 105–112, ISSN 00320633.

[6] K. Lodders, Exoplanet Chemistry, 157, 2010.

[7] M. S. Marley, T. D. Robinson, On the Cool Side: Modeling the Atmospheres of Brown Dwarfs and Giant Planets, ARAA 53 (2015) 279–323, ISSN 0066-4146.

[8] J. J. Fortney, On the Carbon-to-oxygen Ratio Measurement in nearby Sun-like stars: Implications for Planet Formation and the Determination of Stellar Abundances, ApJL 747 L27.

[9] O. Venot, M. Agúndez, F. Selsis, M. Tesenyi, N. Iro, The atmospheric chemistry of the warm Neptune GJ 3470b: Influence of metallicity and temperature on the CH₄/CO ratio, A&A 562 (2014) A51, ISSN 0004-6361.

[10] L. Kreidberg, M. R. Line, D. Thorngren, C. V. Morley, K. B. Stevenson, Water, High-altitude Condensates, and Possible Methane Depletion in the Atmosphere of the Warm Super-Neptune WASP-107b, AJ 858 (1) (2018) L6, ISSN 2041-8213.

[11] A. J. Burgasser, T. R. Geballe, S. K. Leggett, J. D. Kirkpatrick, D. A. Golimowski, A Unified Near Infrared Spectral Classification Scheme for T Dwarfs, AJ 637 (2) (2006) 1067–1093, ISSN 0004-637X.

[12] M. R. Line, G. Vasisht, P. Chen, D. Angerhausen, Y. L. Yung, Thermochemical and Photochemical Kinetics in Cooler Hydrogen-dominated Extrasolar Planets: A Methane-poor GJ436b?, ApJ 738 32.

[13] L. Kreidberg, M. R. Line, D. Thorngren, C. V. Morley, K. B. Stevenson, Water, High-altitude Condensates, and Possible Methane Depletion in the Atmosphere of the Warm Super-Neptune WASP-107b, ApJL 858 L6.

[14] M. R. Swain, P. Deroo, C. A. Griffith, G. Tinetti, A. Thatte, G. Vasisht, P. Chen, J. Bouwman, I. J. Crossfield, D. Angerhausen, C. Afonso, T. Henning, A ground-based near-infrared emission spectrum of the exoplanet HD189733b, Nature 463 (2010) 637–639.

[15] J.-M. Désert, A. Lecavelier des Etangs, G. Hebrard, D. K. Sing, D. Ehrenreich, R. Ferlet, A. Vidal-Madjar, Search for Carbon Monoxide in the Atmosphere of the Transiting Exoplanet HD 189733b, ApJ 699 (2009) 478–485.

[16] J. Wang, D. Mawet, J. J. Fortney, C. Hood, C. V. Morley, B. Benneke, Detecting Water in the Atmosphere of HR 8799 c with L-band High-dispersion Spectroscopy Aided by Adaptive Optics, AJ 156 272.

[17] J. I. Moses, M. R. Line, C. Visscher, M. R. Richardson, N. Nettelmann, J. J. Fortney, T. S. Barman,
A. S. Pine, Self-, N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}, Ar, and He broadening in the ν\textsubscript{3} band Q branch of CH\textsubscript{4}, JCP 97 (1992) 773–785.

A. Pine, T. Gabard, Multispectrum fits for line mixing in the ν\textsubscript{3} band Q branch of methane, JMS 217 (1) (2003) 105–114, ISSN 0022-2852.

K. Fox, D. E. Jennings, Measurements of nitrogen-, hydrogen- and helium-broadened widths of methane lines at 90309120 cm\textsuperscript{-1}, JQSRT 33 (3) (1985) 275–280, ISSN 0022-4073.

K. Fox, D. E. Jennings, E. A. Stern, R. Hunnard, Measurements of argon-, helium-, hydrogen-, and nitrogen-broadened widths of methane lines near 9000 cm\textsuperscript{-1}, JQSRT 39 (6) (1988) 473–476, ISSN 0022-4073.

J.-M. Hartmann, H. Tran, R. Armante, C. Boulet, A. Campargue, F. Forget, L. Gianfrani, I. Gordon, S. Guerlet, M. Gustafsson, J. T. Hodges, S. Kassi, D. Lisak, F. Thibault, G. C. Toon, Recent advances in collisional effects on spectra of molecular gases and their practical consequences, JQSRT 213 (2018) 178–227, ISSN 0022-4073.

P. W. Anderson, Pressure Broadening in the Microwave and Infra-Red Regions, Phys. Rev. 76 (1949) 647–661.

B. S. Frost, A theory of microwave lineshifts, Journal of Physics B: Atomic and Molecular Physics 9 (6) (1976) 1001–1020.

G. D. T. Tejwani, P. Varanasi, Calculation of Collision-Broadened Linewidths in the Infrared Bands of Methane, JCP 55 (1971) 1075–1083.

V. Devi, B. Fridovich, D. Snyder, G. Jones, P. P. Das, Tunable diode laser measurements of intensities and Lorentz broadening coefficients of lines in the 2 band of 12CH\textsubscript{4}, JQSRT 29 (1) (1983) 45 – 47, ISSN 0022-4073.

T. Gabard, Calculated line broadening parameters for methane perturbed by diatomic molecules, JMS 291 (2013) 61 – 68, ISSN 0022-2852.
[52] R. Bretzlauff, T. Bahder, Apodization effects in Fourier transform infrared difference spectra, Revue de Physique Appliquée 21 (12) (1986) 833–844, ISSN 0035-1687.

[53] R. L. Burden, J. D. Faires, A. M. Burden, Numerical analysis, Cengage Learning US, 9th edn., ISBN 9781305253667, 2011.

[54] J. Buldyreva, N. Lavrentieva, V. Starikov, Collisonal Line Broadening and Shifting of Atmospheric Gases: a Practical Guide for Line Shape Modelling by Current Semi-Classical Approaches, World Scientific Publishing Co, 2011.

[55] W. Jin, S. Murray, D. Pinchbeck, G. Stewart, B. Culshaw, Absorption measurement of methane gas with a broadband light source and interferometric signal processing, Optics Letters 18 (16) (1993) 1364, ISSN 0146-9592.

[56] R. Kochanov, I. Gordon, L. Rothman, P. WcisÅo, C. Hill, J. Wilzewski, HITRAN Application Programming Interface (HAPI): A comprehensive approach to working with spectroscopic data, Journal of Quantitative Spectroscopy and Radiative Transfer 177 (2016) 15 – 30, ISSN 0022-4073, xvIIIth Symposium on High Resolution Molecular Spectroscopy (HighRus-2015), Tomsk, Russia.

[57] R. S. Freedman, M. S. Marley, K. Lodders, Line and Mean Opacities for Ultracool Dwarfs and Extrasolar Planets, ApJS 174 (2008) 504–513.

[58] Yurchenko, Sergei N., Al-Refaie, Ahmed F., Tennyson, Jonathan, EXOCROSS: a general program for generating spectra from molecular line lists, A&A 614 (2018) A131.

[59] D. Robert, J. Bonamy, Short range force effects in semiclassical molecular line broadening calculations, Journal de Physique 40 (10) (1979) 923–943.

[60] L. N. Smith, D. Secrest, Close coupling and coupled state calculations of argon scattering from normal methane, JCP 74 (7) (1981) 3882–3897.

[61] M. Baranger, Simplified Quantum-Mechanical Theory of Pressure Broadening, Physical Review 111 (2) (1958) 481–493, ISSN 0031-899X.

[62] J. Lyons, H. Herde, G. Stark, D. Blackie, J. Pickering, N. de Oliveira, VUV pressure-broadening in sulfur dioxide, JQSRT 210 (2018) 156 – 164, ISSN 0022-4073.

[63] R. R. Gamache, B. Vispoel, On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions, JQSRT 217 (2018) 440 – 452, ISSN 0022-4073.

[64] C. E. Keffer, C. P. Conner, W. Smith, Pressure broadening of methane lines in the 6190Åand 6825Åbands at room and low temperatures, JQSRT 35 (6) (1986) 495–499, ISSN 0022-4073.

[65] P. Varanasi, Temperature Dependence of Strengths, Widths and Shifts of CH₄ at Planetary Atmospheric Temperatures, BAAS 21 (1989) 961.

[66] P. Varanasi, S. Chudamani, Measurements of collision-broadened line widths in the ν₄-fundamental band of (C-12)H₄ at low temperatures, JQSRT 41 (1989) 335–343.

[67] P. Varanasi, S. Chudamani, The temperature dependence of lineshifts, linewidths and line intensities of methane at low temperatures, JQSRT 43 (1) (1990) 1–11, ISSN 0022-4073.

[68] V. Devi, D. Benner, M. Smith, C. Rinsland, Temperature dependence of Lorentz air-broadening and pressure-shift coefficients of ¹²CH₄ lines in the 2.3-µm spectral region, JQSRT 51 (3) (1994) 439–465, ISSN 0022-4073.

[69] D. Mondelain, S. Payan, W. Deng, C. Camy-Peyret, D. Hurtmans, A. W. Mantz, Measurement of the temperature dependence of line mixing and pressure broadening parameters between 296 and 90K in the ν₃ band of ¹²CH₄ and their influence on atmospheric methane retrievals, JMS 244 (2) (2007) 130–137, ISSN 0022-2852.
[70] V. Markov, Temperature Dependence of Self-Induced Pressure Broadening and Shift of the 643-550 Line of the Water Molecule, JMS 164 (1) (1994) 233 – 238, ISSN 0022-2852.

[71] G. Baldacchini, G. Buffa, F. D’Amato, F. Pelagalli, O. Tarrini, Variations in the sign of the pressure-induced lineshifts in the 2 band of ammonia with temperature, JQSRT 55 (6) (1996) 741 – 743, ISSN 0022-4073.

[72] A. Pine, Speed-dependent Line Mixing in the $\nu_3$ Band $Q$ Branch of Methane, JQSRT 224 (2019) 62 – 77, ISSN 0022-4073.

[73] E. Es-sebbar, A. Farooq, Intensities, Broadening and Narrowing Parameters in the $\nu_3$ band of Methane, JQSRT 149 (2014) 241 – 252, ISSN 0022-4073.

[74] M. Smith, D. C. Benner, A. Predoi-Cross, V. M. Devi, Multispectrum Analysis of $^{12}$CH$_4$ in the $\nu_4$ band, JQSRT 110 (9-10) (2009) 639–653, ISSN 00224073.

[75] A. S. Pine, N$_2$ and Ar broadening and line mixing in the P and R branches of the $\nu_3$ band of CH$_4$, JQSRT 57 (1997) 157–176.