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Absorption of methane broadened by carbon dioxide in the 3.3 μm spectral region: From line centers to the far wings

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41 by collisions between CH₄ (and H₂) and CO₂. The first modeling of these collision-induced
42 absorptions (CIAs) was based on those of CH₄-N₂ (and H₂-N₂) interacting pairs (Ramirez et
43 al., 2014). In (Wordsworth et al., 2017), theoretical calculations of these CIAs were
44 performed using a semi-empirical model that assumed that the shape of the CIA spectrum of
45 CH₄-CO₂ (H₂-CO₂) can be calculated as a linear combination of the CO₂-CO₂ and CH₄-CH₄
46 (H₂-H₂) CIAs (Richard et al., 2012). The CH₄-CO₂ (H₂-CO₂) CIA integrated intensity was
47 then predicted based on ab initio calculations of the zeroth order spectral moment
48 (Wordsworth et al., 2017). The results showed that the obtained CH₄-CO₂ and H₂-CO₂ CIAs
49 are much more intense than those of CH₄-N₂ and H₂-N₂. The first measurements of these far-
50 infrared CIAs were then performed in (Turbet et al., 2019) where it was shown that the
51 calculated values of (Wordsworth et al., 2017) are overestimated by a factor of 1.6-1.7. In
52 (Turbet et al., 2020), a new set of measurements of both CH₄-CO₂ and H₂-CO₂ CIAs was
53 carried out, confirming the results of (Turbet et al., 2019), with reduced uncertainties. A semi-
54 empirical model was also proposed in (Turbet et al., 2019), based on these measurements,
55 which enabled to calculate CH₄-CO₂ and H₂-CO₂ CIAs over broad spectral (0-1500 cm⁻¹) and
56 temperature (100-600 K) ranges.

57 The present work complements these studies through the measurement and modeling of
58 absorption in the far wings of the lines of the CH₄ monomer broadened by CO₂ in the 3.3 μm
59 spectral region, which can contribute to the greenhouse warming in CO₂-dominated
60 atmospheres. Spectra of CH₄ highly diluted in CO₂ have been recorded, at room temperature
61 and in a wide pressure range, using two different setups. The experimental setups and
62 conditions are presented in Sec. 2. In Sec. 3, the spectral modeling, considering the effect of
63 collisional line mixing, is described, and comparisons between measured and calculated
64 spectra are presented. In Sec. 4, we propose an empirical χ -factor model to represent the
65 spectral shape of CO₂-broadened CH₄ line wings. This model is determined from the most
66 rigorous spectral modeling presented in Sec. 3 and validated using measured spectra. The
67 conclusions of this work are drawn in Sec. 5.

68 2. Experiments

69 2.1 Measurements at ULB

70 Unapodized absorption spectra of CH₄+CO₂ mixtures and of pure CO₂ have been recorded
71 using a Bruker IFS 120 upgraded to 125 HR Fourier transform spectrometer (FTS). For all the
72 spectra, the instrument was fit with a globar source, a 0.8-mm entrance aperture diameter, a
73 KBr beamsplitter, a band pass filter and an InSb detector cooled down to 77 K. Except when
74 stated otherwise, the spectra were recorded at a resolution of 0.1 cm⁻¹, corresponding to a
75 maximum optical path difference of 9 cm. A band-pass optical filter was used to only record
76 the spectral range from 1800 to 5300 cm⁻¹, covering the entire ν_3 band of CH₄. Methane
77 (99.998 % purity) and carbon dioxide (99.995 % purity) were purchased from Air Liquide.
78 During the measurements, the gas mixtures were contained in a high-pressure cell providing
79 an absorption path length of 10.16 m, optically coupled under vacuum to the FTS. The
80 methane pressures were measured using MKS Baratron gauges model 690 of 10 Torr full
81 scale range (Spectrum “No. 1” in Table 1) or model 626 of 1000 Torr full scale range (Spectra
82 “No. 5” and “No. 9” in Table 1). The total pressures were measured using a MKS Baratron
83 gauge model 627F of 25000 Torr full-scale range, directly connected to the high-pressure cell.
84 The model 690 and 627F gauges were temperature stabilized at 45° Celsius. All the gauges

85 are characterized by an accuracy of reading conservatively assumed to be 0.5 %. The cell was
86 wrapped in 5 cm thick stone wool and its temperature measured using 4 PT-111 platinum
87 sensors (Lakeshore Cryotronics) characterized by an accuracy of reading better than 0.1 %,
88 fixed at several locations on the outside wall.

89 Two series of spectra were recorded. In the first one, a mixture of CH₄ and CO₂ (mixture no. 1
90 in Table 1) at an initial total pressure (P_{tot}) of 24.53 atm and initial partial pressure of CH₄
91 (P_{CH_4}) of 0.428 mbar was considered. The mixture was prepared in the cell, filling it with
92 methane followed by carbon dioxide. A first spectrum (identified as “No. 1” in Table 1) was
93 recorded under these sample conditions. The total pressure was then reduced to 12.36 atm and
94 a second spectrum recorded at a resolution of 0.05 cm⁻¹ (“No. 2” in Table 1). Using the same
95 procedure, two other spectra were recorded at total pressures of 6.17 atm (“No. 3” in Table 1)
96 and 3.08 atm (“No. 4” in Table 1) and higher resolution. The corresponding transmission
97 spectra being not saturated, these spectra enable to study the effect of pressure on the
98 absorption in the central region and near wings of the band. To achieve good accuracy on the
99 absorption in a wide spectral range, i.e. from the center of the ν_3 band to its far wing, the
100 second set of transmission spectra (identified as mixtures nos. 2 and 3 in Table 1) involved
101 different CH₄ partial pressures for a fixed value of the total pressure. For mixture no. 2, the
102 cell was first filled with 404 mbar of CH₄ and the total pressure brought to 24903 mbar with
103 CO₂. A first spectrum (“No. 5” in Table 1) was recorded. The total pressure was then reduced
104 by a factor F of about 10, CO₂ added to bring the total pressure to 25003.6 mbar (effectively
105 dividing by F the partial pressure of methane) and spectrum “No. 6” was recorded. This
106 procedure was repeated two more times, leading to spectra “No. 7” and “No. 8”. The cell was
107 evacuated, a new CH₄+CO₂ mixture (no. 3) prepared and spectra “No. 9” to “No. 13” were
108 measured following the procedure applied to mixture no. 2. Pure CO₂ spectra $S_{CO_2}(P_{tot}, \sigma)$
109 were also recorded at the same total pressures and resolutions as spectra No. 1 to 4 (Table 1).

110 The uncertainties on the methane pressures provided in Table 1 were estimated as follows.
111 The uncertainties listed for spectra “No. 5” and “No. 9” are equal to 0.5% of P_{CH_4} . The
112 uncertainty on the low methane pressure measured for spectrum “No. 1” was conservatively
113 set to 2.5% of P_{CH_4} (Cacciani et al., 2022). The uncertainties on P_{CH_4} for spectra of samples
114 resulting from the dilution (i.e. spectra “No. 6” to “No. 8” and “No. 10” to “No. 13”) were
115 estimated by adding in quadrature the estimated uncertainty on P_{CH_4} for the previous
116 spectrum and the uncertainty ΔF on the factor F , estimated to be $\Delta F = \sqrt{2(0.5)^2} \approx 0.71\%$
117 of the reduced methane pressure.

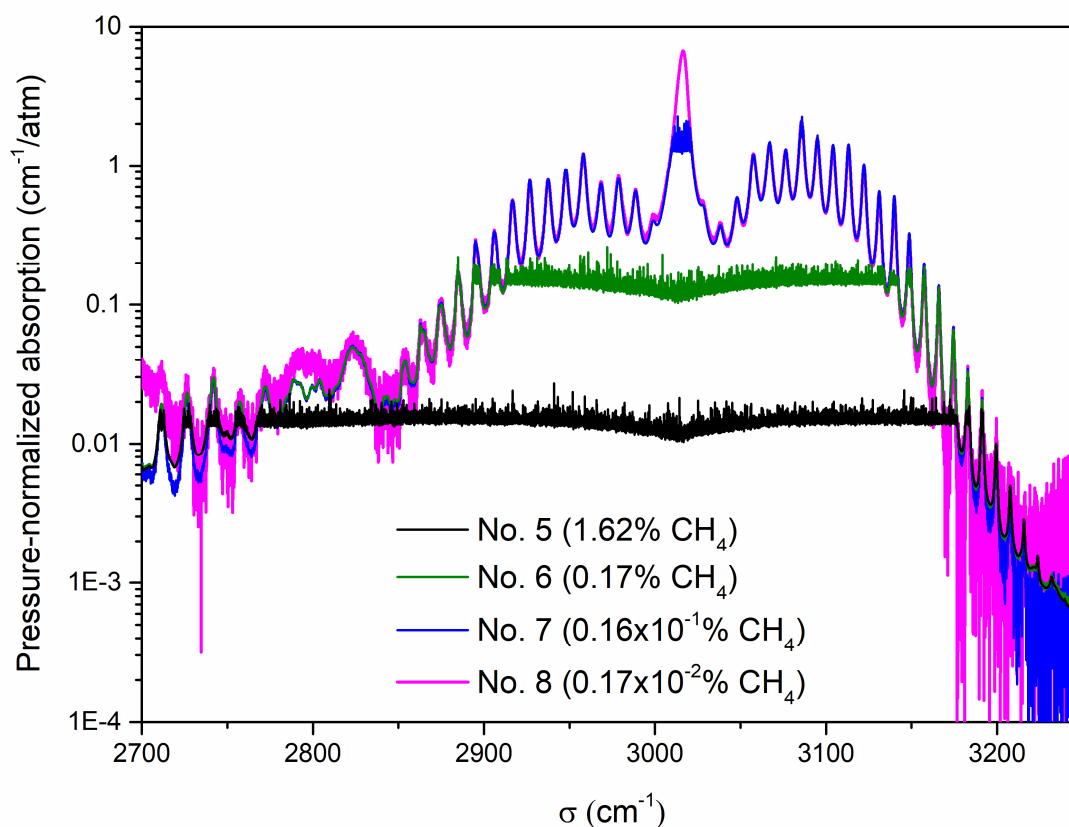
118 The transmissions due to CH₄ broadened by CO₂ were obtained by dividing the signal
119 obtained with the mixture, $S_{CH_4+CO_2}(P_{tot}, \sigma)$, by $S_{CO_2}(P_{tot}, \sigma)$. With this procedure, the
120 contribution of CO₂ absorption (the wings of neighboring CO₂ vibrational bands and some
121 weak collision-induced absorption bands) could be removed. The absorption coefficients were
122 then extracted from the transmissions thus obtained and normalized by the CH₄ partial
123 pressure. Since most of the studied gas samples contain mixing ratios of methane smaller than
124 0.55%, the contribution of CH₄-CH₄ collisions is negligible. The contribution of CH₄-CH₄
125 collisions being not negligible for spectra No. 5 and 9, it was taken into account assuming that
126 the effects of CH₄-CH₄ and of CH₄-CO₂ collisions are the same. This is justified by the fact
127 that the average ratio of self- to air-broadening coefficients of CH₄ is 1.27 (Pine, 1992), very
128 close to the ratio of CO₂ to air-broadenings (1.3, see Sec.3). As shown in Fig. 1 for mixture
129 no. 2, the whole ν_3 band was then reconstructed by combining the spectral windows in which

130 the transmissions were between 0.2 and 0.8. The analysis of the second series of spectra
 131 recorded at ULB therefore resulted in two CH₄ partial-pressure-normalized absorption spectra
 132 of CH₄ broadened by CO₂ measured at average total pressures of 24991 mbar (mixture no. 2)
 133 and 24978 mbar (mixture no. 3) and an average temperature of 295.7 K.

Mixture	No.	$P_{tot}(\Delta P) / \text{mbar}$	$T (\Delta T) / ^\circ\text{C}$	$P_{CH_4}(\Delta P) / \text{mbar}$	Res. / cm^{-1}
1	1	24851 (17)	23.72 (0.12)	0.428 (11)	0.1
	2	12521.2 (2.9)	22.52 (0.01)	0.216 (6)	0.05
	3	6255.1 (2.0)	22.28 (0.08)	0.108 (3)	0.025
	4	3122.9 (1.3)	22.16 (0.02)	0.054 (1)	0.0125
2	5	24903 (12)	23.30 (0.08)	404 (2)	0.1
	6	25003.6 (6.0)	22.68 (0.04)	42.1 (4)	0.1
	7	25029.4 (6.0)	22.68 (0.04)	4.20 (5)	0.1
	8	25029 (13)	22.70 (0.08)	0.428 (6)	0.1
3	9	24764 (14)	22.85 (0.11)	1241 (6)	0.1
	10	24990.2 (8.0)	22.71 (0.06)	130.3 (1.1)	0.1
	11	25025.2 (3.3)	22.62 (0.03)	13.16 (15)	0.1
	12	25052.0 (2.0)	22.62 (0.01)	1.345 (18)	0.1
	13	25074.8 (8.1)	22.63 (0.07)	0.1376 (21)	0.1

134 Table 1: Experimental conditions for the CH₄+CO₂ spectra measured with the ULB setup.
 135 Spectra of pure CO₂ were recorded for the same pressure conditions as spectra No. 1 to 4. The
 136 numbers between parentheses provided for the pressures and temperatures are the estimated
 137 uncertainties. For the total pressure P_{tot} and the temperature T , they are the variations of these
 138 quantities during the recordings, the estimated accuracy of measurement of the pressure (0.5%
 139 of reading) and of the temperature (0.1% of reading) being not included. The estimation of the
 140 uncertainties on the methane pressures is detailed in the text.

141 Note that the measured and reconstructed spectra were corrected to get rid of possible errors
 142 in the partial pressures of methane. This was done by multiplying the experimental results by
 143 a constant factor such that the integrated absorptions of the measured spectrum and of the
 144 corresponding calculated one match. The correction factors vary from 0.96 to 1.1 depending
 145 on the spectrum. They are larger than the estimated uncertainties on the methane pressures
 146 and probably a better assessment of these. No correlation was found between the correction
 147 factors and the CH₄ pressures.



148
 149 Figure 1: CH₄ partial-pressure-normalized absorption spectra of CH₄ broadened by CO₂
 150 measured at an average total pressure of 24991 mbar and for various partial pressures of CH₄
 151 (mixture no. 2 in Table 1).

152 *2.2. Measurements at SOLEIL*

153 CH₄+CO₂ transmittance spectra were also measured using the facilities at the AILES beam
 154 line of the SOLEIL synchrotron. The experimental setup is composed of a Fourier transform
 155 spectrometer Bruker IFS 125 HR equipped with a globar source and a KBr beamsplitter from
 156 which the incident light beam goes into a 2.5 m long multi-pass cell closed with diamond
 157 windows, set for an optical path of 101.3 m. The transmitted light was received by a HgCdTe
 158 detector cooled down with liquid nitrogen. Each spectrum has a usable part between 800 and
 159 4600 cm⁻¹ and results from the average of 1000 interferograms recorded with an unapodized
 160 resolution of 0.5 cm⁻¹.

161 The experiments proceeded as follows. The cell was filled with 54.4 mbar of CH₄ and CO₂
 162 was added until a total pressure of 945.7 mbar was reached (the pressures were measured with
 163 a 0 - 1000 mbar Pfeiffer gauge), resulting in a methane mole fraction of about 5 %. The
 164 mixture was let to evolve freely for 10 to 15 minutes to reach equilibrium and the absorption
 165 spectrum of the mixture was recorded. The total pressure was then reduced to 764.2 mbar, the
 166 mixture given 10 to 15 minutes to reach equilibrium and the spectrum of the mixture
 167 recorded. The procedure was then repeated for total pressures of 607.3, 480.0, 378.3, 171.6,
 168 107.1 and 58.3 mbar. A reference spectrum was also recorded with the cell filled with about 1
 169 bar of pure argon to generate transmittance spectra for all the total pressures.

170 **3. Spectral modeling: line-mixing effect**

171 It is well known that collisional interferences (line-mixing) play an important role in the
 172 infrared absorption spectrum of methane [see (Pieroni et al., 1999; Tran et al., 2006a) for
 173 instance]. Within the impact approximation and including line-mixing effects, the infrared
 174 absorption coefficient α (cm^{-1}) at wavenumber σ (cm^{-1}) of CH_4 broadened by CO_2 is given by
 175 (Hartmann et al., 2021):

$$176 \quad \alpha^{LM}(\sigma, P_{\text{CH}_4}, P_{\text{CO}_2}, T) = \frac{8\pi^2\sigma}{3hc} \left[1 - \exp\left(-\frac{hc\sigma}{k_B T}\right) \right] \times \frac{P_{\text{CH}_4}}{k_B T}$$

$$177 \quad \times \text{Im}\{\sum_{\ell} \sum_k \rho_{\ell}(T) d_{\ell} d_k \langle\langle k | [\mathbf{\Sigma} - \mathbf{L}_0 - iP_{\text{CO}_2} \mathbf{W}(T)]^{-1} | \ell \rangle\rangle\} . \quad (1)$$

178 In Eq. (1), the sums extend over all the absorption lines ℓ and k of CH_4 ; P_{CH_4} and P_{CO_2} are the
 179 partial pressures of CH_4 and CO_2 , respectively; T is the temperature (in kelvin); h , c and k_B
 180 are the Planck constant, the speed of light in vacuum and the Boltzmann constant. ρ_{ℓ} and d_{ℓ}
 181 are the relative population of the initial level and the dipole matrix element of line ℓ . $\mathbf{\Sigma}$, \mathbf{L}_0
 182 and \mathbf{W} are operators in the Liouville space and $\langle\langle k | \dots | \ell \rangle\rangle$ designates a matrix element. The
 183 first two are diagonal, associated with the current wavenumber and the positions of the lines.
 184 \mathbf{W} is the relaxation matrix which describes the effect of collisions between CH_4 and CO_2 on
 185 the CH_4 optical transitions. In this equation, we neglected the self-broadening effect as
 186 explained in Sec. 2.1, the Doppler term and the influence of velocity changes as well as the
 187 speed dependences of the relaxation matrix \mathbf{W} . The latter contains the influence of collisions
 188 on the spectral shape. It depends on the band, on the temperature and on the collisional
 189 partner. Its off-diagonal elements lead to collisional interferences between lines while the real
 190 and imaginary diagonal terms are the pressure-broadening, γ_{ℓ} , and -shifting, δ_{ℓ} , of the
 191 isolated lines, i.e.

$$192 \quad \langle\langle \ell | \mathbf{W}(T) | \ell \rangle\rangle = \gamma_{\ell}(T) - i\delta_{\ell}(T) . \quad (2)$$

193 When line mixing is disregarded, \mathbf{W} is diagonal and Eq. (1) becomes the usual sum of
 194 Lorentzian contributions.

195 The off-diagonal imaginary elements of \mathbf{W} are neglected while the real elements are
 196 computed, as done in (Pieroni et al., 1999; Tran et al., 2006), using:

$$197 \quad \langle\langle k | \mathbf{W}(T) | \ell \rangle\rangle = -A_{k,\ell} \times K(i_k \leftarrow i_{\ell}, T), \quad (3)$$

198 where $K(i_k \leftarrow i_{\ell}, T)$ denotes the state-to-state collisional transfer rates from the initial level of
 199 line ℓ to the initial level of line k ; the parameters $A_{k,\ell}$ enable switching from the state space to
 200 the line space, as explained in (Pieroni et al., 1999).

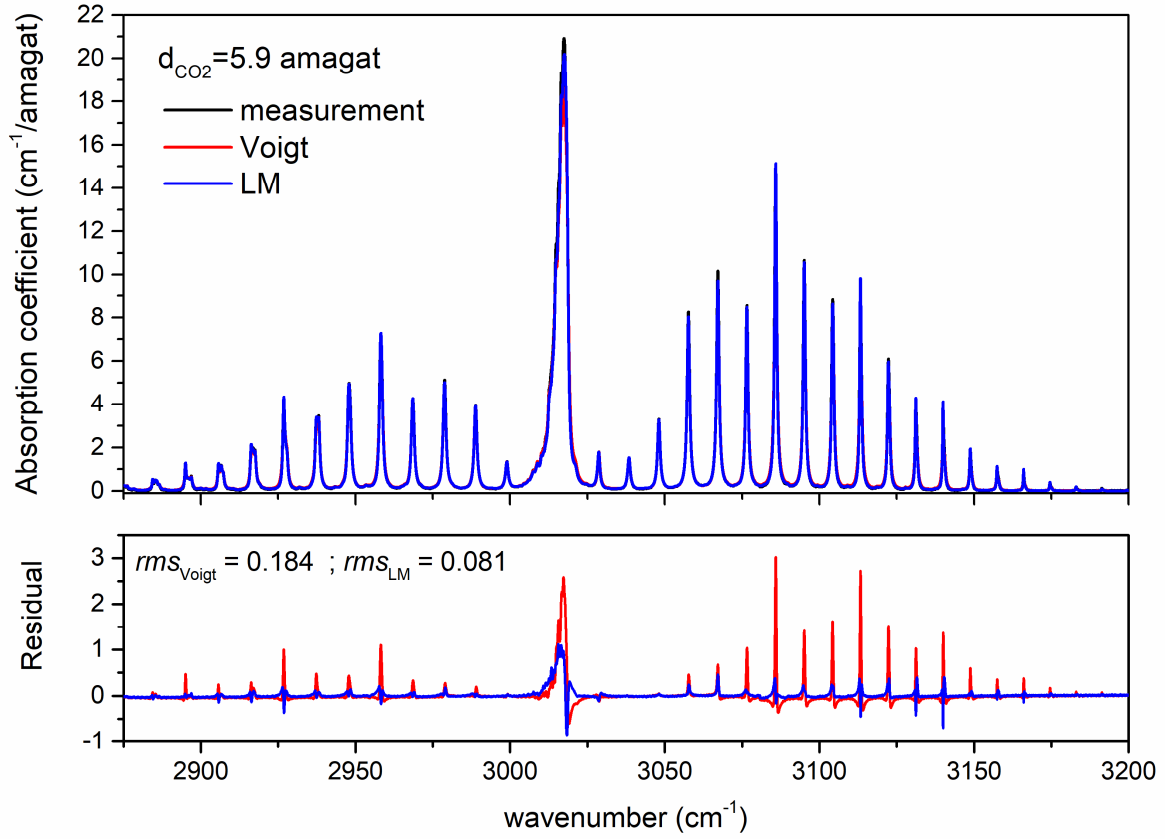
201 Spectra were calculated for the pressure and temperature conditions of the experiments. Since
 202 the considered region is dominated by the ν_3 band of $^{12}\text{CH}_4$, calculations with line-mixing
 203 taken into account were performed only for the lines of this band. The other lines (minor
 204 isotopologues, hot bands) were calculated with the Voigt profile. The individual line
 205 parameters, i.e. the unperturbed line position, integrated intensity, energy of the lower state,
 206 were taken from the 2020 edition of the HITRAN database (Gordon et al., 2022). The
 207 populations and the dipole matrix elements were deduced from these data [as done in (Tran et
 208 al., 2006a)]. The pressure-broadening coefficients of CH_4 lines by CO_2 were obtained by
 209 multiplying by 1.3 the air-broadening coefficients provided by the package of (Tran et al.,
 210 2006a). This factor, which is close to the value of 1.21 obtained by averaging the ratio

211 between the CO₂-broadening coefficients of 28 CH₄ lines measured by (Fissiaux et al., 2014)
212 and the corresponding values for air-broadening [taken from (Tran et al., 2006a) and
213 references therein], was retained because it gives the best agreement between the spectra
214 calculated and measured in the present work. In the absence of available measured or
215 calculated data, we assumed that the pressure-shifting coefficients of CH₄ by collisions with
216 CO₂ are the same as those of CH₄ by air. The latter were also provided by the package of
217 (Tran et al., 2006a). Note that the air-broadening and -shifting coefficients in (Tran et al.,
218 2006a) were obtained from the measured data of (Pine, 1997) in which these parameters were
219 determined with line-mixing effect taken into account. These data are thus consistent with the
220 line-shape model used here.

221 The off-diagonal elements of the relaxation matrix, including the state-to-state rates $K(i_k \leftarrow$
222 $i_\ell, T)$ and the $A_{k,\ell}$ parameters, were assumed to be proportional to those for CH₄ in N₂, also
223 provided in (Tran et al., 2006a), with the same multiplicative factor as for the line broadening
224 coefficients, i.e. $\langle\langle k \| \mathbf{W}^{CH_4/CO_2}(T) \| \ell \rangle\rangle = 1.3 \times \langle\langle k \| \mathbf{W}^{CH_4/N_2}(T) \| \ell \rangle\rangle$. Detailed information
225 on the state-to-state rates $K(i_k \leftarrow i_\ell, T)$ and the $A_{k,\ell}$ parameters can be found in (Tran et al.,
226 2006a) and references therein.

227 Figures 2 and 3 show examples of comparison between measured spectra (mixture no. 1 in
228 Table 1) and those calculated as described above for the same pressure and temperature
229 conditions. In addition to the predictions made taking line-mixing into account, the spectra
230 calculated with the same spectroscopic parameters but using the Voigt profile (i.e. neglecting
231 line-mixing effect) are also displayed. The density of CO₂ was determined from the measured
232 pressure and temperature using NIST-recommended equation of state taking into account the
233 fact that the gas is not ideal.ⁱ As can be observed, the line-mixing calculations, although not
234 perfect, lead to much better agreements with the measurements, the root mean square of the
235 obtained residuals being more than twice smaller than that for the Voigt calculations. These
236 results are consistent with those obtained previously for CH₄ broadened by N₂ (Pieroni et al.,
237 1999; Tran et al., 2006a) in which a detailed analysis of the influence of line-mixing effects
238 on the absorption spectrum can be found.

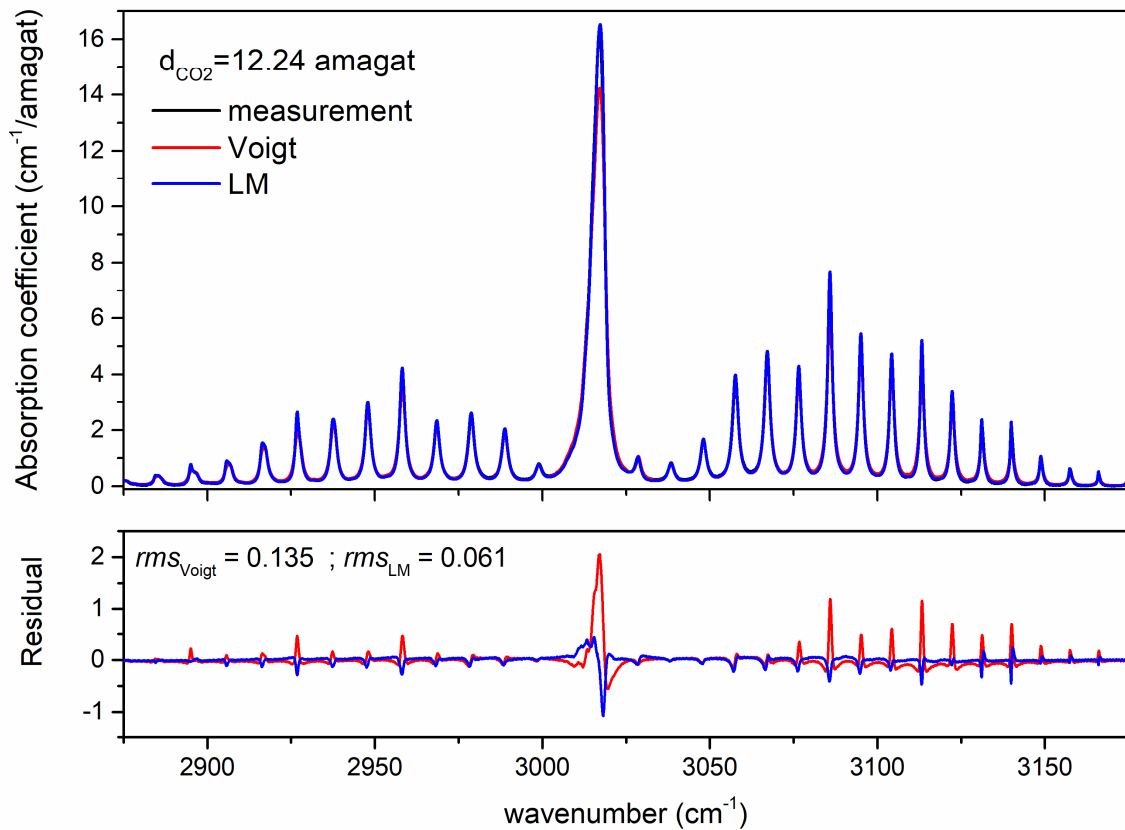
ⁱ <https://webbook.nist.gov/cgi/cbook.cgi?Source=1927LOW%2FERI2729-2734&Units=SI&Mask=7>



239

240 Figure 2: Comparison between the CO₂-broadened CH₄ spectrum measured (black) at room
 241 temperature for a density of CO₂, (d_{CO_2}) of 5.9 amagat (spectrum No. 3 in Table 1; 1 amagat
 242 corresponding to $2.687 \cdot 10^{19}$ molec.cm⁻³ at 273.15 K) and values calculated with (blue) and
 243 without (red) line mixing taken into account.

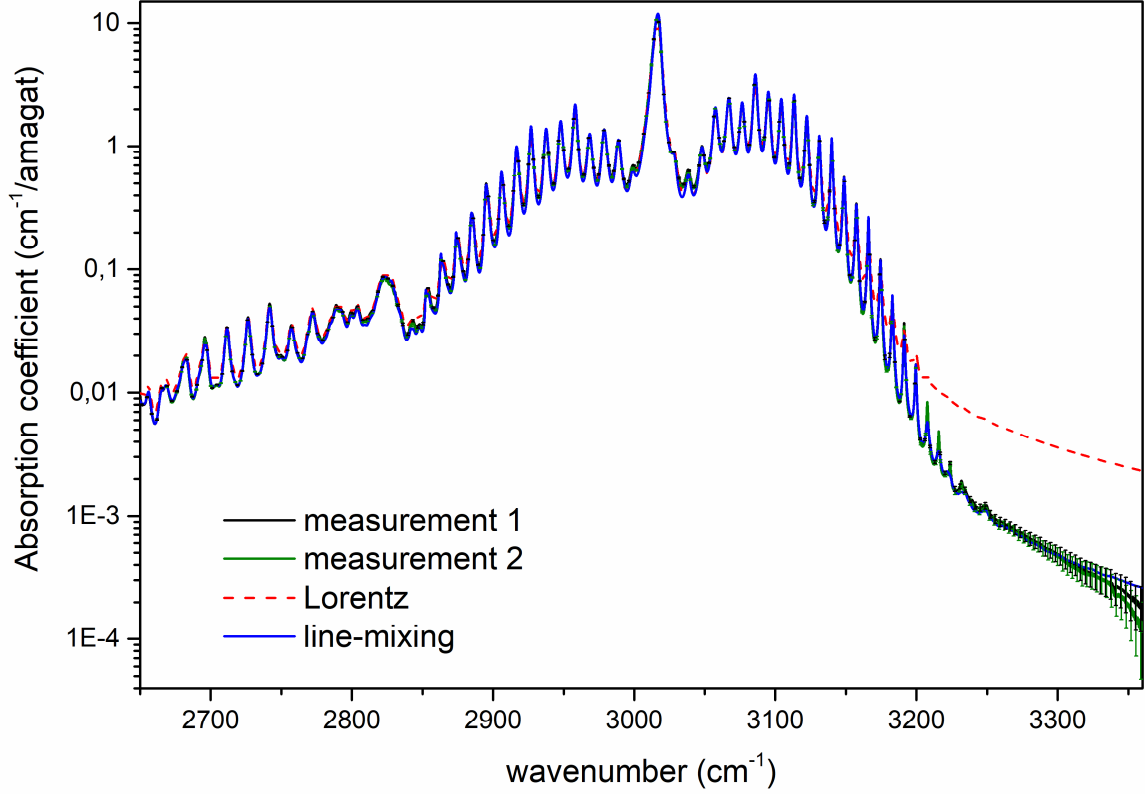
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245

246 Figure 3: Same as Fig. 2 for $d_{CO_2}=12.24$ amagat (spectrum no. 2 in Table 1).

247 The absorption in the band wing is displayed in Fig. 4 where calculations with and without
 248 line-mixing are compared with the spectra reconstructed (see Sec. 2.1) from measurements for
 249 the mixtures nos. 2 and 3 of Table 1. Again, the calculation with line-mixing leads to a good
 250 agreement with the measurements, especially in the blue wing of the band. Absorption in this
 251 spectral region is mainly due to the cumulating far wings of the strong ν_3 lines close to the
 252 center of the band. For CH_4 , it is well known that the Voigt profile strongly overestimates
 253 absorption in the far line wings (Hartmann et al., 2002; Tran et al., 2006a; Tran et al., 2006b),
 254 which is also observed here. Furthermore, in the troughs between the manifolds, particularly
 255 in the R branch, taking line-mixing into account also significantly improves the agreement
 256 with the measurements, when compared with the purely Voigt calculation. This result shows
 257 that our model, although quite simple since based on an approach developed for N_2 -broadened
 258 CH_4 lines, is capable to accurately predict the absorption shape from resonances to the far
 259 wings of CH_4 perturbed by CO_2 .



260

261 Figure 4: Comparison between CO₂-broadened CH₄ spectra measured at $d_{tot} = 26.5$ amagat
 262 (in olive and black, corresponding to mixtures no. 2 and 3 of Table 1) and values calculated
 263 with (blue) and without (red) line-mixing taken into account. The error bars on the measured
 264 absorption coefficient represent the uncertainties due to those of the baselines and the
 265 subtracted CO₂ absorption contributions (estimated to be 1%).

266 4. χ -factor model for the far wings of CO₂-broadened CH₄ lines

267 For practical applications such as simulations of planetary atmospheres spectra, Lorentzian
 268 (or Voigt) line shapes with line wings corrected using a χ -factor are widely used. Within this
 269 simple model, the absorption coefficient of a highly diluted CH₄-CO₂ mixture is written as:

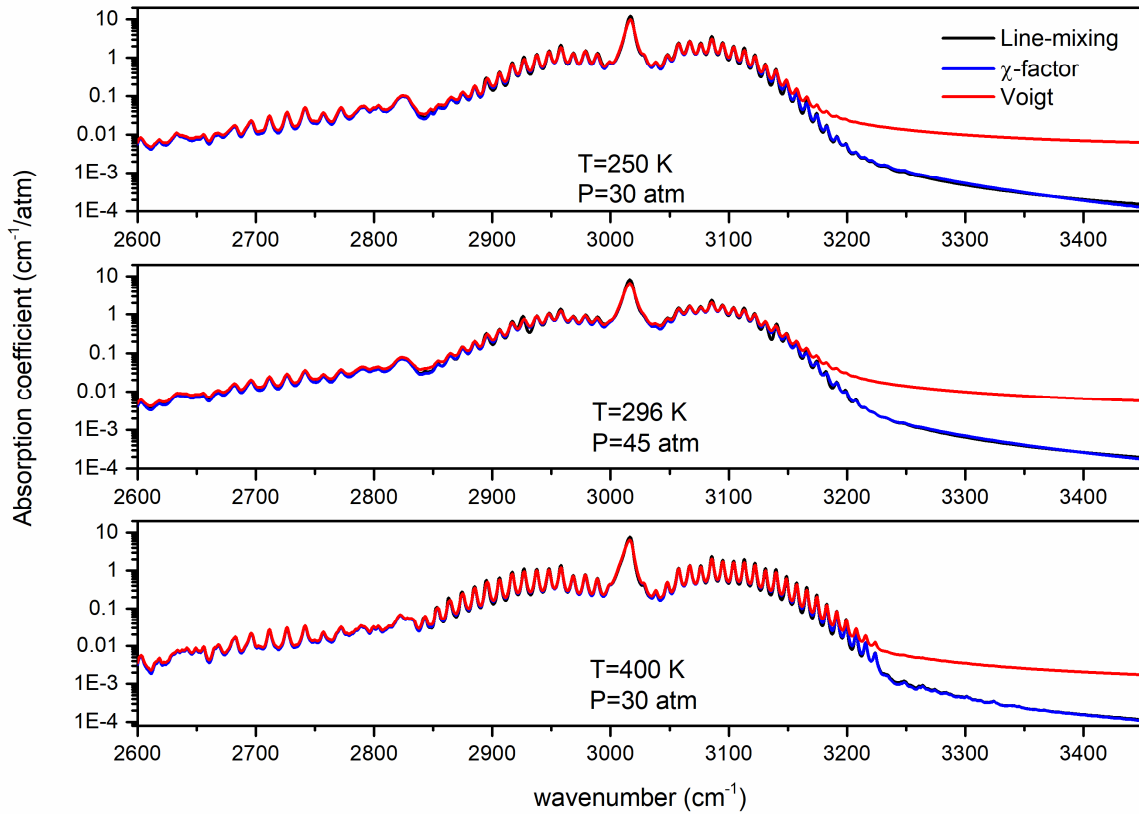
$$\begin{aligned}
 270 \quad \alpha(\sigma, P_{CH_4}, P_{CO_2}, T) &= \frac{1}{\pi} \sum_{\ell} P_{CH_4} S_{\ell}(T) \\
 271 \quad &\times \exp \left[\frac{hc(\sigma - \sigma_{\ell})}{2k_B T} \right] \frac{\sigma}{\sigma_{\ell}} \frac{1 - e^{-\frac{hc\sigma}{k_B T}}}{1 - e^{-\frac{hc\sigma_{\ell}}{k_B T}}} \frac{P_{CO_2} \gamma_{\ell}(T)}{(\sigma - \sigma_{\ell})^2 + (P_{CO_2} \gamma_{\ell}(T))^2} \chi(|\sigma - \sigma_{\ell}|, T) \quad (4)
 \end{aligned}$$

272 The corrective factor χ , which is assumed to be the same for all lines, depends on the
 273 frequency detuning with respect to the line center and on the temperature. It is generally
 274 (Perrin and Hartmann, 1989; Hartmann et al., 2002; Tran et al., 2011) represented by
 275 analytical expressions with parameters deduced from fits of measured spectra. In this work, χ
 276 was determined by fitting Eq. (4) to absorption spectra in the region of the ν_3 band, calculated
 277 using the model described in Sec. 3 (taking line-mixing effect into account) for various
 278 pressure and temperature conditions. Note that the model described in Sec. 3 is based on a

279 theoretical approach developed for CH₄ perturbed N₂ (Pieroni et al., 1999; Tran et al., 2006a),
 280 which showed that it is capable to accurately represent absorption spectra of CH₄ in N₂ for
 281 large range of temperature (i.e. from 200 to 300 K). Here, we assume that the broadening
 282 coefficients and the off-diagonal elements of the relaxation matrix of CH₄ in CO₂ have the
 283 same temperature dependences as those of CH₄ in N₂. Therefore, the model of Sec. 3 can be
 284 used to simulate spectra at various temperatures. The following values for χ were obtained:

$$\begin{aligned}
 285 \quad & |\sigma - \sigma_\ell| = \Delta\sigma < \sigma_1 = 15 \text{ cm}^{-1}, \chi = 1 \\
 286 \quad & \sigma_1 < \Delta\sigma < \sigma_2 = 60 \text{ cm}^{-1}, \chi = \exp[-0.0375(\Delta\sigma - \sigma_1)] \\
 287 \quad & \sigma_2 < \Delta\sigma, \chi = \exp[-0.0375(\sigma_2 - \sigma_1) - \beta(T)(\Delta\sigma - \sigma_2)] \\
 288 \quad & \text{with } \beta(T) = -5.3 \times 10^{-4} + 0.0194e^{-0.0041T}
 \end{aligned} \tag{5}$$

289 Figure 5 shows comparisons between the absorption coefficients calculated using Eqs. (4,5)
 290 and those obtained with the model described in Sec. 3 for three different pressure and
 291 temperature conditions. Very good agreements in the blue wing of the band can be observed.
 292 Note that the χ -factor as proposed in Eqs. (4,5) allows for the correction of sub-Lorentzian
 293 effect in the line wings while it is equivalent to a Lorentzian (or Voigt) line shape in the line
 294 centers and near wings. In the band wings, where absorption is mainly due to the far line
 295 wings, the χ -factor approach leads to good agreements with measured spectra. For instance, at
 296 3400 cm⁻¹ and for $d_{tot} = 26.5$ amagat, the relative difference between the absorption
 297 coefficients computed with the χ -factor model and the measured spectra is about 10% while
 298 the usual Lorentzian profile leads to a relative difference of several order of magnitude.
 299 However, in regions of line centers and near wings, an accurate modeling of the measured
 300 absorptions requires taking into account properly line-mixing effect through the use of the full
 301 relaxation matrix as described in Sec. 3. The χ -factor model therefore should be used to
 302 model absorption in the far line wings only.



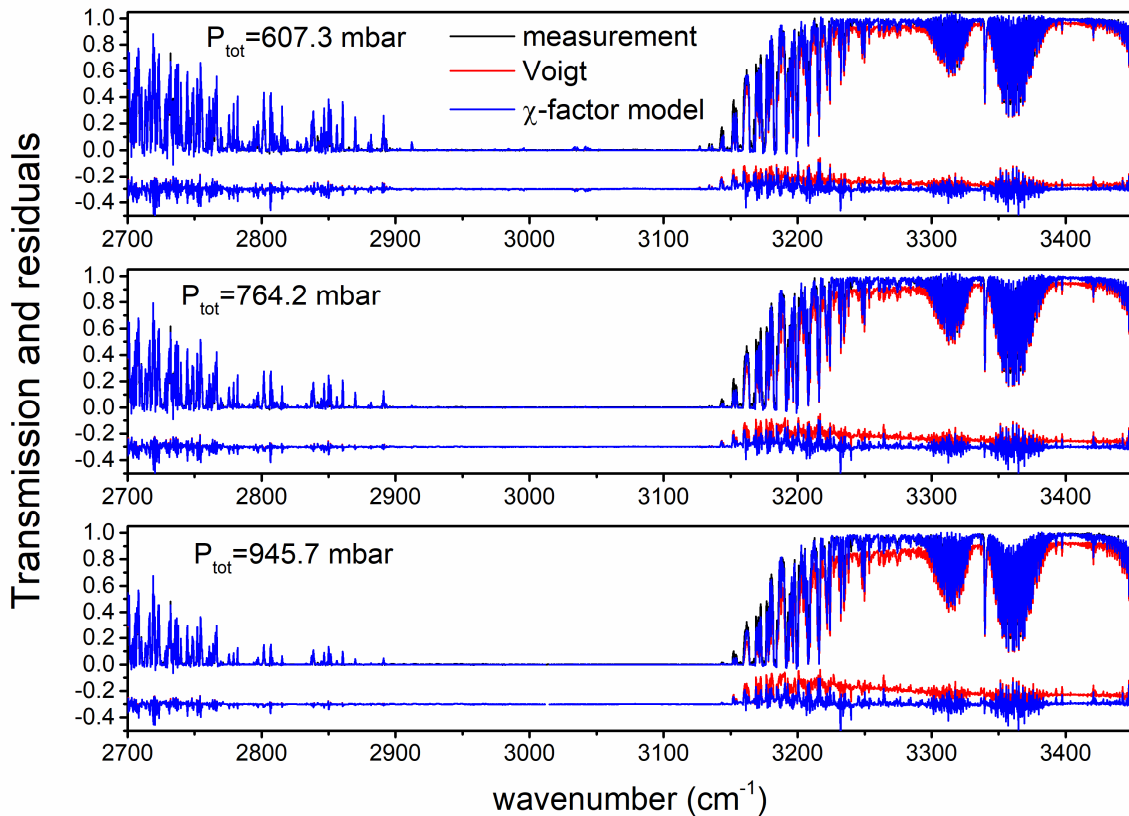
303

304 Figure 5: Absorption coefficients of CH₄ highly diluted in CO₂ calculated with (black line)
 305 and without (red) line mixing, at 250 K and 30 atm (top panel), 296 K and 45 atm (middle
 306 panel) and 400 K and 30 atm (bottom panel). Values calculated with the χ -factor model [see
 307 Eqs. (4,5)] are plotted in blue.

308 In (Gharavi and Buckley, 2005) devoted to the R(3) and R(4) manifolds of the $2\nu_3$ band, it
 309 was shown that the temperature dependences of CO₂- and N₂-broadening coefficients of CH₄
 310 lines can be quite different. The ratio $\gamma_{\text{CO}_2}/\gamma_{\text{N}_2}$ can indeed vary from 1.36 to 1.24 in the 296-
 311 670 K range. It is well known that the absorption coefficient in the line wing is proportional to
 312 the corresponding line width. Therefore, changing $\gamma_{\text{CO}_2}/\gamma_{\text{N}_2}$ from 1.3 to 1.2 or to 1.4 leads to
 313 a difference of about 10% for the absorption coefficient in the wings. This is negligible
 314 compared to the difference between the absorption coefficient calculated with the Voigt line
 315 shape and that computed with the full line-mixing modeling (about one order of magnitude at
 316 3300 cm⁻¹, for instance, see Figs. 4, 5). In the absence of accurate data for CO₂-broadening
 317 coefficients and their temperature dependences, the χ -factor proposed in this work can be
 318 therefore used in the 200 K-400 K temperature range.

319 The obtained χ -factor model was then used to compute spectra for the same conditions as
 320 those of the experiments recorded at SOLEIL (see Sec. 2.2). For the comparison with the
 321 measured spectra, absorption contributions due to CO₂ and to a small amount of water vapor
 322 (a H₂O fraction of $x_{\text{H}_2\text{O}} = 9.5 \times 10^{-5}$ was retrieved from the measured spectra) were
 323 included in the calculation. Voigt profiles were used, and the needed spectroscopic data of
 324 CO₂ and H₂O were taken from (Gordon et al., 2022). Note that calculations using a χ -factor
 325 model for CO₂ line wings (Tran et al., 2011) were also performed to compute CO₂ absorption

326 contributions, showing that CO₂ line wings have negligible influence on the total absorptions.
 327 The CH₄-broadening coefficients of CO₂ lines were assumed to be the same as the air-
 328 broadenings. This approximation should not affect the results since the mole fraction of CH₄
 329 is quite small ($x_{CH_4} = 0.0575$). Figure 6 shows comparisons between the measured spectra
 330 and those computed using the χ -factor model proposed in this work as well as using purely
 331 Voigt line shapes, for the ν_3 band region. As can be observed, the spectra are largely saturated
 332 around the band center. In the red wing of the band, the two calculations are both in good
 333 agreement with the measurements. This can be explained by the large contribution of local
 334 lines in this region. In the blue wing of the band where the relative contribution of the far
 335 wings is more important, the χ -factor model accurately reproduces the measurements,
 336 contrary to the Voigt profile that largely overestimates absorptions. These results thus validate
 337 the χ -factor model [Eqs.(4) and (5)] at room temperature, which can now be used for
 338 applications as those mentioned in Sec. 1. Note that the remaining residuals, namely those
 339 observed around 3200 cm⁻¹, are probably due to the uncertainties of the spectroscopic data of
 340 the local lines (Gordon et al., 2022) but also to the use of a unique scaling factor to deduce
 341 CO₂-broadenings coefficients of methane lines from air-broadening coefficients.



342
 343 Figure 6: Comparison between the SOLEIL spectra measured (black) in the ν_3 band region at
 344 room temperature and various total pressures of a mixture of CH₄ in CO₂ with $x_{CH_4} = 0.0575$
 345 and calculations at the same conditions, using the χ -factor model (blue) and the usual Voigt
 346 line shape (red). The differences between the measured spectra and calculated values are also
 347 displayed in each corresponding panel (minus 0.3).

348

349 5. Conclusion

350 This article presented the first modeling of the spectral shape of methane absorption lines
351 broadened by CO₂ from the line centers to the far wings. The model, based on a theoretical
352 approach previously developed for N₂-broadened CO₂ absorption lines, accounted for the
353 collision-induced line-mixing effects. Comparison with spectra measured in the CH₄ ν₃ band
354 region at room temperature and for a broad pressure range showed that the model is capable
355 to accurately reproduce absorption spectra of CH₄ in CO₂, from the line centers to the far
356 wings, in contrast with the Voigt profile that leads to large discrepancies with the
357 measurements. The model was then used to compute spectra of CH₄ in CO₂ for various
358 pressure and temperature conditions (from 200 to 400 K), which enabled the determination of
359 a simple line-shape correction factor χ in order to correct for the sub-Lorentzian behavior in
360 the far line wings. The latter, successfully validated by comparison with experimental spectra,
361 can be straightforwardly used to model absorption in the line wings, for practical applications
362 such as radiative transfer calculations for a planetary atmosphere. Finally, it is worthy to note
363 that the model can be largely improved in the future when accurate CO₂-broadening
364 coefficients of CH₄ lines, their temperature dependences as well as the state-to-state
365 collisional transfer rates are available.

366

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