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# Absorption of methane broadened by carbon dioxide in the 3.3 $\mu\text{m}$ spectral region: From line centers to the far wings

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41 by collisions between CH<sub>4</sub> (and H<sub>2</sub>) and CO<sub>2</sub>. The first modeling of these collision-induced  
42 absorptions (CIAs) was based on those of CH<sub>4</sub>-N<sub>2</sub> (and H<sub>2</sub>-N<sub>2</sub>) 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 CH<sub>4</sub>-CO<sub>2</sub> (H<sub>2</sub>-CO<sub>2</sub>) can be calculated as a linear combination of the CO<sub>2</sub>-CO<sub>2</sub> and CH<sub>4</sub>-CH<sub>4</sub>  
46 (H<sub>2</sub>-H<sub>2</sub>) CIAs (Richard et al., 2012). The CH<sub>4</sub>-CO<sub>2</sub> (H<sub>2</sub>-CO<sub>2</sub>) 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 CH<sub>4</sub>-CO<sub>2</sub> and H<sub>2</sub>-CO<sub>2</sub> CIAs  
49 are much more intense than those of CH<sub>4</sub>-N<sub>2</sub> and H<sub>2</sub>-N<sub>2</sub>. 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 CH<sub>4</sub>-CO<sub>2</sub> and H<sub>2</sub>-CO<sub>2</sub> 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 CH<sub>4</sub>-CO<sub>2</sub> and H<sub>2</sub>-CO<sub>2</sub> CIAs over broad spectral (0-1500 cm<sup>-1</sup>) 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 CH<sub>4</sub> monomer broadened by CO<sub>2</sub> in the 3.3 μm  
59 spectral region, which can contribute to the greenhouse warming in CO<sub>2</sub>-dominated  
60 atmospheres. Spectra of CH<sub>4</sub> highly diluted in CO<sub>2</sub> 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  $\chi$ -factor model to represent the  
65 spectral shape of CO<sub>2</sub>-broadened CH<sub>4</sub> 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 CH<sub>4</sub>+CO<sub>2</sub> mixtures and of pure CO<sub>2</sub> 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<sup>-1</sup>, 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<sup>-1</sup>, covering the entire  $\nu_3$  band of CH<sub>4</sub>. 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 CH<sub>4</sub> and CO<sub>2</sub> (mixture no. 1  
90 in Table 1) at an initial total pressure ( $P_{tot}$ ) of 24.53 atm and initial partial pressure of CH<sub>4</sub>  
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<sup>-1</sup> (“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  $\nu_3$  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 CH<sub>4</sub> partial pressures for a fixed value of the total pressure. For mixture no. 2, the  
102 cell was first filled with 404 mbar of CH<sub>4</sub> and the total pressure brought to 24903 mbar with  
103 CO<sub>2</sub>. A first spectrum (“No. 5” in Table 1) was recorded. The total pressure was then reduced  
104 by a factor  $F$  of about 10, CO<sub>2</sub> 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 CH<sub>4</sub>+CO<sub>2</sub> mixture (no. 3) prepared and spectra “No. 9” to “No. 13” were  
108 measured following the procedure applied to mixture no. 2. Pure CO<sub>2</sub> 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  $\Delta F$  on the factor  $F$ , estimated to be  $\Delta F = \sqrt{2(0.5)^2} \approx 0.71\%$   
117 of the reduced methane pressure.

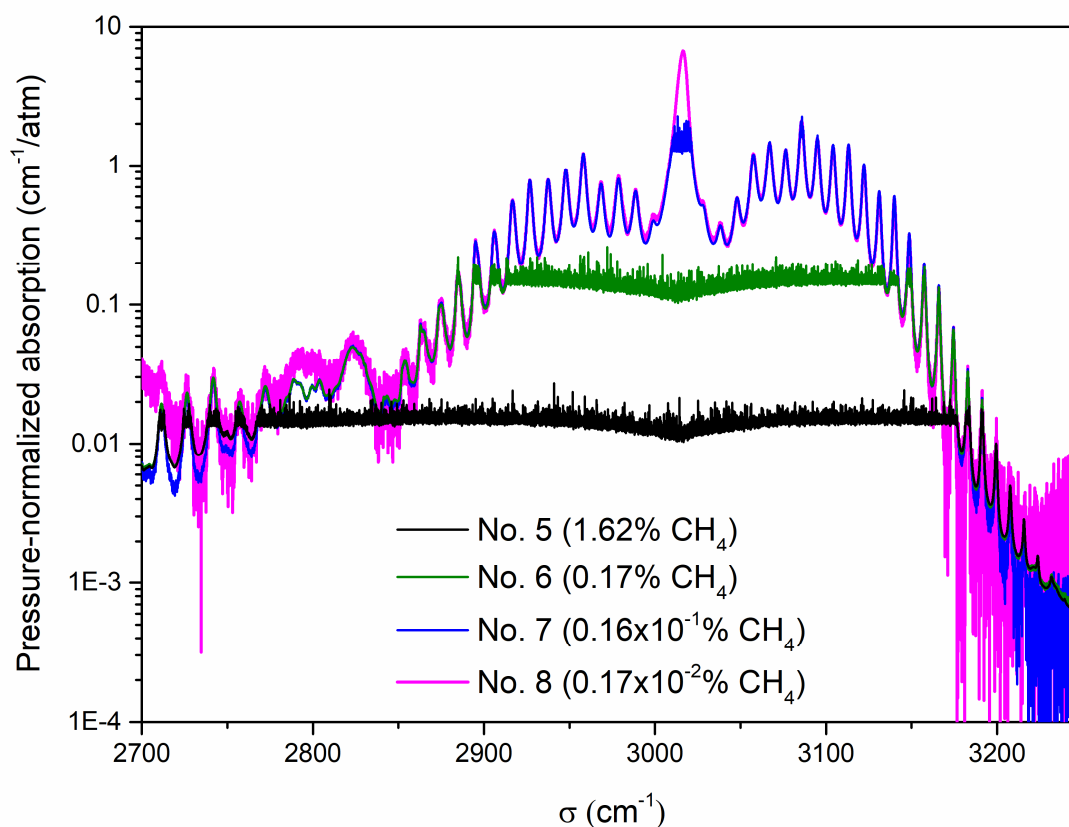
118 The transmissions due to CH<sub>4</sub> broadened by CO<sub>2</sub> were obtained by dividing the signal  
119 obtained with the mixture,  $S_{CH_4+CO_2}(P_{tot}, \sigma)$ , by  $S_{CO_2}(P_{tot}, \sigma)$ . With this procedure, the  
120 contribution of CO<sub>2</sub> absorption (the wings of neighboring CO<sub>2</sub> 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 CH<sub>4</sub> partial  
123 pressure. Since most of the studied gas samples contain mixing ratios of methane smaller than  
124 0.55%, the contribution of CH<sub>4</sub>-CH<sub>4</sub> collisions is negligible. The contribution of CH<sub>4</sub>-CH<sub>4</sub>  
125 collisions being not negligible for spectra No. 5 and 9, it was taken into account assuming that  
126 the effects of CH<sub>4</sub>-CH<sub>4</sub> and of CH<sub>4</sub>-CO<sub>2</sub> collisions are the same. This is justified by the fact  
127 that the average ratio of self- to air-broadening coefficients of CH<sub>4</sub> is 1.27 (Pine, 1992), very  
128 close to the ratio of CO<sub>2</sub> to air-broadenings (1.3, see Sec.3). As shown in Fig. 1 for mixture  
129 no. 2, the whole  $\nu_3$  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 CH<sub>4</sub> partial-pressure-normalized absorption spectra  
 132 of CH<sub>4</sub> broadened by CO<sub>2</sub> 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. / $\text{cm}^{-1}$
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 CH<sub>4</sub>+CO<sub>2</sub> spectra measured with the ULB setup.  
 135 Spectra of pure CO<sub>2</sub> 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 CH<sub>4</sub> pressures.



148  
 149 Figure 1: CH<sub>4</sub> partial-pressure-normalized absorption spectra of CH<sub>4</sub> broadened by CO<sub>2</sub>  
 150 measured at an average total pressure of 24991 mbar and for various partial pressures of CH<sub>4</sub>  
 151 (mixture no. 2 in Table 1).

152 *2.2. Measurements at SOLEIL*

153 CH<sub>4</sub>+CO<sub>2</sub> 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<sup>-1</sup> and results from the average of 1000 interferograms recorded with an unapodized  
 160 resolution of 0.5 cm<sup>-1</sup>.

161 The experiments proceeded as follows. The cell was filled with 54.4 mbar of CH<sub>4</sub> and CO<sub>2</sub>  
 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  $\alpha$  ( $\text{cm}^{-1}$ ) at wavenumber  $\sigma$  ( $\text{cm}^{-1}$ ) of  $\text{CH}_4$  broadened by  $\text{CO}_2$  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  $\ell$  and  $k$  of  $\text{CH}_4$ ;  $P_{\text{CH}_4}$  and  $P_{\text{CO}_2}$  are the  
 179 partial pressures of  $\text{CH}_4$  and  $\text{CO}_2$ , 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.  $\rho_{\ell}$  and  $d_{\ell}$   
 181 are the relative population of the initial level and the dipole matrix element of line  $\ell$ .  $\mathbf{\Sigma}$ ,  $\mathbf{L}_0$   
 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  $\text{CH}_4$  and  $\text{CO}_2$  on  
 185 the  $\text{CH}_4$  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,  $\gamma_{\ell}$ , and -shifting,  $\delta_{\ell}$ , 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  $\ell$  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  $\nu_3$  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  $\text{CH}_4$  lines by  $\text{CO}_2$  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 CO<sub>2</sub>-broadening coefficients of 28 CH<sub>4</sub> 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 CH<sub>4</sub> by collisions with  
216 CO<sub>2</sub> are the same as those of CH<sub>4</sub> 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.

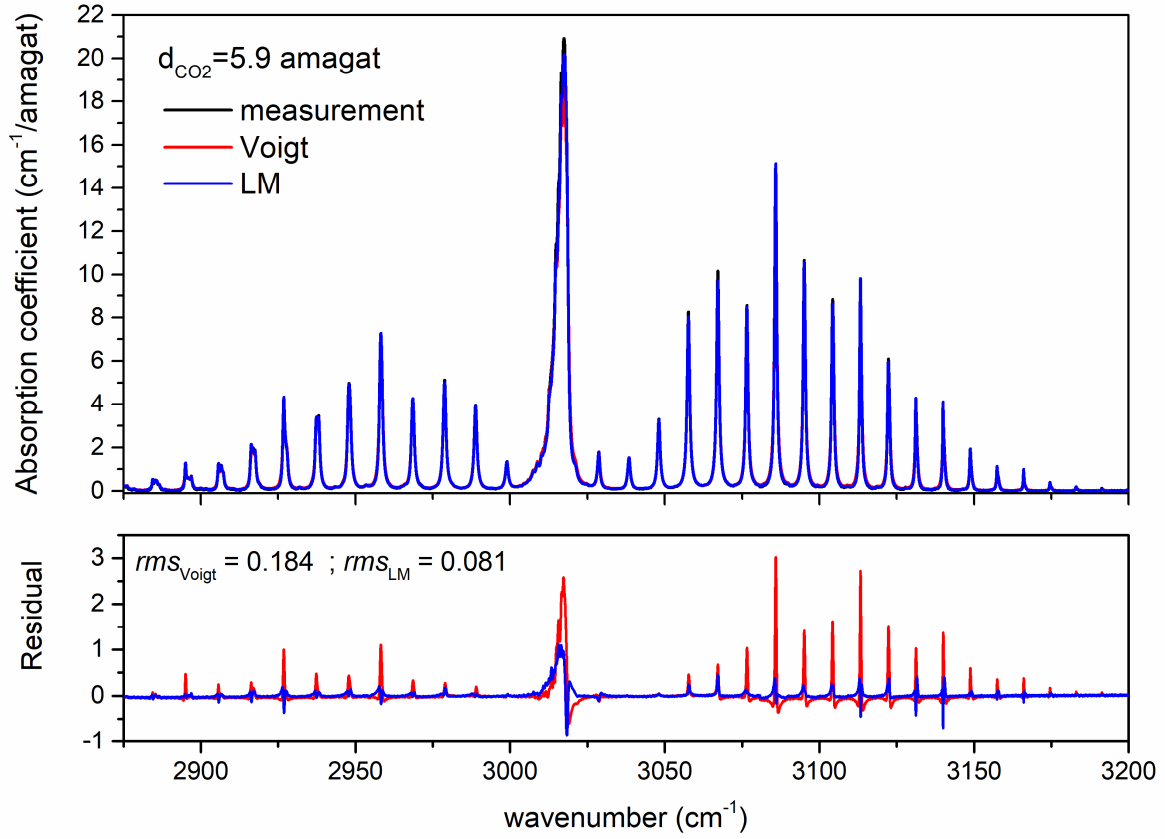
221 The off-diagonal elements of the relaxation matrix, including the state-to-state rates  $K(i_k \leftarrow$   
222  $i_\ell, T)$  and the  $A_{k,\ell}$  parameters, were assumed to be proportional to those for CH<sub>4</sub> in N<sub>2</sub>, also  
223 provided in (Tran et al., 2006a), with the same 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 CO<sub>2</sub> 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.<sup>i</sup> 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 CH<sub>4</sub> broadened by N<sub>2</sub> (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.

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<sup>i</sup> <https://webbook.nist.gov/cgi/cbook.cgi?Source=1927LOW%2FFERI2729-2734&Units=SI&Mask=7>

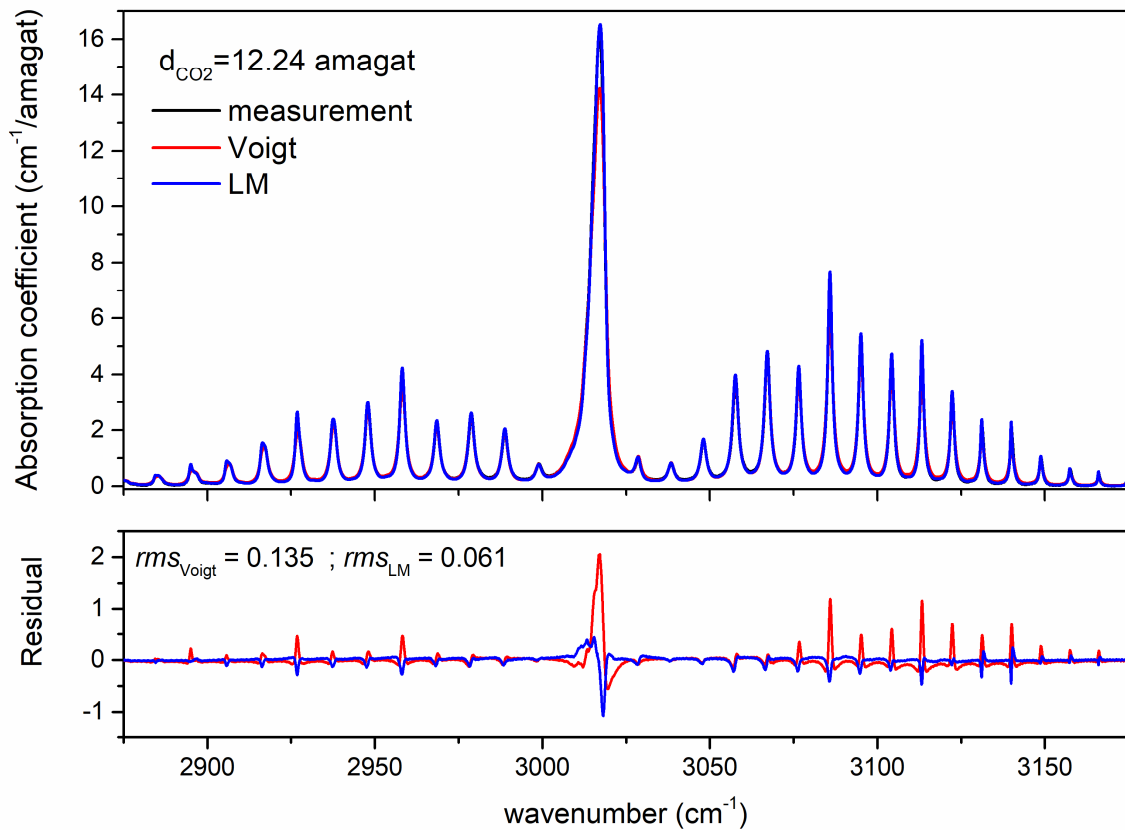




239

240 Figure 2: Comparison between the CO<sub>2</sub>-broadened CH<sub>4</sub> spectrum measured (black) at room  
 241 temperature for a density of CO<sub>2</sub>, ( $d_{CO_2}$ ) of 5.9 amagat (spectrum No. 3 in Table 1; 1 amagat  
 242 corresponding to  $2.687 \cdot 10^{19}$  molec.cm<sup>-3</sup> at 273.15 K) and values calculated with (blue) and  
 243 without (red) line mixing taken into account.

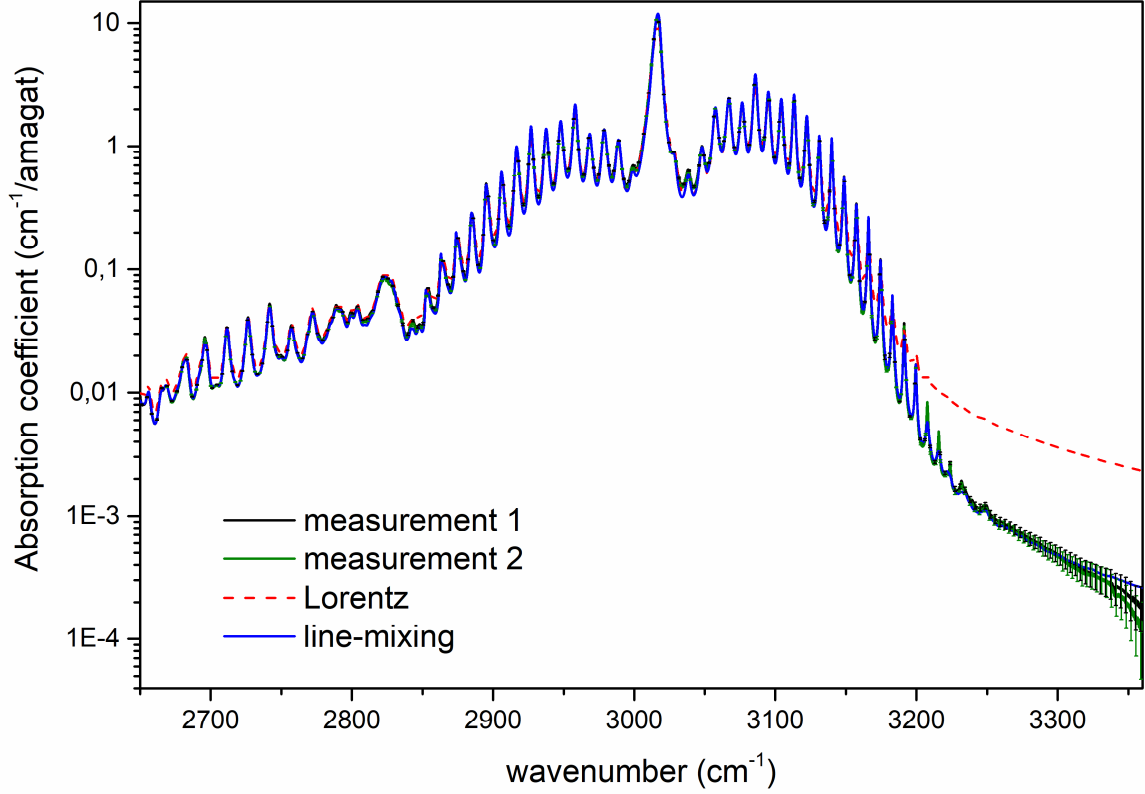
244



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  $\nu_3$  lines close to the  
 252 center of the band. For CH<sub>4</sub>, 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<sub>2</sub>-broadened  
 258 CH<sub>4</sub> lines, is capable to accurately predict the absorption shape from resonances to the far  
 259 wings of CH<sub>4</sub> perturbed by CO<sub>2</sub>.



260

261 Figure 4: Comparison between CO<sub>2</sub>-broadened CH<sub>4</sub> 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 CO<sub>2</sub> absorption contributions (estimated to be 1%).

#### 266 4. $\chi$ -factor model for the far wings of CO<sub>2</sub>-broadened CH<sub>4</sub> lines

267 For practical applications such as simulations of planetary atmospheres spectra, Lorentzian  
 268 (or Voigt) line shapes with line wings corrected using a  $\chi$ -factor are widely used. Within this  
 269 simple model, the absorption coefficient of a highly diluted CH<sub>4</sub>-CO<sub>2</sub> mixture is written as:

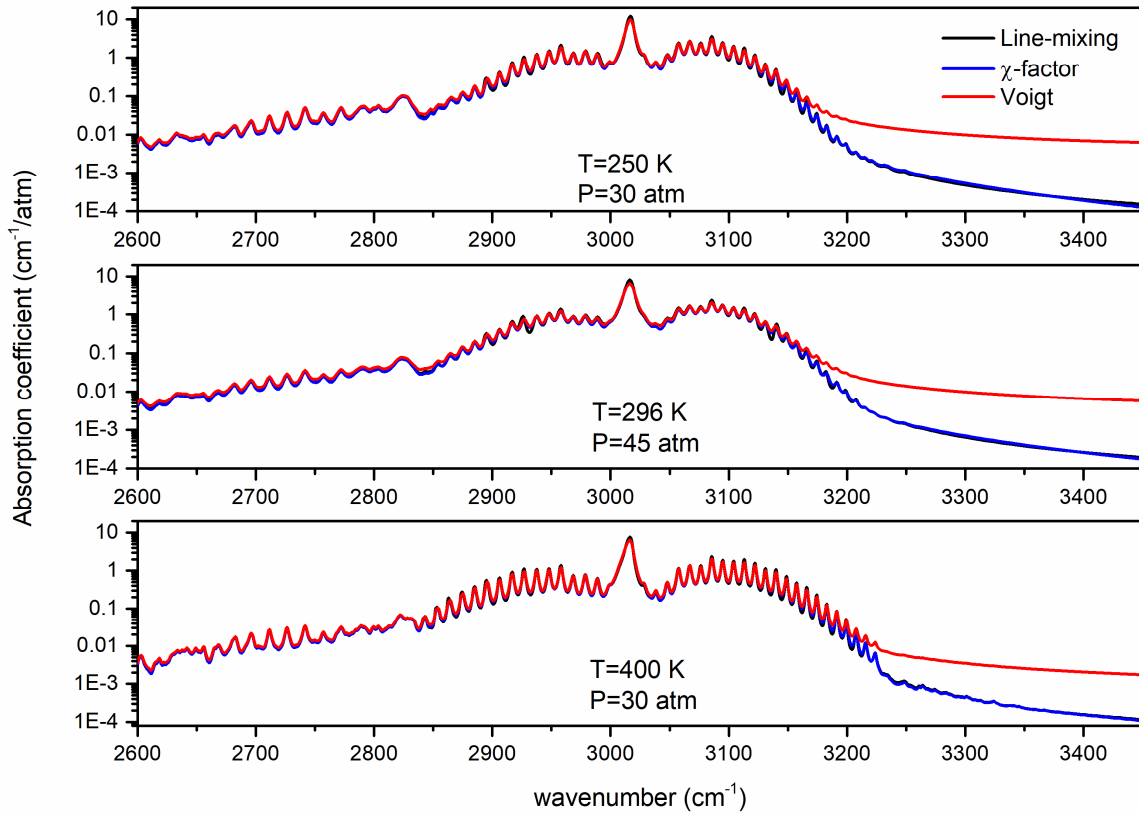
$$\begin{aligned}
 270 \quad \alpha(\sigma, P_{CH_4}, P_{CO_2}, T) &= \frac{1}{\pi} \sum_{\ell} P_{CH_4} S_{\ell}(T) \\
 271 \quad &\times \exp \left[ \frac{hc(\sigma - \sigma_{\ell})}{2k_B T} \right] \frac{\sigma}{\sigma_{\ell}} \frac{1 - e^{-\frac{hc\sigma}{k_B T}}}{1 - e^{-\frac{hc\sigma_{\ell}}{k_B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

272 The corrective factor  $\chi$ , 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,  $\chi$   
 276 was determined by fitting Eq. (4) to absorption spectra in the region of the  $\nu_3$  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 CH<sub>4</sub> perturbed N<sub>2</sub> (Pieroni et al., 1999; Tran et al., 2006a),  
 280 which showed that it is capable to accurately represent absorption spectra of CH<sub>4</sub> in N<sub>2</sub> 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 CH<sub>4</sub> in CO<sub>2</sub> have the  
 283 same temperature dependences as those of CH<sub>4</sub> in N<sub>2</sub>. Therefore, the model of Sec. 3 can be  
 284 used to simulate spectra at various temperatures. The following values for  $\chi$  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  $\chi$ -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  $\chi$ -factor approach leads to good agreements with measured spectra. For instance, at  
 296 3400 cm<sup>-1</sup> and for  $d_{tot} = 26.5$  amagat, the relative difference between the absorption  
 297 coefficients computed with the  $\chi$ -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  $\chi$ -factor model therefore should be used to  
 302 model absorption in the far line wings only.



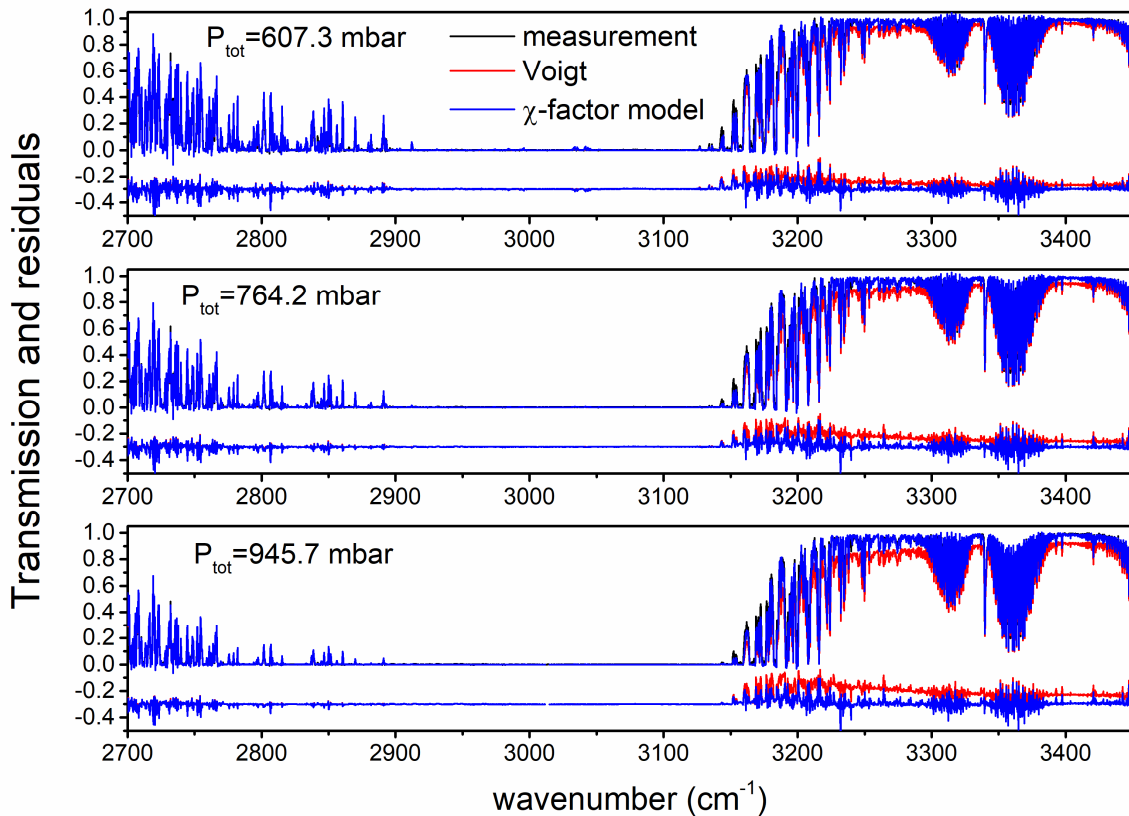
303

304 Figure 5: Absorption coefficients of CH<sub>4</sub> highly diluted in CO<sub>2</sub> 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  $\chi$ -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 CO<sub>2</sub>- and N<sub>2</sub>-broadening coefficients of CH<sub>4</sub>  
 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<sup>-1</sup>, for instance, see Figs. 4, 5). In the absence of accurate data for CO<sub>2</sub>-broadening  
 317 coefficients and their temperature dependences, the  $\chi$ -factor proposed in this work can be  
 318 therefore used in the 200 K-400 K temperature range.

319 The obtained  $\chi$ -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 CO<sub>2</sub> and to a small amount of water vapor  
 322 (a H<sub>2</sub>O 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 CO<sub>2</sub> and H<sub>2</sub>O were taken from (Gordon et al., 2022). Note that calculations using a  $\chi$ -factor  
 325 model for CO<sub>2</sub> line wings (Tran et al., 2011) were also performed to compute CO<sub>2</sub> absorption

326 contributions, showing that CO<sub>2</sub> line wings have negligible influence on the total absorptions.  
 327 The CH<sub>4</sub>-broadening coefficients of CO<sub>2</sub> lines were assumed to be the same as the air-  
 328 broadenings. This approximation should not affect the results since the mole fraction of CH<sub>4</sub>  
 329 is quite small ( $x_{CH_4} = 0.0575$ ). Figure 6 shows comparisons between the measured spectra  
 330 and those computed using the  $\chi$ -factor model proposed in this work as well as using purely  
 331 Voigt line shapes, for the  $\nu_3$  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  $\chi$ -factor model accurately reproduces the measurements,  
 336 contrary to the Voigt profile that largely overestimates absorptions. These results thus validate  
 337 the  $\chi$ -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<sup>-1</sup>, 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 CO<sub>2</sub>-broadenings coefficients of methane lines from air-broadening coefficients.



342  
 343 Figure 6: Comparison between the SOLEIL spectra measured (black) in the  $\nu_3$  band region at  
 344 room temperature and various total pressures of a mixture of CH<sub>4</sub> in CO<sub>2</sub> with  $x_{CH_4} = 0.0575$   
 345 and calculations at the same conditions, using the  $\chi$ -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 CO<sub>2</sub> from the line centers to the far wings. The model, based on a theoretical  
352 approach previously developed for N<sub>2</sub>-broadened CO<sub>2</sub> absorption lines, accounted for the  
353 collision-induced line-mixing effects. Comparison with spectra measured in the CH<sub>4</sub> ν<sub>3</sub> 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 CH<sub>4</sub> in CO<sub>2</sub>, 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 CH<sub>4</sub> in CO<sub>2</sub> for various  
358 pressure and temperature conditions (from 200 to 400 K), which enabled the determination of  
359 a simple line-shape correction factor  $\chi$  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 CO<sub>2</sub>-broadening  
364 coefficients of CH<sub>4</sub> lines, their temperature dependences as well as the state-to-state  
365 collisional transfer rates are available.

366

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## 374 References

- 375 Cacciani, P, Cermák, P, Vander Auwera, J, Campargue, A, 2022. The ammonia absorption spectrum  
376 between 3900 and 4700 cm<sup>-1</sup>. *J. Quant. Spectrosc. Radiat. Transf.* 277, 107961.
- 377 Chassefière, E, Lasue, J, Langlais, B, Quesnel, Y, 2016. Early Mars serpentinization-derived CH<sub>4</sub>  
378 reservoirs, H<sub>2</sub>-induced warming and paleo-pressure evolution. *Meteorit. Planet. Sci.* 51, 2234-45.
- 379 Fissiaux, L, Delière, Q, Blanquet, G, Robert, S, Vandaele, AC, Lepère, M, 2014. CO<sub>2</sub>-broadening  
380 coefficients in the ν<sub>4</sub> fundamental band of methane at room temperature and application to CO<sub>2</sub>-  
381 rich planetary atmospheres. *J. Mol. Spectrosc.* 297, 35-40.
- 382 Gharavi, M, Buckley, SG, 2005. Diode laser absorption spectroscopy measurement of linewidths  
383 and pressure broadening coefficients of the methane 2ν<sub>3</sub> band at elevated temperatures. *J. Mol.*  
384 *Spectrosc.* 229, 78-88.
- 385 Gordon, IE, Rothman, LS, Hargreaves, RJ, R Hashemi, EV Karlovets, FM Skinner, K Conway, C Hill,  
386 RV Kochanov, Y Tan, P Wcisło et al, 2022. The HITRAN2020 molecular spectroscopic database.  
387 *J. Quant. Spectrosc. Radiat. Transf.* 277, 107949. <https://doi.org/10.1016/j.jqsrt.2021.107949>
- 388 Haberle, R, Catling, D, Carr, M, Zahnle, K, 2017. The early Mars climate system. In: Haberle R,  
389 Clancy R, Forget F, Smith M, Zurek R (Eds.). *The Atmosphere and Climate of Mars*. Cambridge  
390 University Press, Cambridge, 526–568 Cambridge Planetary Science.
- 391 Haberle, RM, Zahnle, K, Barlow, NG, Steakley, KE, 2019. Impact degassing of H<sub>2</sub> on early Mars and  
392 its effect on the climate system. *Geophys. Res. Lett.* 46, 13355-62.

393 Hartmann, JM, Boulet, C, Brodbeck, C, Nguyen, VT, Fouchet, T, Drossart, P, 2002. A far wing  
394 lineshape for H<sub>2</sub> broadened CH<sub>4</sub> infrared transitions. *J. Quant. Spectrosc. Radiat. Transf.* 72, 117-  
395 122.

396 Hartmann, JM, Tran, H, Armante, R, Boulet, C, Campargue, A, Forget, F, et al, 2018. Recent  
397 advances in collisional effects on spectra of molecular gases and their practical consequences. *J.*  
398 *Quant. Spectrosc. Radiat. Transf.* 213, 178-227.

399 Hartmann, JM, Boulet, C, Robert, D, 2021. Collisional effects on molecular spectra: laboratory  
400 experiments and models, consequences for applications (2<sup>nd</sup> edition). Elsevier, Amsterdam.

401 Kite, ES, Mischna, M, Gao, P, Yung, YL, Turbet, M, 2020. Methane release on early Mars by  
402 atmospheric collapse and atmospheric reinflation. *Planetary and Space Science* 181, 104820.

403 Perrin, MY, Hartmann, JM, 1989. Temperature-dependent measurements and modeling of absorption  
404 by CO<sub>2</sub>-N<sub>2</sub> mixtures in the far line wings of the 4.3 μm CO<sub>2</sub> band. *J. Quant. Spectrosc. Radiat.*  
405 *Transf.* 42, 311-317.

406 Pieroni, D, Nguyen, VT, Brodbeck, C, Claveau, C, Valentin, A, Hartmann, JM, Gabard, T, Champion,  
407 JP, Bermejo D, Domenech, JL, 1999. Experimental and theoretical study of line mixing in methane  
408 spectra. I. The N<sub>2</sub>-broadened ν<sub>3</sub> band at room temperature. *J. Chem. Phys.* 110, 7717.

409 Pine, AS, 1992. Self-, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, Ar, and He broadening in the ν<sub>3</sub> band Q branch of CH<sub>4</sub>. *J. Chem.*  
410 *Phys.* 97, 773.

411 Pine, AS, 1997. N<sub>2</sub> and Ar broadening and line mixing in the P and R branches of the ν<sub>3</sub> band of CH<sub>4</sub>.  
412 *J. Quant. Spectrosc. Radiat. Transf.* 57, 157-76.

413 Ramirez, RM, Kopparapu, R, Zuger, ME, Robinson, TD, Freedman, R, Kasting, JF, 2014. Warming  
414 early Mars with CO<sub>2</sub> and H<sub>2</sub>. *Nat. Geosci.* 7, 59–63.

415 Ramirez, RM, Kaltenecker, L, 2018. A methane extension to the classical habitable zone. *Astrophys.*  
416 *J.* 858, 72.

417 Richard, C, Gordon, IE, Rothman, LS, Abel, M, Frommhold, L, Gustafsson, M, Hartmann, JM,  
418 Hermans, C, Lafferty, WJ, Orton, GS, Smith, KM, Tran, H, 2012. New section of the HITRAN  
419 database: collision-induced absorption (CIA). *J. Quant. Spectrosc. Radiat. Transf.* 113, 1276-85.

420 Tarnas, JD, Mustard, JF, Sherwood, LB, Bramble, MS, Cannon, KM, Palumbo, AM, Plesa, AC, 2018.  
421 Radiolytic H<sub>2</sub> production on Noachian Mars: implications for habitability and atmospheric  
422 warming. *Earth Planet Sci. Lett.* 502, 133-45.

423 Tran, H, Flaud, JM, Gabard, T, Hase, F, von Clarmann, T, Camy-Peyret, C, Payan, S, Hartmann, JM,  
424 2006a. Model, software and database for line-mixing effects in the ν<sub>3</sub> and ν<sub>4</sub> bands of CH<sub>4</sub> and tests  
425 using laboratory and planetary measurements. I: N<sub>2</sub> (and air) broadenings and the earth atmosphere.  
426 *J. Quant. Spectrosc. Radiat. Transf.* 101, 284-305. <https://doi.org/10.1016/j.jqsrt.2005.11.020>

427 Tran, H, Flaud, PM, Fouchet, T, Garbard, T, Hartmann, JM, 2006b. Model, software and database for  
428 line-mixing effects in the ν<sub>3</sub> and ν<sub>4</sub> bands of CH<sub>4</sub> and tests using laboratory and planetary  
429 measurements – II: H<sub>2</sub> (and He) broadening and the atmosphere of Jupiter and Saturn. *J. Quant.*  
430 *Spectrosc. Radiat. Transf.* 101, 306-324.

431 Tran, H, Boulet, C, Stefani, S, Snels, M, Piccioni, G, 2011. Measurements and modelling of high-  
432 pressure pure CO<sub>2</sub> spectra from 750 to 8500 cm<sup>-1</sup>. I-central and wing regions of the allowed  
433 vibrational bands. *J. Quant. Spectrosc. Radiat. Transf.* 112, 925-936.

434 Tran, H, Turbet, M, Chelin, P, Landsheere, X, 2018. Measurements and modeling of absorption by  
435 CO<sub>2</sub>+H<sub>2</sub>O mixtures in the spectral region beyond the CO<sub>2</sub> ν<sub>3</sub>-band head. *Icarus* 306, 116-21.  
436 <https://doi.org/10.1016/j.icarus.2018.02.009>

437 Tran, H, Turbet, M, Hanoufa, S, Landsheere, X, Chelin, P, Ma, Q, Hartmann, JM, 2019. The CO<sub>2</sub>-  
438 broadened H<sub>2</sub>O continuum in the 100-1500 cm<sup>-1</sup> region: Measurements, predictions and empirical  
439 model. *J. Quant. Spectrosc. Radiat. Transf.* 230, 75-80. <https://doi.org/10.1016/j.jqsrt.2019.03.016>

440 Turbet, M, Tran, H, Pirali, O, Forget, F, Boulet, C, Hartmann, JM, 2019. Far infrared measurements of  
441 absorptions by CH<sub>4</sub>+CO<sub>2</sub> and H<sub>2</sub>+CO<sub>2</sub> mixtures and implications for greenhouse warming on early  
442 Mars. *Icarus.* 321, 189-99.



- 443 Turbet, M, Boulet, C, Karman, T, 2020. Measurements and semi-empirical calculations of CO<sub>2</sub>+CH<sub>4</sub>  
444 and CO<sub>2</sub>+H<sub>2</sub> collision-induced absorption across a wide range of wavelengths and temperature.  
445 Application for the prediction of early Mars surface temperature. *Icarus*. 346, 113762.  
446 Wordsworth, RD, 2016. The Climate of Early Mars. *Ann. Rev. Earth. Planet Sci.* 44, 381-408.  
447 Wordsworth, R, Kalugina, Y, Lokshtanov, S, Vigasin, A, Ehlmann, B, Head, J, Sanders, C, Wang, H,  
448 2017. Transient reducing greenhouse warming on early Mars. *Geophys. Res. Lett.* 44, 665-71.