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Guillaume Janodet, Philippe Rivière, Jean-Michel Lamet, Valérie Rialland, Lionel Tessé, et al.. Statistical Narrow Band model for vibrational nonequilibrium CO₂ radiation. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2024, 314, pp.108856. 10.1016/j.jqsrt.2023.108856 . hal-04220093v1

HAL Id: hal-04220093

<https://hal.science/hal-04220093v1>

Submitted on 27 Sep 2023 (v1), last revised 8 Dec 2023 (v2)

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Statistical Narrow Band model for vibrational nonequilibrium CO₂ radiation

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Abstract

This paper presents the development of a Statistical Narrow Band (SNB) model for CO₂ in a nonequilibrium vibrational state. The population densities of the energy levels are modeled by a three-temperature approach (T, T_{12}, T_3) associated resp. to translation-rotation modes, symmetric-stretching and bending modes, and antisymmetric stretching mode, to compute nonequilibrium line by line (LBL) spectra. The nonequilibrium between vibrational temperatures induces spectral correlation issues between $\eta_\sigma/\kappa_\sigma$ and κ_σ , where η_σ and κ_σ are the emission and absorption coefficients respectively. To overcome this issue, a vibrational splitting of the spectroscopic database is made to separate lines with completely different vibrational transitions. The SNB parameters are obtained by fitting the curves of growth from the LBL approach by a least squares error minimization using a Newton method for pure Lorentz and Doppler broadening regimes for each line class. The total SNB

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transmissivity is obtained by computing the product of each line class transmissivity, and the decorrelation between the spectra of the different classes is checked. Finally, the model is tested in Voigt broadening regime using a mixing rule by computing outlet radiative intensity of uniform and non-uniform columns and agrees well with the LBL approach. SNB parameters are available under request to the corresponding author.

Keywords: CO₂ radiation, Vibrational nonequilibrium, SNB model

1 **1. Introduction**

2 The Local Thermodynamic Equilibrium (LTE) assumption is no longer valid
3 when internal relaxation time scales become comparable or higher than hydrodynamic time scales in gas flows. The gas is then under the Non-Local
4 Thermodynamic Equilibrium (NLTE) state, which means that it contains an
5 excess or a lack of internal energy compared to translational energy or even a
6 non-Boltzmannian distribution of the populations of the different vibrational
7 levels. This nonequilibrium aspect is found, for instance, in atmospheric entry
8 flows [1, 2], electrically excited or gas dynamic CO₂ lasers [3, 4], or
9 expanding flows like rocket plumes at high altitudes [5]. This departure from
10 LTE affects the radiative properties of the radiating species and thus needs
11 to be considered for radiative transfer.

13

14 One of the challenges in studying the radiation of gases under NLTE conditions is the knowledge of the population of each rovibrational energy level.
15 The detailed vibrational state-to-state approach [6] is a priori the most accurate model for predicting level population densities. However, the total
16
17

18 number of vibrational states of CO₂ with energies lower than the dissociation
19 limit is estimated to be of the order of 10⁵ [7]. Although some models
20 attempt to bin vibrational levels based on physical arguments in order to
21 reduce the computational complexity (see e.g., [7, 8]), the vibrational state-
22 to-state approach remains impracticable in the context of radiative transfer
23 calculations for coupled simulations in complex geometries. Moreover, the
24 uncertainty about the kinetic rate constants of high-energy levels makes using
25 the state-to-state approach very difficult. Therefore, the multi-temperature
26 description of the thermodynamic state of CO₂, based on previous works
27 [9, 10], is adopted in this study to compute vibrational level populations.

28

29 Once the spatial distributions of population densities are known, line-by-line
30 (LBL) local absorption and emission spectra can be computed using suitable
31 spectroscopic databases such as HITRAN [11], HITEMP [12] or CDSD-4000
32 [13] for CO₂ at high temperature. Such LBL calculations have been recently
33 undertaken by Binauld et al. [9] to evaluate the effects of vibrational CO₂
34 NLTE on the infrared radiation emitted by an expanding flow in a conical
35 nozzle or by high-altitude rocket plumes. It was shown in this study that the
36 partial freeze of CO₂ vibration excitation, due to the strong expansion of the
37 flow in the low-pressure atmosphere, may significantly increase the emission
38 by the plume compared to the emission predicted from a single translation
39 temperature. However, the LBL calculations were limited to some chosen
40 lines of sight in the plume and 1D radiation calculations in the case of the
41 nozzle flow. As for the state-to-state kinetic approach, the detailed LBL
42 calculations also remain impracticable when the radiative transfer is to be

43 coupled to flow-field calculations. Indeed, spectral, angular, and spatial in-
44 tegrations would require huge CPU time and storage capabilities. The de-
45 velopment of accurate spectral band models is then highly desirable in this
46 perspective.

47

48 In the framework of radiative transfer spectral modelling in nonequilibrium
49 reentry flows, k-distribution models were first developed by Bansal et al. for
50 N and O atomic radiation [14, 15] and then extended by Bansal et al. [16]
51 to diatomic molecular species (N_2 , N_2^+ , NO, and O_2). Several spectral wide-
52 band binning strategies and reduced order models have been compared in
53 [17] for different reentry conditions. However, in the present work, global
54 and wide-band models are excluded since one of the goals of the present
55 study is to develop models suitable for spectrally integrated radiative trans-
56 fer calculations and also for infrared signature simulations, which are limited
57 to narrow spectral bands.

58

59 Among narrow-band models, k-distribution, with or without an extension
60 with fictitious gases [18], remains challenging to apply in the case of react-
61 ing media with spatial change of chemical composition and strong pressure
62 gradients. Statistical narrow-band models have been applied by Lamet et al.
63 [19] for the prediction of radiative transfer in earth reentry flows and show
64 a good ability to deal with diatomic molecules with the imbalance between
65 electronic/vibration and translation/rotation (two-temperature description
66 of the medium).

67

68 It is worth noticing that all NLTE radiation models mentioned above were
69 dedicated to atomic or diatomic radiation, and none of them has consid-
70 ered polyatomic molecules like CO₂, where a disequilibrium may exist be-
71 tween the different vibration modes. Specific models have been developed
72 for NLTE CO₂ radiation in [20]. However, the smeared band model was
73 employed to get tractable simulations, which may fail for low-pressure ap-
74 plications with well-separated non-optically thin rotational lines. Another
75 approach was developed first by Kudryavtsev and Novikov [21], and then
76 by Vitkin et al. [22, 23], on the basis of statistical narrow-band mixing of
77 lines belonging to different vibrational transitions. However, instead of using
78 accurate spectroscopic databases, semi-analytical simplified models were em-
79 ployed to represent the spectral structure of CO₂ bands in the 4.3 and 2.7 μm
80 regions. This approach was followed by Molchanov et al. [24] who used *k*-
81 distribution method to compute partial transmissivities in the narrow bands.

82

83 This paper aims to develop a three-temperature SNB model for CO₂, con-
84 sidering spectral correlations and disequilibrium between vibrational modes
85 (Section 2). CO₂ translational and rotational modes are assumed to be at
86 local equilibrium and are described by a single temperature T due to the
87 fast translation-rotation exchanges. Vibrational levels are assumed to fol-
88 low a Boltzmann distribution at a single temperature T_{12} for the symmetric
89 stretching mode, and the two-fold degenerate bending mode due to Fermi
90 Resonance [25] and a Boltzmann distribution at a different temperature T_3
91 for the antisymmetric stretching mode. The model is then applied in Sec-
92 tion 3 to a simple expanding supersonic nozzle flow and to radiative transfer

93 along selected lines of sight in the high altitude plume of a solid propellant
 94 rocket as in [9]. The model accuracy is assessed through comparisons with
 95 line-by-line calculations.

96 2. SNB formulation

97 2.1. Radiative properties and multi-temperature model

98 The emission and absorption coefficients for wavenumber σ can be expressed
 99 under the assumption of independent lines as:

$$\eta_\sigma = \sum_{u-l} n_u \frac{A_{ul}}{4\pi} hc\sigma_{ul} f_{ul}(\sigma - \sigma_{ul}), \quad (1)$$

$$\kappa_\sigma = \sum_{u-l} (n_l B_{lu} - n_u B_{ul}) hc\sigma_{ul} f_{ul}(\sigma - \sigma_{ul}), \quad (2)$$

101 where n_u and n_l are the populations of levels u and l , A_{ul} , B_{ul} and B_{lu}
 102 are the Einstein coefficients for spontaneous emission, induced emission, and
 103 absorption, σ_{ul} is the central wavenumber, and $f_{ul}(\sigma - \sigma_{ul})$ is the spectral
 104 line profile (assumed to be the same for the three radiative mechanisms) of
 105 the transition $u - l$. Spectroscopic data for CO₂ (Einstein coefficients, level
 106 energies, line positions, collisional broadening parameters) have been taken
 107 from the HITEMP-2010 [12] compilation, which has been recommended for
 108 applications up to 2000 K [13]. The population of any rovibrational level k
 109 of CO₂ in the multi-temperature approach of [9] can be expressed as follows:

$$n_k = n_{CO_2} Ab_I \frac{g_k}{Z_I(T, T_{12}, T_3)} \exp\left(-\frac{E^{rot}\{k\}}{k_B T} - \frac{E^{\nu_{12}}\{k\}}{k_B T_{12}} - \frac{E^{\nu_3}\{k\}}{k_B T_3}\right), \quad (3)$$

110 where n_{CO_2} is the total population density of CO₂, Ab_I is the abundance
 111 of the considered isotopologue I , g_k is the degeneracy of the level k . The

112 partitioning scheme of the energy is composed of a rotational part $E^{rot}\{k\}$, a
 113 vibrational part $E^{\nu_{12}}\{k\}$ associated with the coupled symmetric stretching-
 114 bending modes (ν_1, ν_2) and a vibrational part $E^{\nu_3}\{k\}$ corresponding to the
 115 asymmetric stretching mode ν_3 . For each rovibrational level, these energies
 116 are calculated from the spectroscopic database according to

$$E^{rot}\{v_1, l_2, v_3, r, p, J\} = E\{v_1, l_2, v_3, r, p, J\} - \min_{J'} E\{v_1, l_2, v_3, r, p, J'\}, \quad (4)$$

$$E^{\nu_3}\{v_1, l_2, v_3, r, p, J\} = \min_{J'} E\{0, 0, v_3, 1, e, J'\}, \quad (5)$$

$$E^{\nu_{12}}\{v_1, l_2, v_3, r, p, J\} = \min_{J'} E\{v_1, l_2, v_3, r, p, J'\} - E^{\nu_3}\{v_1, l_2, v_3, r, p, J\}, \quad (6)$$

119 where (v_1, l_2, v_3, r, p, J) are the quantum numbers used in HITEMP-2010 to
 120 identify the rovibrational levels k . v_1 and v_3 are quantum numbers associated
 121 respectively with the vibrational modes ν_1 and ν_3 ; l_2 is associated with the
 122 vibrational angular momentum of mode ν_2 ; the triplet (v_1, l_2, v_3) enables to
 123 identify the Fermi polyad to which the level k belongs; r is the index of the
 124 vibrational level associated to the level k among the $v_1 + 1$ vibrational levels
 125 constituting the Fermi polyad, p is the parity (e or f) and J is the total
 126 angular momentum quantum number excluding nuclear spin of the level k .
 127 The populations of the few non-identified levels (0.9% of the lines see Table
 128 2) have been calculated assuming LTE at temperature T . $Z_I(T, T_{12}, T_3)$
 129 in Eq.(3) is the three-temperature partition function of the isotopologue I ,
 130 which has been calculated using the approximation of the three uncoupled
 131 harmonic oscillators associated with the vibrational modes of CO₂ and the
 132 rigid rotor and is given by:

$$Z_I(T, T_{12}, T_3) = \frac{k_b T}{\alpha_I B_I} \times \frac{1}{1 - \exp(-\omega_{1I}/k_b T_{12})} \frac{1}{[1 - \exp(-\omega_{2I}/k_b T_{12})]^2} \frac{1}{1 - \exp(-\omega_{3I}/k_b T_3)} \quad (7)$$

broadening regime	resolution [cm ⁻¹]	line wing cut-off [cm ⁻¹]	spectral domain [cm ⁻¹]
Lorentz	10 ⁻²	50	[237.5, 8312.5]
Doppler	10 ⁻³	10	[237.5, 8312.5]
Voigt	10 ⁻³	50	[237.5, 8312.5]

Table 1: Input parameters for the LBL calculations

133 where B_I is the rotational constant of isotopologue I , $\alpha_I = 1$ or 2 depending
134 on the isotopologue symmetry, ω_{1I} , ω_{2I} and ω_{3I} are the vibration energies
135 associated with the three fundamental vibration modes taken for the differ-
136 ent isotopologues from [26].

137

138 The models and data presented here are used to perform LBL calculations
139 for building vibrational nonequilibrium SNB models for CO₂ in Doppler, and
140 Lorentz broadening regimes. The Voigt broadening regime will be recov-
141 ered using a mixing approach (see below), whose validation will also require
142 LBL calculations in the Voigt regime. In the following, all calculations were
143 achieved for a CO₂-N₂ mixture with a molar fraction $x_{\text{CO}_2} = 0.5$ using the
144 input parameters provided in Table 1.

145 2.2. Spectral correlation issues

146 The radiative transfer equation (RTE) along a line of sight in nonscattering
147 media is given by

$$\frac{dI_\sigma(s)}{ds} = \eta_\sigma(s) - \kappa_\sigma(s)I_\sigma(s), \quad (8)$$

148 where $I_\sigma(s)$ is the radiative intensity at the abscissa s along the line of sight.

149 The absorption and emission coefficients must be calculated beforehand to

150 solve this equation. This section aims to develop an RTE formulation un-
 151 der nonequilibrium conditions suitable for applying statistical narrow-band
 152 models. From Eq.(8), we can express the intensity escaping from a column
 153 $(0,s)$ at s as:

$$I_\sigma(s) = \int_0^s \eta_\sigma(s') \tau_\sigma(s',s) ds', \quad (9)$$

154 where $\tau_\sigma(s',s) = \exp(-\int_{s'}^s \kappa_\sigma(s'') ds'')$ is the transmissivity of the column
 155 (s',s) and $I_\sigma(s=0)$ is assumed equal to 0.

156

157 To use SNB models for solving the RTE, we must express the intensity av-
 158 eraged over the spectral band $\Delta\sigma$. However, the emission coefficient η_σ and
 159 the transmissivity τ_σ are strongly correlated. To correctly account for self-
 160 correlation, the intensity averaged over the spectral band $\Delta\sigma$ is expressed

161 as

$$\overline{I}_\sigma^{\Delta\sigma}(s) = \int_0^s \overline{\frac{\eta_\sigma(s')}{\kappa_\sigma} \frac{\partial \tau_\sigma}{\partial s'}(s',s)}^{\Delta\sigma} ds'. \quad (10)$$

162 To compute Eq. (10) with SNB models, a further simplification is necessary,

163 which is

$$\overline{I}_\sigma^{\Delta\sigma}(s) \approx \int_0^s \overline{\left(\frac{\eta_\sigma(s')}{\kappa_\sigma}\right)}^{\Delta\sigma} \frac{\partial \overline{\tau}_\sigma^{\Delta\sigma}}{\partial s'}(s',s) ds' \quad (11)$$

164 assuming that $\frac{\eta_\sigma}{\kappa_\sigma}$ and $\frac{\partial \tau_\sigma}{\partial s'}$ are not correlated. This assumption is valid
 165 in LTE conditions because the ratio $\frac{\eta_\sigma}{\kappa_\sigma}$ is equal to the Planck's function
 166 $I_\sigma^0(T)$. However, it is not guaranteed in NLTE conditions since Kirchhoff's
 167 law is no longer valid and the ratio $\frac{\eta_\sigma}{\kappa_\sigma}$ can present important spectral dy-
 168 namics. The Fig.1 presents two nonequilibrium conditions: an imbalance
 169 between vibration and rotation (right) and an imbalance between the vibra-
 170 tional modes and the rotation (left). It is clear that the ratio follows neither

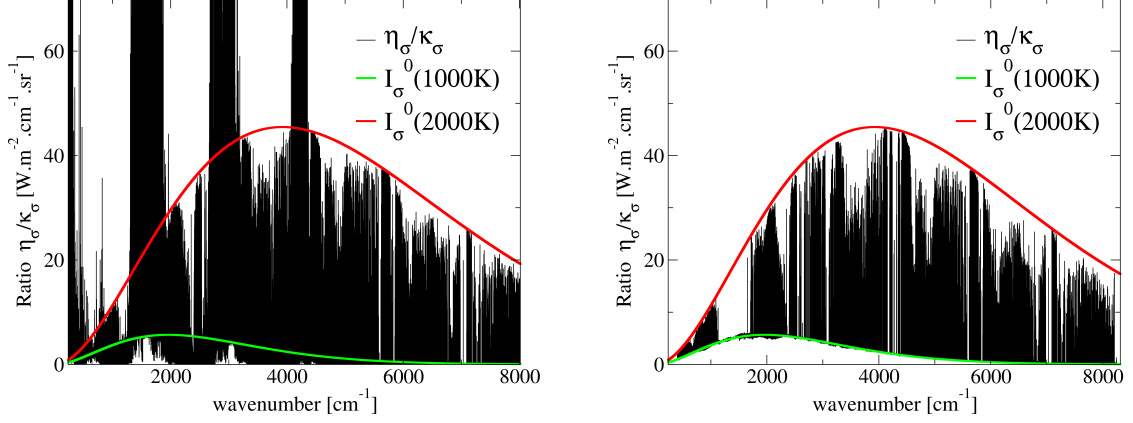


Figure 1: LBL $\eta_\sigma/\kappa_\sigma$ spectrum for $p = 1000$ Pa, $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 300$ K (left) and $p = 1000$ Pa, $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 1000$ K (right)

171 Planck's function at temperature T_{12} nor Planck's function at temperature
 172 T_3 as shown in Fig.1 (left). The spectral dynamics are then more important
 173 than for rotation-vibration nonequilibrium, as shown in Fig.1 (right) and in
 174 [19]. Comparing $\overline{\eta_\sigma}^{\Delta\sigma}$ to $\overline{\eta_\sigma/\kappa_\sigma}^{\Delta\sigma} \times \overline{\kappa_\sigma}^{\Delta\sigma}$ is the most critical test to check the
 175 decorrelation assumption. Indeed, the expression of the intensity averaged
 176 over the spectral band $\Delta\sigma$ exiting of uniform column of length l considering
 177 the decorrelation assumption is given by :

$$\overline{I_\sigma}^{\Delta\sigma}(0 \rightarrow l) = \int_0^l \overline{\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)}^{\Delta\sigma} \frac{\partial \overline{\tau_\sigma}^{\Delta\sigma}}{\partial s'}(s', l) ds' = \overline{\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)}^{\Delta\sigma} (1 - \overline{\tau_\sigma}^{\Delta\sigma}(0 \rightarrow l)). \quad (12)$$

178 The spectral dynamics of the emissivity $1 - \tau_\sigma(0 \rightarrow l)$ is maximum when the
 179 medium is optically thin because the exponential function does not smooth
 180 the absorption coefficient spectral structures. The expression of the radiative

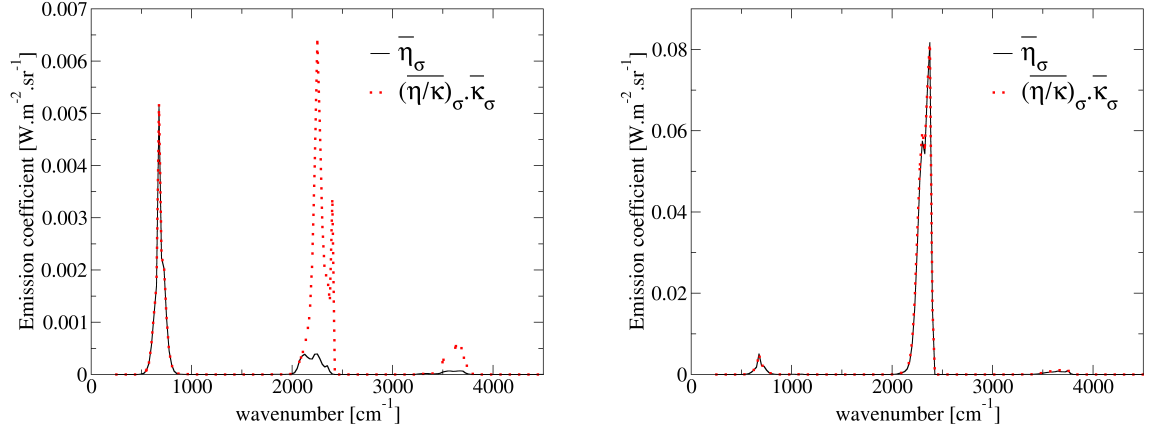


Figure 2: Comparison between $\overline{\eta_\sigma}^{\Delta\sigma}$ and $\overline{\eta_\sigma/\kappa_\sigma}^{\Delta\sigma} \times \overline{\kappa_\sigma}^{\Delta\sigma}$ for $p = 1000$ Pa, $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 300$ K (left) and $p = 1000$ Pa, $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 1000$ K (right)

181 intensity is, considering the decorrelation hypothesis, equal to

$$\overline{I_\sigma}^{\Delta\sigma}(0 \rightarrow l) \underset{\kappa_\sigma l \rightarrow 0}{=} \overline{\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)^{\Delta\sigma}} \overline{\kappa_\sigma}^{\Delta\sigma} l, \quad (13)$$

182 which explains the choice of comparing $\overline{\eta_\sigma}^{\Delta\sigma}$, the exact result, to $\overline{\eta_\sigma/\kappa_\sigma}^{\Delta\sigma} \times$
 183 $\overline{\kappa_\sigma}^{\Delta\sigma}$ for verifying the decorrelation assumption. These tests were performed
 184 for realistic strong nonequilibrium conditions. It turns out that the decorre-
 185 lation assumption between $\eta_\sigma/\kappa_\sigma$ and κ_σ is not valid for cases with a strong
 186 imbalance between the temperatures T_{12} and T_3 and a pressure $P \leq 10^4$ Pa,
 187 as shown in Fig. 2 (left). The influence of pressure on spectral dynamics is
 188 well known. Indeed, the line widths for Lorentz broadening regime are pro-
 189 portional to the pressure. Thus, decreasing the pressure increases the spectral
 190 dynamics and, therefore, the spectral correlation between $\eta_\sigma/\kappa_\sigma$ and κ_σ . Nev-
 191 ertheless, more than pressure's influence is needed to explain these spectral

192 correlations since the decorrelation assumption is always verified at LTE. It
 193 combines being in both moderate pressure conditions and a strong imbalance
 194 between the two vibration temperatures. Fig. 2 (left) shows that the corre-
 195 lation issue arises only for the 2.7 μm and 4.3 μm bands. To understand
 196 further why these spectral bands are problematic under these conditions,
 197 high-resolution spectra of κ_σ and η_σ under the strong vibrational imbalance
 198 condition of Fig.2 (left part) have been plotted in Fig. 3 (lower and middle
 199 part of the figure), for a very narrow spectral range [2247.62, 2247.69] cm^{-1}
 200 belonging to a problematic narrow-band identified in Fig.2. In the upper
 201 part of Fig. 3 are also plotted both $\eta_\sigma/\kappa_\sigma$ and again κ_σ , using a logarithmic
 202 scale, exhibiting a strong anticorrelation between κ_σ and $\eta_\sigma/\kappa_\sigma$: in this re-
 203 gion, the absorption spectrum is dominated by vibrational transitions of the
 204 type $\Delta v_3 = 1$ near 2247.63 and 2247.675 cm^{-1} as mentioned in the lowest
 205 part of the figure; these transitions also contribute to the emission spectrum
 206 near the same spectral locations, but transitions of type ($\Delta v_1 = 1, \Delta l_2 = 1$)
 207 also contribute to the emission spectrum near 2247.655 cm^{-1} as indicated
 208 on the middle part of Fig. 3.¹ Each of these types of vibrational transitions,
 209 considered as an isolated line ($u - l$), will be characterized by very different
 210 values of the ratio $(\eta_\sigma/\kappa_\sigma)_{ul}$, whose general expression is

$$\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)_{ul} = \frac{2hc\sigma_{ul}^3}{\exp\left(\frac{\Delta E_{ul}^{\nu_{12}}}{k_B T_{12}} + \frac{\Delta E_{ul}^{\nu_3}}{k_B T_3} + \frac{\Delta E_{ul}^{rot}}{k_B T}\right) - 1}. \quad (14)$$

211 In the above equation, $\Delta E_{ul}^{\nu_{12}}$, $\Delta E_{ul}^{\nu_3}$, and ΔE_{ul}^{rot} designate the energy varia-

¹Let note that about 16 rovibrational transitions are required to accurately model the spectra shown in Fig. 3: to simplify the analysis, only three dominant vibrational transitions have been mentioned near the local maximum of the spectra.

212 tion associated to resp. vibrational mode 12, vibrational mode 3, and rotation
 213 for the transition ul . For the two types of vibrational transitions identified
 214 above, resp. $\Delta v_3 = 1$ and $(\Delta v_1 = 1, \Delta l_2 = 1)$, the transition energy $hc\sigma_{ul}$ is
 215 mainly defined resp. by $\Delta E_{ul}^{\nu_3}$ and $\Delta E_{ul}^{\nu_{12}}$, while the rotational contribution
 216 $\Delta E_{ul}^{rot}/(k_B T)$ inside the exponential in Eq. (14) is negligible in comparison
 217 with vibrational one at $T = 2000$ K; the associated ratios $(\eta_\sigma/\kappa_\sigma)_{ul}$ may be
 218 therefore approximated according to

$$\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)_{\Delta v_3=1} \approx \frac{2hc\sigma_{ul}^3}{\exp\left(\frac{hc\sigma_{ul}}{k_B T_3}\right) - 1}, \quad (15)$$

$$\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)_{\Delta v_1=1, \Delta l_2=1} \approx \frac{2hc\sigma_{ul}^3}{\exp\left(\frac{hc\sigma_{ul}}{k_B T_{12}}\right) - 1}, \quad (16)$$

219 and will be very different from each other in the condition ($T_3 = 300$ K,
 220 $T_{12} = 2000$ K) considered here. Although the overlapping between lines,
 221 especially at not too low pressures, should moderate this analysis (the ab-
 222 sorption coefficient near 2247.655 cm^{-1} is dominated by the line wings of the
 223 transitions $\Delta v_3 = 1$ even at 1000 Pa), the variability of the $(\eta_\sigma/\kappa_\sigma)_{ul}$ val-
 224 ues of the various contributing transitions to emission or absorption spectra
 225 explains the anticorrelation between κ_σ and $\eta_\sigma/\kappa_\sigma$ observed in Fig. 3, and
 226 thus the overestimation of the emission observed in Fig.2 (left) when using
 227 the decorrelation hypothesis Eq. 13. It is quite obvious from Eq. 14 that the
 228 variability of $(\eta_\sigma/\kappa_\sigma)_{ul}$ values will occur under strong vibrational disequilib-
 229 rium among vibrational transitions of different nature, viz. characterised by
 230 very different vibrational energy variations $(\Delta E_{ul}^{\nu_3}, \Delta E_{ul}^{\nu_{12}})$. Grouping tran-
 231 sitions into classes of similar vibrational energy variations will reduce the
 232 variability of $(\eta_\sigma/\kappa_\sigma)_{ul}$ inside each class and, therefore, improve the accuracy

233 of the decorrelation approximation Eq. 13 when applied to the lines of a given
 234 class. Let note that the good behaviour of this decorrelation assumption in
 235 the 15 μm region (see Fig. 2) is consistent with the above analysis since in
 236 this spectral region, vibrational transitions involving only the mode (ν_1, ν_2)
 237 are dominant.

238 2.3. Definition of line classes

239 Considering that the fundamental vibrational energies of mode ν_1 and ν_2
 240 approximately satisfy $\omega_{1I} \approx 2\omega_{2I}$ for each isotopologue I , the more accurate
 241 approach to ensure the decorrelation assumption's validity would consist of
 242 grouping the lines into classes according to the different observed values of
 243 $(2\Delta v_1 + \Delta l_2, \Delta v_3)$. Such an approach would lead to the introduction of more
 244 than 20 classes leading to a quite tedious model. Observing that in the
 245 two main spectral regions where CO_2 radiation has to be accounted for and
 246 where correlation issues arise, i.e. the 4.3 μm and the 2.7 μm regions, the
 247 main vibrational transitions satisfy $\Delta v_3 = 1$, it appears quite natural to split
 248 the database into lines satisfying $\Delta v_3 = 1$ or $\Delta v_3 \neq 1$. Table 2 presents
 249 the different line classes that have been defined and the distribution of the
 250 transitions per class.

name	$\nu 3$	<i>not_ν3</i>	<i>not_defined</i>
definition	$\Delta v_3 = (v_3)' - (v_3)'' = 1$	$\Delta v_3 \neq 1$	$r' = 0$ or $r'' = 0$
proportion of lines	4554364 (40.9%)	6482107 (58.2%)	99692 (0.9%)

Table 2: Line classes for CO_2

251

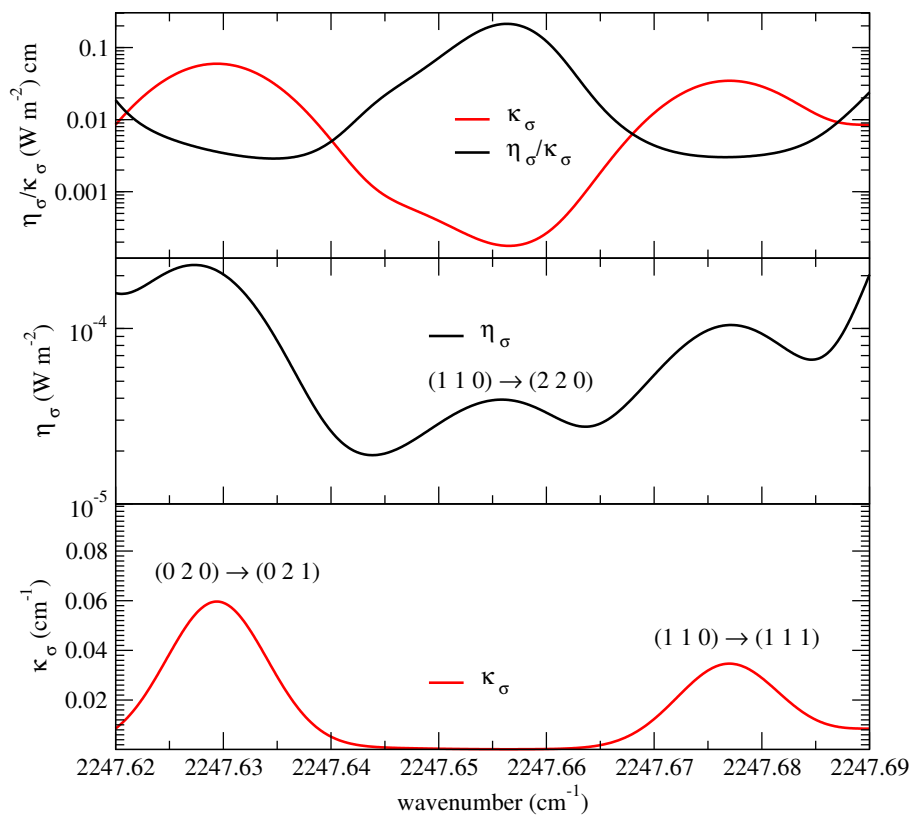


Figure 3: Absorption (κ_σ) and emission (η_σ) spectra of a CO₂-N₂ mixture at $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 300$ K, $p = 1000$ Pa. Typical dominant vibrational transitions (see footnote 1) are indicated near each local maximum of the spectra using the notation $(v_1 l_2 v_3)'' \rightarrow (v_1 l_2 v_3)'$ to designate lower '' and upper ' vibrational states. The upper part of the figure exhibits the anticorrelation between $\eta_\sigma/\kappa_\sigma$ and κ_σ for this strong vibrational imbalance condition.

252 The ν_3 and *not_ν₃* classes represent more than 99% of the database lines. The
 253 class *not_defined* contains the lines for unknown upper or lower vibrational
 254 energy levels. It seems natural to consider these lines separately because we
 255 cannot use vibrational temperatures to predict the population of their asso-

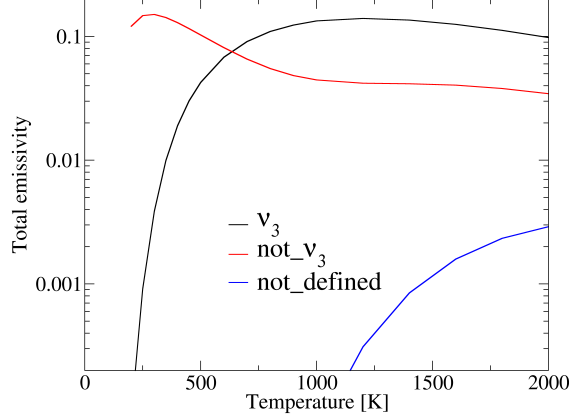


Figure 4: Comparison of emissivities of the three classes vs temperature at LTE for $p = 100000$ Pa, $l = 1$ m and $x_{\text{CO}_2} = 0.5$

256 ciated upper or lower levels; that is why these level populations are assumed
 257 to follow a Boltzmann distribution at the translation/rotation temperature
 258 T . To evaluate the contribution of each class to the gas radiative properties,
 259 a comparison of the total emissivity of each class as a temperature function
 260 (at LTE) is plotted in Fig. 4. The total emissivity is computed following

$$\epsilon_{tot,class}(x,p,l,T) = \frac{\pi}{\sigma_{SB}T^4} \sum_{bands\ b} (1 - \overline{\tau}_b^{\Delta\sigma}(x,p,l,T)) \overline{I}_b^{\Delta\sigma}(T)\Delta\sigma, \quad (17)$$

261 where σ_{SB} is the Stefan-Boltzmann constant and I^0 is Planck's function. The
 262 ν_3 class ($\Delta\nu_3 = 1$) is the one that contributes the most above $T=700$ K, and
 263 the not_nu_3 class ($\Delta\nu_3 \neq 1$) is dominant below. As expected, the contribution
 264 of the $not_defined$ class is weak compared to the other classes.

265

266 Henceforth, a check for the validity of the decorrelation assumption is per-
 267 formed for each class. The one for the $not_defined$ class is useless because

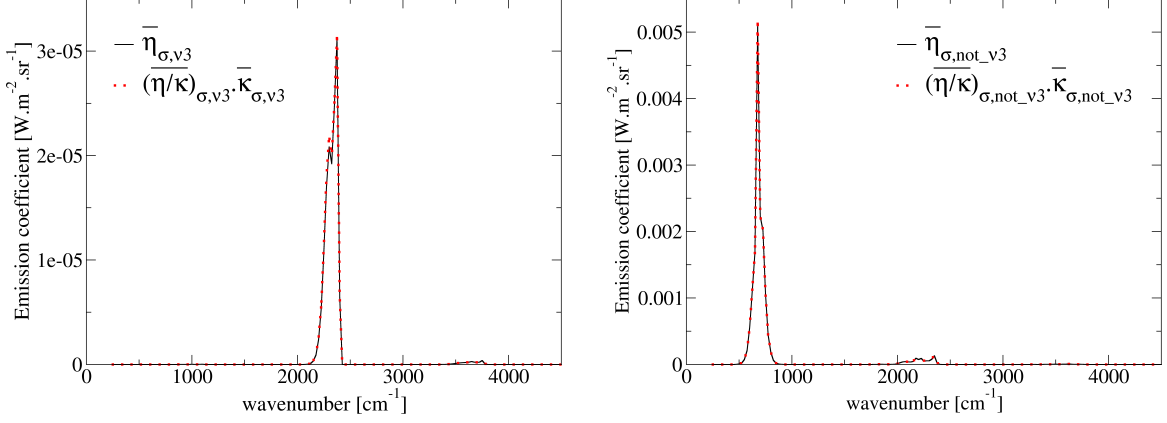


Figure 5: Emission coefficient for $\nu 3$ class (left) and not- $\nu 3$ class (right) for $p = 1000$ Pa, $T = 2000$ K, $T_{12} = 1000$ K and $T_3 = 300$ K

268 level populations for these lines are assumed at LTE. Fig.5 shows that split-
 269 ting into line classes solves the spectral correlation issue between $\eta_\sigma/\kappa_\sigma$ and
 270 κ_σ . The formulation of the RTE equation, averaged over $\Delta\sigma$, with the multi-
 271 class approach for CO₂ is expressed following Lamet et al. [19], as :

$$\bar{I}_\sigma^{\Delta\sigma}(l) = \sum_{j=1}^{N_{class}} \int_0^l \overline{\left(\frac{\eta_\sigma}{\kappa_\sigma}\right)}_j^{\Delta\sigma}(s) \frac{\partial \bar{\tau}_j^{\Delta\sigma}}{\partial s}(s,l) \prod_{j' \neq j} \bar{\tau}_{j'}^{\Delta\sigma}(s,l) ds, \quad (18)$$

272 where a decorrelation assumption between classes has been used. The validity
 273 of this assumption is checked in Fig.6 and shows that the product of the
 274 transmissivities is indeed very close to the total transmissivity $\bar{\tau}_\sigma^{\Delta\sigma}$ of CO₂.

275 2.4. Statistical narrow band model parameters

276 Equation (18) shows that the model requires the computation of parameters
 277 $\overline{(\eta_\sigma/\kappa_\sigma)}_j^{\Delta\sigma}$ and of transmissivities. The parameters $\overline{(\eta_\sigma/\kappa_\sigma)}_j^{\Delta\sigma}$ were directly
 278 tabulated from LBL calculations, and were found to be insensitive to line

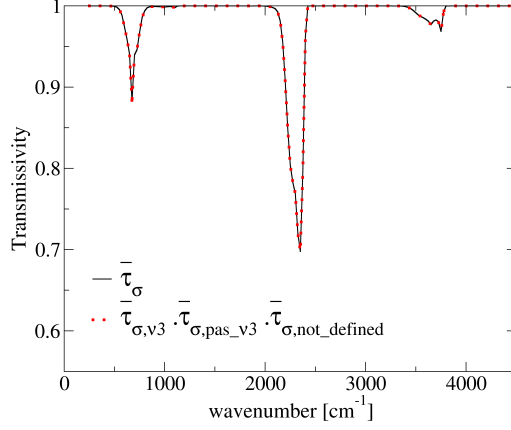


Figure 6: Comparison of the transmissivity product for each class with the total transmissivity

279 broadening regime. For transmissivities, the random SNB model of Mayer
 280 and Goody [27] has been selected in this study since it provides accurate
 281 results for polyatomic molecules at LTE. This model is based on statistical
 282 assumptions concerning line positions and intensities within a narrow band
 283 of width $\Delta\sigma$ and allows to express the transmissivity of a uniform column of
 284 length l , averaged over $\Delta\sigma$ as

$$\bar{\tau}^{\Delta\sigma}(l) = \frac{1}{\Delta\sigma} \int_{\Delta\sigma} \exp(-\kappa_{\sigma}l) d\sigma = \exp\left(-\frac{\bar{W}}{\delta}\right), \quad (19)$$

285 where $\delta = \Delta\sigma/N$ is the mean spacing between the N line positions within
 286 $\Delta\sigma$, and \bar{W} is the mean black equivalent width of these lines, defined as

$$\bar{W} = \frac{1}{N} \sum_{r=1}^N \int_{-\infty}^{+\infty} [1 - \exp(-\kappa_{\sigma}^r l)] d\sigma, \quad (20)$$

287 where κ_{σ}^r is the contribution of the r^{th} line to the absorption coefficient.
 288 Several line intensity distribution functions have been proposed to model

289 \overline{W}/δ for Lorentz and Doppler line broadening. The most used are the Goody
 290 exponential distribution [27], and the Malkmus tailed inverse-exponential
 291 distribution [28]. They are special cases (respectively for $\alpha = -1$ and $\alpha = 0$)
 292 of the generalized Malkmus distribution function of [29]. Its expression is the
 293 following

$$P_\alpha(S) : \frac{C_\alpha}{S} \left(\frac{S_m}{S} \right)^\alpha \left[\exp\left(-\frac{S}{S_m}\right) - \exp\left(-\frac{rS}{S_M}\right) \right], \quad (21)$$

294 where C_α is a normalization constant. In this study, the Malkmus distribu-
 295 tion function is used for the Lorentz broadening regime leading to

$$\frac{\overline{W}_L}{\delta} = \frac{2\overline{\gamma}_L}{\overline{\delta}_L} \left(\sqrt{1 + \frac{\overline{k}_L x p l \overline{\delta}_L}{\overline{\gamma}_L}} - 1 \right). \quad (22)$$

296 In the Doppler broadening regime, P_α distribution leads to the mean equiv-
 297 alent line width expression

$$\frac{\overline{W}_D}{\delta} = \overline{\beta}_D H_\alpha\left(\frac{\overline{k}_D x p l}{\overline{\beta}_D}\right) \quad (23)$$

298 with

$$H_\alpha(y) = \frac{1}{\alpha\sqrt{\pi}} \int_{-\infty}^{+\infty} [(1 + y \exp(-\xi^2))^\alpha - 1] d\xi \quad \text{for } \alpha \neq 0 \quad (24)$$

$$H_0(y) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln[1 + y \exp(-\xi^2)] d\xi \quad \text{for } \alpha = 0, \quad (25)$$

299 where $\overline{\delta}_L$ is a modified mean line spacing and $\overline{\beta}_D$ characterizes the degree of
 300 line overlapping. $\overline{k}_{L/D}$ is the reduced mean absorption coefficient and can be
 301 considered equal for the Lorentz and Doppler broadening regime ($\overline{k}_L = \overline{k}_D =$
 302 $\overline{k} = \overline{\kappa}_\sigma/(x_{\text{CO}_2} p)$) with good accuracy. The parameter $\overline{\gamma}_L$ represents the mean
 303 Lorentz half width at half maximum of the lines and is expressed for CO₂ as

304 [30]

$$\overline{\gamma}_L = \frac{p}{p_s} \left(\frac{T_s}{T} \right)^{0.7} [0.07x_{\text{CO}_2} + 0.058(1 - x_{\text{CO}_2})], \quad (26)$$

305 where $p_s = 1$ atm and $T_s = 296$ K.

306

307 For each broadening regime and each line class, parameters \overline{k} have been
308 obtained directly by averaging over each narrow band ($\Delta\sigma = 25$ cm⁻¹)
309 high-resolution absorption coefficients provided by LBL calculations based
310 on the HITEMP-2010 database. The parameters $\overline{\delta}_L$ and $\overline{\beta}_D$ have been gen-
311 erated from adjustments enabling the corresponding analytical expression of
312 $\overline{W}_{L/D}/\overline{\delta}$, as a function of the column length l , to fit $-\ln(\overline{\tau}^{\Delta\sigma}(l))$ obtained
313 with LBL calculations (called the curve of growth). This adjustment is made
314 by minimizing the least square error thanks to the Newton method. The pa-
315 rameters $\overline{\delta}_L$ and \overline{k} are assumed independent of the pressure and are generated
316 at $p = 1$ bar. For the curve of growth adjustments in the Lorentz broad-
317 ening regime, 20 transmissivities are prescribed from 0.02 to 0.95, and the
318 associated column lengths are computed from these transmissivities. For the
319 adjustments in Doppler broadening regime, 21 column lengths are provided
320 from $x_{\text{CO}_2}pl = 5$ Pa.m to $x_{\text{CO}_2}pl = 5000$ Pa.m with a regular logarithmic
321 step. Indeed, prescribing transmissivities near 0 for the Doppler broadening
322 regime would lead to huge and unrealistic column lengths. The parameter α
323 in the distribution function is equal to 0.3 excepted for narrow band centers
324 $\sigma = 2350/2375/2400$ cm⁻¹ where $\alpha = 0.2$. To quantify the errors introduced
325 by the SNB model for uniform columns, a mean quadratic error is defined

326 for the mean transmissivity $\bar{\tau}^{\Delta\sigma}$ as follows for each spectral band

$$s_\tau(\sigma) = \sqrt{\frac{1}{N_T \cdot N_{T_{12}} \cdot N_{T_3} \cdot N_l \cdot N_{class}}} \times \sqrt{\left(\sum_{i=1}^{N_T} \sum_{j=1}^{N_{T_{12}}} \sum_{k=1}^{N_{T_3}} \sum_{l=1}^{N_l} \sum_{n=1}^{N_{class}} \left((\bar{\tau}_{LBL}^{\Delta\sigma} - \bar{\tau}_{SNB}^{\Delta\sigma})(\sigma, T_i, T_{12,j}, T_{3,k}, l_l, class_n) \right)^2 \right)}, \quad (27)$$

327 and a relative mean quadratic error is defined for $1 - \bar{\tau}^{\Delta\sigma}$ for each spectral
328 band according to

$$s_{rel,1-\tau}(\sigma) = \sqrt{\frac{1}{N_T \cdot N_{T_{12}} \cdot N_{T_3} \cdot N_l \cdot N_{class}}} \times \sqrt{\left(\sum_{i=1}^{N_T} \sum_{j=1}^{N_{T_{12}}} \sum_{k=1}^{N_{T_3}} \sum_{l=1}^{N_l} \sum_{n=1}^{N_{class}} \left(\left(\frac{\bar{\tau}_{LBL}^{\Delta\sigma} - \bar{\tau}_{SNB}^{\Delta\sigma}}{1 - \bar{\tau}_{LBL}^{\Delta\sigma}} \right) (\sigma, T_i, T_{12,j}, T_{3,k}, l_l, class_n) \right)^2 \right)}, \quad (28)$$

329 where $N_T, N_{T_{12}}, N_{T_3}, N_{class}$ are the number of grid points of the variables
330 $T, T_{12}, T_3, class$, respectively, for which parameters have been obtained. For
331 the temperatures, the grid contains the 32 following values: [200, 250, 300,
332 350, 400, 450, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500,
333 1600, 1700, 1800, 1900, 2000, 2200, 2400, 2600, 2800, 3000, 3200, 3400,
334 3600, 3800, 4000]. The N_l lengths l correspond to the ones used to perform
335 the curve of growth adjustments of $\bar{\delta}_L$ and $\bar{\beta}_D$. These error estimators are
336 presented in Fig. 7 and Fig. 8 and show that the adjustment errors are
337 maximum when performed in the absorption bands, which is expected since
338 the curves of growth are linear for small optical thicknesses. The errors for

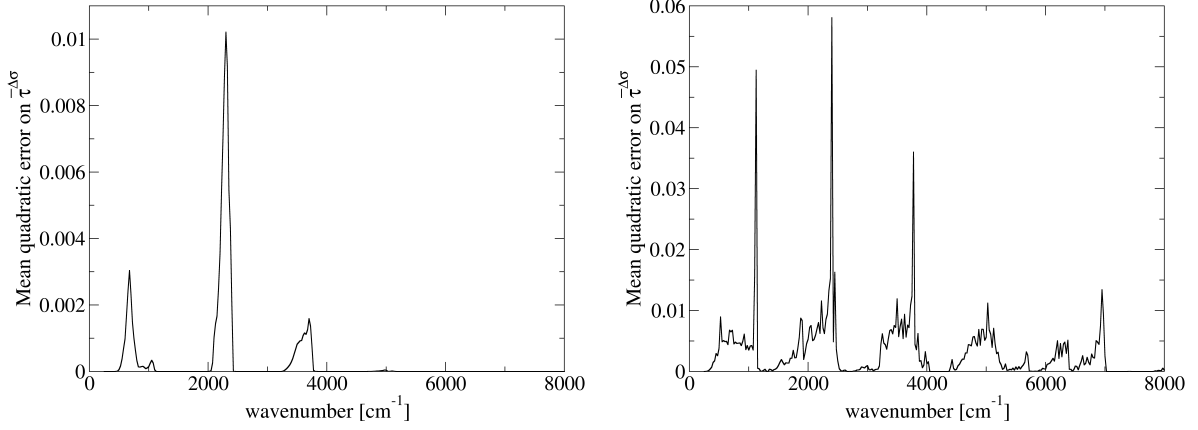


Figure 7: Mean quadratic error on $\bar{\tau}^{-\Delta\sigma}$ for Doppler broadening regime (left) and Lorentz broadening regime (right)

339 Lorentz broadening regime appear higher than for the Doppler regime. How-
 340 ever, transmissivities are prescribed in Lorentz broadening, which means that
 341 the adjustment is made for a wide range of optical thicknesses. Therefore,
 342 the errors displayed for Lorentz broadening involve contributions of all trans-
 343 missivity ranges, unlike for Doppler broadening, where errors are checked on
 344 the optically thin or medium part of the curve of growth.

345

346 In the context of high-altitude rocket plumes, we have to consider the Voigt
 347 broadening regime for which the mean black equivalent line width is calcu-
 348 lated by combining \overline{W}_L/δ and \overline{W}_D/δ expressions, according to the Ludwig
 349 formula

$$\frac{\overline{W}_V}{\delta} = \overline{kxpl} \sqrt{1 - \Omega^{-1/2}} \quad \text{with}$$

$$\Omega = \left[1 - \left(\frac{1}{\overline{kxpl}} \frac{\overline{W}_D}{\delta} \right)^2 \right]^{-2} + \left[1 - \left(\frac{1}{\overline{kxpl}} \frac{\overline{W}_L}{\delta} \right)^2 \right]^{-2} - 1 \quad (29)$$

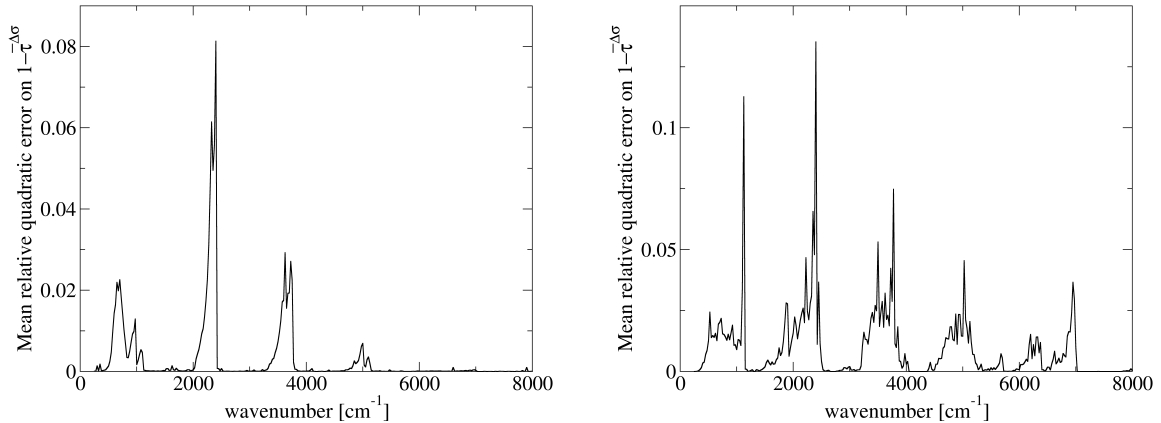


Figure 8: Mean relative quadratic error on $1 - \bar{\tau}^{\Delta\sigma}$ for Doppler broadening regime (left) and Lorentz broadening regime (right)

350 as proposed in [31].

351

352 To validate the SNB model in this regime, we compare the radiative intensity
 353 at the exit of a uniform column from the model expressed as Eq.(18) and
 354 the LBL approach for the nonequilibrium conditions considered in Fig. 2 in
 355 a wide range of pressure. This allows us to check the model in all broadening
 356 regimes and ensure that the mixing formula and the mixing of classes do not
 357 downgrade model accuracy. The comparison in Fig. 9 shows a good agree-
 358 ment between the SNB model and the LBL approach for the two conditions.

359

360 To conclude this subsection, the SNB parameters $\overline{(\eta_\sigma/\kappa_\sigma)^{\Delta\sigma}}$, \bar{k} , $\bar{\delta}_L$, and $\bar{\beta}_D$
 361 have been tabulated as function of the three temperatures T , T_{12} , and T_3 ,
 362 for each class and each narrow band. The temperature grid is the one given
 363 above.

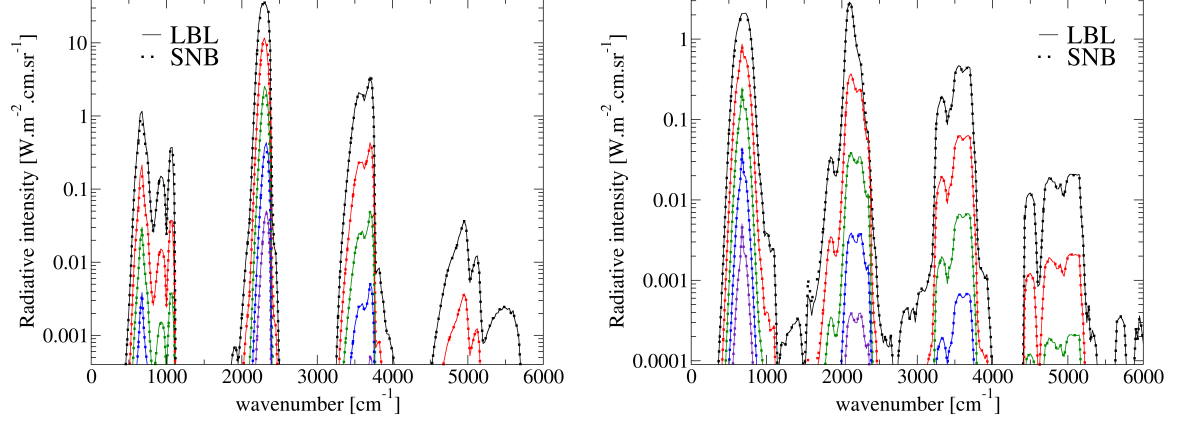


Figure 9: Radiative intensity for a uniform column at $l = 0.1$ m for $x_{\text{CO}_2} = 0.5$, $T = 300$ K, $T_{12} = 1000$ K, $T_3 = 2000$ K (left) and $l = 10$ m for $x_{\text{CO}_2} = 0.5$, $T = 2000$ K, $T_{12} = 1000$ K, $T_3 = 300$ K (right). The pressure is $p = 10000$ Pa (black), $p = 1000$ Pa (red), $p = 100$ Pa (green), $p = 10$ Pa (blue) and $p = 1$ Pa (indigo).

364 3. Application to radiative transfer

365 This model aims to be applied in realistic radiative transfer calculations.
 366 It must, therefore, give satisfactory results for non-uniform columns. The
 367 radiative intensity at the exit of a non-uniform column with N_{col} sub-columns
 368 indexed i from the multi-class SNB model is approximated by

$$\bar{I}^{\Delta\sigma}(N^+) = \sum_{j=1}^{N_{class}} \sum_{i=1}^{N_{col}} \overline{\left(\frac{\eta_{\sigma}}{\kappa_{\sigma}}\right)_j}^{\Delta\sigma} (T^i, T_{12}^i, T_3^i) \times$$

$$\left[\overline{\tau}_j^{\Delta\sigma}(i^+ \rightarrow N^+) - \overline{\tau}_j^{\Delta\sigma}(i^- \rightarrow N^+) \right] \sqrt{\prod_{j' \neq j} \overline{\tau}_{j'}^{\Delta\sigma}(i^+ \rightarrow N^+) \prod_{j' \neq j} \overline{\tau}_{j'}^{\Delta\sigma}(i^- \rightarrow N^+)}, \quad (30)$$

369 where $+$ and $-$ represent resp. the inlet and the outlet of the sub-column i .
 370 The approximation is valid if each sub-column (i^-, i^+) is optically thin.

371

372 The Curtis-Godson (C-G) [32] and Lindquist-Simmons (L-S) [33, 34] ap-
 373 proaches are the most commonly used formulations to express the mean
 374 transmissivity for non-uniform columns with SNB models. In the Curtis-
 375 Godson formulation, it is assumed that the mean transmissivity of a non-
 376 uniform column, bounded by abscissae 0 and l , may be expressed similarly
 377 to Eq.(19)

$$\bar{\tau}_{CG}^{\Delta\sigma}(0,l) = \exp\left(-\frac{\bar{W}^{CG}}{\delta}(0,l)\right). \quad (31)$$

378 For the Lorentz broadening regime, the mean black equivalent width is given
 379 by

$$\frac{\bar{W}_L^{CG}}{\delta} = \frac{\bar{\beta}_L^*}{\pi} \left(\sqrt{1 + \frac{2\pi u^* \bar{k}^*}{\bar{\beta}_L^*}} - 1 \right), \quad (32)$$

380 where u^* , $\bar{\beta}_L^*$ and \bar{k}^* are the effective parameters defined as

$$u^* = \int_0^l x_{\text{CO}_2}(s)p(s) ds, \quad (33)$$

381

$$\bar{k}^* u^* = \int_0^l x_{\text{CO}_2}(s)p(s)\bar{k}(s) ds, \quad (34)$$

382

$$\bar{\beta}_L^* = \frac{1}{\bar{k}^* u^*} \int_0^l x_{\text{CO}_2}(s)p(s)\bar{k}(s)2\pi\frac{\bar{\gamma}_L}{\delta_L}(s) ds. \quad (35)$$

383 The Curtis-Godson formulation for the Doppler broadening regime is ex-
 384 pressed as

$$\frac{\bar{W}_D^{CG}}{\delta} = \bar{\beta}_D^* H_\alpha \left(\frac{u^* \bar{k}^*}{\bar{\beta}_D^*} \right), \quad (36)$$

385 where $\bar{\beta}_D^*$ can be defined in the classical approach according to

$$\bar{\beta}_D^* = \frac{1}{\bar{k}^* u^*} \int_0^l x_{\text{CO}_2}(s)p(s)\bar{k}(s)\bar{\beta}_D(s) ds, \quad (37)$$

386 and in the formal approach leading to

$$\frac{1}{\bar{\beta}_D^*} = \frac{1}{\bar{k}^* u^*} \int_0^l x_{\text{CO}_2}(s) p(s) \bar{k}(s) \frac{1}{\bar{\beta}_D(s)} ds, \quad (38)$$

387 as provided in [19, 29]. The Lindquist–Simmons approaches provide approx-
 388 imate expressions of the path length derivative of the mean black equivalent
 389 width $\overline{W}(s, l)/\delta$ and is defined as follows in [29] for the Doppler and Lorentz
 390 broadening regimes

$$-\frac{1}{\delta} \frac{\partial \overline{W}_D^{LS}}{\partial s}(s, \ell) = \bar{k}(s) x_{\text{CO}_2}(s) p(s) y_\alpha \left(\frac{\bar{k}^*(s) u^*(s)}{\bar{\beta}_D^*(s)}, \frac{\overline{\beta}_D(s)}{\bar{\beta}_D^*(s)} \right), \quad (39)$$

391 with

$$y_\alpha(\tilde{x}, \tilde{\rho}) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{e^{-\xi^2}}{[1 + \tilde{x} \exp(-\tilde{\rho}^2 \xi^2)]^{1-\alpha}} d\xi, \quad (40)$$

392 and

$$-\frac{1}{\delta} \frac{\partial \overline{W}_L^{LS}}{\partial s}(s, l) = x_{\text{CO}_2}(s) p(s) \bar{k}(s) y \left[\frac{\pi \bar{k}^*(s) u^*(s)}{\bar{\beta}_L^*(s)}, \frac{\overline{\beta}_L(s)}{\bar{\beta}_L^*(s)} \right]. \quad (41)$$

393 with

$$y(x, \rho) = \frac{2\rho(1+x) + (1+\rho^2)\sqrt{1+2x}}{\sqrt{1+2x}(\rho + \sqrt{1+2x})^2}, \quad (42)$$

394 As the formulation depends on the parameter $\bar{\beta}_D^*$, there are also classical and
 395 formal approaches for the Lindquist-Simmons formulation in the Doppler
 396 broadening regime.

397

398 To validate the developed SNB model, we consider four cases of non-uniform
 399 columns representative of high-altitude plume applications. The first column
 400 is a quasi-unidimensional expanding isentropic flow in a conical nozzle of
 401 radius $R = 10$ cm at the throat and a cone angle of 15° . The flowing gas is a
 402 non-reacting perfect mixture of N_2 - CO_2 - H_2O with respective molar fractions

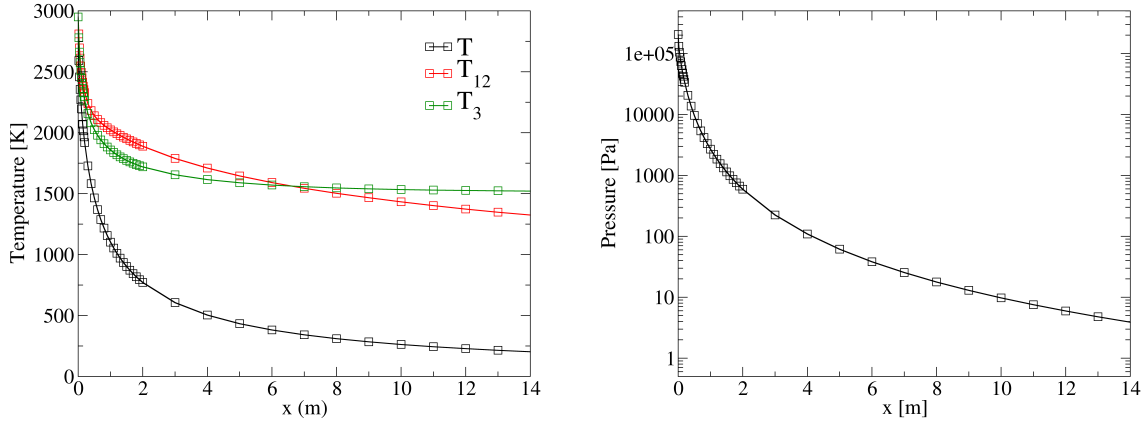


Figure 10: Temperature (left) and pressure (right) profiles of the quasi-unidimensional expanding nozzle flow from [9].

403 of 70%, 20%, and 10%. The flow conditions at the throat are assumed to
 404 be sonic (Mach number=1) with an initial LTE temperature $T_0 = 3000$ K, a
 405 mass flow rate of $9 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, leading to an initial velocity $u_0 = 1118 \text{ m}\cdot\text{s}^{-1}$.
 406 More details about this case are given in [9]. Fig. 10 shows the pressure and
 407 CO_2 temperature profiles during the quasi-unidimensional expansion. The
 408 radiative intensity at the exit of the nozzle axis line of sight is computed
 409 with the LBL and the SNB approaches and is compared in Fig. 11. We
 410 can see that the L-S formal formulation gives the best result in the $15 \mu\text{m}$
 411 band of CO_2 , but the C-G formal approximation is the most accurate one
 412 for the $4.3 \mu\text{m}$ and $2.7 \mu\text{m}$ bands. To sum up, all the models are accurate
 413 for this case and the mean relative errors for the bands presented here are
 414 approximately 2%. For this case, the C-G formal approach seems to best
 415 agree with the LBL approach if we consider the whole spectrum.

416

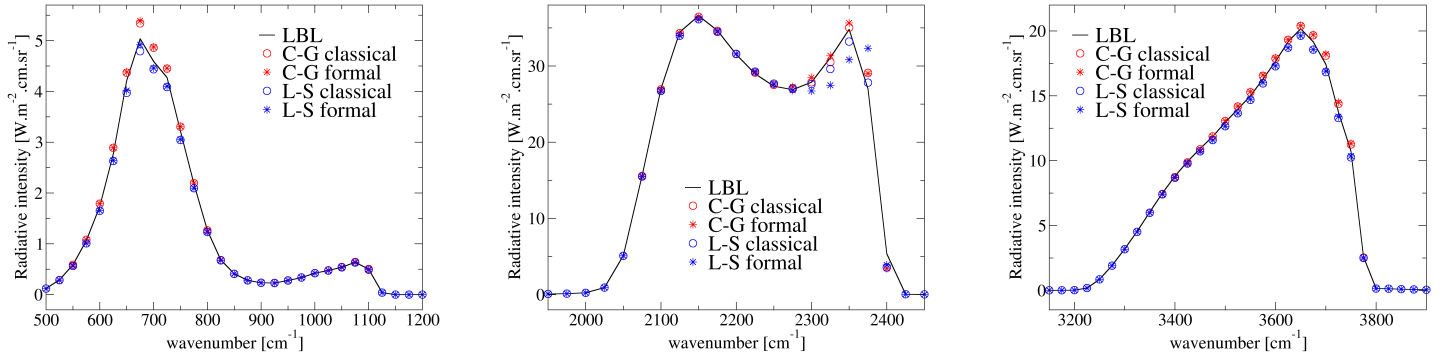


Figure 11: Radiative intensities at the exit of the nozzle axis line of sight in the $15 \mu\text{m}$ (left), $4.3 \mu\text{m}$ (middle) and $2.7 \mu\text{m}$ (right) regions of CO_2 for the quasi-unidimensional expanding flow.

417 The second and third studied cases are non-uniform columns obtained thanks
 418 to a Lagrangian post-processing method applied to LTE simulation of the
 419 plume of the solid propellant motor Antares II from the "Bow Shock Ultra-
 420 violet2" (BSUV2) experiment [35]. This post-processing method was used
 421 on the LTE temperature field of the plume to determine all of the vibrational
 422 temperature fields. An exhaustive explanation of this method is presented in
 423 [9]. The first column considered is 20 m long, starting from the nozzle exit
 424 at $r/2$ from the plume axis of symmetry, where r is the nozzle radius at the
 425 nozzle exit and is parallel to the plume axis of symmetry. This case is called
 426 hereafter the axial column. The second line of sight called the transverse
 427 column, crosses the plume perpendicularly to its axis and intersects this axis
 428 at $x = 2$ m away from the nozzle exit. For these two columns, the molar frac-
 429 tion of CO_2 is $x_{\text{CO}_2} = 0.0136$. Pressure and temperature distributions along
 430 these columns are plotted in Fig.12 and Fig. 14. For the axial column, the
 431 L-S classical approach provides the best agreement with the LBL approach

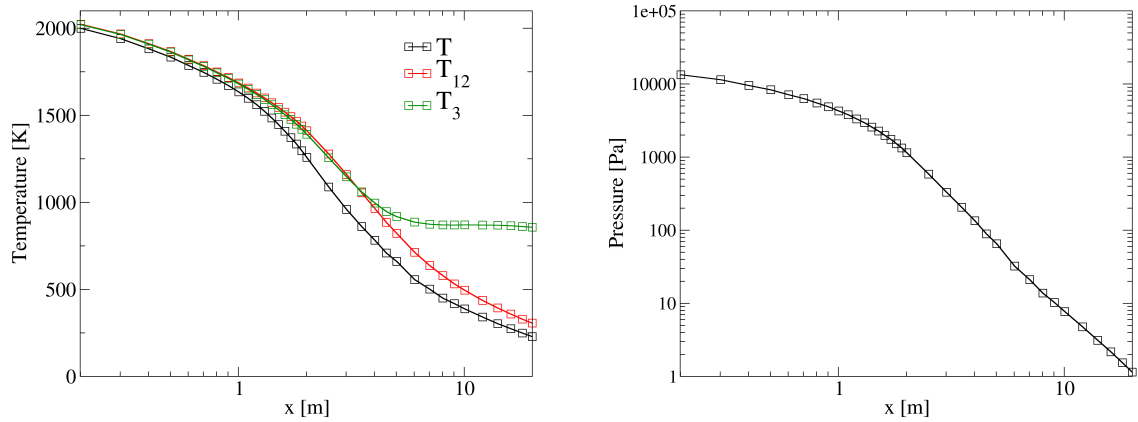


Figure 12: Temperature (left) and pressure (right) profiles of the axial column from [9].

432 in Fig.13. For the transverse column, the L-S formal approach seems more
 433 accurate than the C-G approximation in Fig.15, but the difference is tight.

434

435 The last case is a non-uniform column representative of Mars entry condi-
 436 tions. It is a $\text{CO}_2\text{-N}_2$ mixture discretized in two uniform columns whose
 437 conditions are given in the table 3. The radiative intensity at the exit of
 438 the sub-column 2 in the direction $1 \rightarrow 2$ is computed with the SNB model
 439 and compared with LBL approach results. Although the HITEMP database
 440 might be inaccurate for temperatures around 3500 K, the purpose is to test
 441 the SNB model, not the database. It is clear in Fig. 16 that the classical
 442 Lindquist-Simmons approach is the most accurate for this case. The $2.7 \mu\text{m}$
 443 and $15 \mu\text{m}$ regions are optically thin, so the model degenerates in $\overline{k^*}$ in these
 444 bands. We can conclude that the developed nonequilibrium SNB model gives
 445 satisfactory results for both strong compression and expansion cases.

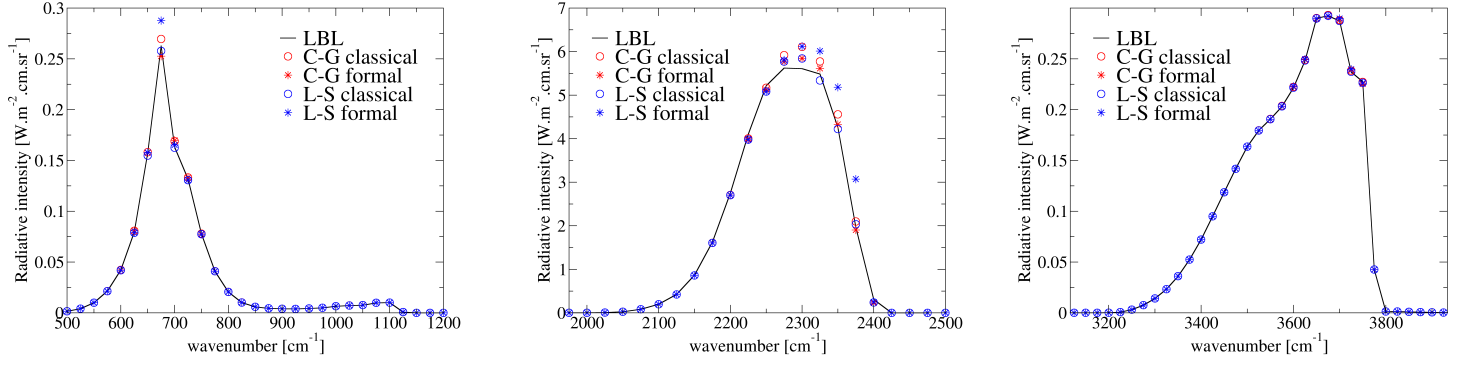


Figure 13: Radiative intensities at the exit of the axial column in the $15 \mu\text{m}$ (left), $4.3 \mu\text{m}$ (middle) and $2.7 \mu\text{m}$ (right) regions of CO_2 .

element	p [Pa]	T [K]	T_{12} [K]	T_3 [K]	length [m]	x_{CO_2}
1	1000	3500	1500	700	0.05	0.6
2	500	3000	500	240	0.05	0.6

Table 3: Conditions of the non-uniform column representative of Mars entry conditions

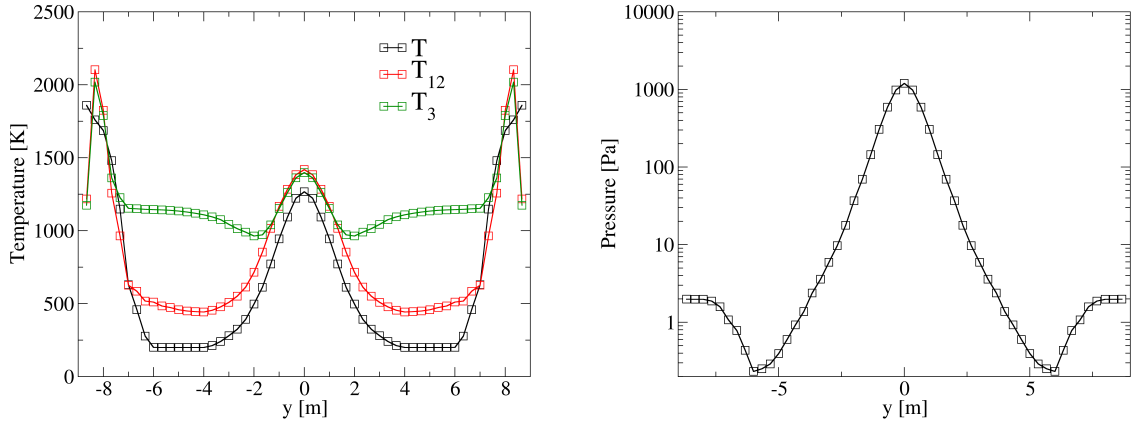


Figure 14: Temperature (left) and pressure (right) profiles of the transverse column from [9].

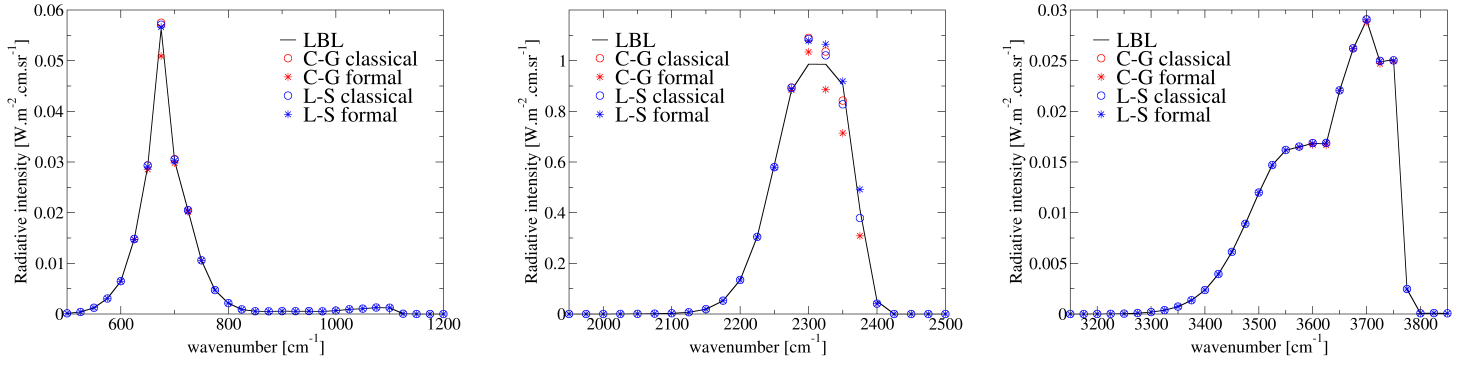


Figure 15: Radiative intensities at the exit of the transverse column in the $15 \mu m$ (left), $4.3 \mu m$ (middle) and $2.7 \mu m$ (right) regions of CO_2 .

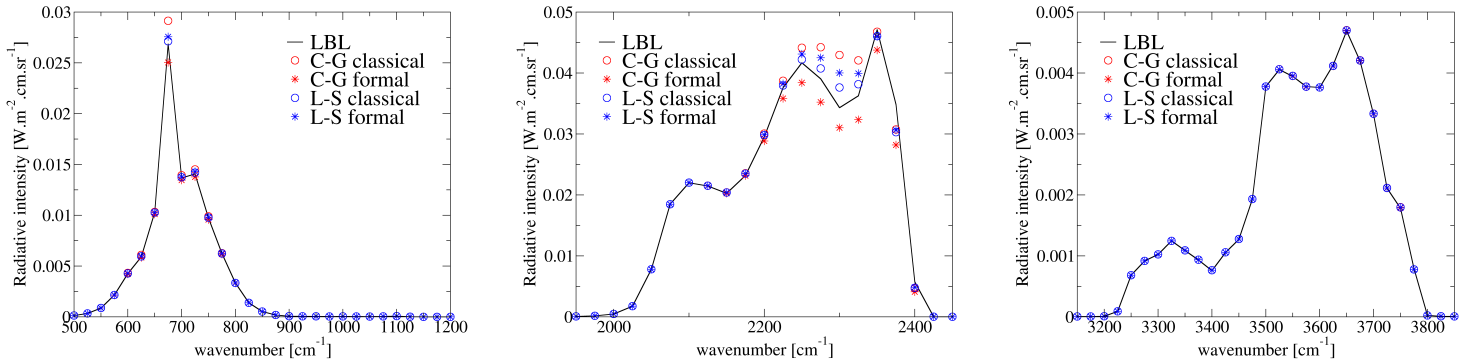


Figure 16: Radiative intensities at the exit of the line of sight in the direction $1 \rightarrow 2$ in the $15 \mu m$ (left), $4.3 \mu m$ (middle) and $2.7 \mu m$ (right) bands of CO_2 for the Mars entry representative conditions.

446 4. Conclusion

447 A vibrational nonequilibrium SNB model for CO₂ has been developed and
448 presented in this paper. The calculation of population densities is based
449 on a three-temperature approach (T, T_{12}, T_3) corresponding resp. to the
450 translational-rotational mode, the symmetric stretching and bending mode,
451 and the antisymmetric stretching mode. Since Kirchhoff's law is no longer
452 valid under these conditions, it is necessary to check the decorrelation be-
453 tween $\eta_\sigma/\kappa_\sigma$ and κ_σ beforehand. With these tests, we highlighted that there
454 are correlation issues between $\eta_\sigma/\kappa_\sigma$ and κ_σ in the 4.3 μm and 2.7 μm re-
455 gions of CO₂ for strong nonequilibrium between the temperatures T_{12} and
456 T_3 . This issue is caused by the proximity of transitions whose $\frac{\eta_\sigma}{\kappa_\sigma}$ ratio is
457 dominated by the T_{12} and the T_3 temperatures. The proposed solution was
458 to define classes of lines with similar vibrational transitions. SNB model
459 parameters were obtained by adjusting the curves of growth obtained from
460 the LBL approach for Lorentz and Doppler broadening regimes for each line
461 class. The quality of the adjustments was then discussed quantitatively us-
462 ing error statistics. Moreover, the SNB model accuracy was studied for the
463 Voigt broadening regime by comparing the radiative intensity escaping from
464 uniform columns for a wide pressure range in two strong nonequilibrium con-
465 ditions. This model was also applied for representative cases of high-altitude
466 expanding plumes and Mars entry conditions and showed satisfactory results.

467

468 **Acknowledgements**

469 The authors acknowledge the financial support of this study from the French
470 Agence de l'Innovation de Défense (AID). This work was granted access to the
471 HPC resources of IDRIS under the allocation 2022-A0102B00209 attributed
472 by GENCI (Grand Equipement National de Calcul Intensif). This work was
473 also performed using HPC resources from the Mésocentre computing center
474 of CentraleSupélec and Ecole Normale Supérieure Paris-Saclay supported by
475 CNRS and Région Île-de-France (<http://mesocentre.centralesupelec.fr/>).

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