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## Simultaneous collision-induced transitions in H<sub>2</sub>O+CO<sub>2</sub> gas mixtures

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### Key words

Absorption spectroscopy; Radiative transfer; Collision Induced Absorption; Continuum

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29

## Abstract

30 A collision induced absorption (CIA) band has been measured near  $6000\text{ cm}^{-1}$  in a spectrum of  
31 humidified  $\text{CO}_2$  recorded by cavity ring down spectroscopy (CRDS) at low pressure ( $<1\text{ atm}$ ). This  
32 absorption adds a contribution to the  $\text{H}_2\text{O}+\text{CO}_2$  continuum mostly originating from far wings of the  $\text{CO}_2$   
33 and  $\text{H}_2\text{O}$  resonance lines broadened by collisions with  $\text{H}_2\text{O}$  and with  $\text{CO}_2$ , respectively. The observed  
34 CIA corresponds to a simultaneous excitation of  $^{12}\text{CO}_2$  and  $\text{H}_2\text{O}$  colliding molecules in the  $\nu_3$   
35 antisymmetric and  $\nu_1$  symmetric stretching mode, respectively. CRDS spectra recorded near  $5940\text{ cm}^{-1}$   
36 with a highly enriched  $^{13}\text{CO}_2$  sample provide a confirmation of the assignment since the measured  
37 CIA isotopic spectral shift (of about  $-68\text{ cm}^{-1}$ ) coincides with that between the  $\nu_3$  bands of  $^{12}\text{CO}_2$  and  
38  $^{13}\text{CO}_2$ . The integrated binary coefficient of the two CIA is evaluated and found to be on the order of  
39  $2.3\times 10^{-3}\text{ cm}^{-2}\text{ amagat}^{-2}$ . Classical molecular dynamics simulations (CMDS) of the considered CIA are also  
40 presented, based on the dominant dipole induction mechanism associated with the vibrational matrix  
41 elements of the dipole of  $\text{CO}_2$  ( $\nu_3$ ) and isotropic polarizability of  $\text{H}_2\text{O}$  ( $\nu_1$ ). The results of the calculations  
42 are found in good agreement with the observations, thus further validating the attribution of the  
43 observed CIA structure to the above mentioned double transitions.

44

45 **I. Introduction**

46 The absorption of light by pure water vapor involves two contributions. The first one is the  
47 monomolecular absorption due to the rovibrational resonance lines which is proportional to the water  
48 vapor pressure. The second one, varying smoothly with the frequency, is the so-called water vapor  
49 self-continuum, which is proportional to the squared molecular density as it is due to interactions  
50 between pairs of water molecules. There are three potential contributions to this continuum, which  
51 include the far wings of the resonance lines, collision-induced absorption (CIA) by interacting pairs of  
52 free (unbound) molecules, and dimers (note that the latter may be considered as a part of the CIA  
53 since they also involve the dipole of a pair of molecules, even though in many cases they negligibly  
54 contribute to it). Similarly, the absorption spectrum of pure carbon dioxide involves resonance lines  
55 and a self-continuum contribution again resulting from the three contributions mentioned above  
56 generating absorptions proportional to the squared gas density. Numerous experimental and  
57 theoretical studies have been devoted to the self-continua of both H<sub>2</sub>O and CO<sub>2</sub> (see [1] and chapters  
58 V and VI of [2]) due to their importance for radiative transfer processes in the atmospheres of the Earth  
59 and Venus, respectively.

60 However, the self-continua are not the only continua relevant for planetary applications. Since  
61 planetary atmospheres are mixtures of various molecular species, there are additional “crossed”  
62 absorption contributions, proportional to the product of the densities of the different colliding  
63 molecules. This leads to non-additive absorption as for example in the Earth atmosphere in which the  
64 H<sub>2</sub>O- and CO<sub>2</sub>-air (or N<sub>2</sub>) continua play, together with the H<sub>2</sub>O self-continuum, a significant role which  
65 has motivated a large number of studies (see [1] and chapters V and VI of [2]). Note that, until recently,  
66 it was generally considered that the associated atmospheric continua were essentially due to the far  
67 wings of the air-broadened lines of H<sub>2</sub>O and CO<sub>2</sub>. The recent demonstration of the importance of an  
68 N<sub>2</sub> absorption band induced by collisions with H<sub>2</sub>O in the H<sub>2</sub>O-N<sub>2</sub> continuum [3,4] pointed out the limits  
69 of this assumption.

70 Due to its potential importance for the atmospheres of Early Mars and exoplanets, the  
71 continuum in H<sub>2</sub>O-CO<sub>2</sub> mixtures has recently received a renewed attention, nearly 30 years after  
72 pioneer studies devoted to the CO<sub>2</sub>-broadened line wings of H<sub>2</sub>O for Venusian studies [5,6].  
73 Measurements and calculations have been made in order to characterize the influence of collisions  
74 with H<sub>2</sub>O on the wings of CO<sub>2</sub> lines [3,7,8] as well as that of collisions with CO<sub>2</sub> on the wings of H<sub>2</sub>O  
75 lines [7,9]. It is worth mentioning that the importance of non-additivity effects in absorption in  
76 H<sub>2</sub>O+CO<sub>2</sub> mixtures (in particular, those related to weak simultaneous transitions – see below) was first  
77 discussed by Vigasin et al. in 1994, on the basis of infrared absorption spectra of moisture-containing  
78 CO<sub>2</sub> in the liquid and gaseous phases [10].

79           Very recently, we have undertaken a series of measurements aiming to characterize the  
80 absorption continuum of H<sub>2</sub>O-CO<sub>2</sub> mixtures in the 1.6 μm and 2.3 μm windows and near 3.5 μm,  
81 corresponding to low opacity regions for both CO<sub>2</sub> and water vapor [11]. The “crossed” absorption  
82 (proportional to the product of the H<sub>2</sub>O and CO<sub>2</sub> densities) was observed to include an unexpected  
83 broad band, centered near 6000 cm<sup>-1</sup>, in addition to the contributions of the far wings of the lines of  
84 the monomers (note that pure CO<sub>2</sub> spectra do not exhibit any CIA band in this spectral region [12]). On  
85 the basis of the spectral position of its center, this band was tentatively assigned to the simultaneous  
86 collision-induced transitions involving a ν<sub>1</sub> (Raman) excitation of H<sub>2</sub>O and a ν<sub>3</sub> (dipole absorption)  
87 excitation of <sup>12</sup>CO<sub>2</sub> [noted ν<sub>3</sub>(CO<sub>2</sub>)+ν<sub>1</sub>(H<sub>2</sub>O), hereafter] but no further analysis was made. Note that such  
88 simultaneous transitions (sometimes also denoted as double transitions), resulting from the  
89 polarization of one molecule (*e.g.* through a vibrational matrix element of the polarizability) by the  
90 vibrating electric field of the collision partner (*e.g.* through a vibrational matrix element of the electric  
91 dipole or quadrupole) have been observed (starting in the early 50’s !) and analyzed for diverse  
92 molecular systems involving H<sub>2</sub> or N<sub>2</sub> (*e.g.* [13,14,15,16,17]), but also for pure CO<sub>2</sub> [18], CO<sub>2</sub>-N<sub>2</sub>  
93 [19,20,21,22,23] and CO<sub>2</sub>-H<sub>2</sub> [24], to cite but a few. Also recall the pioneer work of Colpa and Ketelaar  
94 [24] which set the theoretical bases for practical calculations of their integrated intensity.

95           In this paper, we revisit the ν<sub>3</sub>(CO<sub>2</sub>)+ν<sub>1</sub>(H<sub>2</sub>O) CIA band both experimentally, by complementing  
96 the natural CO<sub>2</sub> measurements reported in Ref. [11] by a new investigation using <sup>13</sup>CO<sub>2</sub>, and  
97 theoretically, by using a simple induction model and molecular dynamics simulations. In the next  
98 section, we summarize the conditions of the acquisition of the humidified CO<sub>2</sub> spectra by cavity ring  
99 down spectroscopy (CRDS). The different steps of the CIA retrieval by successive subtraction of the  
100 different contributions from the measured spectra are also described in this section. In section 3, the  
101 classical molecular dynamics simulations (CMDs) and the input data used for the prediction of the CIA  
102 are described. The measured and calculated results are then presented and discussed in Sec. 4, before  
103 concluding remarks (Sec. 5).

104           **2. CRDS recordings and CIA retrieval**

105           *2.1. Data acquisition*

106           The inherent sensitivity and baseline stability of cavity enhanced techniques make them  
107 particularly suitable to measure weak continua [25]. They, in particular, enable to use samples at sub-  
108 atmospheric pressure while traditional methods are generally combined with pressurized cells. This is  
109 crucial in the case of mixtures involving water vapor at room temperature, the limitation by the  
110 saturation pressure making accurate absorption measurements by FTS with long absorption  
111 pathlengths practically impossible in the atmospheric transparency windows. In contrast,  
112 measurements by CRDS and OFCEAS have recently led to accurate determinations of the self- and

113 foreign (air)-continua of H<sub>2</sub>O [26,27,28,29,30,31]. Another advantage of recordings at sub-atm  
114 pressures is that the contribution of local absorption transitions is easier to calculate and remove, since  
115 line-mixing effects may be disregarded and isolated line shapes can be used. For instance, CRDS was  
116 recently applied to the characterization of the O<sub>2</sub> CIA band at 1.27 μm both at NIST [32] and in our  
117 laboratory [33,34]. The use of low O<sub>2</sub> pressures enabled to minimize the impact of line mixing effects  
118 on the CIA determination obtained with an agreement of less than 1% between the two datasets at  
119 room temperature.

120 The  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  CIA band was observed in CRDS spectra of humidified CO<sub>2</sub> recorded in the  
121 5725-6665 cm<sup>-1</sup> and 5856-5986 cm<sup>-1</sup> intervals, for natural CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> samples, respectively.  
122 Distributed feedback (DFB) laser diodes were used as light sources, each of them covering a spectral  
123 range 20 to 30 cm<sup>-1</sup> wide by temperature variation. The cavity-ring down spectrometer used a 142 cm  
124 long high finesse cavity fitted with two highly reflective dielectric mirrors. Ring down (RD) times were  
125 of the order of 120 to 160 μs. Typically, ten RD times were averaged at each spectral step separated  
126 by 0.005 cm<sup>-1</sup>. A part of the laser light was sent into a wavelength meter (model 621-A IR from Bristol)  
127 to monitor the laser frequency.

128 As detailed in Ref. [11], the spectra with natural CO<sub>2</sub> were recorded in flow regime using  
129 H<sub>2</sub>O+CO<sub>2</sub> mixtures with H<sub>2</sub>O molar fractions between 3000 and 15000 ppmv. The gas flow of the  
130 mixture (typically a few tens sccm inside the CRDS cavity) was produced using a commercial humidity  
131 generator (from Omicron Technologies). The total pressure in the CRDS cavity was monitored by a  
132 sensor from Edwards (1000 mbar full scale, accuracy 0.15 % of reading) and maintained at a fixed value  
133 of 400 or 750 Torr with a solenoid valve and a software-based proportional integral loop acting on the  
134 gas flow. The densities of CO<sub>2</sub> and H<sub>2</sub>O ( $\rho_{\text{CO}_2}$  and  $\rho_{\text{H}_2\text{O}}$ , respectively) were obtained from the partial  
135 pressures and the cell temperature measured with a calibrated Pt100 sensor (2σ-uncertainty ±0.06°C)  
136 fixed on the external wall of the cavity underneath the enveloping thermal insulation foam.

137 In the case of the recordings with humidified <sup>13</sup>CO<sub>2</sub>, the limitation of the gas consumption  
138 (imposed by the cost of the <sup>13</sup>C enriched CO<sub>2</sub> tank) required to record the spectra in static regime. The  
139 cell was thus first filled with about 6.5 Torr of water vapor and <sup>13</sup>CO<sub>2</sub> (from Aldrich, 99 % <sup>13</sup>C  
140 enrichment) was then added up to a total pressure of 400 Torr.

141 The baseline determination of the spectra relied on measurements performed with argon  
142 before and after the recording with the (H<sub>2</sub>O+CO<sub>2</sub>) mixture, with the cavity pumped before each gas  
143 filling (argon or mixture). The two argon spectra ensure that the cavity alignment (and thus the  
144 baseline) is unchanged after pumping/filling cycles. By comparing the two argon spectra, the baseline  
145 stability was found to be of the order of a few 10<sup>-10</sup> cm<sup>-1</sup>. In order to check the proportionality of the  
146 retrieved “crossed” absorption to the  $\rho_{\text{CO}_2}\rho_{\text{H}_2\text{O}}$  densities product, measurements were performed for  
147 several values of the water molar fraction in natural CO<sub>2</sub>. The study with <sup>13</sup>CO<sub>2</sub> being mostly performed

148 for validation of the assignment of the observed CIA structure, a single set of experimental conditions  
149 (~6.5 Torr of water vapor in  $^{13}\text{CO}_2$  at a total pressure of 400 Torr) was retained.

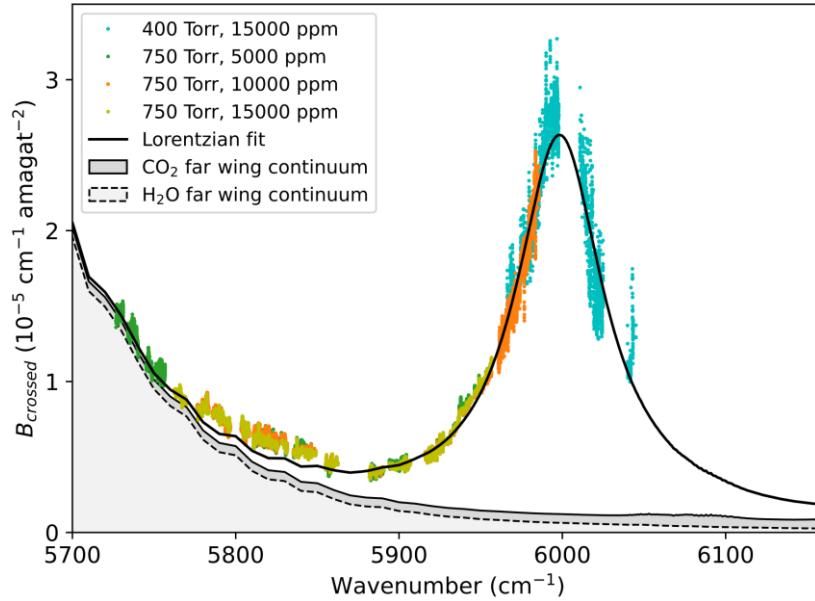
## 150 2.2. CIA retrieval

151 After baseline correction, the absorption coefficient,  $\alpha(\nu)$ , can be expressed as:

$$152 \quad \alpha(\nu) = M_{\text{CO}_2}\rho_{\text{CO}_2} + M_{\text{H}_2\text{O}}\rho_{\text{H}_2\text{O}} + B_{\text{CO}_2}\rho_{\text{CO}_2}^2 + B_{\text{H}_2\text{O}}\rho_{\text{H}_2\text{O}}^2 + B_{\text{crossed}}\rho_{\text{CO}_2}\rho_{\text{H}_2\text{O}} \quad (1)$$

153 where  $M_{\text{CO}_2}\rho_{\text{CO}_2}$  and  $M_{\text{H}_2\text{O}}\rho_{\text{H}_2\text{O}}$  are the contributions due to the monomer local lines of  $\text{CO}_2$  and  $\text{H}_2\text{O}$   
154 (calculated within a  $\pm 25 \text{ cm}^{-1}$  range around the center wavenumber), respectively, and  $\rho$  represents  
155 the density (in  $\text{amagat}^{-1}$ ). The  $B_{\text{H}_2\text{O}}$  and  $B_{\text{CO}_2}$  coefficients (in  $\text{cm}^{-1}\text{amagat}^{-2}$ ) correspond to the self-  
156 continuum coefficients of water and  $\text{CO}_2$ , respectively.  $B_{\text{crossed}}$  is the crossed binary coefficient arising  
157 from the interaction of water and  $\text{CO}_2$  molecules, thus involving both far line wings (of  $\text{CO}_2$ -broadened  
158  $\text{H}_2\text{O}$  transitions as well as of  $\text{H}_2\text{O}$ -broadened  $\text{CO}_2$  transitions) and CIA bands contributions.

159 In the case of natural  $\text{CO}_2$ , the HITRAN2016 database [35] was used to simulate the local  $\text{CO}_2$   
160 and  $\text{H}_2\text{O}$  monomer contributions with Voigt profiles truncated at  $\pm 25 \text{ cm}^{-1}$  excluding the pedestal of  
161 the absorption lines (see details in Ref. [11]). The water self-continuum cross-sections  $B_{\text{H}_2\text{O}}$  were taken  
162 from Ref. [30] while, for  $\text{CO}_2$ , the self-continuum cross-sections  $B_{\text{CO}_2}$  were taken from Ref. [12] or  
163 measured in Ref. [11] below and above  $5800 \text{ cm}^{-1}$ , respectively. The  $B_{\text{crossed}}$  binary coefficients  
164 measured with the natural  $\text{CO}_2$  sample for various water vapor molar fractions (from 3000 to 15000  
165 ppm) and two total pressures (400 and 750 Torr) are presented in **Fig. 1**. While over the various  
166 experimental conditions the  $\rho_{\text{CO}_2}\rho_{\text{H}_2\text{O}}$  density product varied by a factor of 5, the set of retrieved  
167  $B_{\text{crossed}}$  values are found consistent within about 20 % in the CIA region near  $6000 \text{ cm}^{-1}$ . **Fig. 1** also  
168 includes a fit of the observed band, assuming a Lorentzian shape and fixing the far wing continuum  
169 background to its value calculated by the  $\chi$ -factor approach (see [11]). The parameters obtained from  
170 this Lorentzian fit will be discussed in Sec. 4.

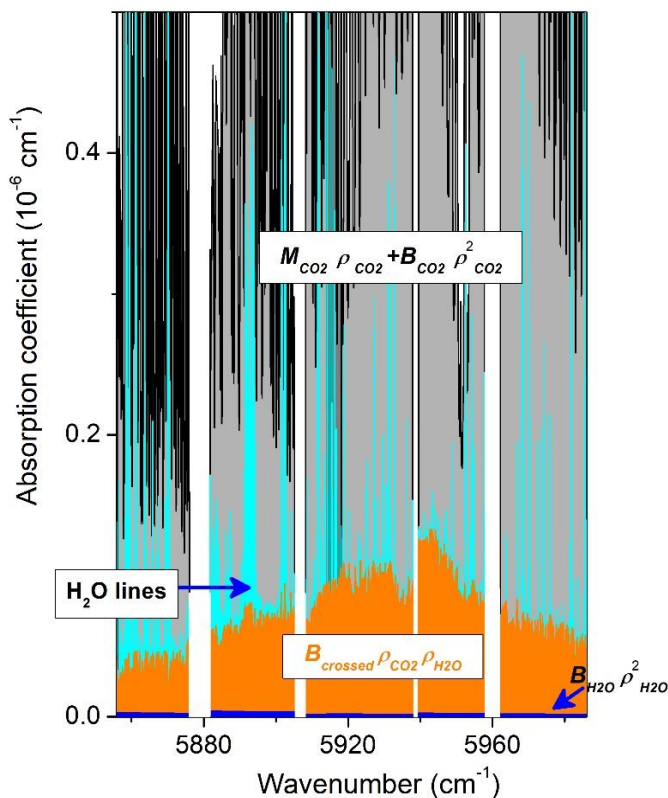


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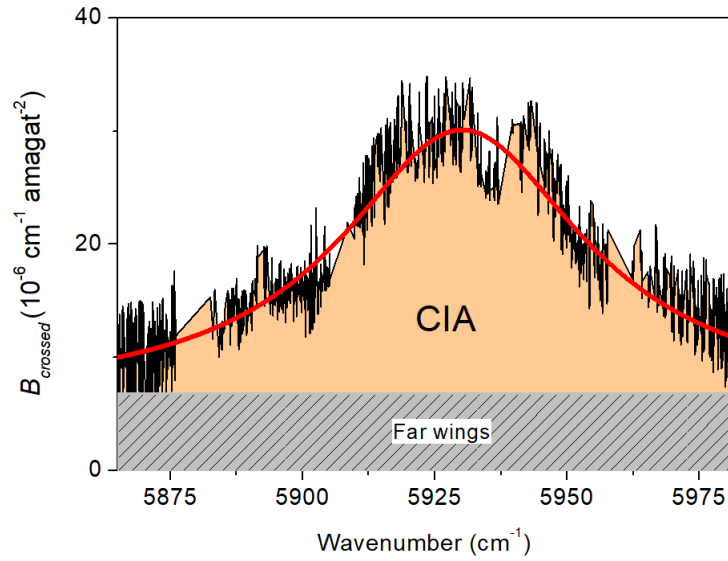
172 **Fig.1:** Overview of the binary coefficients measured in the 5725-6040  $\text{cm}^{-1}$  region including the  $\nu_3(^{12}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$   
 173 CIA band near 6000  $\text{cm}^{-1}$ , for various total pressures and water vapor molar fractions. The best fit of the CIA using  
 174 a Lorentzian function (black solid line) is superimposed to the far wing continuum background which was fixed to  
 175 its value calculated by the  $\chi$ -factor approach (see [11]).

176 In the case of humidified  $^{13}\text{CO}_2$ , the measurement of the CIA band is made more difficult because  
 177 it falls in a region where  $\text{CO}_2$  resonance lines are much stronger than with the natural sample. In order  
 178 to subtract the  $^{13}\text{CO}_2$  contribution  $-(M_{\text{CO}_2}\rho_{\text{CO}_2} + B_{\text{CO}_2}\rho_{\text{CO}_2}^2)$  in Eq. (1) – we did not try to simulate  
 179 separate contributions of the resonance lines and of the self-continuum of  $^{13}\text{CO}_2$  and preferred to  
 180 directly subtract a spectrum of dry  $^{13}\text{CO}_2$  recorded at the same partial pressure of  $^{13}\text{CO}_2$  as in the  
 181 humidified mixture used for the recordings (395 Torr). This, which disregards the effects of collisions  
 182 with  $\text{H}_2\text{O}$  on the central and wing regions of the  $^{13}\text{CO}_2$  lines, is of likely small consequences considering  
 183 the relatively small (1.5 %) amount of water vapor in the humidified sample. **Fig. 2** shows the different  
 184 contributions to the total absorption coefficient measured for a mixture of about 6 Torr of water in  
 185  $^{13}\text{CO}_2$  at a total pressure of 400 Torr. As adsorption on the walls of the CRDS affected the amount of  
 186 water in the cell, for the spectral interval corresponding to the tuning range of each DFB laser diode,  
 187 the water vapor partial pressure,  $p_{\text{H}_2\text{O}}$ , was determined from the integrated absorption coefficient of  
 188 a few observed water lines. The obtained  $p_{\text{H}_2\text{O}}$  values were found to vary from 5.3 to 7.0 Torr for the  
 189 six DFB intervals covering the CIA region (5856-5986  $\text{cm}^{-1}$ ). These  $p_{\text{H}_2\text{O}}$  values were used to calculate  
 190 and subtract the water self-continuum [30] and the water resonance lines contribution (computed  
 191 using the HITRAN2016 line list [35]). As illustrated by **Fig. 2**, in our experimental conditions, the two  
 192 water vapor contributions are much smaller than the  $^{13}\text{CO}_2$  contribution. After subtraction of the  
 193 different contributions, the remaining absorption coefficient  $-B_{\text{crossed}}\rho_{\text{CO}_2}\rho_{\text{H}_2\text{O}}$  shows a clear bell  
 194 shape centered at about 5940  $\text{cm}^{-1}$  corresponding to the  $\nu_3(^{13}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  CIA band. Using the

195 determined  $p_{H_2O}$  values, the corresponding crossed binary coefficients,  $B_{crossed}$ , displayed in **Fig. 3**  
 196 were derived. The obtained curve shows high frequency “noise” due to the imperfect removal of the  
 197 strong  $^{13}CO_2$  resonance lines. An improved description of the CIA band shape is obtained from a  
 198 Lorentzian fit with a baseline (corresponding to the far wing continuum contribution) assumed to be  
 199 constant with frequency. The parameters obtained from this fit will be discussed in Sec. 4.  
 200



201  
 202 **Fig. 2:** Different contributions to the total absorption coefficient measured by CRDS with a mixture of water and  
 203  $CO_2$  highly enriched in  $^{13}C$ . The total pressure was 402 Torr while the water vapor partial pressure varied between  
 204 5.3 and 7.0 Torr over the displayed region. The measured absorption coefficient is first reduced by the  $^{13}CO_2$   
 205 contribution (lines and self-continuum - grey background) measured with a pure  $^{13}CO_2$  sample. Then, the water  
 206 contribution (lines and self-continuum - cyan and blue background, respectively) is simulated and subtracted. The  
 207 absorption remaining after these subtractions (orange background) shows the bell shape profile of the  
 208  $\nu_3(^{13}CO_2)+\nu_1(H_2O)$  CIA band centered near  $5930\text{ cm}^{-1}$ .



209

210 **Fig 3:** Crossed binary coefficients in the region of the  $\nu_3(^{13}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  CIA band. The best fit of the CIA Lorentzian  
 211 shape (red solid line) is superimposed to the continuum background due to the far wing continuum (dashed). The  
 212 background level was adjusted by the fit.  
 213

### 214 3. Classical molecular dynamics simulations (CMDS)

215 The CIA in the region of the  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  simultaneous transitions was calculated using  
 216 classical molecular dynamics simulations (CMDS), exactly as described in Ref. [3] for  $\text{CO}_2+\text{H}_2\text{O}$ , with the  
 217 only difference that the  $\text{H}_2\text{O}$  static isotropic polarizability matrix element  $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v = 0 \rangle$   
 218 used in this previous study was here replaced by the vibrational matrix element  $\langle v =$   
 219  $0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle$  (here,  $v = 0$  and  $v_1 = 1$  stand for the (000) and (100) vibrational states of  $\text{H}_2\text{O}$ ,  
 220 respectively). Since details on the CMDS can be found in Ref. [3] and references cited therein, only the  
 221 main elements are recalled here. The simulations start with the initialization, for each molecule, of its  
 222 center of mass position (inside a cubic box of dimensions defined by the gas density and total number  
 223 of molecules treated) and translational velocity vector, and of its angular orientation and rotational  
 224 angular momentum vector. These are set in order to verify the Boltzmann statistics for the considered  
 225 temperature. The propagation in time of these four molecular parameters is then computed using the  
 226 equations of classical mechanics fed by forces and torques due to intermolecular interactions  
 227 computed using the same input site-site  $\text{CO}_2\text{-H}_2\text{O}$  as in Ref. [3]. Periodic boundary conditions, nearest  
 228 neighbour spheres, the Verlet algorithm, and the quaternions approach [36] were used and about 5  
 229 million molecules were treated. After a temporization time of  $t_0 = 20$  ps to let the system properly  
 230 thermalize, the dipole  $\vec{\mu}_{ij}(t)$  induced in ( $i=\text{CO}_2, j=\text{H}_2\text{O}$ ) colliding pairs was computed. As in Ref. [3], only  
 231 the component of the induced dipole due to the polarization of  $\text{H}_2\text{O}$  (through its isotropic polarizability  
 232  $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle$ ) in the electric field of the  $\text{CO}_2$  dipole (through  $\langle v = 0 | \mu(\text{CO}_2) | v_3 = 1 \rangle$ ,  
 233 where  $v = 0$  and  $v_3 = 1$  stands for the  $(v_1 v_2 l_2 v_3) = (00^0 0)$  and  $(00^0 1)$  vibrational states of  $\text{CO}_2$ ,

234 respectively) was taken into account. This is convenient since the induced dipole – driven by the  
 235  $B_{1012}(R)$  term of Eq. (4.50) of [37] or the first term in Eq. (10) of Ref. [24] – then only depends on the  
 236 orientations of the CO<sub>2</sub> axis and of the vector between the centers of mass of the two molecules, and  
 237 is independent from the orientation of the H<sub>2</sub>O molecule. Note that this disregards other induction  
 238 mechanisms, including the term originating from the anisotropic polarizability of the water molecule  
 239 (*i.e.*  $\langle v = 0 | \Delta\alpha(\text{H}_2\text{O}) | v_1 = 1 \rangle$ ). However note that, as discussed below, this contribution is likely  
 240 relatively small, while many other terms, such as those involving the product of the H<sub>2</sub>O dipole element  
 241  $\langle v = 0 | \mu(\text{H}_2\text{O}) | v_1 = 1 \rangle$  and of the CO<sub>2</sub> polarizability  $\langle v = 0 | \Delta\alpha(\text{CO}_2) \text{ or } \alpha_{iso}(\text{CO}_2) | v_3 = 1 \rangle$ , vanish  
 242 due to symmetry considerations. As in Ref. [3], we used  $\langle v = 0 | \mu(\text{CO}_2) | v_3 = 1 \rangle = 0.13$  a. u. [38, 39].  
 243 For H<sub>2</sub>O,  $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.73$  a. u. was obtained, using the convention of Ref. [37], from  
 244 the value of  $\alpha_0^0$  provided in Ref. [40] with  $\alpha_{iso} = -\alpha_0^0/\sqrt{3}$ . With the method and input data described  
 245 above, the induced dipole was computed from  $t_0 (= 20$  ps) to  $t_0 + \Delta t (= 5$  ps) in the course of the CMDS.  
 246 Then its autocorrelation function was computed using  $t_0$  as the time origin, averaged over all molecules  
 247 and Laplace-Fourier transformed to yield the absorption spectrum [41]. Note that our classical  
 248 calculations lead to a CIA structure that is automatically centered at the sum of the origins of the  
 249  $\nu_3(^{12}\text{CO}_2)$  and  $\nu_1(\text{H}_2\text{O})$  bands,  $2349 + 3657 = 6006$  cm<sup>-1</sup> for <sup>12</sup>CO<sub>2</sub>, because all the  $Q$  transitions of the H<sub>2</sub>O  
 250  $\nu_1$  band, associated with the isotropic polarizability, then have the same imposed wavenumber of 3657  
 251 cm<sup>-1</sup>. This, which leads to a difference of about +6 cm<sup>-1</sup> between the positions of the CIA peak in the  
 252 calculated and measured spectra, does not correspond to reality since the  $(v = 0, J, K_a, K_c) \rightarrow$   
 253  $(v_1 = 1, J, K_a, K_c)$  rovibrational transitions are all shifted to the red with respect to the band origin  
 254 of 3657 cm<sup>-1</sup> and spread over typically 10 cm<sup>-1</sup> [35]. In order to correct for this, the bar spectrum of the  
 255 true  $Q$  lines was convoluted by the raw CMDS-predicted CIA, which red-shifts the peak wavenumber  
 256 by about -6 cm<sup>-1</sup> with respect to 6006 cm<sup>-1</sup>, leading to a very good agreement with the experimental  
 257 findings as discussed below. In the case of <sup>13</sup>CO<sub>2</sub>, CMDS were computed as done for <sup>12</sup>CO<sub>2</sub>, using the  
 258 same value of  $\langle v = 0 | \mu(\text{CO}_2) | v_3 = 1 \rangle$  [42,43], but a change of the  $\nu_3$  band origin from 2349 to 2283  
 259 cm<sup>-1</sup>.

260

#### 261 4. Results and discussion

262 As said above, the <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> CIA bands as obtained from experiments were fitted assuming  
 263 a Lorentzian band shape (see **Figs. 1** and **3**). In the case of the main isotopologue, the underlying far  
 264 wing continuum was fixed to its value calculated by the  $\chi$ -factor approach (see [11]). In the case of  
 265 <sup>13</sup>CO<sub>2</sub>, the baseline was assumed to be constant with frequency and it was adjusted by the fit. The  
 266 CMDS-computed spectra for <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> were fitted by a Gaussian function to determine the  
 267 center position, their integration over wavenumber yielded the intensities, and the widths were

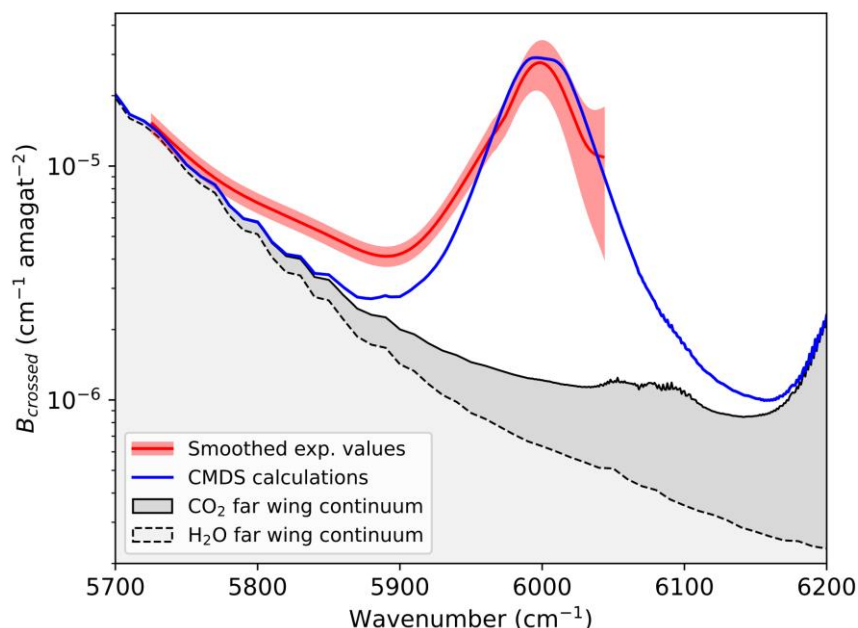
268 determined directly from the computed absorptions. The experimental and calculated centers,  
 269 integrated areas and half-widths at half-maximum (HWHM) are listed in **Table 1**, calling for several  
 270 remarks. The first is that the peak positions obtained for the measured spectra and from those  
 271 computed using CMDS (corrected as explained in Sec. 3 to take the H<sub>2</sub>O Q lines true quantum positions  
 272 into account) agree very well. The measured and calculated differences between the <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>  
 273 values, of about 68 cm<sup>-1</sup>, are in close agreement with the isotopic shift of the  $\nu_3 = 1$  vibrational levels  
 274 of the two isotopologues (66 cm<sup>-1</sup>) [44]. The second is that the measured and computed integrated  
 275 intensities also coincide, with differences well smaller than the experimental uncertainty (roughly  
 276 estimated to 20 % and 30 % for <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, respectively). The integrated band intensities for the  
 277 two isotopologues are close, as could be expected from the fact that the CO<sub>2</sub> dipole matrix elements  
 278 are practically identical [42,43]. Finally, the experimental and predicted HWHM are again consistent,  
 279 both showing a negligible isotope effect, as could be expected from the strong similarity between <sup>12</sup>CO<sub>2</sub>  
 280 and <sup>13</sup>CO<sub>2</sub>.

	$\nu_3(^{12}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$		$\nu_3(^{13}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$	
	Exp	CMDS	Exp	CMDS
Center (cm <sup>-1</sup> )	5998.4	5999.7	5930.2	5932
Integrated binary coefficient (10 <sup>-3</sup> cm <sup>-2</sup> amagat <sup>-2</sup> )	2.6	2.08	2.1	2.06
HWHM (cm <sup>-1</sup> )	33.0	31	28.2	31

281  
 282 **Table 1:** Band centers, integrated intensities and half widths at half maximum (HWHM) of the  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$   
 283 CIA bands measured and CMDS-calculated for natural <sup>12</sup>CO<sub>2</sub> and in <sup>13</sup>CO<sub>2</sub>.  
 284

285 A comparison between the measured and computed H<sub>2</sub>O-<sup>12</sup>CO<sub>2</sub> density-normalized absorption  
 286 coefficients over the spectral range of the 1.6 μm window is displayed in **Fig. 4**. The calculated  
 287 spectrum was obtained by adding the CIA predicted in the present study to the contributions of the  
 288 far wings of the H<sub>2</sub>O-broadened transitions of CO<sub>2</sub> and of the CO<sub>2</sub>-broadened lines of H<sub>2</sub>O. The  
 289 associated values of the binary coefficients,  $B_{\text{CO}_2-\text{H}_2\text{O}}$  and  $B_{\text{H}_2\text{O}-\text{CO}_2}$ , were calculated with the  $\chi$ -factor  
 290 approaches developed in Refs. [8] and [9] respectively. As can be seen, the agreement is quite  
 291 satisfactory which validates the prediction of all three contributions. However there is a noticeable  
 292 discrepancy between measured and computed values on the low frequency side of the CIA peak which  
 293 may be explained by the neglecting of the contribution of the anisotropic polarizability  $\Delta\alpha$  of H<sub>2</sub>O in  
 294 the CMDS computation of the collision-induced dipole. Indeed, first note that, since  $\langle v = 0 | \Delta\alpha(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.54$  a. u. (obtained from the value of  $\alpha_0^2$  provided in Ref. [40] and  $\Delta\alpha =$   
 295  $\sqrt{3/2} \alpha_0^2$ ) which is smaller than  $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.73$  a. u. by a factor of about  $\sqrt{2}$ , the  
 296 integrated intensity due to this dipole induction mechanism should be about 2 times lower. In addition,  
 297 the anisotropic polarizability selection rule allows not only Q but also O and S lines associated with  $J$   
 298  $\rightarrow J \pm 2$  transitions, the latter being spread over a broad spectral range of several 100 cm<sup>-1</sup> on both sides  
 299

300 of the central vibrational frequency. In summary, this contribution, which is weaker and spectrally  
 301 much broader than that of the isotropic polarizability, may explain the above mentioned missing  
 302 "background".



303  
 304 **Fig 4:** Crossed binary coefficients in the region of the  $\nu_3(^{12}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  CIA band. The CIA predicted by CMDS  
 305 calculations (blue) is added to the sum of the H<sub>2</sub>O (light grey) and CO<sub>2</sub> (grey) far wing continua. Also shown are  
 306 the smoothed experimental values from Ref. [11] (red, with a 1 $\sigma$  error band).  
 307

308 It is worth mentioning that the  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  CIA band presently measured in the gas phase  
 309 at sub-atmospheric pressure was pointed out nearly three decades ago in liquid CO<sub>2</sub>+H<sub>2</sub>O mixtures,  
 310 thus at considerably higher molecular densities [10]. Low resolution spectra were recorded with  
 311 grating spectrographs allowing for an estimation of the integrated absorption cross-section. A value of  
 312  $8 \times 10^{-4} \text{ cm}^{-2} \text{ amagat}^{-2}$  was estimated in the liquid phase, about three times smaller than our gas phase  
 313 value ( $2.6 \times 10^{-3} \text{ cm}^{-2} \text{ amagat}^{-2}$ ). Note that a similar tendency between liquid and gas phase CIA  
 314 intensities (normalized to squared density) was reported for the far-infrared CIA of pure CO<sub>2</sub> [45]. Let  
 315 us also mention that the simultaneous CO<sub>2</sub>-H<sub>2</sub>O transitions investigated in the present study have many  
 316 points in common with those of CO<sub>2</sub>-H<sub>2</sub> observed and analyzed more than sixty years ago in [24].  
 317 Indeed, both involve the  $\nu_3$  CO<sub>2</sub> dipole and a vibrational change of the other molecule through the  
 318 polarizability.

319 In general, free collisions are believed to bring most of the contribution to CIA bands, except at  
 320 (very) low temperature, while H<sub>2</sub>O-CO<sub>2</sub> bound complexes, which are disregarded in the CMDS, are not  
 321 expected to contribute significantly to the observed absorption feature. This seems reasonable at the  
 322 room temperature of this study considering the expected very small portion of bound dimers. The  
 323 agreement between the measured and CMDS integrated band intensities seems to confirm this

324 expectation. The H<sub>2</sub>O-CO<sub>2</sub> bound complex which has been observed in matrices (e.g. [46]) and in  
 325 expansion jets (e.g. [47,48]) has a planar T-shaped structure with hydrogens pointing away from CO<sub>2</sub>.  
 326 The dissociation energy  $D_0$  was estimated to be about 730 cm<sup>-1</sup> [49,50]. It is worth mentioning the  
 327 results of anharmonic vibrational calculations of the spectrum of this Van der Waals complex [51],  
 328 based on *ab initio* force field and electro-optical parameters. As expected, most of the predicted  
 329 vibrational bands of the H<sub>2</sub>O-CO<sub>2</sub> complex fall in coincidence with those of pure H<sub>2</sub>O or CO<sub>2</sub> but,  
 330 interestingly, Pavlyuchko et al. concluded their article by noting that "...the combination  
 331 transition  $\nu_{OH}^s + \nu_{CO}^{as}$  [e.g.  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ ] in the vicinity of  $\sim 6000$  cm<sup>-1</sup>, falls occasionally in the  
 332 regions of relative transparency of both isolated monomers and can therefore be discriminated from  
 333 the monomer absorption" [51]. Although our observation cannot be interpreted as an absorption band  
 334 of the H<sub>2</sub>O-CO<sub>2</sub> bound complex, the above statement about the detection of simultaneous transitions  
 335 applies to the CIA in (H<sub>2</sub>O+CO<sub>2</sub>) gas mixtures.

### 336 5. Conclusion

337 The present study, thanks to measurements and classical molecular dynamics calculations made  
 338 for both <sup>12</sup>CO<sub>2</sub>-H<sub>2</sub>O and <sup>13</sup>CO<sub>2</sub>-H<sub>2</sub>O mixtures, has confirmed that the band observed around 6000 cm<sup>-1</sup>  
 339 in Ref. [11] is indeed due to the dipole induced in interacting (CO<sub>2</sub>, H<sub>2</sub>O) pairs through the  
 340  $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  simultaneous transitions, involving a  $\Delta\nu_3 = 1$  change of CO<sub>2</sub> through the dipole and a  
 341  $\Delta\nu_1 = 1$  change of H<sub>2</sub>O through the polarizability. It is worth emphasizing that this is the first  
 342 demonstration of a purely collision-induced absorption contribution to the binary continuum in CO<sub>2</sub> +  
 343 H<sub>2</sub>O gas mixtures, which was so far entirely attributed to the far line wings of the dipole transitions of  
 344 CO<sub>2</sub> broadened by H<sub>2</sub>O and of H<sub>2</sub>O broadened by CO<sub>2</sub>.

345 Note that other simultaneous transitions in H<sub>2</sub>O+CO<sub>2</sub> gas mixtures exist which may be  
 346 detectable, since centered in some relatively transparent regions of the H<sub>2</sub>O+CO<sub>2</sub> spectrum, and thus  
 347 deserve investigation. The first [ $\nu_3(\text{CO}_2)+\nu_3(\text{H}_2\text{O})$ ] is similar to the one studied in this paper, but in which  
 348 a H<sub>2</sub>O  $\nu_3$  Raman vibrational change is involved, which would lead to a CIA centered around 6105 cm<sup>-1</sup>.  
 349 This CIA is expected to be small and broad, since  $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_3 = 1 \rangle = 0$  [40] and thus only  
 350 the  $\langle v = 0 | \Delta\alpha(\text{H}_2\text{O}) | v_3 = 1 \rangle$  matrix element contributes. Another contribution comes from the  
 351  $\nu_2(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$  transition, involving, among others, the contributions of the products  $\langle v =$   
 352  $0 | \Delta\alpha(\text{H}_2\text{O})$  and  $\alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle \langle v = 0 | \mu(\text{CO}_2) | v_2 = 1 \rangle$ , which for <sup>12</sup>CO<sub>2</sub> should peak near 4334  
 353 cm<sup>-1</sup>. The associated CIA band is expected to be less intense than the one investigated in this study due  
 354 to the smaller central wavenumber and weaker CO<sub>2</sub> dipole matrix element ( $\langle v = 0 | \mu(\text{CO}_2) | v_2 = 1 \rangle =$   
 355  $0.071$  a.u. [38,39]). For completeness, note that two other simultaneous transitions should appear  
 356 around 2900 cm<sup>-1</sup>,  $\nu_1(\text{CO}_2)+\nu_2(\text{H}_2\text{O})$  and  $2\nu_2(\text{CO}_2)+\nu_2(\text{H}_2\text{O})$ , associated with the polarization of CO<sub>2</sub> by  
 357 the dipole of H<sub>2</sub>O, through the product  $\langle v = 0 | \Delta\alpha(\text{CO}_2)$  and  $\alpha_{iso}(\text{CO}_2) | v_1 = 1$  or  $v_2 = 2 \rangle \langle v =$   
 358  $0 | \mu(\text{H}_2\text{O}) | v_2 = 1 \rangle$ .

359

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