



HAL
open science

Simultaneous collision-induced transitions in H₂O+CO₂ gas mixtures

H Fleurbaey, Didier Mondelain, W Fakhardji, J M Hartmann, A Campargue

► **To cite this version:**

H Fleurbaey, Didier Mondelain, W Fakhardji, J M Hartmann, A Campargue. Simultaneous collision-induced transitions in H₂O+CO₂ gas mixtures. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2022, 285, 10.1016/j.jqsrt.2022.108162 . hal-03854982

HAL Id: hal-03854982

<https://hal.science/hal-03854982>

Submitted on 21 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

Simultaneous collision-induced transitions in H₂O+CO₂ gas mixtures

H. Fleurbaey^a, D. Mondelain^a, W. Fakhardji^b, J.-M. Hartmann^b, A. Campargue^{a*}

^a *Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

^b *Laboratoire de Météorologie Dynamique/IPSL, CNRS, Ecole Polytechnique, Institut polytechnique de Paris, Sorbonne Université, Ecole Normale Supérieure, PSL Research University, F-91120 Palaiseau, France*

Key words

Absorption spectroscopy; Radiative transfer; Collision Induced Absorption; Continuum

* Corresponding author: alain.campargue@univ-grenoble-alpes.fr; LIPhy, Bat. E, 140 rue de la Physique, 38400 Saint-Martin d'Hères (France).

29

Abstract

30 A collision induced absorption (CIA) band has been measured near 6000 cm^{-1} in a spectrum of
31 humidified 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 CO_2
33 and H_2O resonance lines broadened by collisions with H_2O and with CO_2 , respectively. The observed
34 CIA corresponds to a simultaneous excitation of $^{12}\text{CO}_2$ and H_2O colliding molecules in the ν_3
35 antisymmetric and ν_1 symmetric stretching mode, respectively. CRDS spectra recorded near 5940 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 cm^{-1}) coincides with that between the ν_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 CO_2 (ν_3) and isotropic polarizability of H_2O (ν_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. Various processes may contribute to this continuum, which include
51 the far wings of the resonance lines, collision-induced absorption (CIA), and dimers. Similarly, the
52 absorption spectrum of pure carbon dioxide involves resonance lines and a self-continuum
53 contribution again resulting from the three processes mentioned above generating absorptions
54 proportional to the squared gas density. Numerous experimental and theoretical studies have been
55 devoted to the self-continua of both H₂O and CO₂ (see [1] and chapters V and VI of [2]) due to their
56 importance for radiative transfer processes in the atmospheres of the Earth and Venus, respectively.

57 However, the self-continua are not the only continua relevant for planetary applications. Since
58 planetary atmospheres are mixtures of various molecular species, there are additional “crossed”
59 absorption contributions, proportional to the product of the densities of the different colliding
60 molecules. This is obviously the case for the Earth atmosphere in which the H₂O- and CO₂-air (or N₂)
61 continua play, together with the H₂O self-continuum, a significant role which has motivated a large
62 number of studies (see [1] and chapters V and VI of [2]). Note that, until recently, it was generally
63 considered that the associated atmospheric continua were essentially due to the far wings of the air-
64 broadened lines of H₂O and CO₂. The limits of this assumption were pointed out a few years ago with
65 the demonstration of the importance of an N₂ absorption band induced by collisions with H₂O in the
66 H₂O-N₂ continuum [3,4]. Due to its potential importance for the atmospheres of Early Mars and
67 exoplanets, the continuum in H₂O-CO₂ mixtures has recently received a renewed attention, nearly 30
68 years after pioneer studies devoted to the CO₂-broadened line wings of H₂O for Venusian studies [5,6].
69 Measurements and calculations have been made in order to characterize the influence of collisions
70 with H₂O on the wings of CO₂ lines [7,8,3] as well as that of collisions with CO₂ on the wings of H₂O
71 lines [7,9].

72 Very recently, we have undertaken a series of measurements aiming to characterize the
73 absorption continuum of H₂O-CO₂ mixtures in the 1.6 μm and 2.3 μm windows and near 3.5 μm,
74 corresponding to low opacity regions for both CO₂ and water vapor [10]. The “crossed” absorption
75 (proportional to the product of the H₂O and CO₂ densities) was observed to include an unexpected
76 broad band, centered near 6000 cm⁻¹, in addition to the contributions of the far wings of the lines of
77 the monomers (note that pure CO₂ spectra do not exhibit any CIA band in this spectral region [11]). On
78 the basis of the spectral position of its center, this band was tentatively assigned to the simultaneous
79 collision-induced transitions involving a ν₁ (Raman) excitation of H₂O and a ν₃ (dipole absorption)

80 excitation of $^{12}\text{CO}_2$ [noted $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$, hereafter] but no further analysis was made. Note that such
81 simultaneous transitions (sometimes also denoted as double transitions), resulting from the
82 polarization of one molecule (*e.g.* through a vibrational matrix element of the polarizability) by the
83 vibrating electric field of the collision partner (*e.g.* through a vibrational matrix element of the electric
84 dipole or quadrupole) have been observed and analyzed for diverse molecular systems involving H_2 or
85 N_2 (*e.g.* [12,13,14,15]), but also for pure CO_2 [16] and $\text{CO}_2\text{-N}_2$ [17,18,19,20,21].

86 In this paper, we revisit the $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ CIA band both experimentally, by complementing
87 the natural CO_2 measurements reported in Ref. [10] by a new investigation using $^{13}\text{CO}_2$, and
88 theoretically, by using a simple induction model and molecular dynamics simulations. In the next
89 section, we summarize the conditions of the acquisition of the humidified CO_2 spectra by cavity ring
90 down spectroscopy (CRDS). The different steps of the CIA retrieval by successive subtraction of the
91 different contributions from the measured spectra are also described in this section. In section 3, the
92 classical molecular dynamics simulations (CMDS) and the input data used for the prediction of the CIA
93 are described. The measured and calculated results are then presented and discussed in Sec. 4, before
94 concluding remarks (Sec. 5).

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

96 *2.1. Data acquisition*

97 The inherent sensitivity and baseline stability of cavity enhanced techniques make them
98 particularly suitable to measure weak continua [22]. They, in particular, enable to use samples at sub-
99 atmospheric pressure while traditional methods are generally combined with pressurized cells. This is
100 crucial in the case of mixtures involving water vapor at room temperature, the limitation by the
101 saturation pressure making accurate absorption measurements by FTS with long absorption
102 pathlengths practically impossible in the atmospheric transparency windows. In contrast,
103 measurements by CRDS and OFCEAS have recently led to accurate determinations of the self- and
104 foreign (air)-continua of H_2O [23,24,25,26,27,28]. Another advantage of recordings at sub-atm
105 pressures is that the contribution of local absorption transitions is easier to calculate and remove, since
106 line-mixing effects may be disregarded and isolated line shapes can be used. For instance, CRDS was
107 recently applied to the characterization of the O_2 CIA band at $1.27\ \mu\text{m}$ both at NIST [29] and in our
108 laboratory [30,31]. The use of low O_2 pressures enabled to minimize the impact of line mixing effects
109 on the CIA determination obtained with an agreement of less than 1% between the two datasets at
110 room temperature.

111 The $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ CIA band was observed in CRDS spectra of humidified CO_2 recorded in the
112 $5725\text{-}6665\ \text{cm}^{-1}$ and $5856\text{-}5986\ \text{cm}^{-1}$ intervals, for natural CO_2 and $^{13}\text{CO}_2$ samples, respectively.
113 Distributed feedback (DFB) laser diodes were used as light sources, each of them covering a spectral

114 range 20 to 30 cm⁻¹ wide by temperature variation. The cavity-ring down spectrometer used a 142 cm
 115 long high finesse cavity fitted with two highly reflective dielectric mirrors. Ring down (RD) times were
 116 of the order of 120 to 160 μs. Typically, ten RD times were averaged at each spectral step separated
 117 by 0.005 cm⁻¹. A part of the laser light was sent into a wavelength meter (model 621-A IR from Bristol)
 118 to monitor the laser frequency.

119 As detailed in Ref. [10], the spectra with natural CO₂ were recorded in flow regime using
 120 H₂O+CO₂ mixtures with H₂O molar fractions between 3000 and 15000 ppmv. The gas flow of the
 121 mixture (typically a few tens sccm inside the CRDS cavity) was produced using a commercial humidity
 122 generator (from Omicron Technologies). The total pressure in the CRDS cavity was monitored by a
 123 sensor from Edwards (1000 mbar full scale, accuracy 0.15 % of reading) and maintained at a fixed value
 124 of 400 or 750 Torr with a solenoid valve and a software-based proportional integral loop acting on the
 125 gas flow. The densities of CO₂ and H₂O (ρ_{CO_2} and ρ_{H_2O} , respectively) were obtained from the partial
 126 pressures and the cell temperature measured with a calibrated Pt100 sensor (2 σ -uncertainty $\pm 0.06^\circ\text{C}$)
 127 fixed on the external wall of the cavity underneath the enveloping thermal insulation foam.

128 In the case of the recordings with humidified ¹³CO₂, the limitation of the gas consumption
 129 (imposed by the cost of the ¹³C enriched CO₂ tank) required to record the spectra in static regime. The
 130 cell was thus first filled with about 6.5 Torr of water vapor and ¹³CO₂ (from Aldrich, 99 % ¹³C
 131 enrichment) was then added up to a total pressure of 400 Torr.

132 The baseline determination of the spectra relied on measurements performed with argon
 133 before and after the recording with the (H₂O+CO₂) mixture, with the cavity pumped before each gas
 134 filling (argon or mixture). The two argon spectra ensure that the cavity alignment (and thus the
 135 baseline) is unchanged after pumping/filling cycles. By comparing the two argon spectra, the baseline
 136 stability was found to be of the order of a few 10⁻¹⁰ cm⁻¹. In order to check the proportionality of the
 137 retrieved “crossed” absorption to the $\rho_{CO_2}\rho_{H_2O}$ densities product, measurements were performed for
 138 several values of the water molar fraction in natural CO₂. The study with ¹³CO₂ being mostly performed
 139 for validation of the assignment of the observed CIA structure, a single set of experimental conditions
 140 (~6.5 Torr of water vapor in ¹³CO₂ at a total pressure of 400 Torr) was retained.

141 2.2. CIA retrieval

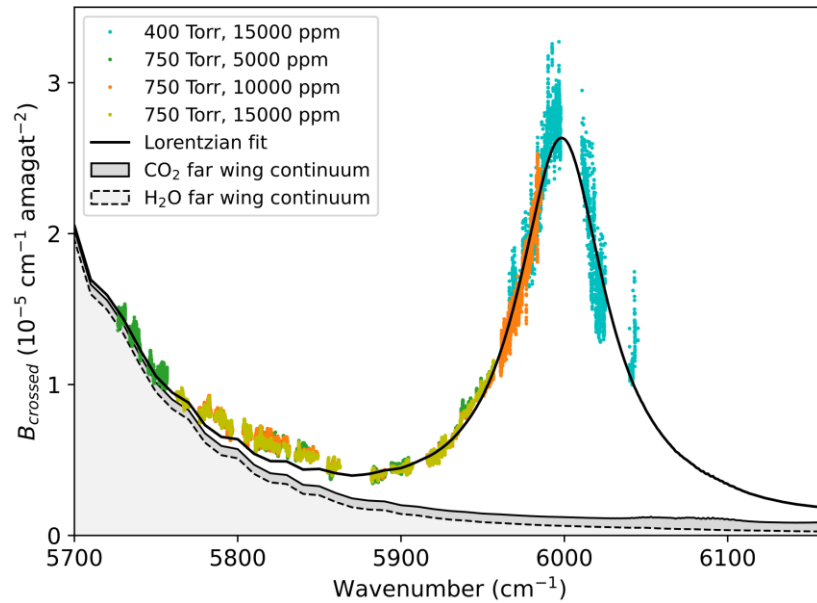
142 After baseline correction, the absorption coefficient, $\alpha(\nu)$, can be expressed as:

$$143 \quad \alpha(\nu) = M_{CO_2}\rho_{CO_2} + M_{H_2O}\rho_{H_2O} + B_{CO_2}\rho_{CO_2}^2 + B_{H_2O}\rho_{H_2O}^2 + B_{crossed}\rho_{CO_2}\rho_{H_2O} \quad (1)$$

144 where $M_{CO_2}\rho_{CO_2}$ and $M_{H_2O}\rho_{H_2O}$ are the contributions due to the monomer local lines of CO₂ and H₂O
 145 (calculated within a ± 25 cm⁻¹ range around the center wavenumber), respectively, and ρ represents
 146 the density (in amagat⁻¹). The B_{H_2O} and B_{CO_2} coefficients (in cm⁻¹amagat⁻²) correspond to the self-
 147 continuum coefficients of water and CO₂, respectively. $B_{crossed}$ is the crossed binary coefficient arising

148 from the interaction of water and CO₂ molecules, thus involving both far line wings (of CO₂-broadened
 149 H₂O transitions as well as of H₂O-broadened CO₂ transitions) and CIA bands contributions.

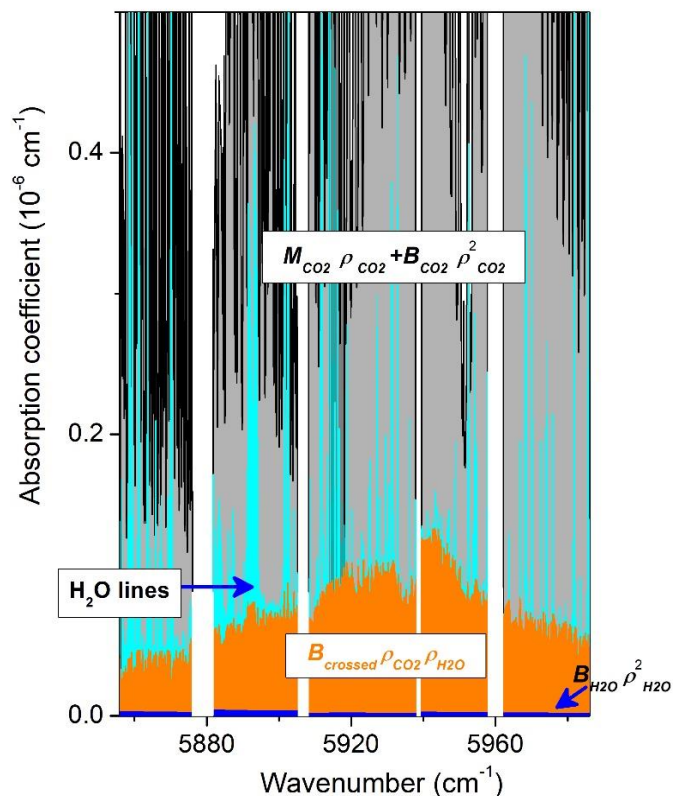
150 In the case of natural CO₂, the HITRAN2016 database [32] was used to simulate the local CO₂
 151 and H₂O monomer contributions with Voigt profiles truncated at $\pm 25 \text{ cm}^{-1}$ excluding the pedestal of
 152 the absorption lines (see details in Ref. [10]). The water self-continuum cross-sections $B_{\text{H}_2\text{O}}$ were taken
 153 from Ref. [27] while, for CO₂, the self-continuum cross-sections B_{CO_2} were taken from Ref. [11] or
 154 measured in Ref. [10] below and above 5800 cm^{-1} , respectively. The B_{crossed} binary coefficients
 155 measured with the natural CO₂ sample for various water vapor molar fractions (from 3000 to 15000
 156 ppm) and two total pressures (400 and 750 Torr) are presented in **Fig. 1**. While over the various
 157 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
 158 B_{crossed} values are found consistent within about 20 % in the CIA region near 6000 cm^{-1} . **Fig. 1** also
 159 includes a fit of the observed band, assuming a Lorentzian shape and fixing the far wing continuum
 160 background to its value calculated by the χ -factor approach (see [10]). The parameters obtained from
 161 this Lorentzian fit will be discussed in Sec. 4.



162
 163 **Fig.1:** Overview of the binary coefficients measured in the 5725-6665 cm^{-1} region including the $\nu_3(^{12}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$
 164 CIA band near 6000 cm^{-1} , for various total pressures and water vapor molar fractions. The best fit of the CIA using
 165 a Lorentzian function (black solid line) is superimposed to the far wing continuum background which was fixed to
 166 its value calculated by the χ -factor approach (see [10]).

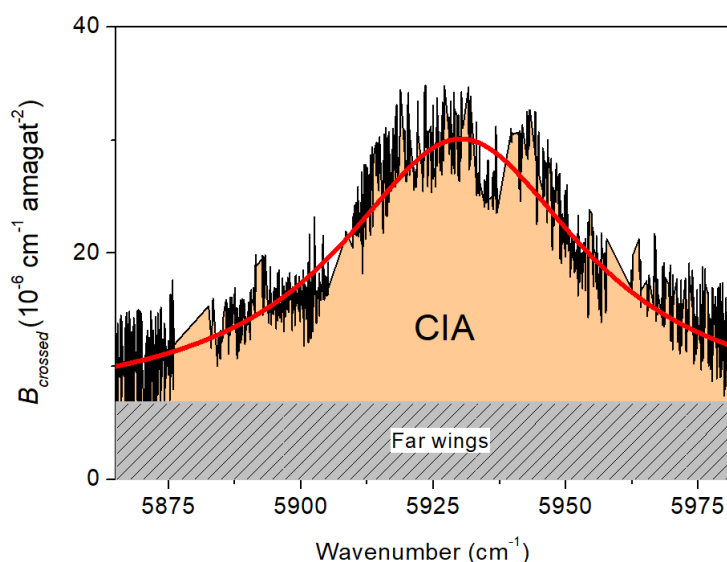
167 In the case of humidified ¹³CO₂, the measurement of the CIA band is made more difficult because
 168 it falls in a region where CO₂ resonance lines are much stronger than with the natural sample. In order
 169 to subtract the ¹³CO₂ contribution – $(M_{\text{CO}_2}\rho_{\text{CO}_2} + B_{\text{CO}_2}\rho_{\text{CO}_2}^2)$ in Eq. (1) – we did not try to simulate
 170 separate contributions of the resonance lines and of the self-continuum of ¹³CO₂ and preferred to
 171 directly subtract a spectrum of dry ¹³CO₂ recorded at the same partial pressure of ¹³CO₂ as in the

172 humidified mixture used for the recordings (395 Torr). This, which disregards the effects of collisions
173 with H₂O on the central and wing regions of the ¹³CO₂ lines, is of likely small consequences considering
174 the relatively small (1.5 %) amount of water vapor in the humidified sample. **Fig. 2** shows the different
175 contributions to the total absorption coefficient measured for a mixture of about 6 Torr of water in
176 ¹³CO₂ at a total pressure of 400 Torr. As adsorption on the walls of the CRDS affected the amount of
177 water in the cell, for the spectral interval corresponding to the tuning range of each DFB laser diode,
178 the water vapor partial pressure, p_{H_2O} , was determined from the integrated absorption coefficient of
179 a few observed water lines. The obtained p_{H_2O} values were found to vary from 5.3 to 7.0 Torr for the
180 six DFB intervals covering the CIA region (5856-5986 cm⁻¹). These p_{H_2O} values were used to calculate
181 and subtract the water self-continuum [27] and the water resonance lines contribution (computed
182 using the HITRAN2016 line list [32]). As illustrated by **Fig. 2**, in our experimental conditions, the two
183 water vapor contributions are much smaller than the ¹³CO₂ contribution. After subtraction of the
184 different contributions, the remaining absorption coefficient - $B_{crossed}\rho_{CO_2}\rho_{H_2O}$ - shows a clear bell
185 shape centered at about 5940 cm⁻¹ corresponding to the $\nu_3(^{13}CO_2)+\nu_1(H_2O)$ CIA band. Using the
186 determined p_{H_2O} values, the corresponding crossed binary coefficients, $B_{crossed}$, displayed in **Fig. 3**
187 were derived. The obtained curve shows high frequency “noise” due to the imperfect removal of the
188 strong ¹³CO₂ resonance lines. An improved description of the CIA band shape is obtained from a
189 Lorentzian fit with a baseline (corresponding to the far wing continuum contribution) assumed to be
190 constant with frequency. The parameters obtained from this fit will be discussed in Sec. 4.
191



192

193 **Fig. 2:** Different contributions to the total absorption coefficient measured by CRDS with a mixture of water and
 194 CO_2 highly enriched in ^{13}C . The total pressure was 402 Torr while the water vapor partial pressure varied between
 195 5.3 and 7.0 Torr over the displayed region. The measured absorption coefficient is first reduced by the $^{13}\text{CO}_2$
 196 contribution (lines and self-continuum - grey background) measured with a pure $^{13}\text{CO}_2$ sample. Then, the water
 197 contribution (lines and self-continuum - cyan and blue background, respectively) is simulated and subtracted. The
 198 absorption remaining after these subtractions (orange background) shows the bell shape profile of the
 199 $\nu_3(^{13}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ CIA band centered near 5930 cm^{-1} .



200

201 **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
 202 shape (red solid line) is superimposed to the continuum background due to the far wing continuum (dashed). The
 203 background level was adjusted by the fit.

204

205 3. Classical molecular dynamics simulations (CMDS)

206 The CIA in the region of the $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ simultaneous transitions was calculated using
207 classical molecular dynamics simulations (CMDS), exactly as described in Ref. [3], with the only
208 difference that the H_2O static isotropic polarizability matrix element $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v = 0 \rangle$ used in
209 this previous study was here replaced by the vibrational matrix element $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle$
210 (here, $v = 0$ and $v_1 = 1$ stand for the (000) and (100) vibrational states of H_2O , respectively). As in Ref.
211 [3], only the component of the induced dipole due to the polarization of H_2O (through its isotropic
212 polarizability $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle$) in the electric field of the CO_2 dipole (through $\langle v =$
213 $0 | \mu(\text{CO}_2) | v_3 = 1 \rangle$, where $v = 0$ and $v_3 = 1$ stands for the $(v_1 v_2^l v_3) = (00^0 0)$ and $(00^0 1)$ vibrational
214 states of CO_2 , respectively) was thus taken into account. This is convenient since the induced dipole
215 then does not depend of the orientation of the H_2O molecule but it disregards other induction
216 mechanisms, including the term originating from the anisotropic polarizability of the water molecule
217 (*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
218 relatively small, while many other terms, such as those involving the product of the H_2O dipole element
219 $\langle v = 0 | \mu(\text{H}_2\text{O}) | v_1 = 1 \rangle$ and of the CO_2 polarizability $\langle v = 0 | \Delta\alpha(\text{CO}_2)$ or $\alpha_{iso}(\text{CO}_2) | v_3 = 1 \rangle$, vanish
220 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. [33, 34].
221 For H_2O , $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.73$ a. u. was obtained, using the convention of Ref. [35], from
222 the value of α_0^0 provided in Ref. [36] with $\alpha_{iso} = -\alpha_0^0/\sqrt{3}$. Note that our classical calculations lead to
223 a CIA structure that is automatically centered at the sum of the origins of the $\nu_3(^{12}\text{CO}_2)$ and $\nu_1(\text{H}_2\text{O})$
224 bands, $2349+3657= 6006$ cm^{-1} for $^{12}\text{CO}_2$, because all the Q transitions of the H_2O ν_1 band, associated
225 with the isotropic polarizability, then have the same imposed wavenumber of 3657 cm^{-1} . This does not
226 correspond to reality since the $(v = 0, J, K_a, K_c) \rightarrow (v_1 = 1, J, K_a, K_c)$ rovibrational transitions are
227 all shifted to the red with respect to the band origin of 3657 cm^{-1} and spread over typically 10 cm^{-1}
228 [32]. In order to correct for this, the bar spectrum of the true Q lines was convoluted by the raw CMDS-
229 predicted CIA, which red-shifts the peak wavenumber by about -6 cm^{-1} with respect to 6006 cm^{-1} . In
230 the case of $^{13}\text{CO}_2$, CMDS were computed as done for $^{12}\text{CO}_2$, using the same value of
231 $\langle v = 0 | \mu(\text{CO}_2) | v_3 = 1 \rangle$ [37,38], but a change of the ν_3 band origin from 2349 to 2283 cm^{-1} .

232 4. Results and discussion

233 As said above, the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ CIA bands as obtained from experiments were fitted assuming
234 a Lorentzian band shape (see **Figs. 1** and **3**). In the case of the main isotopologue, the underlying far
235 wing continuum was fixed to its value calculated by the χ -factor approach (see [10]). In the case of
236 $^{13}\text{CO}_2$, the baseline was assumed to be constant with frequency and it was adjusted by the fit. The
237 CMDS-computed spectra for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ were fitted by a Gaussian function to determine the
238 center position, their integration over wavenumber yielded the intensities, and the widths were

239 determined directly from the computed absorptions. The experimental and calculated centers,
 240 integrated areas and half-widths at half-maximum (HWHM) are listed in **Table 1**, calling for several
 241 remarks. The first is that the peak positions obtained for measured and computed spectra agree very
 242 well. The measured and calculated differences between the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ values, of about 68 cm^{-1} ,
 243 are in close agreement with the isotopic shift of the $\nu_3 = 1$ vibrational levels of the two isotopologues
 244 (66 cm^{-1}) [39]. The second is that the measured and computed integrated intensities also coincide, with
 245 differences well smaller than the experimental uncertainty (roughly estimated to 20 % and 30 % for
 246 $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, respectively). The integrated band intensities for the two isotopologues are close, as
 247 could be expected from the fact that the CO_2 dipole matrix elements are practically identical [37,38].
 248 Finally, the experimental and predicted HWHM are again consistent, both showing a negligible isotope
 249 effect, as could be expected from the strong similarity between $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$.

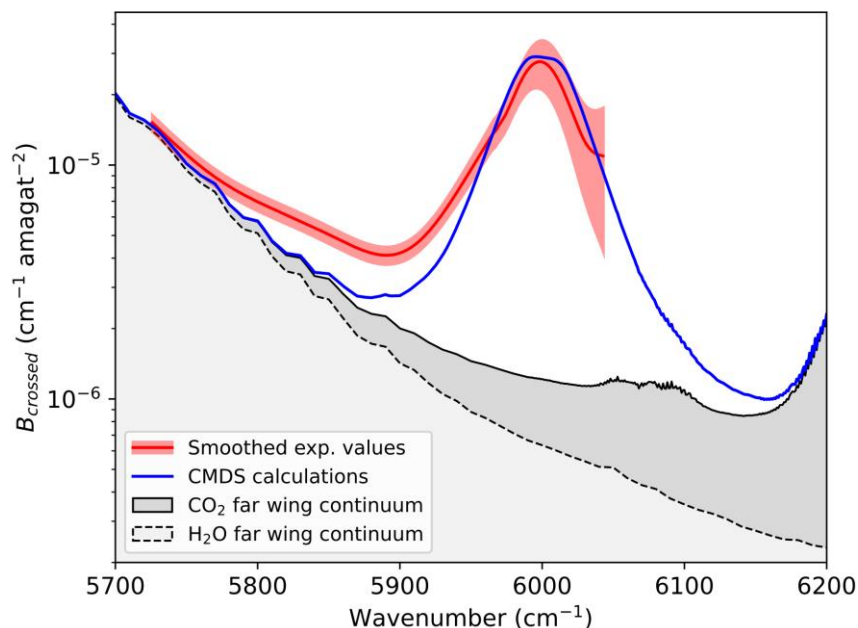
	$\nu_3(^{12}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$		$\nu_3(^{13}\text{CO}_2)+\nu_1(\text{H}_2\text{O})$	
	Exp	CMDS	Exp	CMDS
Center (cm^{-1})	5998.4	5999.7	5930.2	5932
Integrated binary coefficient ($10^{-3}\text{ cm}^{-2}\text{amagat}^{-2}$)	2.6	2.08	2.1	2.06
HWHM (cm^{-1})	33.0	31	28.2	31

250
 251
 252
 253

Table 1: Band centers, integrated intensities and half widths at half maximum (HWHM) of the $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ CIA bands measured and CMDS-calculated for natural $^{12}\text{CO}_2$ and in $^{13}\text{CO}_2$.

254 A comparison between the measured and computed $\text{H}_2\text{O}-^{12}\text{CO}_2$ density-normalized absorption
 255 coefficients over the spectral range of the $1.6\ \mu\text{m}$ window is displayed in **Fig. 4**. The calculated
 256 spectrum was obtained by adding the CIA predicted in the present study to the contributions of the
 257 far wings of the H_2O -broadened transitions of CO_2 and of the CO_2 -broadened lines of H_2O . The
 258 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 χ -factor
 259 approaches developed in Refs. [8] and [9] respectively. As can be seen, the agreement is quite
 260 satisfactory which validates the prediction of all three contributions. However there is a noticeable
 261 discrepancy between measured and computed values on the low frequency side of the CIA peak which
 262 may be explained by the neglecting of the contribution of the anisotropic polarizability $\Delta\alpha$ of H_2O in
 263 the CMDS computation of the collision-induced dipole. Indeed, first note that, since $\langle v = 0 | \Delta\alpha(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.54\text{ a.u.}$ (obtained from the value of α_0^2 provided in Ref. [36] and $\Delta\alpha =$
 264 $\sqrt{3/2}\ \alpha_0^2$) which is smaller than $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_1 = 1 \rangle = 0.73\text{ a.u.}$ by a factor of about $\sqrt{2}$, the
 265 integrated intensity due to this dipole induction mechanism should be about 2 times lower. In addition,
 266 the anisotropic polarizability selection rule allows not only Q but also O and S lines associated with J
 267 $\rightarrow J\pm 2$ transitions, the latter being spread over a broad spectral range of several 100 cm^{-1} on both sides
 268 of the central vibrational frequency. In summary, this contribution, which is weaker and spectrally
 269

270 much broader than that of the isotropic polarizability, may explain the above mentioned missing
 271 "background".



272
 273 **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
 274 calculations (blue) is added to the sum of the H_2O (light grey) and CO_2 (grey) far wing continua. Also shown are
 275 the smoothed experimental values from Ref. [10] (red, with a 1σ error band).
 276

277 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
 278 at sub-atmospheric pressure was pointed out nearly three decades ago in liquid $\text{CO}_2+\text{H}_2\text{O}$ mixtures,
 279 thus at considerably higher molecular densities [40]. Low resolution spectra were recorded with
 280 grating spectrographs allowing for an estimation of the integrated absorption cross-section. A value of
 281 $8\times 10^{-4} \text{ cm}^{-2}\text{amagat}^{-2}$ was estimated in the liquid phase, about three times smaller than our gas phase
 282 value ($2.6\times 10^{-3} \text{ cm}^{-2}\text{amagat}^{-2}$). Note that a similar tendency between liquid and gas phase CIA
 283 intensities (normalized to squared density) was reported for the far-infrared CIA of pure CO_2 [41].

284 In general, free collisions are believed to bring most of the contribution to CIA bands and $\text{H}_2\text{O}-$
 285 CO_2 bound complexes, which are disregarded in the CMDS, are not expected to contribute significantly
 286 to the observed absorption feature. The agreement between the measured and CMDS integrated band
 287 intensities seems to confirm this expectation. The $\text{H}_2\text{O}-\text{CO}_2$ bound complex which has been observed
 288 in matrices (e.g. [42]) and in expansion jets (e.g. [43,44]) has a planar T-shaped structure with
 289 hydrogens pointing away from CO_2 . The dissociation energy D_0 was estimated to be about 730 cm^{-1}
 290 [45,46]. It is worth mentioning the results of anharmonic vibrational calculations of the spectrum of
 291 this Van der Waals complex [47], based on *ab initio* force field and electro-optical parameters. As
 292 expected, most of the predicted vibrational bands of the $\text{H}_2\text{O}-\text{CO}_2$ complex fall in coincidence with
 293 those of pure H_2O or CO_2 but, interestingly, Pavlyuchko et al. concluded their article by noting that

294 “...the combination 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 $\sim 6000 \text{ cm}^{-1}$, falls
 295 occasionally in the regions of relative transparency of both isolated monomers and can therefore be
 296 discriminated from the monomer absorption” [47]. Although our observation cannot be interpreted
 297 as an absorption band of the $\text{H}_2\text{O}-\text{CO}_2$ bound complex, the above statement about the detection of
 298 simultaneous transitions applies to the CIA in $(\text{H}_2\text{O}+\text{CO}_2)$ gas mixtures.

299 5. Conclusion

300 The present study, thanks to measurements and classical molecular dynamics calculations made
 301 for both $^{12}\text{CO}_2-\text{H}_2\text{O}$ and $^{13}\text{CO}_2-\text{H}_2\text{O}$ mixtures, has confirmed that the band observed around 6000 cm^{-1}
 302 in Ref. [10] is indeed due to the dipole induced in interacting $(\text{CO}_2, \text{H}_2\text{O})$ pairs through the
 303 $\nu_3(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ simultaneous transitions, involving an absorption (CO_2) and a Raman (H_2O) process. It
 304 is worth emphasizing that this is the first demonstration of a purely collision-induced absorption
 305 contribution to the binary continuum in $\text{CO}_2 + \text{H}_2\text{O}$ gas mixtures, which was so far entirely attributed
 306 to the far line wings of the dipole transitions of CO_2 broadened by H_2O and of H_2O broadened by CO_2 .

307 Note that other simultaneous transitions in $\text{H}_2\text{O}+\text{CO}_2$ gas mixtures exist which may be
 308 detectable, since centered in some relatively transparent regions of the $\text{H}_2\text{O}+\text{CO}_2$ spectrum, and thus
 309 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
 310 a H_2O ν_3 Raman vibrational change is involved, which would lead to a CIA centered around 6105 cm^{-1} .
 311 This CIA is expected to be small and broad, since $\langle v = 0 | \alpha_{iso}(\text{H}_2\text{O}) | v_3 = 1 \rangle = 0$ [36] and thus only
 312 the $\langle v = 0 | \Delta\alpha(\text{H}_2\text{O}) | v_3 = 1 \rangle$ matrix element contributes. Another contribution comes from the
 313 $\nu_2(\text{CO}_2)+\nu_1(\text{H}_2\text{O})$ transition, involving, among others, the contributions of the products $\langle v =$
 314 $0 | \Delta\alpha(\text{H}_2\text{O})$ 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 $^{12}\text{CO}_2$ should peak near 4334
 315 cm^{-1} . The associated CIA band is expected to be less intense than the one investigated in this study due
 316 to the smaller central wavenumber and weaker CO_2 dipole matrix element ($\langle v = 0 | \mu(\text{CO}_2) | v_2 = 1 \rangle =$
 317 0.071 a.u. [33,34]). For completeness, note that two other simultaneous transitions should appear
 318 around 2900 cm^{-1} , $\nu_1(\text{CO}_2)+\nu_2(\text{H}_2\text{O})$ and $2\nu_2(\text{CO}_2)+\nu_2(\text{H}_2\text{O})$, associated with the polarization of CO_2 by
 319 the dipole of H_2O , through the product $\langle v = 0 | \Delta\alpha(\text{CO}_2)$ and $\alpha_{iso}(\text{CO}_2) | v_1 = 1$ or $v_2 = 2 \rangle \langle v =$
 320 $0 | \mu(\text{H}_2\text{O}) | v_2 = 1 \rangle$.

321

322 Acknowledgements

323 This work was performed in the frame of the ANR project COMPLEAT (ANR-19-CE31-0010-01). H. Tran
 324 and M. Turbet (LMD) are thanked for providing the $B_{\text{CO}_2-\text{H}_2\text{O}}$ and $B_{\text{H}_2\text{O}-\text{CO}_2}$ binary coefficients
 325 calculated with the χ -factor approach. AC is grateful to Andrey Vigasin for useful exchanges. WF and J-
 326 MH thank Prof. Christian Boulet for very helpful discussions.

References

- 330 [1] Hartmann J-M, Tran H, Armante R, Boulet C, Campargue A, Forget F, Gianfrani L, Gordon I, Guerlet S,
331 Gustafsson M, Hodges JT, Kassi S, Lisak D, Thibault F, Toon GC. Recent advances in collisional effect on spectra
332 of molecular gases and their practical consequences. *J Quant Spectrosc Radiat Transf* 2018;213:178–227.
333 doi:10.1016/j.jqsrt.2018.03.016.
- 334 [2] Hartmann J-M, Boulet C, Robert D. Collisional effects on molecular spectra: laboratory experiments and
335 models, consequences for applications. Elsevier; 2021. Second Edition Amsterdam.
- 336 [3] Hartmann J-M, Boulet C, Tran DD, Tran H, Baranov Y. Effect of humidity on the absorption continua of CO₂
337 and N₂ near 4 μm: Calculations, comparisons with measurements, and consequences for atmospheric spectra.
338 *J Chem Phys* 2018;148:054304. doi:10.1063/1.5019994.
- 339 [4] Hartmann J-M, Armante R, Toon GC, Scott N, Tran H, Crevoisier C, Chédin A, Capelle V. Indirect influence of
340 humidity on atmospheric spectra near 4 μm. *Geophys Res Lett* 2018;45:12593–12601.
341 doi:10.1029/2018GL079582.
- 342 [5] Ma Q, Tipping RH. A far wing line shape theory and its application to the foreign-broadened water continuum
343 absorption. III. *J Chem Phys* 1992;97:818–828. doi:10.1063/1.463184.
- 344 [6] Pollack JB, Dalton JB, Grinspoon D, Wattson RB, Freedman R, Crisp D, Allen DA, Bézard B, DeBergh C, Giver
345 LP, Ma Q, Tipping RH. Near-Infrared Light from Venus' Nightside: A Spectroscopic Analysis. *Icarus* 1993;103:1–
346 42. doi:10.1006/icar.1993.1055.
- 347 [7] Baranov YI. On the significant enhancement of the continuum-collision induced absorption in H₂O+CO₂
348 mixtures. *J Quant Spectrosc Radiat Transf* 2016;175:100–6. doi:10.1016/j.jqsrt.2016.02.017.
- 349 [8] Tran H, Turbet M, Chelin P, Landsheere X. Measurements and modeling of absorption by CO₂+H₂O mixtures
350 in the spectral region beyond the CO₂ v₃-band head. *Icarus* 2018;306:116–121.
351 doi:10.1016/j.icarus.2018.02.009.
- 352 [9] Tran H, Turbet M, Hanoufa S, Landsheere X, Chelin P, Ma Q, Hartmann J-M. The CO₂-broadened H₂O
353 continuum in the 100–1500 cm⁻¹ region: Measurements, predictions and empirical model. *J Quant Spectrosc
354 Radiat Transf* 2019;230:75–80. doi:10.1016/j.jqsrt.2019.03.016.
- 355 [10] Fleurbaey H, Campargue A, Carreira Mendès da Silva Y, Grilli R, Kassi S, Mondelain D. Characterization of the
356 foreign water vapor continuum in CO₂ within the infrared transparency windows. *J Quant Spectrosc Radiat
357 Transf* submitted.
- 358 [11] Mondelain D, Campargue A, Čermák P, Gamache RR, Kassi S, Tashkun SA, Tran H. The CO₂ absorption
359 continuum by high pressure CRDS in the 1.74 μm window. *J Quant Spectrosc Radiat Transfer* 2017;203:530–
360 537. doi:10.1016/j.jqsrt.2017.02.019.
- 361 [12] Brodbeck C, Bouanich J-P, Figuiere P, Szwarc H. Simultaneous infrared transitions in N₂ + SF₆ mixtures. *J
362 Chem Phys* 1981;74:77–80. doi:10.1063/1.440796.
- 363 [13] Bouanich J-P, Brodbeck C. Collision-induced simultaneous transitions in H₂+CF₄ and H₂+SF₆ mixtures. *J Quant
364 Spectrosc Radiat Transf* 1977;17:777–82. doi:10.1016/0022-4073(77)90041-3.
- 365 [14] Abu-Kharma M. Analysis of the collision-induced absorption spectra of H₂ in H₂-N₂ in the range 5600–9500
366 cm⁻¹. *J Phys B: At Mol Opt Phys* 2007;40:2345–50. doi:10.1088/0953-4075/40/12/010.
- 367 [15] Stamp S, Prasad RDG, Gillard PG, Paddi Reddy S. Analysis of the collision-induced absorption spectra of
368 double vibrational transitions in H₂-N₂", AIP Conference Proceedings 1999;467:453–456.
369 doi:10.1063/1.58384.
- 370 [16] Tonkov MV, Filippov NN, Bertsev VV, Bouanich JP, Nguyen Van Thanh, Brodbeck C, et al. Measurements and
371 empirical modelling of pure CO₂ absorption in the 2.3 μm region at room temperature: far wings, allowed
372 and collision-induced bands. *Appl Opt* 1996;35:4863–70. doi:10.1364/AO.35.004863.
- 373 [17] Fahrenfort J, Ketelaar JAA. Simultaneous Vibrational Transitions in the Infrared Absorption Spectra of
374 Compressed Gases. *J Chem Phys* 1954;22:1631. doi:10.1063/1.1740502.

- 375 [18] Keteelar JAA. Infra-red spectra of compressed gases. *Spectrochim Acta* 1959;14:237–248. doi:10.1016/0371-
376 1951(59)80231-9.
- 377 [19] Brodbeck C, Bouanich J-P, Penner AR, Meinander N, Tabisz GC. Band-shape analysis of an infrared double
378 transition in CO₂ + N₂ gas mixtures. *Can J Phys* 1987;65:1073–1076. doi:10.1139/p87-177.
- 379 [20] Maté B, Fraser GT, Lafferty WJ. Intensity of the simultaneous vibrational absorption CO₂ (ν₃=1) + N₂ (ν=1) ←
380 CO₂ (ν₃=0) + N₂ (ν=0) at 4680 cm⁻¹. *J Mol Spectrosc* 2000;201:175–177. doi:10.1006/jmsp.2000.8074.
- 381 [21] Brown A, Tipping RH, Maté B. Theoretical Study of the Collision-Induced Double Transition CO₂ (ν₃=1) + N₂
382 (ν₁=1) ← CO₂ (ν₃=0) + N₂ (ν₁=0) at 296 K. *J Mol Spectrosc* 2000;204(1):153–158. doi:10.1006/jmsp.2000.8214.
- 383 [22] Kassi S, Campargue A, Mondelain D, Tran H. High pressure Cavity Ring Down Spectroscopy: Application to
384 the absorption continuum of CO₂ near 1.7 μm. *J Quant Spectrosc Radiat Transf* 2015;167:97–104.
385 doi:10.1016/j.jqsrt.2015.08.014.
- 386 [23] Campargue A, Kassi S, Mondelain D, Vasilchenko S, Romanini D. Accurate laboratory determination of the
387 near infrared water vapor self-continuum: A test of the MT_CKD model. *J Geophys Res Atmos*
388 2016;121:13180–13203. doi:10.1002/2016JD025531.
- 389 [24] Lechevallier L, Vasilchenko S, Grilli R, Mondelain D, Romanini D, Campargue A. The water vapour self-
390 continuum absorption in the infrared atmospheric windows: new laser measurements near 3.3 and 2.0 μm.
391 *Atmos Meas Tech* 2018;11:2159–2171. doi:10.5194/amt-11-2159-2018.
- 392 [25] Richard L, Vasilchenko S, Mondelain D, Ventrillard I, Romanini D, Campargue A. Water vapor self-continuum
393 absorption measurements in the 4.0 and 2.1 μm transparency windows. *J Quant Spectrosc Radiat Transf*
394 2017;201:171–179. doi:10.1016/j.jqsrt.2017.06.037.
- 395 [26] Ventrillard I, Romanini D, Mondelain D, Campargue A. Accurate measurements and temperature
396 dependence of the water vapor self-continuum absorption in the 2.1 μm atmospheric window. *J Chem Phys*
397 2015;143:134304. doi:10.1063/1.4931811.
- 398 [27] Vasilchenko S, Campargue A, Kassi S, Mondelain D. The water vapour self- and foreign-continua in the 1.6
399 μm and 2.3 μm windows by CRDS at room temperature. *J Quant Spectrosc Radiat Transf* 2019;227:230–238.
400 doi:10.1016/j.jqsrt.2019.02.016.
- 401 [28] Fleurbaey H, Grilli R, Mondelain D, Campargue A. Measurements of the water vapor continuum absorption
402 by OFCEAS at 3.50 μm and 2.32 μm. *J Quant Spectrosc Radiat Transf* 2022;278:108004.
403 doi:10.1016/j.jqsrt.2021.108004.
- 404 [29] Fleurbaey H, Reed ZD, Adkins EM, Long DA, Hodges JT. High accuracy spectroscopic parameters of the 1.27
405 μm band of O₂ measured with comb-referenced, cavity ring-down spectroscopy. *J Quant Spectrosc Radiat*
406 *Transf* 2021;270:107684. doi:10.1016/j.jqsrt.2021.107684.
- 407 [30] Mondelain D, Kassi S, Campargue A. Accurate laboratory measurement of the O₂ collision-induced
408 absorption band near 1.27 μm. *J Geophys Res: Atmospheres* 2019;124:414–423. doi:10.1029/2018JD029317.
- 409 [31] Kassi S, Guessoum S, Abanto JCA, Tran H, Campargue A, Mondelain D. Temperature dependence of the
410 collision-induced absorption band of O₂ near 1.27 μm. *J Geophys Res: Atmospheres*
411 2021;126:e2021JD034860. doi:10.1029/2021JD034860.
- 412 [32] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, Birk M, Boudon V, Campargue A, et al. The
413 HITRAN2016 Molecular Spectroscopic Database. *J Quant Spectrosc Radiat Transf* 2017;203:3–69.
414 doi:10.1016/j.jqsrt.2017.06.038.
- 415 [33] Kolomiitsova TD, Lyaptsev AV, Shchepkin DN. Determination of parameters of the dipole moment of the CO₂
416 molecule. *Opt Spectrosc* 2000;88:648–60. doi:10.1134/1.626856.
- 417 [34] Liang Z, Tsai HL. Determination of vibrational energy levels and transition dipole moments of CO₂ molecules
418 by density functional theory. *J Mol Spectrosc* 2008;252:108–14. doi:10.1016/j.jms.2008.07.008.
- 419 [35] Frommhold L. Collision Induced Absorption in Gases. Cambridge Monographs on Atomic, Molecular, and
420 Chemical Physics. Cambridge University Press, Cambridge, (2006).
- 421 [36] Avila G, Fernández JM, Tejada G, Montero S. The Raman spectra and cross-sections of H₂O, D₂O, and HDO in
422 the OH/OD stretching regions. *J Mol Spectrosc* 2004;228:38–65. doi:10.1016/j.jms.2004.06.012.
- 423 [37] Johns JWC. Absolute intensities in CO₂: The 4.3- and 2.7-μm regions revisited. *J Mol Spectrosc* 1989;134:433-
424 9. doi:10.1016/0022-2852(89)90328-7.

- 425 [38] Gordon IE, Rothman LS, Hargreaves RJ, Hashemi R, Karlovets EV, Skinner FM, Conway EK, Hill C, et al. The
426 HITRAN2020 Molecular Spectroscopic Database. *J Quant Spectrosc Radiat Transf* 2022;277:107949.
427 doi:10.1016/j.jqsrt.2021.107949.
- 428 [39] Rothman LS, Hawkins RL, Wattson RB, Gamache RR. Energy levels, intensities, and linewidths of atmospheric
429 carbon dioxide bands. *J Quant Spectrosc Radiat Transf* 1992;48:537–66. doi:10.1016/0022-4073(92)90119-
430 O.
- 431 [40] Vigasin AA, Adiks TG, Tarakanova EG, Yukhnevich GV. Simultaneous infrared absorption in a mixture of CO₂
432 and H₂O: The role of hydrogen-bonded aggregates. *J Quant Spectrosc Radiat Transf* 1994;52:295-301.
433 doi:10.1016/0022-4073(94)90159-7.
- 434 [41] Ho W, Birnbaum G, Rosenberg A. Far-infrared collision-induced absorption in CO₂. I. Temperature
435 dependence. *J Chem Phys* 1971;55:1028. doi:10.1063/1.1676181
- 436 [42] Schriver A, Schriver-Mazzuoli L, Chaquin P, Dumont E. FTIR and ab Initio Study of the 1/1 Complex between
437 Water and Carbon Dioxide in Solid Nitrogen. *J Phys Chem A* 2006;110:51–56. doi:10.1021/jp0581328.
- 438 [43] Zhu Y, Li S, Sun P, Duan C. Infrared diode laser spectroscopy of H₂O–CO₂ and D₂O–CO₂ complexes in the ν₂
439 bend region of water. *J Mol Spectrosc* 2013;283:7–9. doi:10.1016/j.jms.2012.12.002.
- 440 [44] Bogomolov AS, Roucou A, Bejjani R, Herman M, Moazzen-Ahmadi N, Lauzin C. The rotationally resolved
441 symmetric 2OH excitation in H₂O–CO₂ observed using pulsed supersonic expansion and CW-CRDS. *Chem Phys*
442 *Letters* 2021;774:138606. doi:10.1016/j.cplett.2021.138606.
- 443 [45] Makarewicz J. Intermolecular potential energy surface of the water-carbon dioxide complex. *J Chem Phys*
444 2010;132:234305. doi:10.1063/1.3439693.
- 445 [46] Andersen J, Heimdal J, Mahler DW, Nelander B, Wugt Larsen R, et al. Communication: THz absorption
446 spectrum of the CO₂–H₂O complex: Observation and assignment of intermolecular van der Waals vibrations.
447 *J Chem Phys* 2014;140:091103. doi:10.1063/1.4867901.
- 448 [47] Pavlyuchko AI, Orlinson BS, Vigasin AA. Variational Solution of Anharmonic Vibrational Problems for
449 Polyatomics and Molecular Pairs. In: Camy-Peyret C, Vigasin AA (eds) *Weakly Interacting Molecular Pairs:
450 Unconventional Absorbers of Radiation in the Atmosphere*. NATO Science Series (Series IV: Earth and
451 Environmental Sciences), vol 27. Springer, Dordrecht. 2003, pp. 73–82. doi:10.1007/978-94-010-0025-3_5.