

The H2O–CO2 continuum around 3.1, 5.2 and 8.0 μ m: New measurements and validation of a previously proposed χ factor

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Highlights

The $H_2O - CO_2$ continuum around 3.1, 5.2 and 8.0 µm: New measurements and validation of a previously proposed χ factor

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- $H_2O CO_2$ continuum measurements at room temperature
- Confirmation of previous measurements for the $1400-1500~{\rm cm^{-1}}$ spectral region
- New measurements in the 1800 2000 and 3100 3300 cm⁻¹ regions
- Validation of a previous χ factor model

The H₂O - CO₂ continuum around 3.1, 5.2 and 8.0 $_{2}$ µm: New measurements and validation of a previously $_{3}$ proposed χ factor

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12 Abstract

The $H_2O - CO_2$ continuum has been measured, at room temperature, at 13 discrete spectral points in the 1100 - 1500, 1800 - 2000, and 3100 - 3300 cm⁻¹ intervals. Our results are in good agreement with previous experimental 15 values in the low frequency wing of the ν_2 band of H₂O when the associated 16 uncertainties are taken into account. Furthermore, they confirm the quality, 17 in this region, of a χ factor previously adjusted on measurements in the 100 18 -1500 cm^{-1} range, and prove its validity in the blue side of the ν_2 band as 19 well as in the region around 3.1 µm, which have been experimentally studied 20 for the first time in this work. Together with recent measurements in the 1.6 21 μ m, 2.3 μ m and far infrared regions, our results contribute to the progressive 22 building-up of a data set for the modeling of the absorption by $CO_2 + H_2O$ 23 mixtures throughout the infrared, which is needed for studies of CO_2 -rich 24 planetary atmospheres. 25

²⁶ Keywords: $CO_2 - H_2O$ continuum, measurements, χ -factor model,

²⁷ CO₂-rich atmospheres

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28 1. Introduction

The accurate knowledge and modeling of spectra of $H_2O + CO_2$ mixtures for various temperature and pressure conditions is required for planetary science. In particular, the effect of CO_2 on the water vapor greenhouse effect must be known to model the atmospheres of Venus and Early Mars and it will likely be soon needed for some exoplanets [see, e.g. (Lebonnois et al., 2015; Turbet et al., 2021; Turbet et al., 2020; Pluriel et al., 2019)].

The absorption by gas samples containing water vapor is generally split into 35 several contributions, which, in the present case of $H_2O + CO_2$ mixtures, 36 are those of the local lines of the H_2O and CO_2 monomers, and those 37 of the so-called continua associated with intermolecular interactions within 38 $H_2O - H_2O$, $CO_2 - CO_2$ and $H_2O - CO_2$ pairs. This separation, which was 39 introduced many years ago [see, e.g. (Burch, 1982; Burch and Alt, 1984)] 40 and kept since then (Mlawer et al., 2012), has a practical interest since the 41 continua are proportional to the product of the densities of the molecules 42 involved (provided that the local transitions contributions are computed up 43 to a distant to the line centers significantly larger than the pressure broadened 44 widths). Recall that the continua potentially include contributions of the 45 far wings of the pressure-broadened absorption lines of the monomers, of 46 collision-induced absorption, and of bound and quasi-bound bi-molecular 47 complexes. 48

In a pioneer study carried three decades ago, a quasistatic theoretical 49 approach was developed (Ma and Tipping, 1992; Pollack et al., 1993) for 50 the prediction of the $H_2O - CO_2$ continuum due to the far wings of the 51 CO_2 -broadened lines of H_2O . In the absence of any experimental results, 52 the associated calculated spectra and line-shape correction-factor $\chi_{\rm H_2O-CO_2}$ 53 provided the very first data throughout the infrared. Twenty five years 54 later came the first measurements of the $H_2O - CO_2$ continuum, which 55 investigated the $1100-1300 \text{ cm}^{-1}$ region (Baranov, 2016). Then, Tran et 56 (2019) produced new data from 100 to 1500 $\rm cm^{-1}$, which confirmed al. 57 the results of Baranov (2016) and extended the investigated spectral range. 58 Note that this latter study also provided a line-shape factor $\chi_{\rm H_2O-CO_2}$ for 59 CO_2 -broadened H_2O transitions, obtained by adjusting the measured values 60 between 100 and 1500 $\rm cm^{-1}$, with which the calculated continuum agrees 61 well with the experiments. For the H_2O -broadened wings of CO_2 lines, 62 the situation is somehow similar, with first results and data obtained only 63 recently. These include measurements in the high frequency wing of the CO_2 64

 ν_3 band (Baranov, 2016; Tran et al., 2018) from which a $\chi_{CO_2-H_2O}$ absorption 65 factor was deduced (Tran et al., 2018), and direct predictions using molecular 66 dynamics simulations (Hartmann et al., 2018a). Finally, recall that another 67 process participating to the continua is collision-induced absorption (CIA) 68 (Frommhold, 1993). In the particular case of $H_2O + CO_2$ mixtures such a 69 contribution was pointed out recently by a cavity ring down spectroscopy 70 study (Fleurbaey et al., 2022a). This investigation, which provided values of 71 the continuum of $H_2O + CO_2$ mixtures at some points around 1.60, 2.3 and 72 3.5 μ m, also evidenced the presence of a CIA peak around 6000 cm⁻¹. The 73 latter was soon after attributed (Fleurbaey et al., 2022b) to the simultaneous 74 transitions involving the ν_3 -band dipole of CO₂ and the ν_1 -band polarizability 75 of H_2O . 76

In the present work, we continue the efforts made to build up a H₂O + CO₂ continuum throughout the infrared by measuring the absorption, at room temperature, on both sides of the ν_2 band as well as around 3.1 µm. The experimental procedure is presented in Section 2 and the data analysis is described in Section 3. Finally, the results are shown in Section 4 and compared to previous experiments and predictions based on the line-shape factor $\chi_{\rm H_2O-CO_2}$ proposed in Tran et al. (2019).

84 2. Measurements

The spectra were measured using the facilities at the AILES beam line 85 of the SOLEIL synchrotron, previously used for similar experiments (Tran 86 et al., 2019; Fakhardji et al., 2022). A high resolution Fourier transform 87 spectrometer (FTS, Bruker IFS 125 HR) was used, equipped with a globar 88 source and a KBr beam splitter. The light exiting the FTS passed through 89 a 2.5 m long multi-pass cell with diamond windows, set for an optical path 90 of 101.3 m. The transmitted intensity was then measured with a liquid 91 nitrogen-cooled HgCdTe detector. For each spectrum, whose usable part lies 92 between about 700 and 4600 $\rm cm^{-1}$, an average of 1000 scans was made with 93 an unapodized resolution of 0.5 cm^{-1} . In the measurements of the absorption 94 by $H_2O + CO_2$ mixtures, all carried at 295 K, the cell was first filled with 95 purified water vapor at a pressure of ~ 15 mb (measured using a 0-1000 96 mb Pfeiffer model CMR361 capacitive gauge which has a stated accuracy 97 of 0.2%). Then CO₂ was introduced step by step, progressively increasing 98 the total pressure from ~ 500 mb to ~ 1000 mb (measured using the same 99 capacitive gauge) and a spectrum was recorded after each step (awaiting 100

about 10 to 15 min each time to allow the gas mixture to reach equilibrium). 101 In addition to this "ascendant" procedure, we also recorded spectra using a 102 "descendant" procedure, i.e. starting from the highest pressure of ~ 1000 mb 103 and progressively reducing it down to ~ 500 mb. Note that these two ways of 104 collecting data are not equivalent since the mole fractions of H_2O (~ 1.5%) 105 and CO_2 (~ 98.5 %) are kept constant in the descendant procedure while they 106 vary in the ascendant one (the proportion of water vapor then decreasing from 107 $\sim 3\%$ down to $\sim 1.5\%$). In order to obtain the 100% transmittance levels, 108 reference spectra were also recorded with the cell filled with pure argon at \sim 109 1 bar, before and after each of the series with $H_2O + CO_2$ mixtures described 110 above. 111

112 3. Data analysis

In a first step, the transmission associated with each $H_2O + CO_2$ sample was obtained by dividing the corresponding recording by the reference spectrum (recorded with argon). Then, various contributions to the absorption needed to be removed in order to obtain the targeted continuum due to the CO₂-broadened far wings of the H₂O lines. Indeed, for a CO₂+H₂O mixture at temperature T with densities d_{CO_2} and d_{H_2O} , the total absorption coefficient α_{tot} at wavenumber σ can be written as:

$$\alpha_{tot}(\sigma, d_{CO_2}, d_{H_2O}, T) = \alpha_{loc}^{CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T) + \alpha_{loc}^{H_2O}(\sigma, d_{CO_2}, d_{H_2O}, T) + \alpha_{CA}^{CO_2 - CO_2}(\sigma, d_{CO_2}, T) + \alpha_{CA}^{H_2O - H_2O}(\sigma, d_{H_2O}, T) + \alpha_{CA}^{H_2O - CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T)$$

$$(1)$$

where $\alpha_{loc}^{CO_2}$ and $\alpha_{loc}^{H_2O}$ are the contributions of local lines of the two molecules, computed including all transitions within a given interval (see below) around the current wavenumber. The coefficient $\alpha_{CA}^{CO_2-CO_2}$ and $\alpha_{CA}^{H_2O-H_2O}$ denote the continuum absorptions by pure CO₂ and H₂O respectively. Finally $\alpha_{CA}^{H_2O-CO_2}$ is the continuum absorption due to interacting H₂O + CO₂ pairs. In order to deduce $\alpha_{CA}^{H_2O-CO_2}$ we have computed all the other contributions as described below.

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¹²⁸ 1 – Computation of the local lines absorption $(\alpha_{loc}^{CO_2}, \alpha_{loc}^{H_2O})$ – The ¹²⁹ calculation of the associated absorption coefficients was carried using Voigt ¹³⁰ profiles [truncated ± 5 cm⁻¹ for CO₂, for consistency with Perrin and

Hartmann (1989) and $\pm 25 \text{ cm}^{-1}$ for H₂O, for consistency with Mlawer et 131 (2012) and Clough et al. (1989), away from their centers] with line al. 132 positions and intensities taken from the HITRAN database (Gordon et al., 133 2022). Since the latter provides only self- and air-broadening coefficients, 134 the needed values of the broadenings of H_2O lines by CO_2 were taken from 135 Brown et al. (2007), while we used the data of Sung et al. (2009) for the H_2O 136 broadenings of CO_2 transitions, as done in Tran et al. (2019). The pressure 137 shifts of the CO_2 lines induced by collisions with H_2O and those of H_2O lines 138 by CO_2 being not available, they are considered to be the same as the ones 139 with air. The impact of this approximation is expected to be negligible given 140 the small value of the line shift in comparison to the spectral resolution of 141 the recorded spectra. The partial pressure of H_2O for each recording was 142 also determined by fitting some absorption lines. The obtained results are 143 consistent (with a difference around only $\sim 2\%$) with the values deduced 144 from the H_2O mole fraction and the total pressure of the mixture (both a 145 priori known through the pressure readings during the making of the mixture 146 and the successive recordings). 147

2 – Computation of the pure CO_2 continuum $(\alpha_{CA}^{CO_2-CO_2}) - \alpha_{CA}^{CO_2-CO_2}$ was 148 computed taking into account two contributions. The first, due to the wings 149 of CO_2 lines broadened by collisions with CO_2 , was computed using the 150 $\chi_{\rm CO_2-CO_2}$ factor from Perrin and Hartmann (1989). Note that this model was 151 preferred to a line-mixing model because it leads to much better agreement 152 with the measurements in the line-wings (Tran et al., 2011). The second, 153 due to two collision-induced absorption bands around 1350 cm^{-1} (Baranov 154 and Vigasin, 1999) was taken from Karman et al. (2019). 155

¹⁵⁶ $3 - Computation of the pure H_2O continuum - Finally, the contribution$ $¹⁵⁷ of the H_2O self-continuum was computed using the version v3.2 (available$ $¹⁵⁸ at http://rtweb.aer.com/continuum_frame.html) of the MT_CKD model$ ¹⁵⁹ (Mlawer et al., 2012).

Note that, since data are available for its computation, the contribution of the H₂O-broadened wings of CO₂ lines were computed using the $\chi_{CO_2-H_2O}$ from Tran et al. (2018), and removed from $\alpha_{CA}^{H_2O-CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T)$. Note that it makes a practically negligible contribution in the investigated spectral regions.

Once all these contributions have been calculated, the associated spectral transmission $\tau_{Calc}(\sigma)$ is predicted and convolved by the FTS instrument function $F_{inst}(\sigma)$. The targetted continuum due to the far wings of the CO₂-broadened H₂O monomer lines was then obtained from the measured transmission $\tau_{Meas}(\sigma)$ by using:

$$\alpha_{CA}^{H_2O-CO_2}(\sigma) = -ln \left[\tau_{Meas}(\sigma) / (\tau_{Calc}(\sigma) * F_{inst}(\sigma)) \right] / L$$
(2)

where L is the optical path in cm and * denotes a convolution. Note that for consistency with the usual definition of the H₂O continua (Mlawer et al. 2012; Clough et al., 1989), the values of $\alpha_{CA}^{H_2O-CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T)$ provided by this procedure are corrected by adding the "pedestal" (since it was not substracted from $\alpha_{loc}^{H_2O}$) defined by:

$$P(\sigma, d_{CO_2}, d_{H_2O}, T) = \frac{d_{CO_2} d_{H_2O}}{\pi} \sum_{l \text{ if } |\sigma - \sigma_l| < 25} \frac{S_l(T)\gamma_l(T)}{(25)^2}$$
(3)

where the sum extends over all H₂O lines centered within $\pm 25 \text{ cm}^{-1}$ around the current wavenumber. $S_l(T)$ is the the integrated intensity of line *l* in cm⁻²/amagat, and $\gamma_l(T)$ (in cm⁻¹.amagat⁻¹) is the CO₂-broadening coefficient of the line. Note that the amagat density unit is used here as in previous studies, 1 amagat corresponding to $2.687 \times 10^{19} \text{ molec/cm}^3$.

Using the above described procedure, the $\alpha_{CA}^{H_2O-CO_2}$ continuum can 180 potentially be retrieved for each wavenumber where the absorption by H_2O 181 is measurable under our experimental conditions. However, the values 182 obtained are very uncertain when the computed absorption that has been 183 removed represents a very large part of the total absorption. Hence, as 184 done in Tran et al. (2019), we selected only the spectral points located 185 in troughs between lines and sufficiently distant from the latter. In order 186 to determine the density-normalized $CA^{H_2O-CO_2}(\sigma,T)$ continuum from the 187 values of $\alpha_{CA}^{H_2O-CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T)$, we used the fact that, for binary 188 collisions (an assumption valid at the pressures of our measurements), they 189 are related through: 190

$$\alpha_{CA}^{H_2O-CO_2}(\sigma, d_{CO_2}, d_{H_2O}, T) = d_{CO_2} d_{H_2O} C A^{H_2O-CO_2}(\sigma, T)$$
(4)

We thus performed a linear fit of $\alpha_{CA}^{H_2O-CO_2}$ versus the product of the densities 191 $d_{CO_2}d_{H_2O}$ for each retained spectral point. Some examples of this exercise 192 are displayed in Fig. 1, which shows that our measured values do quite well 193 follow the proportionality law of Eq. (4). Note that, in order to obtain 194 these results, the level of the reference spectrum (corresponding to the 100%195 transmittance recorded with the cell filled with argon) was also adjusted by 196 multiplying it by a linear function of wavenumber assumed independent of 197 the pressure. 198



Figure 1: Examples of linear fits (dashed lines) of the measurements (represented with filled and empty dots respectively for increasing and decreasing pressure ramps) for fixed values of the wavenumber. The value of the H₂O - CO₂ continuum $CA^{\rm H_2O-CO_2}(\sigma)$ is directly given by the slope of the line.

199 4. Results and discussion

Figure 2 displays a comparison of our experimental values (provided in 200 the supplementary material) for the $H_2O - CO_2$ continuum with the other 201 measurements available in the considered spectral region (Baranov, 2016; 202 Tran et al., 2019). The uncertainties on our determinations, shown by the 203 error bars in Fig. 2, were obtained taking into account three major sources 204 of error. The first one comes from the dispersion of the measurements and 205 it was obtained from the 1σ statistical error in the linear fits exemplified 206 in Fig. 1. In addition, the calculations of the other contributions to the 207 absorption (presented in Sec. 3) that have been removed propagate errors 208

due to uncertainties on the spectroscopic parameters used (in particular 209 for the contribution of the H_2O local lines). This additional source of 210 errors was computed using the uncertainties on the H_2O line intensities 211 and air-broadening coefficients provided, for each line, by the HITRAN 212 database (Gordon et al., 2022) [we thus assumed the same values for the 213 CO_2 -broadening coefficients of Brown et al. (2007)]. Even though they 214 are not expected to play a major role, the uncertainties on the intensities 215 and self-broadening coefficient for CO_2 are also taken in account. For both 216 H_2O and CO_2 lines, we disregarded the uncertainties on their positions since 217 the associated uncertainties are negligible. The third source of error is the 218 uncertainty on the self H_2O continuum that we estimated by comparing the 219 MT CKD model with the measurements made by Ptashnik et al., (2019). 220 The difference observed was on average about ~ 10 % and we then supposed 221 this level for the uncertainties and added them to the error bars. Note 222 that the first and the two other sources of error mentioned above behave 223 differently according to the spectral region of interest. Indeed, the dispersion 224 of the measurements becomes less important as the absorption increases, 225 and the associated statistical error decreases. In contrast, the uncertainties 226 on the spectral parameters and those on the self H_2O continuum naturally 227 play a larger role near the center of the ν_2 band, while their impact is less 228 pronounced in the far wings regions. Hence the first source of error dominates 229 in the weak absorption regions, while the uncertainty associated with the 230 calculation of the removed absorption is predominant near the band center. 231 Finally, in our results we have selected only the values of the continuum 232 which are larger than their associated uncertainty. 233

The first thing to be noticed is that, between 1100 and 1200 $\rm cm^{-1}$, our 234 continuum values are on average larger than the previous measurements 235 (Baranov, 2016; Tran et al., 2019) (although all are compatible when 236 uncertainties are taken into account) while at higher frequencies in the 237 red wing of the ν_2 band the agreement is better. The center of the ν_2 238 absorption band being saturated it is not possible to extract information on 239 the continuum but, in the $1800 - 2000 \text{ cm}^{-1}$ range we were able to determine 240 it, providing the first determination of the $H_2O - CO_2$ continuum, which is 241 also the case for the $3100-3300 \text{ cm}^{-1}$ interval. 242

As is well known, the self and foreign H_2O continua include four contributions, all proportional to the product of densities of the species involved: (i) What is left of the wings of the pressure-broadened monomer lines after the removal of the contribution of the transitions within ± 25

 cm^{-1} . (ii) The absorption due to the interaction-induced dipole within free 247 colliding pairs (see e.g. Fleurbaey et al., 2022a,b). The participation of 248 (iii) bound and (iv) meta-stable or quasi-bound dimers. In the case of the 249 water vapor continua the related importance of these four contributions has 250 been a controversial and still open issue for decades (see e.g. Hartmann et 251 al., 2018b and references therein), whose discussion is largely beyond the 252 scope of the present study. However, an empirical approach was proposed 253 by Tran et al. (2019) to compute the $H_2O - CO_2$ continuum. The authors 254 rightly or wrongly assumed that the continuum in the 100-1500 $\rm cm^{-1}$ region, 255 is entirely due to the far wings of the monomer lines. They consequently 256 adjusted a $\chi_{CO_2-H_2O}$ correction factor on the experimental data as was done 257 many years ago for the self- and air-broadened H_2O continua (Clough et 258 al, 1989). In the absence of any other theoretical approach for comparison 259 with our measurements, we used this model, with results displayed in Fig. 260 2. As can be seen, the agreement between calculations and experiments in 261 the newly studied regions is quite good, which demonstrates the predictive 262 capabilities of the χ factor approach. However, note that concluding from 263 this that the continuum in whole studied regions is only due to the monomer 264 far wings would be highly hazardous. 265

Finally, the top panel in Fig. 2 enables to compare the H_2O-CO_2 continuum 266 with those, taken from Mlawer et al. (2012), for pure H_2O and H_2O -air. As 267 can be seen the values for H_2O-CO_2 are slightly larger than those for H_2O -air 268 and significantly smaller than those for $H_2O - H_2O$ (Brown et al., 2007). This 269 is consistent with the quasi static predictions of Ma and Tipping (1992) and 270 with the fact that the broadening coefficients of H_2O lines by CO_2 (Brown et 271 al., 2007) are slightly larger than those by air and significantly smaller than 272 those for pure H_2O (Gordon et al., 2022). 273

274 5. Conclusion

We measured the H_2O-CO_2 continuum on both sides of the ν_2 absorption 275 band, as well as around $3.1 \,\mu\text{m}$. The data obtained in the spectral range 1100 276 -1400 cm^{-1} are consistent with previous measurements (Baranov, 2016; Tran 277 et al., 2019) when their respective uncertainties are taken into account. For 278 the first time, the continuum has been measured on the high frequency side 279 of the ν_2 band from 1800 cm⁻¹ to 2000 cm⁻¹ as well as between 3100 and 280 3300 cm^{-1} . In addition to providing new measured data, this study also 281 enabled a successful further test of the $\chi_{H_2O-CO_2}$ factor model proposed in 282



Figure 2: H_2O-CO_2 continuum – The data measured in this study are shown with red dots and are compared to the results of previous experiments (Baranov, 2016; Tran et al., 2019) respectively displayed in blue and green. The black line represents the values predicted using the $\chi_{H_2O-CO_2}$ factor model developed by Tran et al. (2019). For comparison, we also show the self- and air-broadened H₂O far line wings continuum [computed using the latest version available at http://rtweb.aer.com/continuum_frame.html of the MT_CKD model (Mlawer et al., 2012)] with dashed and dashdoted lines, respectively. The top panel (a) displays the results in log scale while the two bottom plots (b) and (c) show respectively the 1100–1300 cm⁻¹ and 3100–3300 cm⁻¹ regions in linear scale.

Tran et al. (2019). This demonstration of the predictive capabilities of a line-shape correction-factor fitted to experimental results below 1500 cm⁻¹ is of considerable interest, particularly for spectral regions where measurements have not yet been made. However recall that our experimental data have been collected at room temperature only, which stresses the crucial need of investigations at various temperatures.

It is worth mentioning that our knowledge of the continua associated with 289 $H_2O - CO_2$ pairs has significantly increased in the last four years, and 290 that much progress has been made after the first computations of Ma et 291 al. (1992) and measurements of Baranov (2016). Many new experimental 292 data have been provided which confirmed the latter data and considerably 293 extended the spectral range in which values of the continuum are available. 294 In addition, the original $\chi_{H_2O-CO_2}$ factor of Ma et al. (1992) has been 295 significantly improved (Tran et al., 2019). This provides a computational 296 approach with which a satisfactory agreement with measurements is obtained 297 at almost all experimentally investigated wavelengths, provided that it 298 is complemented, around 6000 cm^{-1} , by a description (Fleurbaey et al., 299 2022b) of the collision-induced simultaneous transitions. However, much 300 still remains to be done: First, new measurements are needed to test the 301 model in so far unstudied regions, e.g. $2200 - 3000 \text{ cm}^{-1}$, while experiments 302 of improved precision are desirable around 3.1 µm. Last but not least, the 303 temperature dependence, for which the only information available comes from 304 the early theoretical study of Pollack et al. (1993) must be investigated 305 experimentally. 306

307 Declaration of Competing Interest

³⁰⁸ The authors declare no conflicts of interest

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³¹⁴ Supplementary material

The measured data of the $H_2O - CO_2$ continuum presented in this work are available in the supplementary material

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