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# High sensitivity CRDS of CO<sub>2</sub> in the 1.18 μm transparency window. Validation tests of current spectroscopic databases

E.V.Karlovets<sup>1,2</sup>, S. Kassi<sup>2</sup>, A. Campargue<sup>2\*</sup>

<sup>1</sup>*Tomsk State University, Laboratory of Quantum Mechanics of Molecules and Radiative Processes, 36, Lenin Avenue, 634050, Tomsk, Russia*

<sup>2</sup>*Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

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\* Corresponding author: [alain.campargue@univ-grenoble-alpes.fr](mailto:alain.campargue@univ-grenoble-alpes.fr)

## Abstract

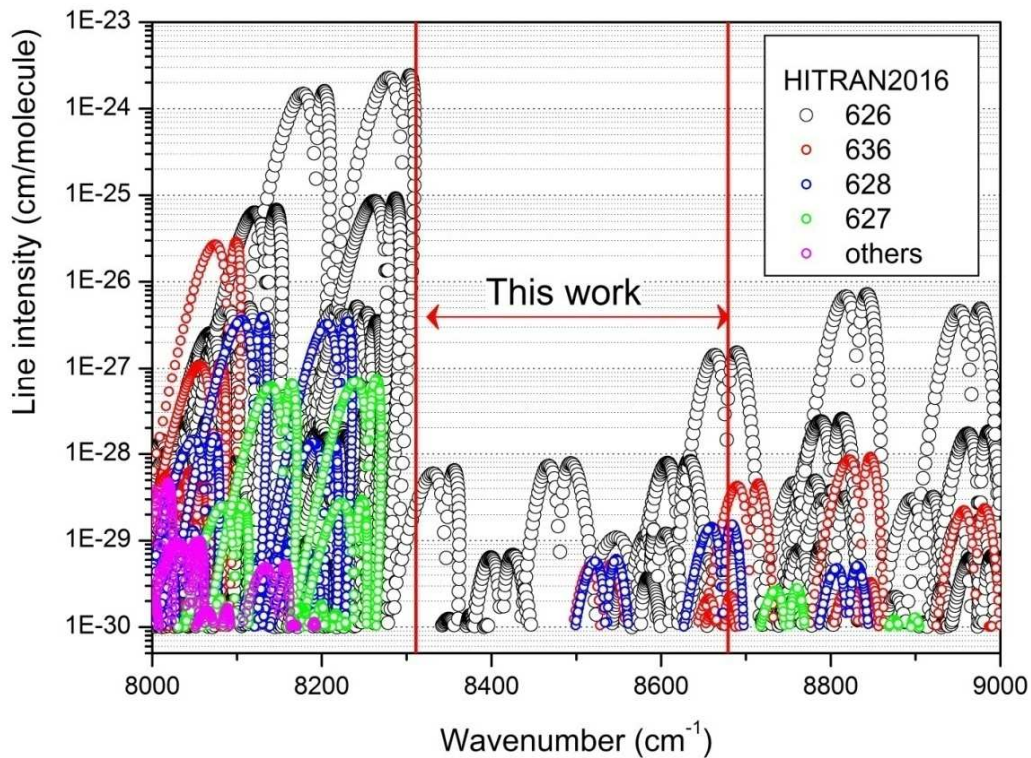
The very weak absorption spectrum of natural CO<sub>2</sub> is studied at high sensitivity near 1.18μm. The investigated region corresponds to a transparency window of particular interest for Venus. Low pressure (10 Torr) spectra are recorded with unprecedented sensitivity in the 8311-8679 cm<sup>-1</sup> interval. A noise equivalent absorption,  $\alpha_{min}$ , on the order of 5×10<sup>-12</sup> cm<sup>-1</sup> is achieved using a cavity ring down spectrometer (CRDS) coupled with a self-referenced frequency comb. 669 lines are accurately measured and rovibrationally assigned to 15 bands of the three first carbon dioxide isotopologues, <sup>12</sup>C<sup>16</sup>O<sub>2</sub>, <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O. For all but one band, line intensities are smaller than 10<sup>-28</sup> cm/molecule at 296 K and the weakest lines have intensity as low as 5×10<sup>-31</sup> cm/molecule. In the large 8310- 8645 cm<sup>-1</sup> interval where no CO<sub>2</sub> absorption lines were previously detected, about 500 lines are measured. In spite of the weakness of the considered transitions, line centers could be accurately determined and spectroscopic parameters are determined from standard band-by-band fit of the line positions (typical *rms* deviations are 5×10<sup>-4</sup> cm<sup>-1</sup>).

These newly observed bands provide critical validation tests for the most recent spectroscopic databases of carbon dioxide. The comparison to the recent updated version of the Carbon Dioxide Spectroscopic Databank (CDSD2019), to the current HITRAN2016 database and *ab initio* line lists is presented. The CDSD and HITRAN positions deviate from the measurements by less than 0.01 cm<sup>-1</sup>. Measured line intensities show an overall good agreement in particular with *ab initio* values but reveal that a few bands have inaccurate intensities in HITRAN2016 and CDSD2019. Three very weak bands are missing in CDSD2019. The reported experimental information will help to improve the quality of the CO<sub>2</sub> spectroscopic databases in the region.

## I. Introduction

In recent years, we have performed systematic investigations of the near infrared absorption spectrum of carbon dioxide by high sensitivity cavity ring down spectroscopy (CRDS) in the 5850–8370  $\text{cm}^{-1}$  region [1-20]. The spectra were recorded not only with natural carbon dioxide [1-10] but also with  $^{13}\text{C}$  [11-15],  $^{18}\text{O}$  [16-18] and  $^{17}\text{O}$  [19,20] enriched samples. The unprecedented sensitivity of the recordings provided a considerable amount of new information which was used to improve the spectroscopic databases in the region, in particular the Carbon Dioxide Spectroscopic Databank (CDSD2019) [21].

Transparency windows of carbon dioxide corresponding to spectral regions of very low absorption are of particular importance to study the atmosphere of Venus. For instance, the 1.10 and 1.18  $\mu\text{m}$  windows are used to sound the deep atmosphere and the surface [22-24]. High sensitivity laboratory studies are thus suitable for a detailed characterization of the residual absorption in these windows. Indeed, in absence of measurements, the current spectroscopic databases provide extrapolated line parameters which should be validated. For instance, our recent CRDS studies in the 1.74  $\mu\text{m}$  window [1,12,18] revealed inconsistencies in the construction of the HITRAN2016 database [25] due to the mixing, within a same vibrational band, of *ab initio* and CDSD intensity values.



**Fig. 1**

The HITRAN2016 list [25] of natural carbon dioxide in the region of the 1.18  $\mu\text{m}$  window (8000-9000  $\text{cm}^{-1}$ ). The central zone (8311-8679  $\text{cm}^{-1}$ ) corresponds to the present CRDS recordings. The region below 8370  $\text{cm}^{-1}$  was previously studied by CRDS [2].

The HITRAN2016 line list between 8000 and 9000  $\text{cm}^{-1}$  is presented in **Fig. 1**. The 1.18  $\mu\text{m}$  window is located just above the band head of the strong 10031-00001 band near 8310  $\text{cm}^{-1}$ . The strongest lines of the 10031-00001 band have intensity on the order of  $3 \times 10^{-24}$   $\text{cm}/\text{molecule}$  while all the transitions located between 8310 and 8635  $\text{cm}^{-1}$  are weaker by more than four orders of magnitude (less than  $10^{-28}$   $\text{cm}/\text{molecule}$ ). A few lines of the 20031-10002 band centered near 8346  $\text{cm}^{-1}$  were detected in a previous CRDS study covering the 7909-8370  $\text{cm}^{-1}$  region [2] and the 50015-00001 band centered near 8677  $\text{cm}^{-1}$  was detected in Venus spectra [26] but no  $\text{CO}_2$  absorption lines were previously detected in the large 8310- 8645  $\text{cm}^{-1}$  interval, neither in the laboratory nor in Venus spectra. In the present work, about 500  $\text{CO}_2$  lines with intensity values down to  $5 \times 10^{-31}$   $\text{cm}/\text{molecule}$  are measured in this interval.

The present study is thus an extension to higher energy of our previous CRDS studies by using a newly acquired fiber-coupled External Cavity Diode Laser (ECDL) as light source. The sensitivity of the set-up made possible to use low pressure values (10 Torr) while the coupling of the CRDS spectrometer to a self-referenced frequency comb provided an important gain on the accuracy of the line center determination. The experimental set-up and spectra acquisition are presented below, in Part 2, together with the line list construction. The rovibrational assignments were performed using available spectroscopic databases. In Part 3, the measured positions are used to derive the spectroscopic constants of the upper levels and we present the position and intensity comparisons to the recently updated version of the Carbon Dioxide Spectroscopic Databank (CDSD2019) [21], to the current 2016 version of the HITRAN database [25] and to the *ab initio* lists computed at NASA Ames [27,28].

## 2. Experimental set-up and line list construction

The present CRDS recordings benefit from the coupling of the CRD spectrometer to a self-referenced frequency comb that provides an accurate frequency value for each ring down event. The "on the fly" measurement of the laser optical frequency values, first implemented in Refs. [29-33], allows for a gain in accuracy of about one order of magnitude and thus a better line profile description. In addition, compared to our previous CRDS studies below 7920  $\text{cm}^{-1}$  [1,3-13], the use of an external cavity diode laser (ECDL) instead of distributed feedback laser diodes provides a more efficient light injection into the CRDS cell and thus a better detectivity [2].

A major difficulty of the experiment was to minimize the amount of water present in the CRDS cell. Numerous strong absorption lines with intensity larger than  $10^{-23}$   $\text{cm}/\text{molecule}$  are located throughout the entire spectral interval while the  $\text{CO}_2$  lines of interest are typically six orders of magnitude weaker. Consequently, the spectra were recorded in flow regime. The flow of  $\text{CO}_2$  (AlphaGaz2 from Air Liquide, impurities < 0.1 ppm) was roughly adjusted to 5 sccm with a downstream

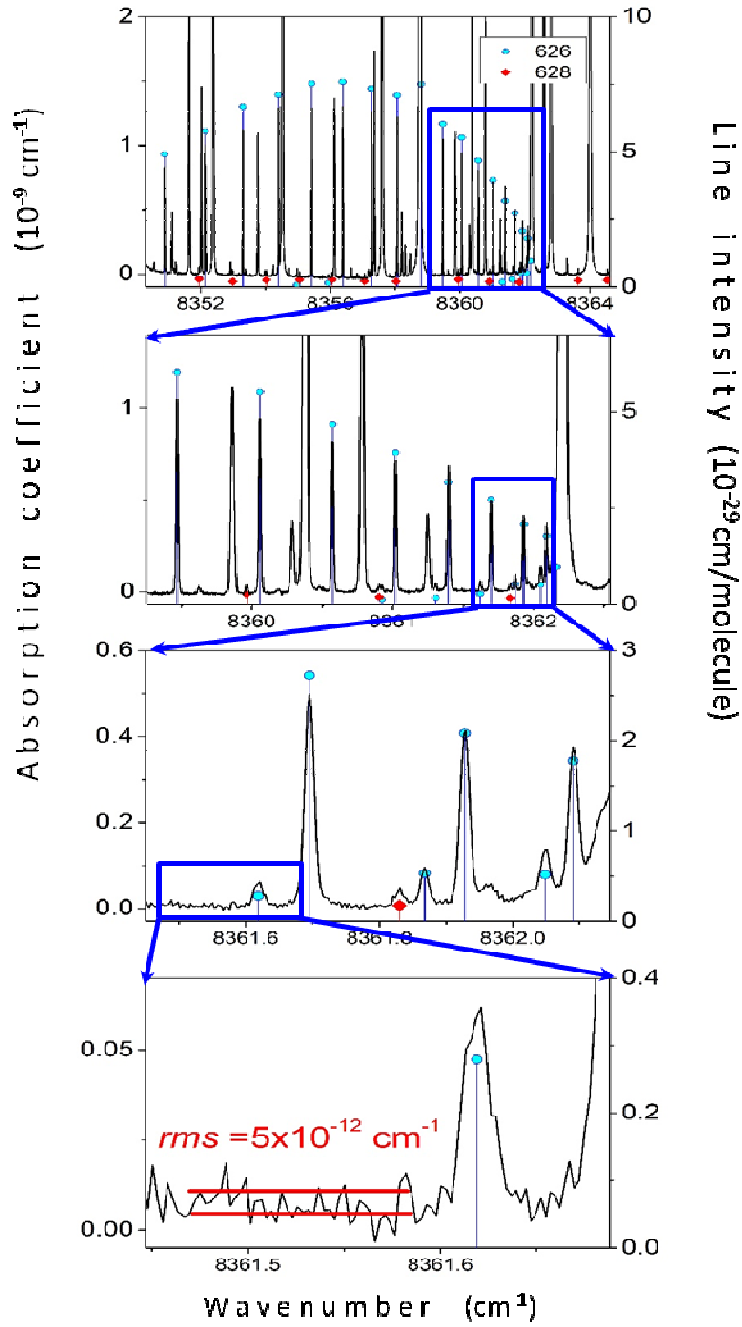
manual needle valve and the pressure was actively regulated at 10.00 Torr using capacitance gauge (MKS Baratron, 10 Torr range, 0.15% accuracy of the reading) recording the total pressure. The temperature of the outer wall of the stainless steel gas cell was monitored with a PT 1000 resistive probe (class Y,  $\pm 0.15$  K accuracy at room temperature) and an analog temperature sensor (TSic 501, IST-AG,  $\pm 0.1$  K accuracy) both fixed on the cell surface.

The reader is referred to Ref. [33,34] for a detailed description of the cavity ring down spectrometer. Briefly, the ECDL light is first sent into a polarization maintained fiber coupler which directs about 10% of the emitted light for the frequency measurement and the remaining 90% into a fibered acousto-optic modulator (AOM) inserted before the 1.4-meter-long high-finesse cavity ( $F \approx 130,000$ ). The AOM interrupts the excitation, leading to a ring down (RD) event measured with an InGaAs photodiode. The determination of the absolute ECDL emission frequency relies on the frequency of the beat note (BN) between the tooth,  $n$ , of the self-referenced frequency comb and the ECDL, the number  $n$  being deduced from the ECDL emission frequency measured by a Fizeau wavemeter (High Finesse WS-U-30 IR). The beat note frequency, updated 1000 times per second, was used to actively lock the ECDL emission frequency, ensuring the ECDL frequency to be stable to 300 kHz *rms*, corresponding to the uncertainty on the absolute ECDL frequency.

The frequency tuning of the ECDL (from Toptica) was achieved by acting on its internal grating angular position and the laser chip current (see Ref. [33] for details). The grating angular position was roughly set with an external step motor and finely adjusted with an internal piezo electric element (PZT). The ECDL has a mode-hop-free tuning range of  $1.3 \text{ cm}^{-1}$  obtained with a linear scan of the PZT voltage. Broadband spectra were therefore obtained by concatenation of series of  $1.1 \text{ cm}^{-1}$  wide partly overlapping individual spectra ( $\sim 40$  MHz step by step sampling and  $\sim 20$  minutes duration). Each spectrum was obtained following a repetitive step/lock/measure/release sequence. After each ECDL step, the frequency lock was engaged according an actualized BN frequency until 40 RDs ( $\sim 80$  Hz repetition rate) were acquired, averaged then recorded together with the BN frequency, raw wavelength, cell pressure, cell temperature and ECDL scan parameters. The ECDL lock was then released, allowing the ECDL to be freely tuned for the new sequence.

In all the recordings, the sampling step was chosen to be about  $1.3 \times 10^{-3} \text{ cm}^{-1}$  to be compared to a Doppler line width of about  $7 \times 10^{-3} \text{ cm}^{-1}$  (HWHM). **Fig. 2** illustrates the sensitivity and high dynamical range on the intensity scale and the importance of the residual water lines. The noise equivalent absorption evaluated as the *rms* of the baseline fluctuations is around  $5 \times 10^{-12} \text{ cm}^{-1}$ . In spite of our efforts to reduce the water concentration, the spectrum is dominated by a number of strong water vapor interfering lines. The relative concentration of water vapor in the CRDS cell retrieved from the observed lines is on the order of 0.1 %. Assigned  $^{12}\text{C}^{16}\text{O}_2$  (626) and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  (628)

lines are indicated in **Fig. 2**. Note that the  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  lines belonging to the 30023-00001 band (discussed hereafter) have intensity on the order of  $2 \times 10^{-30}$  cm/molecule.



**Fig. 2.**

CRDS spectrum of carbon dioxide in the region of the *R* branch of the 20031-10002 hot band centered at  $8345.932 \text{ cm}^{-1}$  recorded at a pressure of 10.0 Torr. The enlargements illustrate the dynamics achieved on the intensity scale and the noise equivalent absorption ( $\alpha_{\min} \approx 5 \times 10^{-12} \text{ cm}^{-1}$ ). The stick spectrum shows the  $^{12}\text{C}^{16}\text{O}_2$  (626) and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  (628) lines assigned in the region (blue and red symbols, respectively). The  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  lines belong to the 30023-00001 band missing in CDSD2019 and HITRAN2016. The spectrum shows a number of strong interfering lines due to water vapor present in the CRDS cell with a relative concentration on the order of 0.1 %.

The line centers and intensities were determined using a homemade interactive least squares multi-line fitting program. Considering the important contribution of water vapor and the frequent line overlapping with CO<sub>2</sub> lines of interest, we first performed an HITRAN simulation for a mixture of carbon dioxide and water vapor with water line intensities pondered by an abundance factor of  $1.5 \times 10^{-3}$ . As a result of the quality of the HITRAN lists of CO<sub>2</sub> and H<sub>2</sub>O in the region, the obtained simulation provided a good starting point for the fit and an immediate identification of the majority of the lines observed in the CRDS spectrum. The line identification was used to fix the Gaussian width to the Doppler width calculated with the correct isotopologue mass. For the few lines which could not be identified using the HITRAN list, the  $^{12}\text{C}^{16}\text{O}_2$  mass was used by default.

CO<sub>2</sub> lines being weak, a Voigt profile (VP) was found sufficient to reproduce the observed line shape of CO<sub>2</sub>. The ECDL line width ( $\sim 100$  kHz HWHM) is much smaller than the Doppler width ( $\sim 7 \times 10^{-3} \text{ cm}^{-1}$  HWHM) leading to a line profile mostly Doppler limited in the adopted pressure conditions (the pressure broadening at 10 Torr is about  $10^{-3} \text{ cm}^{-1}$ ). Nevertheless, the small Lorentzian width could be generally adjusted. Otherwise, it was constrained to the pressure broadened width calculated using the HITRAN self-broadening coefficient [25]. The multi-line fit provides the line center, line intensity, Lorentzian width and the corresponding local baseline (assumed to be a linear function of the wavenumber).

For a large fraction ( $\approx 40\%$ ) of the water lines, the VP fit residuals were found to exhibit the typical W signature due to collisional narrowing effects (see for instance Ref. [35]). The VP residuals of water lines were drastically reduced using a Nelkin-Ghatak Voigt profile which accounts for Dicke narrowing effects.

As result a global list of 2771 lines was obtained for the  $8311\text{--}8679 \text{ cm}^{-1}$  region. More than 2000 lines are due to water vapor. On the basis of the HITRAN list and of additional considerations presented below, 669 lines were assigned as CO<sub>2</sub> transitions leaving about 80 lines unassigned. Note that, in spite of the low concentration of water vapor in the CRDS cell (partial pressure of about 0.015 Torr), some water lines were observed significantly shifted compared to their HITRAN positions. The analysis of the water list of 2000 lines will be reported elsewhere together with a systematic comparison of the line centers to HITRAN values.

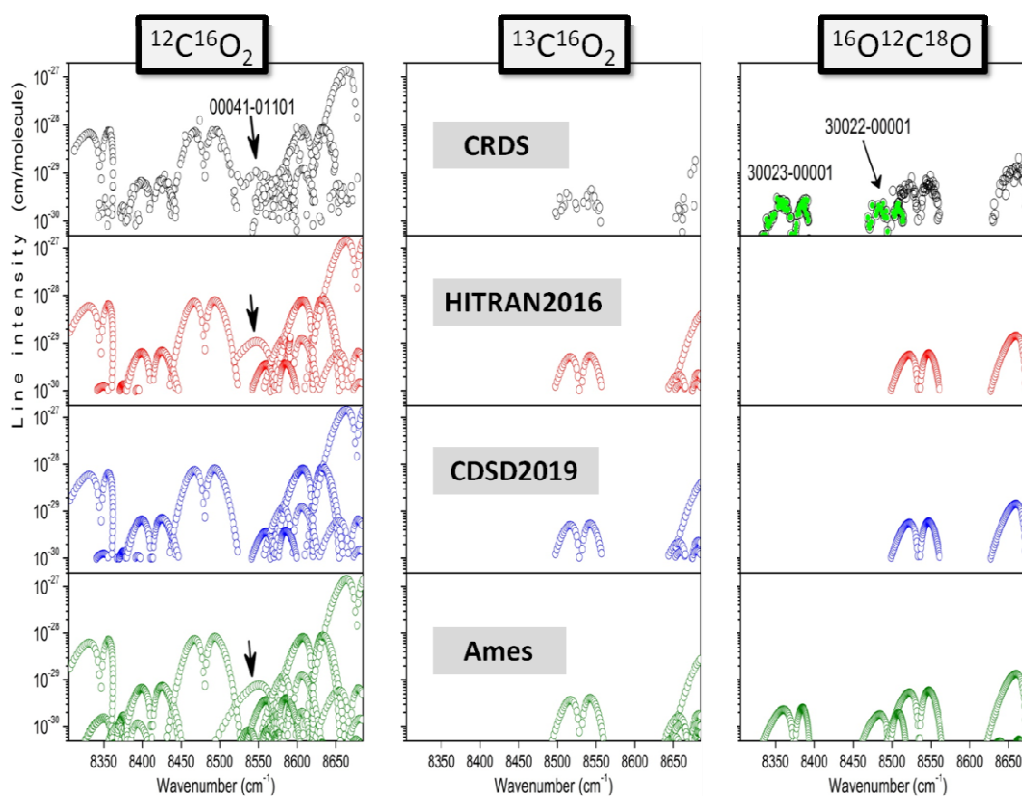
The error bars on the CO<sub>2</sub> line centers and line intensities can be only roughly estimated. The accuracy on the center of well isolated lines is on the order of  $5 \times 10^{-4} \text{ cm}^{-1}$  while the uncertainties on the line intensities are estimated to be 2% for the strongest lines (which are in fact very weak- line intensities smaller than  $10^{-27} \text{ cm/molecule}$ ).

### 3. Rovibrational assignments and band-by-band fit

The sensitivity of the recordings being at the level of the HITRAN intensity cut-off ( $10^{-30} \text{ cm/molecule}$ ), at the final stage of the analysis we also considered the Ames *ab initio* line list [27,28]

which provides CO<sub>2</sub> transitions with intensities as low as 10<sup>-42</sup> cm/molecule at 296 K. Indeed, the Ames predictions allowed us identifying two very weak <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O bands which are absent in the HITRAN2016 list and in CDSD2019, although their line intensities are slightly above the 10<sup>-30</sup> cm/molecule cut off. Overall, transitions belonging to 10, 1 and 4 bands of the <sup>12</sup>C<sup>16</sup>O<sub>2</sub>, <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O isotopologues were assigned, respectively. Including a few lines located near the borders of the investigated region and belonging to three additional bands, it leads to a total of 669 assigned transitions provided as Supplementary Material. The listed intensity values were converted from the measurement temperature (294.6 K) to the reference temperature of 296 K.

**Fig. 3** shows an overview comparison between the observations and the HITRAN2016, CDSD2019 and Ames line lists for the three isotopologues contributing to the spectrum. The 30023-00001 and 30022-00001 bands of <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O missing in HITRAN2016 and CDSD2019 are indicated together with the 00041-01101 of <sup>12</sup>C<sup>16</sup>O<sub>2</sub> missing in CDSD2019.



**Fig. 3**

Overview comparison between the CRDS observations between 8311 and 8679 cm<sup>-1</sup> to various spectroscopic line lists: HITRAN2016 (red) [25], CDSD2019 (blue) [21] and NASA Ames (green) [27,28].

**Table 1.** Spectroscopic constants ( $\text{cm}^{-1}$ ) of the  $\text{CO}_2$  bands identified in CRDS spectrum recorded in the  $8311\text{--}8679\text{ cm}^{-1}$  region.

$\Delta P^a$	Band	$\Delta G_v^b$	$G_v$	$B_v$	$D_v \times 10^7$	$H_v \times 10^{12}$	$rms^c$	$N_{\text{fit}}/N_{\text{obs}}^d$	$J_{\text{max } P/Q/R}^e$	Note <sup>f</sup>
<b><math>^{12}\text{C}^{16}\text{O}_2</math></b>										
11	20031e-10002e	8345.931963(63)	9631.340303(63)	0.38123963(15)	0.92214(52)		0.23	42/42	P32/R54	
11	21131e-11102e	8364.59953(94)	10297.06966(94)	0.3814042(73)	1.59(12)		0.49	11/12	P21/P21	
11	21131f-11102f	8364.59768(15)	10297.06781(15)	0.3813768(84)	0.77(10)		0.51	8/11	P22/R24	
13	51116e-01101e	8412.19035(15)	9079.57031(15)	0.38943557(52)	2.0915(31)		0.43	34/36	P41/R41	
13	51116f-01101f	8412.19020(15)	9079.57016(15)	0.39179223(51)	2.4403(32)		0.37	30/37	P42/R38	
13	50016e-00001e	8480.233319(84)	8480.233319(84)	0.39038314(32)	3.2663(29)	7.185(67)	0.25	48/50	P56/R54	
13	52215e-02201e	8573.29012(30)	9908.42173(30)	0.3893293(12)	1.2864(91)		0.61	21/26	P36/R36	
13	52215f-02201f	8573.29013(32)	9908.42174(32)	0.3893259(12)	1.9130(86)		0.61	19/25	P35/R37	
11	00041e-01101e	8579.55455(32)	9246.93451(32)	0.37792198(68)	1.3147(30)		0.53	22/26	P45/R47	1
13	60016e-10002e	8593.90888(30)	9879.31722(30)	0.3908977(70)	19.71(28)		0.45	13/38	P44/R38	2
13	51115e-01101e 51115e-01101f	8620.71216(18)	9288.09212(18)	0.38742277(35)	1.85185(12)		0.37	46/48 3/5	P57/R55 Q10	
13	51115f-01101f 51115f-01101e	8620.71215(10)	9288.09211(10)	0.38954780(22)	2.09596(74)		0.34	39/41 1/2	P54/R54 Q9	
13	60015e-10001e	8667.77734(38)	10055.96166(38)	0.3851777(18)	0.866(12)		0.75	11/18	P40/R14	
13	50015e-00001e	8676.707698(90)	8676.707698(90)	0.38811948(22)	2.3229(13)	2.463(20)	0.21	30/31	P68/R0	
<b><math>^{13}\text{C}^{16}\text{O}_2</math></b>										
13	50015e-00001e	8529.67299(43)	8529.67299(43)	0.3885843(15)	3.224(10)		0.74	19/22	P38/R36	
<b><math>^{16}\text{O}^{12}\text{C}^{18}\text{O}</math></b>										
12	30023e-00001e	8374.23070(16)	8374.23070(16)	0.36173352(54)	1.3777(34)		0.47	45/58	P41/R41	3
12	30022e-00001e	8497.45686(38)	8497.45686(38)	0.3623124(21)	0.795(21)		0.70	21/31	P31/R30	3
13	50015e-00001e	8535.29938(17)	8535.29938(17)	0.36527441(64)	1.9489(43)		0.63	50/60	P42/R42	
13	50014e-00001e	8672.68957(16)	8672.68957(16)	0.36350498(49)	0.9830(27)		0.47	28/33	P48/R8	

**Notes**

The confidence interval (1SD) is in the units of the last quoted digit.

<sup>a</sup>  $\Delta P = P' - P''$  ( $P = 2V_1 + V_2 + 3V_3$  is the polyad number).

<sup>b</sup>  $\Delta G_v = G_v' - G_v''$  is the band center.

<sup>c</sup> Root mean square of the (Obs.-Calc.) differences of the position values ( $10^{-3}\text{ cm}^{-1}$ ).

<sup>d</sup>  $N$  is number of the observed lines;  $n$  is number of transitions included in the fit.

<sup>e</sup> Observed branch with maximum value of the total angular momentum quantum number.

<sup>f</sup> Note: 1 – Absent in CDSD2019, R branch overestimated in HITRAN.

2 – Perturbed band. The 60016 upper level is in Coriolis resonance interaction with the 71105 level [37].

3 – Absent in CDSD2019 and HITRAN2016.

The different bands are listed in **Table 1** in increasing order of their band centre. The identified bands of the symmetric isotopologues ( $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$ ) belong to the  $\Delta P=11$  and  $\Delta P=13$  series of transitions ( $P=2V_1+V_2+3V_3$  is the polyad number,  $V_i$  being the vibrational quantum numbers). Let us mention that the vibrational term value of the upper level of the 00041e-01101e hot band ( $\Delta P=11$ ) is larger than those of a number of bands belonging to the  $\Delta P=13$  series. The  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  bands belong to the  $\Delta P=12$  and  $\Delta P=13$  series.

The spectroscopic parameters of the upper level of fifteen bands were derived from a fit of the measured wavenumbers. The standard expression of the energies of the vibration-rotational levels was used:

$$F_v(J) = G_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 \quad (1)$$

where  $G_v$  is the vibrational term value,  $B_v$  is the rotational constant,  $D_v$  and  $H_v$  are the centrifugal distortion constants,  $J$  is the angular momentum quantum number. The lower state rotational constants were constrained to the values of Ref. [36]. As the *e* and *f* sub bands may be perturbed in a different way, they were fitted independently. The derived constants are listed in **Table 1**. The *rms* values of the fits are on the order of  $5 \times 10^{-4} \text{ cm}^{-1}$ , which is very satisfactory considering that most of the transitions have intensities smaller than  $10^{-28} \text{ cm/molecule}$ . All but two bands are unperturbed. The 60016-10002 hot band of  $^{12}\text{C}^{16}\text{O}_2$  is perturbed due to a Coriolis resonance interaction between the 60016 upper level and the 71105 level [37]. Only low  $J$  values transitions were used to derive the 60016 spectroscopic parameters. Another Coriolis interaction affects the 00041 and 11131 states of the  $P=11$  polyad [37]. The detailed results of the band-by-band fit of the spectroscopic parameters are provided as Supplementary Material.

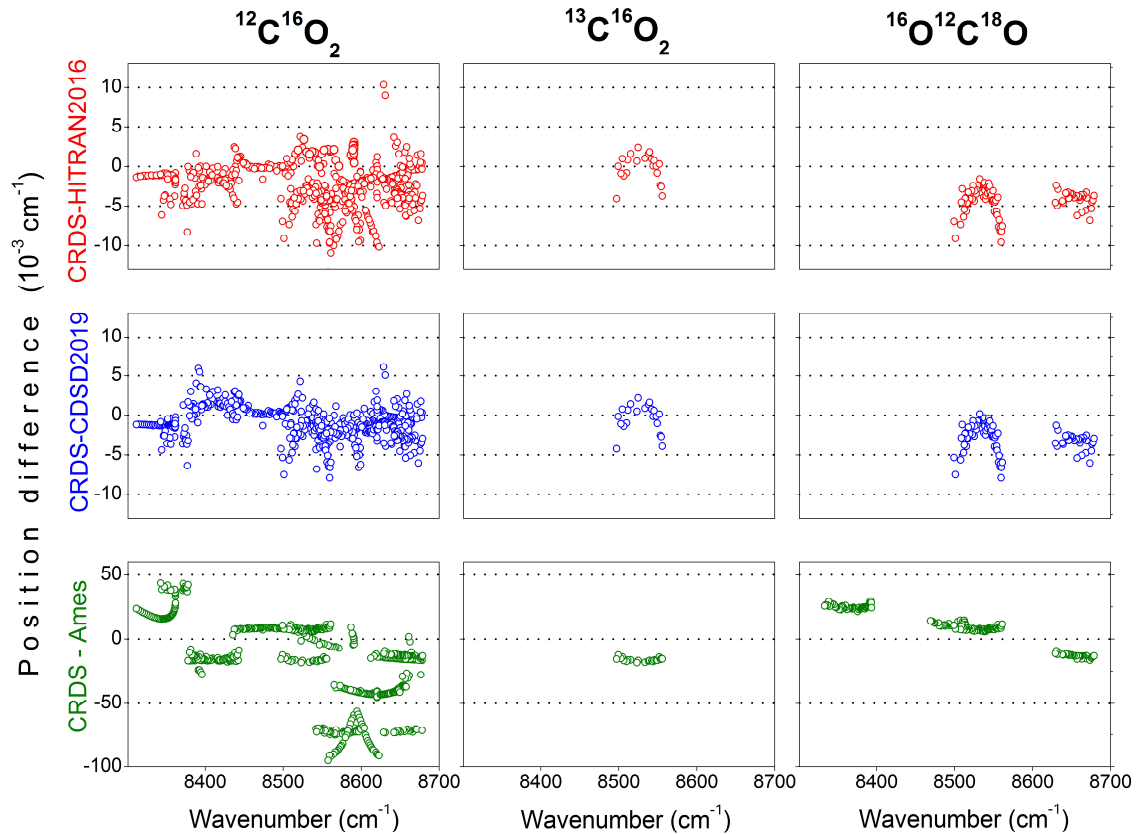
#### 4. Comparison to spectroscopic databases

The present new observations provide an opportunity to discuss the status of the most recent spectroscopic databases of carbon dioxide in a region where previous observations were practically absent.

##### 4.1. Line positions

The line list of natural  $\text{CO}_2$  provided by the Carbon Dioxide Spectroscopic Databank (CDSD) [21] is a computed line list based on a global modeling of the line positions and line intensities using the effective operator approach [38,39]. For each isotopologue, the effective Hamiltonian (EH) parameters and effective dipole moment (EDM) parameters are fitted to experimental positions and line intensities, respectively [3,4,9,11,17]. The developed EHs are able to reproduce the exhaustive datasets of measured line positions collected in the literature with an accuracy close the experimental accuracy and have very good predictive capabilities. Most of the line positions provided in the HITRAN2016 and GEISA2015 databases are CDSD2015 values [40]. The set of EH and EDM

parameters are regularly refined on the basis of new observations. We consider here the most recent CDSD2019 version [21], which will be used for HITRAN2020. The differences between the measured line positions and those provided by the HITRAN2016 database (*i.e.* CDSD2015), CDSD2019 and the NASA-Ames line lists [27,28] are plotted in **Fig. 4**. Overall the agreement is very good. As expected the Ames positions relying on an empirically adjusted potential energy surface, show larger deviations than the CDSD positions extrapolated using parameters fitted on measurements available in the region. For  $^{12}\text{C}^{16}\text{O}_2$ , the average values of the (meas.- ref.) deviations are -2.3, -1.0 and -20.6 in  $10^{-3} \text{ cm}^{-1}$  unit, for HITRAN2016, CDSD2019 and Ames list, respectively, with corresponding standard deviations of 2.7, 2.0 and 32.1. Considering the fact that most of the transitions are newly measured, the present results illustrate the very good predictive capabilities of the effective operator approach used in CDSD. The already good agreement with CDSD2015 (*i.e.* HITRAN2016) is improved with CDSD2019. Only a few bands show significant deviations compared to CDSD2019. For the two minor isotopologues,  $^{13}\text{C}^{16}\text{O}_2$  and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ , CDSD2019 and HITRAN2016 mostly coincide and maximum deviations are less than  $0.01 \text{ cm}^{-1}$ .

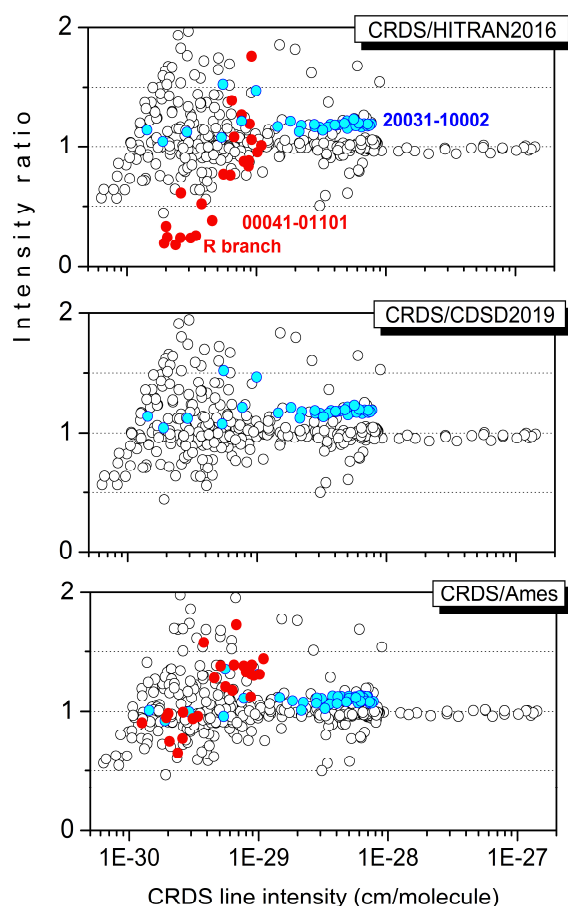


**Fig. 4**

Differences between the positions of the  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$  and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  lines measured in the 8311-8679  $\text{cm}^{-1}$  region and the values included in HITRAN2016 database [25], the Carbon Dioxide Databank in its last version (CDSD2019) [25] and NASA Ames database [27,28]. Note the different scale adopted for the lower panels.

#### 4.2. Line intensities

The ratios between the measured intensity values and the HITRAN2016, CDSD2019 and Ames values are plotted in **Fig. 5** versus the CRDS line intensities. The overall agreement is very good for line intensities larger than  $10^{-29}$  cm/molecule, a larger dispersion of the ratios being observed for the weaker lines, due to experimental uncertainties. While, below  $8000\text{ cm}^{-1}$ , the HITRAN2016 CO<sub>2</sub> line list combines CDSD2015 line intensities and variational line intensities from University College London (UCL) [41-44], in the present region above  $8000\text{ cm}^{-1}$ , CDSD2015 [40] is the only intensity source of the HITRAN list. The comparison to HITRAN2016 is thus in fact a comparison to CDSD2015. Note that the UCL list, limited to the  $0\text{--}8000\text{ cm}^{-1}$ , cannot be used for comparison to the present measurements contrary to the Ames list which extends up to  $25000\text{ cm}^{-1}$  [27,28].



**Fig. 5**

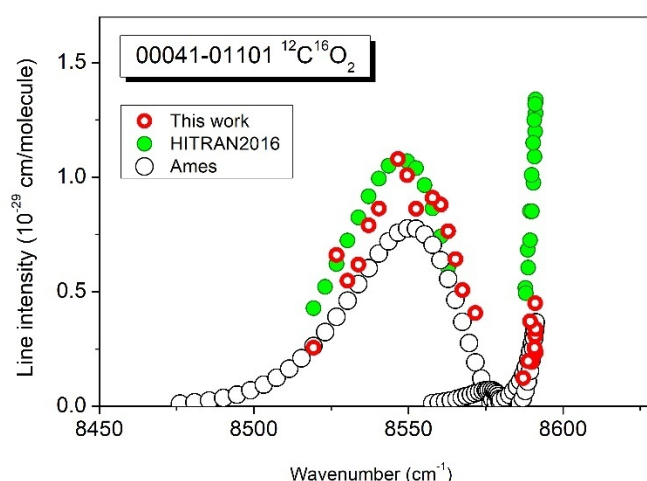
Intensity ratios at 296 K for the  $^{12}\text{C}^{16}\text{O}_2$  lines measured in the  $8311\text{--}8679\text{ cm}^{-1}$  region and HITRAN2016 database [25], the Carbon Dioxide Databank (CDSD2019) [21] and NASA Ames database [27,28]. The 20031-10002 and 00041-01101 bands discussed in the text are highlighted (red and blue symbols, respectively).

**Fig. 5** indicates that the changes between CDSD2015 and CDSD2019 are small. In particular, an underestimation of the 20031-10002 hot band intensity by about 17% is apparent for the two CDSD

versions. We examine in more details the intensities of this band already reported in our previous CRDS below  $8360\text{ cm}^{-1}$  [2]. Although the sensitivity presently achieved is improved compared to Ref. [2], the overall agreement between the two CRDS measurements is within 5 %. The comparison to Ames intensities shows a systematic underestimation of the *ab initio* intensities of about 12 % and 8% in the *P* and *R* branch, respectively. Although reduced compared to CDSD, these deviations seem to be significant in regards of the experimental uncertainty which is better than 5 %.

Interestingly, in HITRAN2016, a line intensity error code (3) corresponding to more than 20% is attached to all the  $^{12}\text{C}^{16}\text{O}_2$  bands of our region, except the 20031-10002 band to which is associated the error code (5), corresponding to a 5-10 % uncertainty. Our measurements deviate by more than the HITRAN error bar for this specific 20031-10002 band while the >20% error bar of the other HITRAN values appear to be conservative, at least for the strongest bands of the region. For instance, for the strongest band (50015-00001), HITRAN intensities are confirmed by our measurements within 2%.

A significant difference between HITRAN2016 and CDSD2019 concerns the very weak 00041-01101 hot band. This perpendicular band is absent in CDSD2019 (see **Fig. 3**) and it is the only one in HITRAN2016 for which the intensity source is not CDSD2015 but a previous CDSD version (2008) [45]. **Fig. 6** compares to the experimental rotational distribution of this band in HITRAN2016 and in the Ames list. While in the *P*-branch, the intensity comparison is not conclusive, a good agreement is achieved between CRDS and Ames intensities in the *R*-branch while HITRAN2016 intensities are overestimated by more than a factor of 3. Note that the HITRAN uncertainties associated to this band are larger than 20%.



**Fig. 6**

Rotational distribution of the 00041-01101 band of  $^{12}\text{C}^{16}\text{O}_2$ : CRDS measurements (red circles) HITRAN2016 database (green circles) [25] and Ames list [27,28] (open circles).

## 5. Conclusion

The very weak absorption spectrum of natural carbon dioxide in the 1.18  $\mu\text{m}$  window has been investigated for the first time at high sensitivity. The reported dataset includes some of the weakest  $\text{CO}_2$  lines ever measured (line intensities smaller than  $10^{-30}$   $\text{cm}/\text{molecule}$ ).

The measurements of near 700  $\text{CO}_2$  lines in a region where previous observations were practically absent provided valuable tests of the recent 2019 version of the Carbon Dioxide Spectroscopic Databank (CDSD2019) [21], the current HITRAN2016 database [21] and Ames *ab initio* line list [27,28]. This kind of tests are particularly stringent in the windows [1] where the absorption is due to “exotic” bands such as very hot bands, perturbed bands and bands of minor isotopologues.

Overall, the obtained agreement with the different databases is very good although some observations indicate that the present experimental results will be valuable to refine the characterization of the  $\text{CO}_2$  absorption spectrum in the region:

- i. Line positions of  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$  and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  reported with an experimental accuracy on the order of  $5 \times 10^{-4}$   $\text{cm}^{-1}$  show deviations from HITRAN and CDSD values by up to 0.01  $\text{cm}^{-1}$ . They will help to improve the respective effective model parameters used to generate the CDSD in the region,
- ii. The very weak 30023-00001 and 30022-00001 bands of  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  are missing in HITRAN2016 list and in CDSD2009,
- iii. The 00041-01101 of  $^{12}\text{C}^{16}\text{O}_2$  is missing in CDSD2019 and included in HITRAN2016 from an old version of CDSD [45]. The *R*-branch intensities of this band are found in good agreement with the Ames values while HITRAN values are largely overestimated (**Fig. 6**),
- iv. Except for the 20031-10002 band, the CRDS intensities values reported with an error bar of a few % show an agreement to HITRAN values significantly better than the >20 % error bar attached HITRAN intensities. We thus conclude that HITRAN error bars are overestimated, at least for the line intensities larger than  $10^{-29}$   $\text{cm}/\text{molecule}$ .

The observations confirm the benefits of the *ab initio* variational lines lists computed at NASA-Ames [27,28] and at UCL [41,44], in terms of completeness and quality of the predicted intensities. Below 8000  $\text{cm}^{-1}$ , most of the HITRAN line intensities have CDSD origin but UCL variational values were adopted for a number of transitions in regions where experimental data were not sufficient to derive the effective parameters requested for the global CDSD model, in particular for the minor isotopologues. Our previous studies in the 1.74  $\mu\text{m}$  window [1,12,18] revealed some examples where *ab initio* calculations should have been preferred to the CDSD intensities reproduced in HITRAN (see Fig. 5 of Ref. [12]). In the present work, above 8000  $\text{cm}^{-1}$ , this is confirmed by the intensity distribution in the 00041-01101 band of  $^{12}\text{C}^{16}\text{O}_2$  and by the two  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  bands missing in HITRAN and CDSD despite their intensities are above the intensity cut-off. Note that these effects mainly

concern very weak bands and generally have a marginal impact on the overall opacity in the considered window.

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