Line parameters including temperature dependences of air- and self-broadened line shapes of $^{12}\text{C}^{16}\text{O}_2$: 2.06- μm region

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Abstract

This study reports the results from analyzing a number of high resolution, high signal-to-noise ratio (S/N) spectra in the 2.06- μm spectral region for pure CO_2 and mixtures of CO_2 in dry air. A multispectrum nonlinear least squares curve fitting technique has been used to retrieve the various spectral line parameters. The dataset includes 27 spectra: ten pure CO_2 , two 99% ^{13}C -enriched CO_2 and fifteen spectra of mixtures of ^{12}C -enriched CO_2 in dry air. The spectra were recorded at various gas sample temperatures between 170 and 297 K. The absorption path lengths range from 0.347 to 49 m. The sample pressures for the pure CO_2 spectra varied from 1.1 to 594 Torr; for the two $^{13}\text{CO}_2$ spectra the pressures were ~ 10 and 146 Torr. For the air-broadened spectra, the pressures of the gas mixtures varied between 200 and 711 Torr with CO_2 volume mixing ratios ranging from 0.014 to 0.203%. The multispectrum fitting technique was applied to fit simultaneously all these spectra to retrieve consistent set of line positions, intensities, and line shape parameters including their temperature dependences; for this, the Voigt line shape was modified to include line mixing (via the relaxation matrix formalism) and quadratic speed dependence. The new results are compared to select published values, including recent *ab initio* calculations. These results are required to retrieve the column averaged dry air mole fraction (X_{CO_2}) from space-based observations, such as the Orbiting Carbon Observatory-2 (OCO-2) satellite mission that NASA launched in July 2014.

Key words: CO_2 ; Lorentz widths; pressure shifts; temperature dependences; spectral line shapes; relaxation matrix element coefficients; speed dependence

1. Introduction

The 2.06- μm spectral region is used extensively for remote sensing of atmospheric carbon dioxide (CO_2) column mixing ratios [1-10]. CO_2 IS BOTH LONG-LIVED AND WELL MIXED THROUGHOUT THE EARTH'S ATMOSPHERE, BUT CONCENTRATIONS OF THIS GAS IS CONTINUALLY INCREASING IN THE ATMOSPHERE, IN TURN PRODUCING GLOBAL WARMING. CLIMATE MODELING REQUIRES PRECISE KNOWLEDGE OF THE CO_2 CONCENTRATIONS AT SOURCES AND SINKS FOR THE ATMOSPHERE. Satellite missions such as the Orbiting Carbon Observatory (OCO-2) and the Greenhouse Gases Observing Satellite (GOSAT) rely on reflected sunlight in the near-infrared region to obtain column-average mixing ratios of CO_2 . WITHIN SPATIAL SCALES OF 1000 KILOMETERS, THE TYPICAL VARIATIONS ARE NO LARGER THAN 0.25% (1 PART PER MILLION (PPM) OUT OF THE AMBIENT 400 PPM BACKGROUND). THIS PLACES STRINGENT REQUIREMENTS ON THE PRECISION AND ACCURACY OF SPACE-BORNE CO_2 MEASUREMENTS, WHICH IN TURN PLACES STRINGENT REQUIREMENTS ON THE PRECISION AND ACCURACY OF THE SPECTROSCOPIC LINE PARAMETERS USED IN THE RETRIEVALS. The present study (4700-4930 cm^{-1}) focuses on our efforts to provide the best line parameters for CO_2 in the 2.06- μm region.

During the past several years, many research groups have reported high-resolution measurements for the 2- μm region of CO_2 (*e.g.*, [11-24]) including a number of line shape parameters (*e.g.*, Lorentz half-widths and pressure-shift coefficients). In **Table 1** are shown recent line shape measurements obtained for the 2.06- μm $^{12}\text{C}^{16}\text{O}_2$ band, 20013 $\leftarrow$ 00001 [12,13,18-23]. The most comprehensive measurements by Toth et al. [11-15] included line center positions, intensities (and band strengths) and self- and air-broadened half-width coefficients. Those studies reported measurements of hundreds of CO_2 bands covering the 4550-7000 cm^{-1} spectral region (2.2–1.43- μm), including the most abundant $^{12}\text{C}^{16}\text{O}_2$ species, as well as several rarer isotopologues such as $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. However, these line shape studies considered neither line mixing nor speed dependence, both of which are important for atmospheric monitoring in the 2.06- to 2.0- μm region (*e.g.*, [6,25]). In addition, these studies used laboratory data obtained only at room temperature.

In general, the temperature dependences of line shape coefficients are not well characterized for CO₂. Suarez and Valero [17] measured temperature dependence exponents of self-broadened half-width coefficients for 14 lines of the nearby 2.0-μm CO₂ band (20012←00001) using spectra obtained with a BOMEM FTS, but these few values did not fulfill the need for a comprehensive, self-consistent set of spectral line parameters for remote sensing of atmospheric CO₂ in the 2.06-μm region. In our previous work [16], the multispectrum fitting approach applied to only room temperature spectra derived a self-consistent set of spectral line parameters using a quadratic speed-dependent Voigt line shape and *nearest neighbor* line-mixing coefficients using the off-diagonal relaxation matrix formalism [26]. These parameters were validated against atmospheric spectra from a ground-based Fourier transform spectrometer (FTS) from the Total Carbon Column Observing Network (TCCON) [6,9,10]. However, the temperature dependence of line shape parameters remained an outstanding source of uncertainty.

In addition to the line shape studies listed in **Table 1**, there have been a number of new measurements employing different experimental techniques concerning the 2-μm spectral region [*e.g.*, 27,28]. While valuable, these do not provide all the parameters needed for atmospheric remote sensing. We began a new study of this region in 2007 and presented preliminary results at a conference [16] but later expanded our analysis to include more high-quality data (acquired with the Bruker IFS-125 HR FTS at JPL) to investigate the temperature dependence of line shapes using a wider range of optical densities.

Table 1 comes here (Prior studies)

We employed our multispectrum fitting approach [29,30] to simultaneously analyze a large number of spectra [27] in order to minimize the random errors in the fit residuals and to reduce correlations between fitted line parameters. The precise results presented in this study represent the first extensive and most precise measurements of spectral line parameters (including the temperature dependence of line shapes) for CO₂ and CO₂ + air at 2.06-μm. Our results are directly applicable to space-borne CO₂ retrievals from missions such as OCO-2.

2. Experimental Details

2.1. *Instrument setups, summary of experimental conditions*

Spectra used in the present analysis were recorded using two different spectrometers: 1) McMath-Pierce Fourier transform spectrometer (FTS) facility at the National Solar Observatory (NSO) on Kitt Peak, Arizona, and 2) the Bruker IFS-125HR FTS located at the Jet Propulsion Laboratory (JPL), California Institute of Technology at Pasadena, California. The experimental setups and the system configuration details are listed in **Table 2**. The fitted spectra were selectively chosen from a larger dataset, in order to judiciously select gas sample pressure and temperature ranges that would best determine the temperature dependences of the line shape parameters. Twenty-seven spectra obtained with seven different absorption cells were included in the final fit. Five of these were recorded at Kitt Peak, while the other twenty-two were recorded at JPL. A summary of the experimental conditions of spectra analyzed is given in **Table 3**.

Insert Table 2 (Experimental setups)

The spectra recorded at Kitt Peak were obtained at $\sim 0.01 \text{ cm}^{-1}$ unapodized resolution. The Kitt Peak FTS was configured with a quartz halogen source, two liquid nitrogen cooled InSb detectors and a CaF_2 beam splitter. The experimental setup for spectra recorded at JPL consisted of a tungsten lamp for the source, a CaF_2 beam splitter and an InSb detector. The unapodized resolutions for the 22 spectra varied between ~ 0.004 and 0.011 cm^{-1} . The absorption path lengths for the 22 spectra recorded at JPL range from 0.2038 m to 29.3 m. For the Kitt Peak data, a natural sample of CO_2 was used for three of the spectra while a 99% ^{13}C -enriched CO_2 was used for the other two. The absorption path length of the cells varied between 0.347 m and 49.0 m. For the majority of the JPL (0.2038 and 20.941 m cells) spectra, 99.99% ^{12}C -enriched CO_2 samples were used for self and air-broadening while 99.98% ^{12}C -enriched CO_2 sample was used for the air-broadened spectra obtained with a room temperature multipass cell set to 29.30 m cell.

Table 3 comes here

For the Kitt Peak FTS data, the 49 m path was obtained using the 6-m base path White cell. The 0.347 m and the 2.46 m cells were newly built to be efficient thermally-insulated chambers such that the temperature sensors could be kept in direct contact with the gas samples. Each spectrum covered the region from 3800 to 7200 cm^{-1} . Spectrum #1 (**Table 3**), with the largest path length (49 m) with 80 Torr CO_2 included in the fit, was particularly useful in determining and validating the abundances of various rarer isotopologues in the JPL data.

For the JPL Bruker spectra, the 29.30 m path cell was used to obtain room temperature air-broadened spectra. The 0.2038 m straight path cell and the 20.941 m Herriott cell were both coolable and used for recording self-broadened and air-broadened spectra ($\sim 170\text{--}250$ K), respectively. The design, construction and the performance details for the two cells are detailed in Sung et al. [31] and Mantz et al. [32], respectively. For the air-broadened spectra recorded at JPL (using the 20.941 m Herriott cell) NIST standard air sample was used, while synthetic dry air was used for all other Bruker spectra (*i.e.*, 0.2038 m and the 29.3 m long cell). 99.98% ^{12}C -enriched sample of CO_2 was used for the 29.3 m spectra, while the purity of the CO_2 sample was 99.99% for spectra recorded with both the coolable cells (0.2038 m and 20.941 m). More details about the experimental setups are given in **Table 2**.

2.2. Calibrations of wavenumber scales

The calibration of the wavenumber scales of the Kitt Peak spectra was determined by placing a second cell in the optical beam so that CO and/or C_2H_2 line positions could be used as standards [33,34]. This approach has been described in several of our previous studies (*e.g.*, [35]). Calibration correction factors for the Bruker data were determined relative to the $2\leftarrow 0$ band of HCl line positions from the HITRAN2008 database [36]. It was important that these two sets of calibration factors provided good internal consistency between both sets of spectra (Kitt Peak FTS and JPL Bruker). The multispectrum fitting software [29] used here provides the capability to adjust the wavenumber scales, interactively, if appropriate. This capability was applied for the two separate sets of data obtained with both coolable cells (see **Table 3**).

In order to maintain good knowledge and control of the experimental conditions, sample pressures and temperatures were continually monitored during the entire data acquisition process. For the Kitt Peak data, gas sample pressures were monitored using calibrated capacitance manometers of appropriate pressure ranges. For the 49 m White cell, sample temperatures were determined using thermocouples attached to three different places on the outside surface of cell. For the shorter path cells, temperatures were determined using high accuracy (± 0.05 K) platinum resistance thermometers (Hart Scientific) inserted into the cell at four different positions (temperature sensors installed inside the cells), and these recorded temperatures varied by ± 0.2 K at most during the data acquisition period. For recording the Bruker spectra, the pressure gauges were periodically calibrated and the recommended calibration factors from the manufacturers were applied to the temperature sensors. The coolable cells used in recording the Bruker spectra are specially built with very good temperature stability and homogeneity across the length of the cells. Further details on the experimental precautions followed for the Kitt Peak spectra are listed in Miller et al. [35], while details on monitoring the gas pressures and temperatures for the data taken with the two coolable cells at JPL are described in Sung et al. [31] and Mantz et al. [32].

3. Analysis and data retrievals

3.1. General procedures and equations applied

As was done in several of our previous studies on linear molecules, such as CO₂ and CO [e.g., 35, 37, 38], we followed the whole band retrieval technique originally applied by Shaw and co-workers [39] and Lin and Shaw [40], and later developed and expanded extensively by Benner et al. [29] using a better formulation of the Voigt profile [30]. Rather than adjusting the transition positions on a line-by-line basis, the multispectrum retrieval software was modified to solve for the values of the ro-vibrational constants G , B , D and H for the upper and lower state energies (where possible lower state constants were constrained to the best literature values). For line intensities, the vibrational band strength S_v and the Herman-Wallis factor F defined by the parameters a_1 , a_2 , a_3 and a_4 (given below) were adjusted instead of individual line intensities. Thus our individual “measured” positions and “measured” intensities are the constrained values calculated with **Eqs. (1-3)**.

$$\nu_i = G' - G'' + (B'J'[J' + 1] - D'\{J'[J' + 1]\}^2 + H'\{J'[J' + 1]\}^3) - (B''J''[J'' + 1] - D''\{J''[J'' + 1]\}^2 + H''\{J''[J'' + 1]\}^3) \quad (1)$$

$$S_i = \frac{S_v \nu_i L_i F}{Q_r \nu_0} \exp\left(\frac{-C_2 E''}{T_0}\right) \left[1 - \exp\left(\frac{-C_2 \nu_i}{T_0}\right)\right] \quad (2)$$

where,

$$F = [1 + a_1 m + a_2 m^2 + a_3 m^3 + a_4 J(J + 1)]^2 \quad (3)$$

and $m = -J''$ for P-branch and $J''+1$ for R-branch lines. ν_0 is the band center (equal to $G' - G''$), ν_i and S_i correspond, respectively, to the transition wavenumber (cm^{-1}) and the line intensity ($\text{cm}/(\text{molecule})$) of the i^{th} line, where prime and double prime refer to the upper and lower levels; J is the rotational quantum number and Q_r , the rotational quantum partition function.

For the present study, the lower state ro-vibrational constants in **Eq. (1)** are constrained to the values from Miller and Brown [41] for $^{12}\text{C}^{16}\text{O}_2$ and Elliot et al. [42] for $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{17}\text{O}$. In **Eq. (2)**, E'' is the lower state energy of the transition, and T_0 is the reference temperature (296 K). L_i are the Hönl-London factors, S_v is the vibrational band intensity ($\text{cm}/\text{molecule}$), and C_2 is the second radiation constant. The values of the rotational quantum partition function, Q_r , at $T=296$ K are 263.87063 for $^{12}\text{C}^{16}\text{O}_2$, 527.71608 for $^{13}\text{C}^{16}\text{O}_2$ and 559.30454 for $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ [43]. The term $a_4 J(J+1)$ in **Eq. (3)** is indistinguishable from the a_2 term in the P- and R-branches, so for bands without Q branches, the reported a_2 is actually very nearly $a_2 + a_4$.

Uncertainties are minimized with constraints in the multispectrum retrievals (1) by fitting the entire band and fitting all spectra simultaneously, (2) by applying constraints using theoretical quantum mechanical equations (eigenfunction expressions Eqs. (1) and (2)) for line positions and intensities of all major (stronger) bands, (3) by adjusting Lorentz half-widths, pressure shifts, off-diagonal relaxation matrix element coefficients and speed dependence for each line separately, (4) by including all absorption features within the fitted interval (*e.g.*, hot bands, weak bands, and isotopologue bands), and (5) by using line mixing (relaxation matrix element coefficients) and quadratic speed dependence parameter when required as judged from fit residuals.

The size of the fitted interval, number of spectra and the resolution of each spectrum were carefully chosen for this analysis. In the fitted interval 4700-4930 cm^{-1} with 27 spectra, absorption features were observed from 42 vibrational bands (24, 9, 2, 3, and 4) belonging respectively, to $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$. For several very weak bands, their parameters were held fixed to predicted values from HITRAN2004 [44] (see the **Supplemental file** discussed later). Other very weak bands belonging to the rarer isotopologues (*e.g.*, ^{18}O) were not significant, and no effort was made to obtain their line parameters. In all, 21 of 42 bands were measured in the fitting. The band identifications with their upper and lower vibrational levels, range of quantum numbers of transitions fitted in the P, Q (when present), and R branches, and the isotopologue identifications for these 21 bands are listed in **Table 4**.

Table 4 appears here (major bands included in the analysis)

3.2. Constraints

The least squares fittings were initialized using the line list from HITRAN2004 [44]. The final input file contained 3040 spectral lines from the initial line list used in [16] from HITRAN2004 with additional lines (*e.g.*, for $^{12}\text{C}^{16}\text{O}^{18}\text{O}$) added later from Toth et al. [14] to include all observable features in the 4700-4930 cm^{-1} region of the fitted spectra. In order to extract the most information for the stronger bands, the least squares fit solves for the ro-vibrational constants; for this the positions were calculated from the ro-vibrational constants extending to the highest J for which position constraints are written and is the same as in HITRAN [44]. When two different bands involve the same vibrational state, there is a further reduction in the number of degrees of freedom in the solution since those bands will access some of the same ro-vibrational constants. Similarly the individual line intensities are calculated from the vibrational band strength (S_v) and Herman-Wallis-type parameters measured in this study along with the known quantum numbers. The multispectrum fit then solves for only the vibrational band strength (S_v) and the Herman-Wallis parameters for each band. Positions and intensities of several of the stronger bands are also constrained. For the very weak bands, the line positions and intensities are either fixed to the initial values assumed from HITRAN 2004 [44] or the values of Toth et al. [11,14,15], since the analysis of the present study started in 2006 was initially begun with only

room temperature spectra [16]. Positions and intensities for a number of weak transitions (where no constraints were setup) were also adjusted during the fittings, as judged from the fit residuals.

3.3. Sample spectra and multispectrum fits

As example, a set of (unfitted) experimental spectra included in the present analysis is shown in **Fig. 1**.

Insert Fig. 1 here

Fig. 1(a-e) shows the signal levels (0–100% scale) vs. wavenumber (cm^{-1}) for 5 of the 27 spectra analyzed in this work. The spectra plotted in the top two panels **(a)** and **(b)** represent majority of the transitions observed in the entire fitted region. Panel **(a)** represents the spectrum with the longest absorption path length of 49 m in the dataset, with CO_2 at natural isotopologue abundance with 80 Torr and at room temperature, while panel **(b)** represents one of the (only) two spectra with the highest isotopologue abundance of (99% ^{13}C -enriched) $^{13}\text{CO}_2$. It is clear that the $^{13}\text{CO}_2$ features in **(b)** are practically absent in panels **(c-d)** but appear in **(a)**. The $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ bands appear in **(a)** and **(c)**, even though data in **(c)** were obtained with a 99.99% ^{12}C -enriched carbon dioxide. The first hot band (21113←01101) transitions of $^{12}\text{C}^{16}\text{O}_2$ centered at 4807.694 cm^{-1} are seen in **(a)**, **(c)** and **(d)**. In the bottom panel **(e)**, most of the transitions are from the strongest 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ located at 4853.523 cm^{-1} , because the other weaker bands almost disappear when the sample is cooled to $\sim 170 \text{ K}$. Weak absorptions from the 20013←00001 band of $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ are still visible near 4910 cm^{-1} . In fitting all 27 spectra, the abundances for each of the isotopologues in every spectrum must be determined accurately enough such that when fitted simultaneously, the residuals are reduced to the noise levels of the spectra as was done in the present study (**PS**).

The final multispectrum fit of all 27 spectra is plotted in **Fig. 2**. The top panel **(a)** shows the observed spectra, and the bottom panel **(b)** shows the global weighted observed minus calculated (O-C) fit residuals.

Insert Fig.2 here

Some small but persistent residuals (corresponding to the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ around 4850 cm^{-1}) are still present, as seen in **Fig. 2(b)**. The sources of these residuals are not understood at this time, but they could be due to line mixing from non-neighboring lines not included in this study, missing transitions from rarer isotopologues or other causes of unknown origin. **Fig. 3** shows the fit residuals grouped by temperature ranges (from the multispectrum fit). Persistent residual features are not obvious in the $^{13}\text{C}^{16}\text{O}_2$ spectrum (room temperature spectrum and not high enough pressure to have line mixing) in **(c)**, but they are clearly visible in the cold temperature residuals in **(d)** and **(e)**. Spectra plotted in **Figs. 2** and **3** have been given weights in accordance with their different signal-to-noise ratios. The largest weighted residual anywhere on the fit for any spectrum is $< 0.2\%$. The standard deviation of the fit for unit weight (the highest signal-to-noise ratio spectra in the solution) was 0.037% .

Insert Fig. 3 here

3.4. Lorentz half-width and pressure-shift coefficients

The Lorentz half-width coefficients, pressure-shift coefficients, and their temperature dependences were measured on a line-by-line basis and defined by **Eqs. (4-6)** given below [38]:

$$b_L = p \times \left[b_{L,air}^0 \times (1 - \chi) \left(\frac{T_0}{T} \right)^{n_1} + b_{L,self}^0 \times \chi \left(\frac{T_0}{T} \right)^{n_2} \right] \quad (4)$$

$$\nu = \nu_0 + p \times [\delta_{air} \times (1 - \chi) + \delta_{self} \times \chi] \quad (5)$$

$$\delta = \delta^0 + \delta' \times (T - T_0) \quad (6)$$

In **Eqs. (4-6)**, b_L^0 and δ^0 represent pressure broadening and pressure-shift coefficients (in $\text{cm}^{-1}\text{ atm}^{-1}$ at 296 K), respectively. b_L is the Lorentz half-width (in $\text{cm}^{-1}/\text{atm}$) of the spectral line at pressure p and temperature T , $b_{L,air}^0$ and $b_{L,self}^0$ are the Lorentz half-width coefficient of the line for air- and self-broadening, respectively, at the reference pressure p_0 (1 atm) and temperature T_0 (296 K), and χ is the ratio of the partial pressure of CO_2 to the total sample pressure in the cell. Similar to air- and self-broadened width and shift coefficients, temperature dependences of air- and self-broadened half-width and pressure-shift coefficients were also measured individually for each transition. As shown in **Eq. (6)** a linear model was used for the temperature dependence of pressure-shift coefficients.

Applying the above expressions, Lorentz half-width and pressure-shift coefficients have been measured for a few hundred individual transitions. Where ro-vibrational constants were measured rather than individual line positions, the pressure-shift coefficients were well determined because of the more precise zero-pressure line position retrievals and the large reduction of correlation between the zero-pressure line positions and the pressure-shift coefficients. Similarly, correlations were also reduced between the line intensities and the Lorentz half-width coefficients which are characteristics for strong transitions due to the constraints upon the line intensities.

The measured line parameters and number of CO₂ measurements from this study are provided in **Table 5**.

Table 5 comes here

The number of positions and intensity measurements given under columns 2 and 4 (first row) lists two values: the top number corresponds to constrained values while the number beneath (within parentheses) correspond to the total number of measured positions and intensities including those that were retrieved as part of the constrained parameters (top row). The number of measured intensities in **Table 5** is slightly greater than the number of measured positions because those positions greatly blended with other lines are excluded in the count. Generally, more self-broadening and self-shift coefficients are measured than air-broadening and air-shift coefficients since there are higher carbon dioxide amounts in pure sample data than for the air-broadened spectra. Further details about each measured parameter will be discussed in the following sections.

4. Discussion of results and comparison with databases

The CO₂ line parameters have undergone several improvements/modifications in the last three editions of the HITRAN databases [36,44,45]. For HITRAN2004 [44], values from the Direct Numerical Diagonalization (DND) technique [46] were replaced by combining selected experimental results with calculated line positions and intensities from the 2003 version of the

Carbon Dioxide Spectroscopic Databank, CDSD-1000 [47]. The line parameters compilation by Toth et al. in [15] was used for further improvements in the positions and intensities for HITRAN2008 [36]. In HITRAN2012 [45], the database has been greatly expanded and improved using an updated CDSD-296 databank [48] that includes line parameters for 12 CO₂ isotopologues providing spectroscopic information not only for positions and intensities but also for air- and self-broadened Lorentz half-width coefficients, temperature dependences of air-broadened half-width coefficients and air- pressure-induced shift coefficients. The CDSD-296 [48] line list includes CO₂ transitions with intensities as low as $\sim 1 \times 10^{-30} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ at 296 K. Comparisons of present line parameters with the CDSD-296 [48] are shown in several graphs and discussed in the section describing estimated total error budget. In addition to the CDSD-296 [48] databank, there are two other sources of line parameters that are theoretically computed [49,50] with which present results are compared. In the following subsections we detail how our new ¹²CO₂ measurements for the 20013←00001 band compare with HITRAN values, selected laboratory measurements [*e.g.*, Refs. 11-13,] and recent theoretical calculations [48–50].

4.1. Line positions

Detailed descriptions of constraints and the theoretical quantum mechanical expressions used for determining the line positions were provided in **Section 3.1**. Line positions from **PS** are compared to values reported in the HITRAN databases [36,44,45] and Toth et al. [11] for the 20013←00001 band of ¹²C¹⁶O₂ and are plotted in **Fig. 4**. Since the initial line list used in our earlier analysis of room temperature spectra [16] was from HITRAN2004 [44], values from HITRAN2004, HITRAN2008 [36], and the more recent HITRAN2012 [45] compilations are included in the comparisons. The means and standard deviations of the position differences between **PS** and [11,36,44,45] are given in the plot. The mean difference **PS**–Toth et al. [11] shows the smallest value.

Insert Fig. 4 here

The position differences between **PS** and HITRAN [36,44,45] are larger than the difference between this work and Toth et al. [11] because Toth et al. measured positions for P58–R58 only

while the constrained positions from **PS** extend up to $J''=84$. The position differences between **PS** and HITRAN2004 [44] are slightly smaller compared to the differences between **PS** and HITRAN [36,45]. Positions and uncertainties extrapolated to higher- J ($J''>70$) in the present study assume that the ro-vibrational model used here is correct, which is likely to be close to the truth for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$. However, a few % difference exists between the vibrational band strength (S_v) and the total integrated band strength (S_{band}) that is attributed to small vibration-rotation interactions, as discussed in a later section. The constrained positions also depend upon the ro-vibrational constants for both the upper state (determined from **PS**) and the lower state (fixed to literature values given in **Table 6(a)**). If line positions from **PS** are compared to only P58-R58 transitions corresponding to [11], the mean and standard deviation for all the four comparisons shown in **Fig. 4** would be $0.0001716(8) \text{ cm}^{-1}$.

4.2. Line Intensities

Fig. 5 displays the measured line intensities vs. m along with uncertainties for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$. The uncertainties shown in **(b)** assume that the model used for constraining the intensities is correct. This is likely to be true as long as there are no unrecognized local or non-local resonances for unobserved lines at high J (*i.e.*, $J'' \geq 70$). The advantage of constraining the intensities to theory is that the uncertainties remain small at high J even when the lines are disappearing in the data (especially at cold temperatures). At $J=80$ the internal uncertainties are about 0.1% (discussed and shown in a later figure). However, the sample pressures, temperatures, and absorption path lengths are only known to this level of uncertainty at best, so the absolute error in intensities of all lines plotted could be several tenths of a percent to one percent. Further details on absolute error estimates are given in the discussion section.

Insert Fig. 5 here

The retrieved line intensities for the strongest $^{12}\text{C}^{16}\text{O}_2$ band, 20013←00001, are plotted vs. m in **Fig. 5** on both a linear **(5a)** and a logarithmic **(5b)** scale. The corresponding intensity uncertainties are also plotted in **(5b)**. The **PS** intensities are compared to HITRAN2004 [44], HITRAN2008 [36] and HITRAN2012 [45] as well as to Toth et al. [11]. Similar to line positions, line intensities for this band (along with hundreds of other CO_2 bands) from Toth et al.

[11,15] were used in [36,45]. As seen in **Fig. 5(b)**, the uncertainties in intensities are J -dependent since both intensities and their uncertainties are constrained to follow **Eqs. (2) and (3)**.

The ratios of line intensities between **PS** and HITRAN2012 [45] and **PS** and Toth et al. [11] are plotted in **Fig. 5(c)**. The comparison between **PS** and Toth et al. [11] is limited to measured transitions listed in [11], while the comparison with HITRAN2012 applies to all constrained line intensities ($J''=84$) and even higher J . The ratios between **PS** and HITRAN2004 showing the largest variability are also included since the intensities in our initial room temperature fittings [16] were from [44]. The line intensities in [36,45] for the P58-R58 are nearly the same [11] and hence indistinguishable in **Fig. 5(c)**. The reason for the discontinuity observed near $m=58$ and 60 [45] is likely associated with some small discrepancies while combining intensity files from different sources (see Refs. [45,48] for details). Although Toth et al. [11] used a Voigt line shape model and performed a spectrum-by-spectrum analysis, the mean ratios of intensities (**PS**/Toth et al.) = 0.992(5) for P58-R58. The ratios of intensities computed between **PS** and Refs. [36,44,45] are given in panel **5(c)**. No other *extensive* experimental measurements of intensities have been recently reported for this band (see **Table 1**).

The measured ro-vibrational (G , B , D , H) and the transition moment constants (vibrational band strength S_v and the Herman-Wallis terms, a_1 , a_2 , a_3 , a_4) for several bands that were constrained to theory using **Eqs. (2) and (3)** are listed in **Table 6(a)**. In the present study, the a_1 , a_2 and a_3 terms were determined for seven of the eight bands listed in **Table 6(a)**, and were found sufficient to describe the strongest $^{12}\text{C}^{16}\text{O}_2$ 20013 $\leftarrow$ 00001 band, its hot band 21113 $\leftarrow$ 01101 and six other bands. For the weaker 30013 $\leftarrow$ 10002 band of $^{12}\text{C}^{16}\text{O}_2$, only the a_1 and a_2 terms were needed to obtain a good fit. **Table 6(a)** also lists the correlation coefficients between appropriate pairs of the fitted parameters. These correlation coefficients are required to calculate the uncertainties of the positions and intensities of the individual lines (see the discussion section for details). These values also provide confidence in the global least squares fits. The correlation coefficients between *any two* unconstrained line parameters determined in this work are internally calculated in the multispectrum software and used for the uncertainty analysis. This matrix contains over 610000 entries $\{n(n-1)/2\}$, n being the number of adjusted parameters in the multispectrum fit and hence is not reported here. Correlation coefficients for the upper state ro-vibrational

constants for the 21113←01101 *e*, 21113←01101 *f* and the 40002 ←10002 bands (interacting bands) of $^{12}\text{C}^{16}\text{O}_2$ are listed in **Table 6(b)**.

Insert Table 6(a) and 6(b) here

Comparisons of the vibrational band strengths (cm/molecule at 296 K) for a few selected bands measured in the **PS** with Toth et al. [11] are provided in **Table 7**. Only those bands whose vibrational band strengths, S_v , have been determined using theoretical quantum mechanical expressions (constraints) are listed in this table. Recall that measurements in [11] were made without using constraints.

Table 7 comes here

Vibrational band strengths (S_v) for nine bands (five for the main isotopologue $^{12}\text{C}^{16}\text{O}_2$, two for $^{13}\text{C}^{16}\text{O}_2$ and two for $^{12}\text{C}^{16}\text{O}^{18}\text{O}$) are given in **Table 7**. The upper and lower levels for the bands with approximate band centers (for identification of bands) are also provided. For all cases, including the enriched samples, appropriate abundances for the various isotopologues for a natural carbon dioxide sample were used in determining the intensities.

Often the vibrational band strength, S_v , differs from the integrated band strength, S_{band} , which is defined as the sum of the intensity of all lines in the band. The following discussion shows the relationship between the sum of the line intensities and the vibrational band strength and presents the results determined from present measurements whose values are listed in **Tables 6 and 7**.

Starting from the general expression for the intensity of a line in terms of the total transition moment squared, which in general contains all interactions (for example see **Eq. (38)** of Ref. [51] or **Eq. (17)** of Ref. [52]), the vibrational band strength can be defined as follows. Assuming no interactions, the total transition moment squared can be written as a product of a rotationless (vibrational) transition moment squared times the transition moment squared for a rigid rotor (Hönl-London factors). Further, assuming $Q_{\text{tot}} = Q_{\text{vib}} \times Q_{\text{rot}}$, *i.e.*, the product approximation for

the partition sum, the line intensity expression can be written as a vibrational part times a rotational part. S_v is defined by the vibrational part,

$$S_v = \frac{8\pi^3}{3hc} \nu_{v' \leftarrow v''} \left(\frac{e^{-C_2 E_{v''}/T}}{Q_v} \right) |R_{v' \leftarrow v''}|^2 \quad (7)$$

where, h is Planck's constant, c is the speed of light, $\nu_{v' \leftarrow v''}$ is the vibrational band center corresponding to ν_0 in Eq. (2), $E_{v''}$ is the lower state vibrational energy, C_2 is the second radiation constant ($\text{cm}^{-1} \cdot \text{K}$), T is the temperature in Kelvin, Q_v is the vibrational partition sum, and $|R_{v' \leftarrow v''}|^2$ is the vibrational transition moment squared. Furthermore, if the line intensity expression is summed over all lines of a band, a sum rule can be applied reducing the rotational part to 1 giving $S_v = S_{\text{band}}$. Note, this is only for the case for no vibration-rotation interactions. Further details are available in Ref. [52].

When vibration-rotation interactions are present, the line intensity formula is generally augmented with the Herman-Wallis factor, which defines the departure of line intensities from rigid-rotor behavior (see **Eq. (2)**). In such cases S_v does not equal S_{band} . The difference between the two can be used as a proxy to the strength of the vibration-rotation interactions. For most parallel bands the differences are only a few percent. In the present study, the ratio of the integrated band strength, S_{band} , to the vibrational band strength, S_v , is 1.033, indicating a small vibration-rotation interaction for this band. When the vibration-rotation interactions are strong, significant differences between S_{band} and S_v are observed, see for example Rinsland et al. [53].

The integrated band strength S_{band} for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$ from **PS** is obtained by summing up the measured (or calculated) individual line intensities to be 7.110×10^{-21} cm/molecule at 296 K and shows excellent agreement (except Ref. 44)) with the band strength values of 7.127×10^{-21} [11], 7.145×10^{-21} [36,45], 8.042×10^{-21} [44] and 7.134×10^{-21} [50] cm/molecule at 296 K. The vibrational band strength S_v for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$ from **PS** obtained directly from our multispectrum least squares fittings and listed in **Table 6(a)** is 6.884×10^{-21} cm/molecule at 296 K. Thus we find that the ratio of the integrated band strength

S_{band} (7.110×10^{-21} cm/molecule) to the vibrational band strength S_v (6.884×10^{-21} cm/molecule) for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$ is 1.033, indicating a small vibration-rotation interaction for this band. For the same band, a similar ratio (1.033) has been obtained between S_{band} and S_v by Toth et al. [11].

4.3. Interacting bands and Fermi resonance

Two pairs of bands in this study have interacting levels involved in Fermi resonance. The first of these interacting pairs, the 12212 $\leftarrow$ 00001 and the 23301 $\leftarrow$ 00001 bands of $^{12}\text{C}^{16}\text{O}_2$, is located near the high wavenumber limit of the fitted interval. This interaction is due to an unusual resonance where the predicted level crossing near $J = -25$ is avoided. While $J < 0$ is not physically allowed, this mathematical “crossing” still affects the energy of the allowed levels for $J > 0$. The interacting vibrational energies are separated by just over 2 cm^{-1} . The 12212 $\leftarrow$ 00001 band is very weak; also no lines of the weaker 23301 $\leftarrow$ 00001 band could be identified to report the corresponding intensities. This prevented us from modeling the interaction between these bands. However, for the weak 12212 $\leftarrow$ 00001 band, 24 line positions and 25 line intensities between P50 and R52 were individually measured; the remaining higher J line parameters were fixed to the values of the HITRAN2004 database [44].

The second interacting pair consists of a very weak 40002 $\leftarrow$ 01101 band which interacts with the e component of the much stronger 21113 $\leftarrow$ 01101 band of $^{12}\text{C}^{16}\text{O}_2$ (first hot band of 20013 $\leftarrow$ 00001 and the second strongest band in the spectral region after 20013 $\leftarrow$ 00001). Without the interaction, the 40002 $\leftarrow$ 01101 band would not be seen in our data. The modeling is complicated because the 21113 f level is not interacting and its transitions are visible in the spectrum. This prevents the solution from overly adjusting the interaction to compensate for other uncertainties in the solution. Line parameters for both interacting bands were adjusted and the unperturbed lines (f components) of the 21113 $\leftarrow$ 01101 band were constrained to the same position and intensity constraints as for the perturbed lines. The same interaction coefficient was forced to be used for both the positions and intensities of the two bands. **Eqs. (1-3)** were used to compute the unperturbed positions and intensities of all lines with only the rotation-vibrational constants, vibrational band strengths and Herman-Wallis constants varied in the solution. A

single interaction coefficient was then used to compute the perturbed positions and intensities of the lines involved in the interaction using the formulation of Ref. [54]. The perturbed energies, E , of the upper levels at each J were found from the two unperturbed energies, E_1 and E_2 and the interaction constant W_{12} [55].

$$E = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{4|W_{12}|^2 + \delta^2} \quad (8)$$

$$\delta = (E_1 - E_2) \quad (9)$$

$$W_{12} = \Omega\sqrt{J(J+1)} \quad (10)$$

Ω is the interaction coefficient for the two bands. The perturbed intensities, I^p , of the spectral lines are computed from the unperturbed intensities, I^0 , and the parameters above by the following relationships.

$$\sqrt{I_1^p} = c\sqrt{I_1^0} - d\sqrt{I_2^0} \quad (11)$$

$$\sqrt{I_2^p} = d\sqrt{I_1^0} + c\sqrt{I_2^0} \quad (12)$$

$$c = \left(\frac{\sqrt{4|W_{12}|^2 + \delta^2} + \delta}{2\sqrt{4|W_{12}|^2 + \delta^2}} \right)^{0.5} \quad (13)$$

$$d = \left(\frac{\sqrt{4|W_{12}|^2 + \delta^2} - \delta}{2\sqrt{4|W_{12}|^2 + \delta^2}} \right)^{0.5} \quad (14)$$

This interaction shares many of the features of the weaker interacting pair (12212←00001 and the 23301←00001 bands of $^{12}\text{C}^{16}\text{O}_2$) discussed earlier. The mathematical crossing for this interacting pair is near $J = -15$, but the separation of the upper state vibrational levels is only 0.48 cm^{-1} (compared to $\sim 2 \text{ cm}^{-1}$ for the other weaker interacting pair). This smaller separation makes

the interaction much stronger. The result is that up to 8% of the intensity of the stronger band is transferred to the weaker band and the positions of the lines in the two bands are moved as much as 0.15 cm^{-1} . **Fig. 6(a)** displays the shift of each spectral line in position as a function of J' of this band. The shift in position starts at $J'=0$ since the interaction coefficient is multiplied by $J'(J'+1)$. The shift grows rapidly due to the rapid change in $J'(J'+1)$, but then eventually slows and turns around near $J'=50$ at a shift of about 0.15 cm^{-1} due to the increasing value of δ (separation between the unperturbed energies).

The fraction of the intensity of the stronger band borrowed by the weaker band is plotted in **Fig. 6(b)**; the effect is zero at $J'=0$ due to the $J'(J'+1)$ factor in the interaction constant. Around $J'=15$, the intensity borrowing peaks at about 8% and then starts a slow decline due to the increasing distance from the mathematical crossing until a minimum of about 4.5% occurs near $J'=50$. The $J'(J'+1)$ factor then overcomes the larger δ very slowly until a peak of about 4.5% occurs near $J'=70$. The interaction coefficient is determined to be 0.019295(5) compared to 0.019300(140) as found by Toth et al. [11]. This few percent of intensity of the stronger band is still about 2000 times the intrinsic intensity of the weaker band (see **Table 6(a)**). While the effect is small (a few percent) on the stronger band, the effect on the weaker band is very large and the characterization of the interaction is crucial.

Figs. 6(a) and 6(b) come here (interacting band)

The band strength of the weaker band ($40002 \leftarrow 01101$) was too small to be determined in our solution, but by trial and error, an approximate value was found. The weaker band's intrinsic intensity is about 50000 times smaller than that of the stronger band (**Table 6(a)**), but the lines are visible because the interaction transfers significant intensity into the weaker band. Note that the interaction coefficient that affects both the intensities and positions of both bands is determined with an uncertainty of 0.03%.

4.4. Lorentz half-width coefficients and their temperature dependences

Numerous pressure-broadened half-width and pressure-shift coefficients were also determined from the present study. The best information on the width and shift coefficients is from spectra with large amounts of carbon dioxide and high pressures. With traditional single spectrum analysis, these spectra pose a number of difficulties. First, the broader lines are more likely to be blended, and it is difficult to retrieve reliable individual half widths. Second, for lines having larger optical depths, retrieval of the Lorentz half width is highly inversely correlated with the intensity of the line. Thus, constraining line intensities of both the strong and weak transitions to the same theoretical formula using multispectrum fitting technique provides internally consistent retrievals. With the better-determined intensities, the measured values of the individual half-widths are more precise.

The measured air- and self-broadened Lorentz half-width coefficients, pressure-shift coefficients, and their corresponding temperature dependences along with line positions and intensities are listed in the **Supplemental file** (discussed later). The majority of the half-width and pressure-shift coefficients were measured for the strongest band (20013←00001) and its first hot band (21113←01101) of $^{12}\text{C}^{16}\text{O}_2$. Similar parameters could be measured only for a fewer number of transitions in other bands. Temperature dependences of half-widths, pressure-shifts and off-diagonal relaxation matrix elements were measured only for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$.

As example, in **Table 8**, all measured line parameters (except the off-diagonal relaxation matrix element coefficients) for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ are listed for the P20-R20 transitions. In the **Supplemental file**, the air- and self-broadening parameters (widths, shifts and their temperature dependences) for all measured transitions are listed under separate columns. In the sample **Table 8**, the line parameters for air-broadening are given at the top of each row, and the self-broadening parameters are given underneath. The identification of each transition, its position and intensity (with corresponding uncertainties) are provided. For the line intensities, half-width coefficients and their temperature dependence exponents, uncertainties in % are given in the column next to their values while the uncertainties for positions, pressure-shift coefficients and their temperature dependences are provided in parentheses corresponding to the last quoted digits. The last two columns in **Table 8** list the quadratic speed dependence

parameter for each transition and their % uncertainties. We have assumed that the speed dependence parameter is independent of both the broadening gas (CO₂ and air in this study) and the temperature of the gas sample, hence a single value common to both CO₂-CO₂ and CO₂-air broadening has been assumed. Lisak et al. [56] recently published theoretical prediction for the temperature dependence of the quadratic speed dependence parameter. Future analysis could include this model as an appropriate physical constraint on the speed-dependent parameter.

Insert Table 8 here

The values in **Table 8** are representative of the high precision achieved in our multispectrum fittings (for strong, unblended lines) where the random errors are minimized to the noise levels of the spectra. All listed uncertainties correspond to one-sigma internal statistical errors in the last quoted digit(s) obtained from the multispectrum fit. The uncertainties listed above do not include any systematic errors that might arise due to unknown sources (*e.g.*, uncertainties in the physical conditions of spectra, absorption path lengths, line shape model used).

The measured air- and self-broadened half-width coefficients for the 20013←00001 are plotted vs. m ($m = -J''$ for P-branch lines and $J''+1$ for R-branch lines) in **Fig. 7**, where the values are compared to those measured by Toth et al. [12,13], Régalia Jarlot et al. [18], and HITRAN2012 [45]. Even though there are no theoretical constraints to the half-width coefficients, the values still follow a fairly smooth curve; however, at high J , the half-width coefficients are less well determined because of the weakness of those absorptions (even in spectra with the largest gas amounts, especially at cold sample temperatures). The uncertainties are also plotted, but they are not visible in most cases since their values are smaller than the symbol size. Toth et al. [12,13] fitted their measured half-width coefficients to a model (polynomial expression in m) after measuring each value individually; as seen in **Fig. 7**, the trend with J is smooth. The width coefficients in HITRAN2012 [45] also follow a smooth curve since those were calculated using an empirical polynomial expressions in m obtained by fitting measured values. Also included are the predicted Lorentz air- and self-broadened half-width coefficients by Gamache and Lamouroux [57] which are in very good agreement with other measurements and calculations.

Insert Fig. 7 comes here (half-width coefficients)

The ratios of self- and air-broadened half-width coefficients from **PS** to Toth et al. [12,13] as a function of m are plotted in **Figs. 7(b)** and **7(c)**, respectively. The ratios of self- to air-broadened half-width coefficients as a function of m from **PS**, Toth et al. and HITRAN2012 are shown in **Fig. 7(d)**. As expected, the self-width to air-width ratios are m -dependent and vary from 1.19(13) to about 1.28(10) in the three cases compared. The mean ratios from **PS** and Toth et al. [12,13] agree well while the mean ratio from HITRAN2012 [45] gives a smaller value, but all three ratios agree within the mutual scatter from the other two ratios.

The temperature dependence exponents for air- and self- broadened half-width coefficients (n_1 and n_2 , respectively) for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ have been determined in the **PS**. A power law model shown in **Eq. (4)** was applied to fit all the spectra (see **Table 3**) simultaneously. These power law parameters (n_1 and n_2) are needed on a line-by-line basis for accurate remote sensing of CO_2 . The measured n_1 and n_2 are shown as a function of m in **Fig. 8(a)**. The black horizontal dashed line corresponds to the value of $n = 0.75$, usually assumed when no measured values are available.

Fig. 8 comes here (T-dep. Widths)

Since no extensive measurements for temperature dependence exponents of half-width coefficients for air- or self-broadening have been published in the literature, the present values for n_2 are compared to the experimental measurements reported for the 20012←00001 band of $^{12}\text{C}^{16}\text{O}_2$ by Suarez and Valero [17]. Although measurements in [17] were available only for $m = 6-32$, the general pattern of the variation of n_2 vs. m is similar to what is observed in the present work. In the **PS**, the variations are almost identical in the P and R branches. The n_2 values beyond $m=50-54$ are uncertain because when the sample is cooled, high J lines become weak and often disappear from lower temperature spectra. For air broadening, there are no previous measured temperature dependence exponents available for this band. The temperature dependence exponents for air-broadening are larger than those for self-broadening, and the variation of n_1 vs. m mirrors the m -variation seen in n_2 .

In **Fig. 8(b)** we have plotted previously measured values for the 30013←00001 (1.6- μm) band of $^{12}\text{C}^{16}\text{O}_2$ [58]. The behavior of n_1 and n_2 vs. m is similar to that obtained for the 20013←00001 band shown in **Fig. 8(a)**. A similar pattern was observed in calculated temperature dependence exponents for self-broadening reported by Predoi-Cross et al. [59] for the 30012←00001 and the 30013←00001 bands of $^{12}\text{C}^{16}\text{O}_2$ where the authors modeled their self-broadened half-width coefficients using semi-classical calculations based upon the Robert-Bonamy formalism [60]. The values in [61] for n_1 and in [59] for n_2 are not included in **Fig. 8(b)** for two reasons: (1) these 1.6 μm bands were measured using a different [59] line mixing approach, and (2) the results were more scattered, especially for n_2 , making it difficult to decipher. In **Fig. 8(c)** we have included the predicted temperature dependence exponents for n_1 and n_2 by Gamache and Lamouroux [57]. The variations in n_1 and n_2 with m [57] show overall similar patterns observed in **(a)** and **(b)**.

4.5. Air- and self-shift coefficients and their temperature dependences

Air- and self- pressure-shift coefficients, $\delta^0(\text{air})$ and $\delta^0(\text{self})$, and their temperature dependences $\delta'(\text{air})$ and $\delta'(\text{self})$ are measured for lines of the dominant 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$. Measurements were also obtained for a number of transitions in the 21113←01101 hot band of $^{12}\text{C}^{16}\text{O}_2$. Similar to the Lorentz half-width coefficients, the pressure-shift coefficients were also measured for a number of the stronger transitions in a few other bands (see the **Supplemental file**).

The measured parameters for the 20013←00001 band are displayed in **Fig. 9**. The pressure-shift coefficients are plotted in the top panel **(a)**. Values from the **PS** are compared to the measured values by Toth et al. [12,13] and values from the HITRAN2012 compilation. For m (-20 to +20), the self-shift coefficients from **PS** are larger (more negative) compared to [12] while the air-shift coefficients are more consistent to those in [13]. The air-shift coefficients in HITRAN2012 are calculated values using experimental measurements modeled with empirical polynomial expressions and therefore follow a smooth curve with m . The HITRAN2012 compilation does not list self-shift coefficients.

Insert Fig. 9 here

The self-shift coefficients from **PS** (**solid red up triangles**) are more strongly negative than those from Toth et al. [12] and follow a strange pattern, especially for m in the -20 to +20 range. The reason for this is not obvious, but it could arise from strong correlation between pressure shifts and line mixing, resulting in some interplay in the observed pressure shifts and the large relaxation matrix element coefficients seen for CO₂-CO₂ mixing between the P-branch transitions (discussed later in the line mixing section). Normally, self-shift coefficients are measured more precisely than the air-shift coefficients due to the larger optical densities in pure sample spectra. In the **PS**, the self-shift coefficients do show more scatter and higher uncertainties than the air-shift coefficients (**solid blue triangles**).

The temperature dependences of the air- and self-shift coefficients, $\delta'(\text{air})$ and $\delta'(\text{self})$, are shown in **Fig. 9(b)**. Similar to the temperature dependence exponents for air- and self-broadened Lorentz half-width coefficients, the patterns seen in the temperature dependences of pressure-shift coefficients are also quite different. Panel **(b)** shows that $\delta'(\text{self})$ is more negative compared to $\delta'(\text{air})$ until $m=30-34$, beyond which $\delta'(\text{self})$ are more positive compared to $\delta'(\text{air})$. $\delta'(\text{self})$ shows the largest negative value of nearly $-0.000045 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$ near the lowest J and slowly becomes less negative until its value reaches zero near $m=30-34$ and increases slowly to a positive value close to $+0.00002 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$ near $m=50$ and higher. Beyond $m=50$, their values are subject to higher uncertainty due to weakness of these lines at low temperatures.

$\delta'(\text{air})$, starts near $-0.00001 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$ around $m=0$ and becomes slightly more negative in the R branch for $m=20-24$ and remain close to zero until $m=50$; while its value in the P branch remain close to zero from $m=10$ until $m=50$; $\delta'(\text{self})$ and $\delta'(\text{air})$ cross *zero* temperature dependence coefficient near $m=30$. This mirror behavior in $\delta'(\text{air})$ and $\delta'(\text{self})$ is also seen in **Fig. 9(c)** where plots for the 30013←00001 band of ¹²C¹⁶O₂ are shown [58], except the crossing occurs near $+0.000015 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$ for $m=40-44$. The differences in magnitudes between $\delta'(\text{air})$ and $\delta'(\text{self})$ for the 20013←00001 band shown in panel **(b)** and the 30013←00001 band shown in panel **(c)** may be related to the differences between the magnitudes of the pressure-shift coefficients themselves (wavenumber dependence of pressure-shift coefficients).

4.6. Off-diagonal relaxation matrix element coefficients and their temperature dependences

As higher pressure spectra were added to the global least squares fittings, the need to include line mixing became obvious. Line mixing using the off-diagonal relaxation matrix element coefficients (W_{ij} in $\text{cm}^{-1} \text{ atm}^{-1}$) were included using the formalism of Lévy et al. [26]. In the analysis we included the mixing only between the nearest neighbor transitions. To make the fitting program work smoothly, initially, the relaxation matrix element coefficients were slowly activated for a few transition pairs in the P and the R branches, and for CO_2 -air and CO_2 - CO_2 mixing starting from the center of the band (*i.e.*, lowest J) and slowly adding higher- J transitions. Statistical weights of $2J''+1$ were assigned to each line with the appropriate J'' .

In principle, if the dataset contains spectra at multiple temperatures, the temperature dependence exponents of the relaxation matrix element coefficients should also be determinable. Similar to building the relaxation matrix elements starting with zero values initially, the temperature dependence exponents for both CO_2 - CO_2 and CO_2 -air states could also be setup in both P and R branches with initial default values (*e.g.*, 0.75, a value similar to the temperature dependence exponents for the Lorentz half-width coefficients) and their values carefully adjusted until all residuals characteristic of line mixing disappear. In practice, fitting the temperature exponents of the line mixing has proved challenging. In our analysis of the 1.6- μm CO_2 band [58] as well as the $2\nu_3$ band of CH_4 [62], we have not been very successful in retrieving the temperature dependence exponents for all of the measured relaxation matrix element coefficients. In this study, we have measured the temperature dependence exponents for low- J to mid- J transitions for both CO_2 - CO_2 and CO_2 -air mixing in the P and R branches (*e.g.*, P6 & P8 – P30 & P32 and R6 & R8–R28 & R30 and listed in **Table 9**). In determining these temperature dependence exponents, we have assumed the same power-law model (**Eq. 4**) applied to the temperature dependence exponents of the Lorentz half-width coefficients.

The off-diagonal relaxation matrix element coefficients for CO_2 - CO_2 and CO_2 -air mixing listed in **Table 9** have been measured in the **PS** for the maximum J up to 50 in the P branch and up to $J=46$ in the R branch. All other W_{ij} elements that could not be retrieved were fixed to a default value of $0.004\text{-}0.005 \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K (for the nearest neighbor transitions) up to P58 & P60

in the P branch and R48 & R50 in the R branch (corresponding to J for which Lorentz half-width coefficients were obtained).

Table 9 comes here

The measured values of W_{ij} ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K) are plotted in **Fig. 10(a)** as a function of m . The measured W_{ij} vary from 0.0047 to 0.047 for $\text{CO}_2\text{-CO}_2$, and between 0.0064 and 0.0022 for $\text{CO}_2\text{-air}$ mixing in the P branch. In the R branch, the range of W_{ij} ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K) varies between 0.0043 and 0.028 for $\text{CO}_2\text{-CO}_2$, and from 0.0025 to 0.023 for $\text{CO}_2\text{-air}$. From **Table 9** and **Fig. 10(a)** it is apparent that the value of the relaxation matrix element coefficients slowly increase from the center of the band and reach the maximum value around $m = 20$ and then fall off slowly until the highest J for which measurements are made. The W_{ij} coefficients are not the same (but close) for the same m in both the P and R branches. Generally the measured W_{ij} for $\text{CO}_2\text{-CO}_2$ are larger compared to $\text{CO}_2\text{-air}$, perhaps analogous to the corresponding self- and air-broadened Lorentz half-width coefficients as observed in our previous and recent studies of the $1.6 \mu\text{m}$ CO_2 band [e.g., 58]. In **Fig. 10(a)** we have plotted the results from our earlier room temperature measurements for the 20013←00001 band [16] for purpose of comparison with the present measurements. It is clear that the relaxation matrix element coefficients from **PS** for $\text{CO}_2\text{-air}$ (**blue inverted triangles**) are comparable to those measured in [16] (**purple stars**) in both the P and R branches. However, the line mixing coefficients for the P branch from **PS** for $\text{CO}_2\text{-CO}_2$ (**solid black up triangles**) are higher than those determined from room temperature measurements (**solid green squares**) and extend to a few more higher- J transition pairs while those for the R branch are nearly the same in both the **PS** and in [16]. In the R branch, range for $\text{CO}_2\text{-CO}_2$ mixing extends only up to R34 & R36 transition pairs in the **PS**, but it was measured to slightly larger J range (R36 & 38) in [16]. The maximum value for W_{ij} in the R branch is $\sim 0.03 \text{ cm}^{-1} \text{ atm}^{-1}$. In the P branch, the range of W_{ij} for $\text{CO}_2\text{-CO}_2$ extends to P46 & P48 in the **PS** and the maximum W_{ij} is $0.047 \text{ cm}^{-1} \text{ atm}^{-1}$ compared to the range P42–P44 and maximum W_{ij} of $\sim 0.035 \text{ cm}^{-1} \text{ atm}^{-1}$ in [16]. In the **PS**, the maximum value of W_{ij} for $\text{CO}_2\text{-CO}_2$ is shifted to higher J (~ 36) compared to the room temperature study for J (~ 28). A small upward shift in the P branch W_{ij} for the $\text{CO}_2\text{-CO}_2$ mixing starts near P20–P22 and reaches a maximum of $0.047 \text{ cm}^{-1} \text{ atm}^{-1}$ for P38 & P40 transitions; this is nearly 55% higher than the value in the R branch. We are not able to

explain this peculiar behavior, except for the fact that the hot band 21113←01101 (centered near the P-branch side of 20013←00001 band) is in Fermi resonance with the 40002←10002 band. Since line mixing is strongly correlated with pressure shifts, this peculiar pattern of W_{ij} in **Fig. 10(a)** could be responsible for the odd pattern for self-shift coefficients shown in **Fig. 9(a)**. Temperature dependence exponents of the relaxation matrix element coefficients were obtained only for low- J to mid- J transitions; their values are listed in **Table 9** (but not included in the plots). For all unmeasured transition pairs, their values were fixed to either 0.8 or 0.7 (see **Table 9**). To avoid complexity in the plots, the relaxation matrix element coefficients, W_{ij} , for the 30013←00001 band [58] are not included in **Fig. 10(a)**.

Line mixing was also measured for a few transition pairs for both CO₂-CO₂ and CO₂-air in the Q branch of the 21113←01101 band of ¹²C¹⁶O₂. The results are appended at the end of **Table 9**. Although it was required to include line mixing for the Q branch of this hot-band to obtain a better fit, those values should be considered only as approximate at best. Temperature dependence exponents for those relaxation matrix element coefficients were fixed to a default value of 0.7. Statistical weights of $2J''+1$ were applied while retrieving those relaxation matrix element coefficients.

Fig. 10 comes here (Line mixing and speed dependence)

4.7. Speed dependence

Speed dependence of the Lorentz half-width coefficients were measured for 112 transitions mostly belonging to the 20013←00001 and the 21113←01101 bands of ¹²C¹⁶O₂. These correspond to ~20% of the constrained lines for the strong and medium strength transitions (see **Table 5**). Measurement of this parameter requires measuring well into the wings of the Lorentz profile, so spectra with more carbon dioxide (stronger lines) and good signal-to-noise ratios were required. The measured speed dependence parameters for the 20013←00001 band are plotted as a function of m in **Fig. 10(b)** and compared to values from previous room temperature measurements [16].

The quadratic speed dependence of the Lorentz half-width coefficients was measured using the following expression from Ref. [63] and given in **Eq. (15)** below, similar to our previous studies [*e.g.*, 37,38,58,62].

$$b_L^0(v) = b_L^0(v_m) \left\{ 1 + S \left[\left(\frac{v}{v_p} \right)^2 - c \right] \right\} \quad (15)$$

In the above expression, v is the speed of the molecular collision, v_m is the mean speed of the molecular collision, v_p is the most probable speed of the collision, S is the speed dependence parameter (SD) reported in this study, and c is a constant whose value is taken to be 1.5. When **Eq. (15)** is implemented into the Voigt expression and integrated over all velocities of collision, the resulting real (K_s) and imaginary (L_s) parts for the line shape are given by **Eq. (16)**.

$$K_s(x, y, S) = \frac{2}{\pi} \int_{-\infty}^{\infty} e^{-v^2} v \tan^{-1} \left\{ \left[\frac{v+x}{y(S\{v^2-c\}+1)} \right]^2 \right\} dv \quad (16a)$$

$$L_s(x, y, S) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-v^2} v \ln \left\{ \left[\frac{v+x}{y(S\{v^2-c\}+1)} \right]^2 + 1 \right\} dv \quad (16b)$$

Where,

$$x = \sqrt{\ln 2} |v - v_0| / \alpha_D, y = \sqrt{\ln 2} b_L^0 / \alpha_D, \text{ and } \alpha_D \text{ is the Doppler half-width (cm}^{-1}\text{)}.$$

For transitions for which speed dependence was not measured, values were fixed to 0.08 for P52-P84 and for R40-R84 (see the last two columns in the **Supplemental file**). The measured values of the speed dependence plotted in **Fig. 10(b)** are compared to values from our room-temperature analysis [16]. It is clear that the results obtained in the **PS** are about 8-10% larger compared to the peak values for the R- and P-branch transitions [16]; the change is more pronounced for the $|m|$ values between 10 and 20. No obvious reason could be offered for this discrepancy except for the fact that the present study included a number of low-temperature spectra while the previous study involved only room-temperature data. We also assumed that the speed dependence parameter is independent of both the broadening gas (CO₂ and air in this study) and the temperature of the gas sample, hence a single value common to both CO₂-CO₂ and CO₂-air

broadening has been assumed. As stated earlier, Lisak et al. [56] recently published theoretical prediction for the temperature dependence of the quadratic speed dependence parameter.

Speed dependence parameters were also measured for a number of transitions of the P- and R-branches of 21113←01101 band, but they are not included in **Fig. 10(b)**. Some of the new line shape models and updated databases including software for line mixing in CO₂ should be considered for improving the accuracy in future analysis of laboratory data requiring atmospheric remote retrievals [57, 64-68].

4.8. Influence of line mixing in fitting laboratory spectra

To illustrate the influence of line mixing in the retrieved parameters, we plot in **Fig. 11(a)** an air-broadened carbon dioxide spectrum and its fit residuals in **(b)** where line mixing was excluded in the final fit, and in **(c)** with line mixing included. The final fit shown was obtained from the multispectrum fit of all 27 spectra, and the graphs in panels **(a)**, **(b)** and **(c)** are shown for one spectrum, as an example, taken from the multispectrum fit. The plots clearly demonstrate the point that except for the residuals under the strongest 20013←00001 band due to neglect of line mixing, the entire wavenumber interval (4700-4930.5 cm⁻¹) has been fitted with no other detectable residuals **(c)**. The plots also illustrate that line mixing was not required in any other bands under the present experimental conditions of the spectra fitted. The graphs in **Fig. 11** compare remarkably well to **Fig. 6** by Hartmann et al. [25] illustrating the influence of line mixing on atmospheric retrievals of CO₂ from space. Theoretically, line mixing could be measurable for all the bands producing absorption in the fitted region. In experimental data, it would be necessary to include spectra with very large optical densities *and* carbon dioxide molecules, such as those obtained with cavity ring-down and photo-acoustic techniques, not only for the major carbon dioxide isotopologue but also for each of the rarer isotopologues producing absorption.

Insert Fig. 11 here (influence of line mixing)

5. Uncertainties in some measured parameters

To estimate the total error budget in our measurements it would be useful to provide a few details illustrating the precision (excluding systematic errors) obtained. We present the best precision achieved in all of the line parameters by simultaneously fitting a number of spectra with careful choice of their experimental physical conditions for the gas samples.

5.1. Line positions and intensities

Uncertainties in zero pressure line positions are plotted in **Fig. 12** as a function of J' for the strongest band in the measured region, 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$. The theoretical expressions (**Eqs. 1-3**) used in the fittings result in the smooth J -dependence of these uncertainties that follow a simple function as displayed in **Eq. (17)**.

$$\begin{aligned} \varepsilon_v^2 = & \varepsilon_{G'}^2 + 2q\rho_{G'B'}\varepsilon_{G'}\varepsilon_{B'} + q^2(\varepsilon_{B'}^2 - 2\rho_{G'D'}\varepsilon_{G'}\varepsilon_{D'}) + 2q^3(\rho_{G'H'}\varepsilon_{G'}\varepsilon_{H'} - \rho_{B'D'}\varepsilon_{B'}\varepsilon_{D'}) \\ & + q^4(\varepsilon_{D'}^2 + 2\rho_{B'H'}\varepsilon_{B'}\varepsilon_{H'}) - 2q^5\rho_{D'H'}\varepsilon_{D'}\varepsilon_{H'} + q^6\varepsilon_{H'}^2 \end{aligned} \quad (17)$$

Here ε is the one standard deviation uncertainty in the parameter in the subscript, q is $J'(J'+1)$ and ρ is the correlation coefficient in the solution between the two parameters in the subscript. For the constrained interacting bands this expression requires several more terms involving the upper state constants for both interacting bands and the interaction coefficient. Both the values of ε and ρ are given in **Table 6** for the constrained bands.

The uncertainties in positions for $0 \leq J \leq 40$ are between 0.6×10^{-7} and $1.1 \times 10^{-6} \text{ cm}^{-1}$, less than $1.1 \times 10^{-5} \text{ cm}^{-1}$ for J' up to 60, less than $1.1 \times 10^{-4} \text{ cm}^{-1}$ for J' up to 80. As always, the extrapolation of the uncertainties beyond the range of measured lines are only an estimate assuming that there are no local or non-local resonances or higher order ro-vibrational terms used in the equations.

Insert Fig. 12 (Position uncertainty vs. m)

The uncertainties in the constrained non interacting intensities are computed as indicated in **Eqs. (18-21)**.

$$\varepsilon_{S_i}^2 = S_i^2 \left\{ \frac{\varepsilon_{S_i}^2}{S_v^2} + \frac{A_1}{F^2} + \frac{2}{F} \left[\frac{\varepsilon_{S_i} A_2}{S_v} + \frac{A_3}{F} \right] \right\} \quad (18)$$

where, F is the Herman-Wallis factor as defined in **Eq. (3)**, and

$$A_1 = m^2 \varepsilon_{a_1}^2 + m^4 \varepsilon_{a_2}^2 + m^6 \varepsilon_{a_3}^2 + [J'(J' + 1)]^2 \varepsilon_{a_4}^2 \quad (19)$$

$$A_2 = \rho_{S_i a_1} m \varepsilon_{a_1} + \rho_{S_i a_2} m^2 \varepsilon_{a_2} + \rho_{S_i a_3} m^3 \varepsilon_{a_3} + \rho_{S_i a_4} J'(J' + 1) \varepsilon_{a_4} \quad (20)$$

$$A_3 = \rho_{a_1 a_2} m^3 \varepsilon_{a_1} \varepsilon_{a_2} + \rho_{a_1 a_3} m^4 \varepsilon_{a_1} \varepsilon_{a_3} + \rho_{a_1 a_4} m J'(J' + 1) \varepsilon_{a_1} \varepsilon_{a_4} \quad (21)$$

$$+ \rho_{a_2 a_3} m^5 \varepsilon_{a_2} \varepsilon_{a_3} + \rho_{a_2 a_4} m^2 J'(J' + 1) \varepsilon_{a_2} \varepsilon_{a_4} + \rho_{a_3 a_4} m^3 J'(J' + 1) \varepsilon_{a_3} \varepsilon_{a_4}$$

The definitions of uncertainties, ε and ρ , appearing in the various terms in **Eqs. (18)-(21)** are the same as those in **Eq. (17)**. Expressions for the interacting bands will require many additional terms for the upper states of both the bands involved in the interaction and the interaction coefficient than provided in the above Equations. The values of ε and ρ for the constrained interacting bands are listed in **Table 6**.

The percent uncertainties in the fitted intensities (ratio of intensity uncertainty to intensity $\times 100$) are plotted as a function of m in **Fig. 13** for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$. The percent uncertainty in intensity varies between 0.005% and 0.01% for $|m|$ $0 \leq 10 \leq 50$ and to $\sim 0.1\%$ for $|m|=100$ (notice that there is a minimum percent intensity of $\sim 0.003\%$ near P24). Such high precision in positions (**Fig. 12**) and intensities (**Fig. 13**) was achieved by using the constraints as discussed earlier. The absolute error in measured individual line intensities is limited by the uncertainty due to possible dimer formation that may occur in the sample at cold temperatures or if there is any Collision Induced Absorption (CIA) in addition to systematic errors arising from knowledge of absorption path lengths, pressure and temperature readings and model deficiencies.

Insert Fig. 13 (Percent intensity uncertainty vs. m)

5.2. Lorentz half-width coefficients vs. sample temperature

In order to simulate the spectrum of a molecule or its band(s) at a specific temperature, the uncertainties associated with the spectral line parameters at that temperature are even more important than the uncertainties in their values themselves. If we measure only the half-width coefficients at $T=296$ K and apply its temperature dependence from another source (such as the calculated values available in the HITRAN compilation), it is assumed that the half-width coefficients near 296 K are the best determined values, and the uncertainty in the knowledge of temperature dependence exponent (n) increases the uncertainty in half-width coefficients as the sample temperature moves farther from 296 K (at which our measurements are reported). This is not always the case as we illustrate in the following discussion supported by the present measurements.

In **Fig. 14**, we have plotted the uncertainties (internal one sigma values) in the measured Lorentz half-width coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$) vs. gas sample temperatures (in K) for a set of self- and air-broadened transitions for the $20013 \leftarrow 00001$ band of $^{12}\text{C}^{16}\text{O}_2$. We have shown the variations of half-width uncertainties vs. gas temperature for P4, P18, and R42 transitions to represent low- J , medium- J and high- J transitions. For each graph, the uncertainties without considering the correlations are also plotted to illustrate the significance of incorporating correlations in calculating the uncertainties. For the low- to medium J transitions, the minimum uncertainty tends to be towards the low temperature (200-230 K) range, whereas for the higher J transitions, the minimum uncertainty gets shifted to higher temperature (typically between 270 and 290 K). There are no experimental data above room temperature from this study to see the pattern in uncertainty (the curves drawn above room temperature and below 170 K are extrapolated).

For high- J transitions, the intensities of the transitions become weak at low temperatures and the fit does not determine the half-width coefficients well. Therefore, the temperature region where the half-width coefficients are best determined narrows to only the higher temperatures of the fitted region. It is obvious that the trend toward lower uncertainties at higher temperature for higher J transitions (*e.g.*, R42 self- at the top curve) is akin to the trend towards lower uncertainties at lower temperature for the low- J and mid- J values (*e.g.*, P4 self-).

Insert Fig. 14 (uncertainty in Lorentz width vs. temp)

In **Fig. 15**, graphs showing the relative uncertainty (ratios of half-width uncertainty to half-width coefficients) are plotted vs. gas sample temperature (in K) for the same set of transitions shown in **Fig. 14**. The relative uncertainties with and without considering the correlations among fitted parameters are shown by dashed curves. As in **Fig. 14**, the percent uncertainties remain small for low to mid- J transitions. Similar in **Fig. 14**, to minimize congestion, only few transitions are labeled.

The uncertainty in the Lorentz halfwidth coefficient at temperature T is given **Eq. (22)**.

$$\varepsilon_{b_L^0(T)}^2 = b_L^0(T)^2 \left\{ \frac{\varepsilon_{b_L^0(T_0)}^2}{b_L^0(T_0)^2} + \left[\ln \left(\frac{T_0}{T} \right) \right]^2 \varepsilon_n^2 + 2\rho_{b_L^0(T_0),n} \frac{\ln \left(\frac{T_0}{T} \right) \varepsilon_{b_L^0(T_0)} \varepsilon_n}{b_L^0(T_0)} \right\} \quad \text{Eq. (22)}$$

Here ε is the one standard deviation uncertainty in the parameter in the subscript, and ρ is the correlation coefficient in the solution between the two parameters in the subscript.

Insert Fig. 15 (Relative uncertainty in Lorentz width vs. temp)

5.3. Uncertainties in pressure shift coefficients vs. sample temperature

Uncertainties in air- and self- pressure-shift coefficients vs. gas sample temperature (in K) for the P18, P42, R4 and R18 transitions are plotted in **Fig. 16** for the $^{12}\text{C}^{16}\text{O}_2$ 20013←00001 band. Similar to **Fig. 14**, the uncertainties in the pressure-shift coefficients vs. temperature also tend to be smallest near the middle of the temperature range of the fitted spectra. Uncertainties in air-shift coefficients are smaller than those for self-shift coefficients for all transitions plotted. In the present study, such large differences in pressure-shift uncertainty between air- and self-shift coefficients could be due to the much larger relaxation matrix element coefficients for $\text{CO}_2\text{-CO}_2$ mixing obtained from present study (**Fig. 10(a)**), and the large correlations with self-shift coefficients. Graphs with correlations included in the fit are not shown in this figure. For low- J and medium- J transitions, the uncertainty in air-shift coefficients is small for all temperatures in the fitted temperature range. **Eq. (23)** is used for determining the pressure-shift uncertainty.

$$\varepsilon_{\delta}^2 = \varepsilon_{\delta_0}^2 + (T - T_0)^2 \varepsilon_{\delta'}^2 + 2\rho_{\delta_0\delta'}(T - T_0)\varepsilon_{\delta_0}\varepsilon_{\delta'} \quad (23)$$

Similar to **Eqs. (17)-(22)**, here ε is the one standard deviation uncertainty in the parameter indicated by the subscript, and ρ is the correlation coefficient in the solution between the two parameters in the subscript.

Insert **Fig. 16** (uncertainty in pressure shift vs. gas temperature)

5.4. *Uncertainties in measured relaxation matrix coefficients vs. sample temperature*

Uncertainty in the measured off-diagonal relaxation matrix element coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$) are plotted vs. gas sample temperature (in K) in **Fig. 17**. Plots are shown for two transition pairs, P12 & P14 and R12 & R14 (for $\text{CO}_2\text{--CO}_2$ and $\text{CO}_2\text{--air}$) as marked in the panel. Uncertainties without and with correlations are computed as a function of sample temperature to illustrate their importance in reducing the measured uncertainty which are clearly observed for the two cases of $\text{CO}_2\text{--CO}_2$ mixing. As seen in **Fig. 17**, the uncertainty is much larger for $\text{CO}_2\text{--CO}_2$ than for $\text{CO}_2\text{--air}$. This behavior could be related to the peculiar relaxation matrix element coefficients mentioned earlier and shown in **Fig. 10(a)** and listed in **Table 9**. Compared to $\text{CO}_2\text{--CO}_2$, the uncertainty for $\text{CO}_2\text{--air}$ mixing is smaller by a factor of three or more.

Eq. (22) used for uncertainty in Lorentz half-width coefficients could be applied for the line mixing uncertainty (except replacing half-width coefficient b_L^0 with the line mixing coefficient W_{ij}).

Insert **Fig. 17** (Uncertainty in relaxation matrix coefficients
vs. gas sample temperature)

Plots similar to **Figs. 14-17** could be made for all measured line parameters obtained from this study. Representative cases only are discussed here to show that for the accurate simulation of spectra it is not the uncertainties in the Lorentz half-width or pressure shift at 296 K of those

transitions that are important, but the uncertainties in those parameters at the temperature at which the spectrum is to be calculated.

6. Estimated total error budget

With several spectral line parameters investigated in the present study, it is important to provide the absolute errors we estimate in the various measured quantities. Where possible, each measured parameter was listed with its associated uncertainty (in various **Tables**). These values correspond to the formal one-sigma *precisions* resulting from the simultaneous fitting of several spectra. To judge the absolute errors in the retrieved parameters, the errors in the experimental conditions of the spectra and reference standards used in the calibration of wavenumber scales must be evaluated. These errors include uncertainties in the knowledge of absorption cell path lengths, knowledge of gas pressures and temperatures, calibration errors in their monitoring systems, errors due to line shape model deficiencies, weak absorption features whose parameters could not be adjusted in the fits and hence fixed to some theoretical or default values in the least squares solution. Understanding, evaluating and fixing those errors is not trivial, and every effort was made to minimize these errors sources. Simultaneous fitting of several spectra recorded at different gas conditions and using various absorption path cells, including non-Voigt line shapes and the best-fit obtained (**Figs. 1** and **2**) with no significant fit residuals clearly indicate that most such uncertainties are small. The absolute one sigma standard deviations in our measured parameters are *estimated* conservatively to be 0.0001 cm^{-1} for positions, $\leq 1\%$ for line intensities, $< 2\text{-}3\%$ for the Lorentz half-width coefficients (for the strong, unblended lines), $5\text{-}10\%$ in pressure-shift coefficients and in the temperature dependences of width and shift coefficients. The absolute errors in the off-diagonal relaxation matrix elements and their temperature dependence exponents, and the speed dependence parameters are estimated to be in the $5\text{-}20\%$ (depending on individual lines, their rotational quantum numbers, S/N etc.).

To compute the absolute accuracies in our measured line intensities we have estimated the various contributions due to systematic error sources: (a) $0.3\text{-}0.4\%$ in the knowledge of path lengths, (b) $0.1\text{-}0.2\%$ in pressure readings, (c) $0.1\text{-}0.2\%$ in temperature readings, and (d) $0.1\text{-}0.2\%$ background polynomial fits, field of view corrections, residual phase errors, zero level determinations, and some undetermined contribution due to model deficiencies in our analysis.

The global standard deviation of weighted observed minus calculated fit residuals are only 0.045%, thus eliminating almost all random errors to within the noise levels of the fitted spectra.

After we completed our analysis and in the process of documenting the results, new calculations of line intensities became available. In **Fig. 18** we provide comparisons of our measured line intensities to the only other extensive experimental measurements of Toth et al. [11], calculated line intensities from HITRAN2012 [36,45] and the recent *ab initio* calculations by Zak et al. [50]. In the top panel we have shown the four sets of line intensities (cm/molecule at 296 K) plotted vs. m . In the middle panel (b) we show the position differences between present values and those from Zak et al. The mean and standard deviation of the position differences, (PS-Zak et al.) for P68-R68 is 0.00022(4) cm⁻¹. In the bottom panel (c) the ratios of present line intensities to HITRAN database [36,45], Toth et al. [11] and the *ab initio* values [50] are shown. The following mean ratios with standard deviations are obtained: PS/HITRAN2012=0.993(5); PS/HITRAN2008=0.988(8); PS/Toth et al. [11]=0.992(5) and PS/*ab initio* =0.994(2). Similar observations were made in our study of the 1.6 micron CO₂ band [58].

Insert **Fig. 18** here [Comparisons of Intensities with *ab initio* calculations]

Judging the various plots in **Fig. 18(c)**, very good agreement is seen between present measurements and with those in [45] and [50] for the entire P84-R84 range. Similar agreement is also seen between PS and Toth et al., where the range in J is limited to P58-R58. A small curvature in the intensity ratios between this study and the *ab initio* calculations is clear which could be related to the differences in the models used in the two methods.

Calculations of new line positions and intensities for CO₂ including the 2-μm region have been reported recently [48-50]. For a comprehensive understanding of the changes in the CO₂ line positions and intensities (including the 20013←00001 band of ¹²C¹⁶O₂) listed in HITRAN databases [36,44,45], and to compare our results with the most recent calculations [46-50], we include two figures [Figs. 19 and 20]. In **Fig. 19(a)** comparison of line position differences between HITRAN2012 [45] and CDSD-296 [48] vs. m and in **19(b)** percent intensity differences between HITRAN2012 and CDSD-296 vs. m are shown. In both (a) and (b) the values corresponding to higher m (~60 and beyond shown by **solid red circles**) are predicted values

from various sources (see **Section 4**). As seen in **Fig. 19**, the position differences between HITRAN2012 and CDSD-296 lie between $+0.000033$ and $+0.000184$ cm^{-1} for P58–R62, and beyond that the differences range from -0.00012 to $+0.00283$ cm^{-1} . For the same range in J , the % intensity differences between HITRAN2012 and CDSD-296 are small and vary approximately from -0.9 to $+1.1$ and from -0.3 to -1.0 , respectively.

Insert Fig. 19 here (Comparisons between HITRAN2012 vs. CDSD-296)

In **Fig. 20**, the ratios of line intensities between **PS** and [11,36,45,48-50] vs. m are plotted. We find that line intensities from present study agree well with all the comparisons plotted in **(a)**. The mean and standard deviations of the ratios of line intensities between this study with Toth et al. [11] = 0.992(5); HITRAN2012 = 0.993(5); HITRAN2008 = 0.988(7), Zak et al. = 0.994(3); CDSD-296 = 0.990(3); and Huang = 0.981(5). While the comparisons with Toth et al. are limited to their measured values for P58-R62, all other comparisons are for P84-R84. In panel **(b)**, the following mean ratios for the plots shown are obtained: Zak et al./CDSD-296 = 0.996(5); Zak et al./Huang = 0.997(2), and CDSD-296/Huang = 0.991(6). It is interesting to see that the curvature observed in the intensity ratios between **PS**/Zak et al. and between **PS**/CDSD-296 seen in panel **(a)** is also seen in the plots showing the intensity ratios among other *ab initio* [49,50] and calculated [48] intensities, though to a lesser degree.

Line mixing (off-diagonal relaxation matrix formalism) included in the **PS** could influence line intensities, although its magnitude is not quantified at this time. The very good agreement (0.994 ± 0.003) in line intensities between **PS** and the *ab initio* calculated intensities [50] is very encouraging.

In addition to plotting the intensity ratios discussed above, we have shown several other comparisons in panels **(c) – (f)**. In **(c)** line position differences **PS**-Zak et al. and **PS**-CDSD-296 are shown, **(d)** Ratios of Lorentz air- and self-broadened half-width coefficients between **PS** and CDSD-296, **(e)** temperature dependence exponents of Lorentz air-broadened half-width coefficients from **PS** and CDSD-296, and **(f)** air- pressure-shift coefficients from **PS** and CDSD-296. In addition to the good agreement seen between present measurements and CDSD-296 for

line positions and intensities as seen in panels (a) and (c) for P64-R64, it is very encouraging to see also the good agreements in the self- and air-broadened half-width coefficients, temperature dependence exponents for air-broadened half-width coefficients and air- pressure-shift coefficients obtained from **PS** and the CDSD-296.

Insert Fig. 20 here (Comparisons of several parameters)

Comparisons of line positions and intensities between the present results and the CDSD-296 databank [48], Huang [49] and Zak et al. [50] and line shape parameters with CDSD-296 are compared and plotted.

7. Conclusions

The principal objective of this investigation was to support accurate X_{CO_2} remote retrievals for the OCO-2 mission. As for the 1.6 μm region [58], the present results will be used to generate the absorption coefficients for the OCO-2 retrieval algorithm; these results can also be applied to model spectra for other instruments (such as GOSAT) measuring the 2.06 and 1.6 μm CO_2 bands.

Recent multiple studies have shown that accurate simulations of remote retrievals for well-mixed atmospheric gases (e.g., CO_2 , CH_4) require spectroscopic characterization of molecular line parameters beyond the use of traditional Voigt line shapes to minimize measurement uncertainties without systematic residuals. In the present work we have reduced the fit residuals in our laboratory absorption spectra of pure CO_2 and mixtures of CO_2 in air by including speed dependence and line mixing via off-diagonal relaxation matrix element coefficients. We have further improved the analysis by reducing random errors through simultaneously fitting a large number of experimental spectra (recorded at high resolution and high S/N acquired at various opacities, absorption path lengths, gas amounts and sample temperatures). Important precautionary measures were followed with great care in collecting the laboratory data by carefully monitoring the physical conditions of the data while data were being recorded. New fitting methodologies were implemented for determining the ro-vibrational and band intensity

parameters by constraining the individual line positions and intensities to the known theoretical quantum mechanical expressions. Spectroscopic parameters were determined for several bands that reproduce detectable absorptions in the fitted region by including many weaker features and interfering bands to increase the accuracy of the fits. The high correlations between line intensities and Lorentz half-width coefficients were reduced by appropriate choice of the experimental conditions of the spectra.

The goal of the OCO-2 mission is to retrieve X_{CO_2} with accuracy of 1 part in 400 (0.25 %). Spectroscopy is only one part of the OCO-2 error budget [69]. Therefore, in order to achieve the OCO-2 accuracy goal, the spectroscopic parameters must be known to even higher accuracy. Through the results presented in this work, we have demonstrated that with careful planning and implementing a state-of-the art analysis technique, it was possible to characterize CO_2 spectral line parameters (positions, intensities and line shape parameters) with precision close to ~0.3%. There is still room for improvement in future analyses. For example, off-diagonal relaxation matrix elements for only the neighboring pairs of transitions have been considered, but it is possible that line mixing between non-neighboring transitions could occur. Furthermore, speed dependence associated with only the Lorentz half-width coefficients was included in this study. However, new studies involving different line shape models are appearing in the literature, such as more sophisticated line shapes including speed dependence of pressure-shift coefficients and temperature dependence of speed dependence are being evaluated. Also, assumptions were made in this work for retrieving the temperature dependences of Lorentz half-width (power-law) and pressure-shift coefficients (linear model); the speed dependence was assumed to be independent of the broadening gas and independent of gas temperatures. Perhaps a standard line shape model including line mixing, speed dependence and other more subtle effects such as Dicke narrowing and collision-induced absorption could be required to establish inter-laboratory comparisons and standardization of spectra databases. The situation is complicated by the fact that a single choice of line shape/line mixing formalism is unlikely to produce optimal results under all pressure-temperature combinations of all broadening gases.

We emphasize that the parameterization presented in this study is intended for specific applications for CO_2 retrievals for earth's atmospheric remote sensing. The present

measurements of the temperature dependences for the air- and self-broadened Lorentz widths, pressure shifts and the relaxation matrix element coefficients along with speed dependence result in best precision for the 2.06 μm region for the pressure and temperature conditions applicable to earth's atmosphere. We conclude that, while simulating the spectrum of CO_2 , the full accuracy will be achieved *only* by using the complete, consistent set of parameters; the full accuracy will be reduced if some of the parameters from the present study are applied to another line shape/line mixing model or mixed with parameters obtained from other studies.

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Table titles

1. Summary of line shape measurements^a reported for CO₂ bands near 2 μm .
2. Experimental setups and physical conditions of analyzed CO₂ spectra.
3. Summary of experimental conditions of spectra analyzed.
4. Major bands included in the 2 μm region^a of the fitted interval.
5. Measured line parameters and number of CO₂ measurements.
6. (a) Ro-vibrational constants, vibrational band strengths (S_v), and correlation coefficients of measured CO₂ bands: 4700-4930 cm^{-1} . (b) Correlation coefficients for the upper state ro-vibrational constants for the 21113 $\leftarrow$ 01101 e, 21113 $\leftarrow$ 01101 f and the 40002 $\leftarrow$ 10002 interacting bands of $^{12}\text{C}^{16}\text{O}_2$.
7. Comparisons of vibrational band strengths, S_v (cm/molecule) at 296 K, for select bands^a measured in the 2- μm region of CO₂.
8. A sample of measured line parameters for the P20-R20 transitions in the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$.
9. Measured off-diagonal relaxation matrix element coefficients, W_{ij} ($\text{cm}^{-1} \text{ atm}^{-1}$) at 296 K, and their temperature dependence exponents for CO₂-CO₂ and CO₂-air for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$.

Figure captions

Fig. 1. Five laboratory absorption spectra ($4700\text{--}4930\text{ cm}^{-1}$) of pure CO_2 and dilute mixtures of CO_2 in air in the $20013\leftarrow 00001$ region recorded at high resolution ($0.004\text{--}0.012\text{ cm}^{-1}$) using two different FTS. Spectra shown in (a) and (b) were recorded using the Kitt Peak FTS with a natural sample of CO_2 and a 99% ^{13}C -enriched CO_2 near room temperature. Spectra shown in panels (c)–(d) were recorded at JPL with a Bruker IFS-125HR FTS using a 99.99% ^{12}C -enriched CO_2 and CO_2 +air: (c) Pure CO_2 at 170.3 K, (d) 0.051% CO_2 in air at 295.7 K and (e) $\sim 0.03\%$ CO_2 in air at 169.8 K. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 2. The multispectrum fit of the $4700\text{--}4930\text{ cm}^{-1}$ region covering the strongest $20013\leftarrow 00001$ band of $^{12}\text{C}^{16}\text{O}_2$ and a number of other bands of CO_2 . All 27 experimental spectra are overlaid in the top panel (a) and the weighted observed minus calculated (O-C) fit residuals are plotted in the lower panel (b). The dashed horizontal line in (a) corresponds to the 100% absorption level. Color codes: (Refer Table 3) **Black:** (self-broadened); **Red:** (air-broadened); **Blue:** ($^{13}\text{C}^{16}\text{O}_2$). (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 3. This figure is a re-plot of Fig. 2 with the weighted fit residuals grouped according to different ranges of the sample temperatures. Similar to Fig. 2, the top panel (a) displays all the 27 spectra fitted simultaneously. Panel (b) shows the fit residuals from all 27 spectra at various pressures, temperatures and volume mixing ratios of CO_2 ; (c) shows the two 99% ^{13}C -enriched CO_2 at room temperature; (d) has two pure $^{12}\text{CO}_2$ spectra at 170 and 180 K, and (e) shows five air-broadened CO_2 spectra between 170 and 195 K (see Table 3).

Fig. 4. The comparisons of line position differences (cm^{-1}) plotted vs. m (where $m = -J'', J''+1$ for P- and R-branch lines of the $20013\text{--}00001$ band of $^{12}\text{C}^{16}\text{O}_2$, respectively): Present study [PS]-HITRAN2012 [45] **open black circles**, PS-Toth et al. [11] **open green diamonds**, PS-HITRAN2004 [44] **solid blue triangles**, and PS-HITRAN2008 [36] **solid red stars**. If line positions from PS are compared to only P58-R58 transitions measured in Toth et al. [11], the means and standard deviations for all four comparisons shown above would very nearly be the same: $0.0001716(8)\text{ cm}^{-1}$. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 5. Line intensities (cm/molecule at 296 K) in natural abundance determined for the P and R branches for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ plotted as a function of m ($m = -J''$ for P-branch and $J''+1$ for R-branch lines). A linear scale is used in (a) and a logarithmic scale in (b). In (b) the line intensities and their uncertainties are plotted. In panel (c), ratios of line intensities between **PS**/HITRAN [36,44,45]; and **PS**/Toth et al. [11] are plotted. The error bars in (c) are dominated by the uncertainties in Toth et al. [11]. The reason for the discontinuity observed near P(58) and R(60) may be due to some difficulties in merging intensities beyond Toth et al. [11] experimental values and other calculated intensities [45,48]. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 6(a). The effect on line positions due to crossing interaction (due to Fermi resonance) in the 21103←01101 and 40002←01101 bands of $^{12}\text{C}^{16}\text{O}_2$. The shift in the position of each spectral line as a function of J' is plotted. The shift in position at $J'=0$ is zero but grows rapidly as a function of $J'(J'+1)$ but turns around near $J' = 50$ at a shift of about 0.15 cm^{-1} . See the text for details.

Fig. 6(b). The fraction of intensity borrowed from the stronger band (21103←01101) to the weaker band (40002←01101) of $^{12}\text{C}^{16}\text{O}_2$ plotted vs. J (see the text for details).

Fig. 7. (a) The measured Lorentz air- and self-broadened half-width coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K) for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ plotted as a function of m ($m = -J''$ for P-branch and $J''+1$ for R-branch lines). The half-width coefficients are compared to those by Toth et al. [11,12], HITRAN2012 [45] and Régalia-Jarlot et al. [18] and the predicted air- and self-width coefficients by Gamache and Lamouroux [57]. The ratios of air-broadened widths from **PS** to Toth et al. [13] and for self-broadened widths from **PS** to Toth et al. [12] are plotted in (b) and (c), respectively. The ratios of self- to air-broadened half-width coefficients from **PS**, Toth et al. [12, 13] and HITRAN [45] are plotted in panel (d). Where error bars are not visible the uncertainties are smaller than the size of the symbols used. The means and standard deviations of the ratios are also given, when appropriate.

Fig. 8. Measured temperature dependence exponents for the air- and self-broadened half-width coefficients (n_1 and n_2 , respectively) for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ as a function of m . Upper panel: (a) Measured n_2 (red solid up triangles) and n_1 (solid blue down triangles). The

values for n_2 are from Suarez and Valero (**green open circles**) for the 20012←00001 band of $^{12}\text{C}^{16}\text{O}_2$. Middle panel: **(b)** Measured n_2 (**red solid stars**) and n_1 (**solid blue stars**) for the 30013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ [58]. In the bottom panel: **(c)** The predicted n_2 (**red semi-filled squares**) and n_1 (**blue semi-filled circles**) from Gamache and Lamouroux [57]. The horizontal black dashed line in all three panels corresponds to the temperature dependence exponent $n = 0.75$ (default values normally used). (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 9. Measured air- and self- pressure-shift coefficients, $\delta^0(\text{air})$ and $\delta^0(\text{self})$, and their temperature dependences $\delta'(\text{air})$ and $\delta'(\text{self})$, respectively, are plotted in panels **(a)-(c)**. In **(a)** the air- and self-shift coefficients from PS, Toth et al. [12,13], and HITRAN [45] are shown; in the middle panel **(b)** the temperature dependences $\delta'(\text{air})$ and $\delta'(\text{self})$ for the 20013←0001 band is plotted; in the bottom panel **(c)** the temperature dependences $\delta'(\text{air})$ and $\delta'(\text{self})$ for the 30013←00001 [57] are shown for comparisons. The horizontal black dashed line in **(b)** and **(c)** represents zero temperature dependence. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 10. (a) Measured off-diagonal relaxation matrix element coefficients, W_{ij} , ($\text{cm}^{-1} \text{ atm}^{-1}$) at 296 K for $\text{CO}_2\text{-CO}_2$ and $\text{CO}_2\text{-air}$ plotted vs. m ($m = -J''$ for P branch and $J''+1$ for R-branch lines) for the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$ and comparison to the corresponding room temperature measurements [16], **(b)** The measured speed dependence parameter in the P and R branches for the 20013←00001 band plotted against m . from present study and [16, **indicated here by green ****]. Where error bars are not visible, the uncertainties are smaller than the plot symbol. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 11. Influence of line mixing in fitting the laboratory spectra plotted vs. wavenumber (cm^{-1}). The fit was performed with a Voigt line shape with quadratic speed dependence and no line mixing in the multispectrum fit. **(a)** One spectrum (5.1% CO_2 with a total pressure of 649.73 Torr, 20.941 m path and $T=220.2$ K) plotted from the simultaneous fit of 27 spectra. **(b)** The weighted observed minus calculated fit residuals for the spectrum shown in **(a)**. The characteristic fit residuals associated with line mixing are apparent. **(c)** The same spectrum in **(a)** with relaxation matrix elements included in the fit. Notice the improvement in the fit residuals.

Fig. 12. Uncertainties in the fitted line positions (cm^{-1}) are plotted as a function of J' for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$. With the multispectrum fitting and using the theoretical quantum mechanical formulae, very precise determination of line positions are achieved. At $J'=40, 60$ and 80 , for example, the obtained position uncertainties are nearly 1×10^{-6} , 1×10^{-5} , and 1×10^{-4} (cm^{-1}), respectively.

Fig. 13. The percent intensity uncertainties (ratio of intensity uncertainty to intensity $\times 100$) plotted as a function of m ($-J''$ and $J''+1$ for the P and R branches, respectively) for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$ for P and R branches. See the text for details.

Fig. 14. Uncertainty in measured Lorentz half-width coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$) plotted as a function of gas sample temperature (in K) for the 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$. The graphs are plotted for select J transitions for both self- and air-broadening. These plots illustrate that the minimum uncertainty in measured half-width coefficients does not always correspond to $T=296$ K (where half-width coefficients are usually reported). The inset lists the various transitions for which the graphs are shown. To avoid confusion only P4 self and R42 air are labeled. The dashed curves signify the importance of correlations in reducing the uncertainties in measured half-width coefficients.

Fig. 15. Relative uncertainty (ratios of half-width uncertainty to half-width coefficients) are plotted vs. gas sample temperature (in K) for the same set of transitions shown in **Fig. 14**. The relative uncertainties with and without considering correlations among fitted parameters are shown by dashed curves. As in **Fig. 14**, to minimize the congestion, only few lines are labeled.

Fig. 16. Uncertainty of self- and air- pressure-shift coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$) plotted as a function of gas sample temperature (in K) for 20013 $\leftarrow$ 00001 band of $^{12}\text{C}^{16}\text{O}_2$ illustrating that the minimum uncertainty does not always correspond to $T=296$ K (where pressure shift coefficients are reported). The curves represent uncertainties for both self- and air-shift coefficients for P18, P42, R4, and R18 transitions. Uncertainties in self-shift coefficients are rather higher than for air-shift coefficients (perhaps related to the large $\text{CO}_2\text{-CO}_2$ mixing observed in self broadening). Plots for only a few J -transitions are labeled. Minimum uncertainty occurs generally at lower gas temperatures than at 296 K.

Fig. 17. Uncertainty in the measured off-diagonal relaxation matrix element coefficients ($\text{cm}^{-1} \text{atm}^{-1}$) are plotted vs. gas sample temperature (in K). Plots are made for two transition pairs, P12&P14 and R12&R14 (for $\text{CO}_2\text{-CO}_2$ and $\text{CO}_2\text{-air}$) as marked in the panel. Uncertainties without and with correlations are displayed as a function of temperature to illustrate the importance of correlations in reducing the uncertainty.

Fig. 18. Line intensities from present study are compared to the only other extensive experimental measurements by Toth et al. [11], calculated intensities from the latest HITRAN2012 database [45] and the most recent *ab initio* calculations by Zak et al. [50]. **(a)** Line intensities vs. m . **(b)** Line position differences between **PS** and Zak et al. **(c)** The line intensity ratios for the same set as in **(a)** plotted as a function of m . (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 19. **(a)** Comparison of line position differences between HITRAN2012 [45] and CDSD-296 [48] vs. m . **(b)** Percent intensity differences between HITRAN2012 and CDSD-296 vs. m . In **(a)** and **(b)**, the CDSD-296 data points for P58-P2 and R0-R62 (open black circles and open black triangles, respectively) were calculated using the experimental values from Toth et al. [11] and for the higher m values (**solid red stars** and **solid brown circles**, respectively) from Refs. [48] (See the text for details). (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 20. **(a)** Ratios of line intensities: **PS**/HITRAN2012; **PS**/Toth et al. [11]; **PS**/HITRAN2008; **PS**/Zak et al. [50]; **PS**/CDSD-296 [48]; **PS**/Huang [49], **(b)** Ratios of line intensities between Zak et al./CDSD-296, Zak et al./Huang, and CDSD-296/Huang, **(c)** Line position differences **PS**-Zak et al. and **PS**-CDSD-296, **(d)** Ratios of Lorentz air- and self-broadened half-width coefficients between **PS** and CDSD-296, **(e)** Temperature dependence exponents of Lorentz air-broadened half-width coefficients from **PS** and CDSD-296, and **(f)** air- pressure-shift coefficients from **PS** and CDSD-296. See the text for details. (For interpretation of the reference to color in this figure legend, the reader is referred to the electronic version of this article).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. (6a)

Fig. 6(b)

Fig. 7

Fig. 8

Fig. 9

Figure

Fig. 10

Fig.11

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Figure

Fig. 19

Fig. 20

Table 1

Summary of line shape measurements^a reported for CO₂ bands near 2 μm .

Instrument type	Line shape Model used	Wavenumber Range (cm ⁻¹)	Reference	Gas sample	# Widths (CO ₂ , air)	# T-dep. (widths) CO ₂ , air	# Shifts (CO ₂ , air)	# T-dep Shifts; CO ₂ , air
Bruker IFS-125 HR FTS	Speed dependent Voigt, relaxation matrix	4700-4930	Present Study [PS] ^b	CO ₂ , air	339,246	175,179	320,228	175,175
Bomem DA3 FTS ^c	Voigt	Near 4978 cm ⁻¹	Suarez & Valero 1990 [17]	CO ₂	16	14	None	None
Kitt Peak FTS	Voigt	4750-7000	Toth et al. 2006,2007 [12,13]	CO ₂ , air	Several hundreds (11–15 bands)	None	Several hundreds (11– 15 bands)	None
Diode lasers and FTS	Voigt	P48-R42 (4813-4883)	Régalia-Jarlot et al. 2006 [18]	CO ₂	43	None	None	None
Diode laser	Voigt, Rautian	P8,P10,P12 (4843-4848)	Joly et al. 2008 [19]	CO ₂ , air	3,3	None	None	None
Diode laser ^d	Voigt	R26-R34	Joly et al. 2009 [20]	CO ₂	5	None	None	None
Diode laser ^d	Voigt	R22-R36	Li et al. 2011 [21]	air	None	None	8	8
Diode laser ^d	Voigt	R22-R36	Li et al. 2012 [22]	CO ₂	None	None	8	8
Diode laser ^d	Voigt with Rosenkranz line mixing	R16-R40	Christensen et al. 2012 [23] ^e	CO ₂	None	None	None	None
Diode laser ^e	Several line shapes VP, SDVP, NGP, GP	R2-R18 (4980-4992)	Casa et al, 2009 [24]	CO ₂	9	None	None	None

^aThis table lists examples of recent line shape measurements performed using different experimental techniques and analysis methods. For further details, see the original publications. Measurements that involve only line positions and intensities are not included in this table, though they are referenced in the text.

^b Line mixing for CO₂-air and CO₂-CO₂ via off-diagonal relaxation matrix elements formalism are also obtained for a number of transition pairs (~ 50) for the 20013←00001 band of ¹²C¹⁶O₂.

^c 20012←00001 band of ¹²C¹⁶O₂.

^d Wavenumber coverage is not specified in these papers.

^e Rosenkranz line mixing for CO₂-air for 13 lines.

Table 2

Experimental setups and physical conditions of analyzed CO₂ spectra.

Parameters	Kitt Peak FTS	JPL Bruker IFS-125HR FTS
Light Source	Quartz halogen Lamp	Tungsten Lamp
Bean Splitter	CaF ₂	CaF ₂
Detector	Two matched InSb	InSb
Focal length of the collimating lens (mm)	2260	418
Source aperture diameter (mm)	8	1.3
Filter band pass (cm ⁻¹)	3000-9000	4200-6400
Resolution (cm ⁻¹) Unapodized	~0.01	0.004-0.011
Maximum Optical Path Difference (cm)	50	45-113
Sample Pressure (Torr)	10-252	1.1-594
Total pressures of CO ₂ +air (Torr)	None	200-711
Volume mixing ratio	1.0	0.014-.203
Temperature (K)	292-297	170-296
Cell path length (m)	0.347, 2.46, 49.0	0.2038,13.09, 29.30,20.941
Scanning time (h)	1.3	5-8
Signal-to-noise	800-1000	>2000
Gas Samples	¹² CO ₂ ^b , ¹³ CO ₂ ^c	¹² C-enriched CO ₂ ^d
Calibration standards ^a	CO, C ₂ H ₂	HCl, H ₂ O

^a Calibration of wavenumber scales of spectra was achieved using CO/C₂H₂/HCl, as appropriate (See the text for details).

^b CO₂ sample with natural isotopologue abundances was used.

^c 99% ¹³C-enriched CO₂ was used.

^d 99.98% ¹²C-enriched CO₂ sample was used with the 29.3 m cell while a 99.99% ¹²C-enriched CO₂ sample was used for spectra obtained with the 0.2038 and 20.941 m cells.

Table 3

Summary of experimental conditions of spectra analyzed

Serial #	File name	Cell length (m) ^e	Total Pressure (Torr) ^f	Gas temperature (K) ^g	Volume mixing ratio of CO ₂
Pure gas spectra					
1	4600x714.bus ^a	49.0	80.00	297.40	1.0
2	4600x23671.urs ^b	13.09	1.108	293.80	1.0
3	4600x1688.urs ^a	2.46	10.005	292.38	1.0
4	4600x1690.urs ^a	2.46	252.01	293.37	1.0
5	4600x1705.ars ^c	2.46	10.04	296.61	1.0
6	4600x1677.ars ^c	0.347	146.56	293.54	1.0
7	4600x2526.urs ^b	0.2038	594.00	240.00	1.0
8	4600x2529.urs ^b	0.2038	403.60	240.00	1.0
9	4600x3805.ars ^b	20.941	0.304	220.20	1.0
10	4600x2519.urs ^b	0.2038	80.00	181.65	1.0
11	4600x2522.urs ^b	0.2038	173.10	181.15	1.0
12	4600x3831.ars ^b	20.941	29.70	170.30	1.0
Air broadened CO ₂ spectra					
13	4600x2507.urs ^d	29.30	598.90	294.10	0.014495
14	4600x2508.urs ^d	29.30	401.60	294.80	0.014464
15	4600x2509.urs ^d	29.30	207.30	293.75	0.014530
16	4600x2514.urs ^d	29.30	787.71	295.70	0.05060
17	4600x2515.urs ^d	29.30	599.80	296.10	0.05058
18	4600x3800.ars	20.941	711.68	249.90	0.04402
19	4600x3802.ars	20.941	499.00	249.90	0.04432
20	4600x2527.urs	0.2038	605.90	240.00	0.1940
21	4600x3809.ars	20.941	649.73	220.20	0.0509
22	4600x3811.ars	20.941	502.02	220.20	0.0510
23	4600x3819.ars	20.941	301.25	195.00	0.03086
24	4600x2523.urs	0.2038	610.34	180.00	0.2028
25	4600x2520.urs	0.2038	357.15	180.00	0.1930
26	4600x3827.ars	20.941	400.43	169.80	0.02985
27	4600x3829.ars	20.941	200.41	170.10	0.03000

Notes:

1 atm = 101.3 kPa = 760 Torr.

^a Natural CO₂ sample.^b 99.99% ¹²C-enriched CO₂.^c 99% ¹³C-enriched CO₂.^d 99.98% ¹²C-enriched CO₂ was used with the 29.30 m cell and a 99.99% ¹²C-enriched sample was used for the data taken with the 0.2038 and 20.941 m cells.^e Cell lengths are known with uncertainties of 0.01-0.3% depending on the cell (see the text for details).^f Gas pressures are measured with uncertainties $\pm 0.05\%$ of full-scale pressure readings.^g Cell (gas sample) temperatures are measured with uncertainties of ± 0.02 -0.2 K.

Table 4

Major bands included in the 2 μm region^a of the fitted interval.

# of band	V'	V''	P branch Range in J	Q branch Range in J	R branch Range in J	Iso.
1	20013	00001	2-84		0-84	$^{12}\text{C}^{16}\text{O}_2$
2	20012	00001	2-72		0-72	$^{13}\text{C}^{16}\text{O}_2$
3	20013	00001	2-60		0-64	$^{13}\text{C}^{16}\text{O}_2$
4	40002	01101	3-55	2-20	1-55	$^{12}\text{C}^{16}\text{O}_2^{\text{a}}$
5	21113	01101 $_{e,f}$	2-73	1-38	1-72	$^{12}\text{C}^{16}\text{O}_2^{\text{a}}$
6	20013	00001	1-64		0-64	$^{12}\text{C}^{16}\text{O}^{18}\text{O}$
7	30014	10002	2-64		0-64	$^{12}\text{C}^{16}\text{O}_2$
8	20012	00001	48-88			$^{12}\text{C}^{16}\text{O}_2$
9	21112	01101 $_{e,f}$	36-77			$^{12}\text{C}^{16}\text{O}_2$
10	30013	10002	12-68			$^{12}\text{C}^{16}\text{O}_2$
11	20012	00001	1-67		0-49	$^{12}\text{C}^{16}\text{O}^{18}\text{O}$
12	30012	10001	30-66			$^{12}\text{C}^{16}\text{O}_2$
13	22212	02201 $_{e,f}$	24-64			$^{12}\text{C}^{16}\text{O}_2$
14	30013	10001	2-60		0-60	$^{12}\text{C}^{16}\text{O}_2$
15	22213	02201 $_{e,f}$	3-60	2-28	2-60	$^{12}\text{C}^{16}\text{O}_2$
16	21112	01101 $_{e,f}$	2-57	1-14	1-58	$^{12}\text{C}^{16}\text{O}_2$
17	20013	00001	1-53		0-53	$^{12}\text{C}^{16}\text{O}^{17}\text{O}$
18	20012	00001	8-58			$^{12}\text{C}^{16}\text{O}^{17}\text{O}$
19	31113	11102 $_{e,f}$	2-53	1-8	1-2	$^{12}\text{C}^{16}\text{O}_2$
20	12212	00001	12-70		10-64	$^{12}\text{C}^{16}\text{O}_2^{\text{b}}$
21	23301	00001	No line observed			$^{12}\text{C}^{16}\text{O}_2^{\text{b}}$

^a Some of the bands are fragmentary and only the P-branch transitions appear in the fitted interval. Line parameters for a number of weaker transitions were kept fixed in the least squares solution.

V': Upper vibrational level

V'': Lower vibrational level

The numbers (*e.g.*, 2-84) under P, Q and R branch denote the range in J'' for observed transitions

Iso: Isotopologue ($^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$).

^a Bands that are interacting.

^b 23301 $\leftarrow$ 00001 is a dark state and no lines were observable in our spectral data; however, it interacts with the band 12212 $\leftarrow$ 00001.

Transitions from a total of 42 vibrational bands (24, 9, 2, 3 and 4 bands belonging to $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$) were considered in the fitted region (several of which are very weak and their parameters were held fixed in the fittings). see **Supplemental file #3**.

Table 5**Measured line parameters and number of CO₂ measurements.**

Parameters	Number of measurements	Parameters	Number of measurements
Position (ν) ^a	533 constrained (1464 total)	Intensity (S) ^b	625 constrained (1514 total)
Air-broadened width Coefficient (air-Width) ^c	246	Self-broadened width Coefficient (self-Width) ^c	339
Temperature dependence of air-broadened width coefficient ^d (n_1)	179	Temperature dependence of self-broadened width coefficient ^d (n_2)	175
Air- pressure-shift coefficient (δ^0 air) ^c	228	Self- pressure-shift coefficient (δ^0 self) ^c	320
Temperature dependence of air- pressure-shift coefficient ^e (δ')	175	Temperature dependence of self- pressure-shift coefficient ^e (δ')	175
Off-diagonal relaxation matrix elements for CO ₂ +air mixing (W_{ij}) ^c	54	Off-diagonal relaxation matrix elements for CO ₂ +CO ₂ mixing (W_{ij}) ^c	49
Temp. dependence of off- diagonal relaxation matrix element coefficients for CO ₂ +airmixing ^c	26	Temp. dependence of off- diagonal relaxation matrix element coefficients for CO ₂ +CO ₂ mixing ^c	25
Speed dependence	112	Auxiliary parameters ^f	98

^aThe number of measured positions (in cm⁻¹) is less than the measured line intensities; positions of many lines were held fixed due to their weakness, blends and proximity to stronger lines. First row: Number of measured positions and intensities with constraints are given first, followed by all measured positions and intensities at the bottom in parentheses (this number also includes the number given above).

^b Line intensity in cm/molecule at 296 K.

^c Lorentz half-width and pressure-shift coefficients and the off-diagonal relaxation matrix element coefficients in cm⁻¹ atm⁻¹ at 296 K.

^d Temperature dependence exponents of half-width coefficients and the off-diagonal relaxation matrix element coefficients, and the speed dependence parameters have no units.

^e Temperature dependence of pressure-shift coefficients in cm⁻¹ atm⁻¹ K⁻¹.

^f Examples include ro-vibrational constants, vibrational band strengths (S_v) (see text for details).

Table 6(a)

Ro-vibrational constants, vibrational band strengths (S_v) and correlation coefficients of measured CO₂ bands: 4700-4930 cm⁻¹.

Band/iso.	UpperState Rotational Constants in cm ⁻¹				Intensity Constants							
	<i>G</i> '- <i>G</i> ''	<i>B</i> '	<i>D</i> 'x 10 ⁷	<i>H</i> 'x 10 ¹²	<i>S_V</i> × 10 ²³	<i>a</i> ₁ × 10 ⁴	<i>a</i> ₂ × 10 ⁵	<i>a</i> ₃ × 10 ⁸				
20013←00001 (626)	4853.623370 (1)	0.3881977360(44)	1.817979 (43)	0.5833 (10)	688.420(2)	+2.342 (6)	+3.0063(16)	-0.371(80)				
21113←01101 <i>e</i> (626) ^a 21113←01101 <i>f</i>	4807.694373 (12)	0.388134609 (160) 0.389436575 (53)	1.624471(115) 1.759166 (57)	0.396 (24) 0.233 (15)	65.488(6) ^c	-0.07 (11)	-15.5 (10)	+2.85(5)				
40002←01101 (626) ^b	4808.173871(83)	0.39008047 (47)	0.76606 (57)	1.68 (19)	0.00123 ^c	+641.(25)	+958.(51)	-3789.(280)				
30014←10002 (626)	4790.571556 (57)	0.388906302 (272)	2.1322(29)	1.647(84)	3.3311 (41)	-0.69(35)	0.11(3)	0.003(4)				
30013←10002 (626)	4942.508758(112)	0.38671049(36)	1.71496(307)	1.052(75)	11.229(8)	-49.8(3)	-8.60(5)	0.0 (fixed)				
20012←00001 (636)	4887.384605 (8)	0.386855580 (30)	1.51655 (30)	0.566(8)	26.690 (8)	1.841(8)	1.288(2)	-1.90(6)				
20013←00001 (636)	4748.059367(24)	0.388854741(116)	1.8910 (14)	10.52(7)	2.7080 (2)	2.76(25)	2.94(8)	-4. (3)				
20013←00001 (628)	4791.259512(19)	0.365760127(111)	1.5943(15)	0.401(50)	4.8692(4)	4.32(25)	1.43(8)	-9.4(32)				
20012←00001 (628)	4904.859743(21)	0.364844268(107)	1.1049(13)	0.846(42)	12.9875 (58)	2.66 (14)	-6.78 (50)	-12.9 (18)				
	LowerState Constants											
00001 (fixed) (626)	0.	0.390218949	1.334088	1.918								
01101 <i>e</i> (fixed) (626)	667.3798265	0.390639109	1.353930	2.967								
01101 <i>f</i> (fixed) (626)		0.391254698	1.361606	3.040								
10001 (fixed) (626)	1388.1840918	0.390188916	1.1494271	1.86596								
10002 (fixed) (626)	1285.4081123	0.390482292	1.5715707	2.33398								
00001 (fixed) (636)	0.	0.390237280	1.332981	1.34								
00001 (fixed) (628)	0.	0.368184557	1.187385	62.60								
Band	Correlation Coefficients for UpperState Constants				Correlation Coefficients for Intensity Constants							
	<i>G</i> '- <i>G</i> ''& <i>B</i> '	<i>G</i> '- <i>G</i> ''& <i>D</i> '	<i>G</i> '- <i>G</i> ''& <i>H</i> '	<i>B</i> '& <i>D</i> '	<i>B</i> '& <i>H</i> '	<i>D</i> '& <i>H</i> '	<i>S_V</i> & <i>A</i> ₁	<i>S_V</i> & <i>A</i> ₂	<i>S_V</i> & <i>A</i> ₃	<i>A</i> ₁ & <i>A</i> ₂	<i>A</i> ₁ & <i>A</i> ₃	<i>A</i> ₂ & <i>A</i> ₃
20013←00001 (626)	-0.7798	-0.6211	-0.4985	+0.9355	+0.8129	+0.9478	-0.0540	-0.5935	+0.0900	+0.1154	-0.8130	-0.2405
30014←10002 (626)	-0.8464	-0.7250	-0.6106	+0.9576	+0.8582	+0.9663	+0.0560	-0.7540	-0.0311	-0.0382	-0.8392	-0.0096
30013←10002 (626)	-0.9652	-0.9104	-0.8350	+0.9804	+0.9242	+0.9782	+0.9886	+0.9567	----	+0.9878	----	----
20012←00001 (636)	-0.7951	-0.6183	-0.4689	+0.9234	+0.7806	+0.9511	+0.0185	-0.7140	-0.0198	-0.0161	+0.7872	+0.0214
20013←00001 (636)	-0.8535	-0.7072	-0.5860	+0.9465	+0.8449	+0.9625	-0.0703	-0.7680	+0.0812	+0.0617	-0.8489	-0.1110
20012←00001 (628)	-0.7941	-0.6183	-0.4689	+0.9234	+0.7806	+0.9511	+0.0185	-0.7140	-0.0198	-0.0161	-0.7872	+0.0214
20013←00001 (628)	-0.8253	-0.6713	-0.5432	+0.9385	+0.8185	+0.9506	+0.0447	-0.7307	-0.0203	-0.0084	-0.8187	-0.0126

Notes: The bands identified with superscripts (^a and ^b) are in Fermi resonance. The interaction coefficient determined in this study = 0.019295(5).

^c The strength of this band was too small to be determined and hence fixed to the listed value after several trials during the least squares solution. Because of the presence of a very weak Q branch, the a_4 term of the Herman-Wallis parameter needed adjustments and its value is determined to be: For the 21113←01101 band, a_4 (even Q) = +0.000177 (10) and for the 40002←100002 band a_4 (odd Q) = -0.0054(5)

The band centers and rotational constants are in cm^{-1} . The rotational constants for the lower states (ground state, 01101, 10001, 10002) are from Miller and Brown [41].

L'' (10001) = $0.5663 \times 10^{-18} \text{ cm}^{-1}$ and L'' (10002) = $-0.9928 \times 10^{-18} \text{ cm}^{-1}$ where L'' corresponds to the higher order (octal) term, $L''\{J''[J'' + 1]\}^4$, after the $H''\{J''[J'' + 1]\}^3$ term in **Eq. (1)**, for the lower vibrational state. We did not include this term in our analysis. However, this term was determined by Miller and Brown [41] and hence we listed the L'' values for completeness. Since our present study involved the lower states 10001 and 10002 in some of the bands, we listed the L'' values for these two lower states. The lower level 10001 was involved in the fragmentary band (30012←100001 of $^{12}\text{C}^{16}\text{O}_2$) that appeared at the upper wavenumber limit in our fitted interval with band center located at $\sim 4959.66689(5) \text{ cm}^{-1}$.

The intensity constants are the same for the e and f levels of the 21113←01101 band. The lower state rotational constants for the 636 and 628 bands were taken from Elliot et al. [42].

The vibrational band strengths (S_v) are in $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2}) \times 10^{-23}$ at 296 K. CO_2 samples with natural abundance ($^{16}\text{O}^{12}\text{C}^{16}\text{O}=0.9842$) and high-purity $^{12}\text{C}^{16}\text{O}_2$ samples with (99.99% ^{12}C -enriched) abundances (see text for details) were used in recording the spectra. The rotational partition sums used for $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ at 296 K are from R.R. Gamache [43] and their values are: 263.87063, 527.71608, and 559.30454, respectively. Contribution due to vibrational partition function for the lower vibrational levels was applied in computing the vibrational band strengths (S_v) listed in the Table above.

Table 6(b)

Correlation coefficients for the upper state ro-vibrational constants for the 21113←01101 *e*, 21113←01101 *f* and the 40002 ←10002 interacting bands of $^{12}\text{C}^{16}\text{O}_2$

	21113 <i>e</i>			21113 <i>f</i>			40002				
	B'_e	D'_e	H'_e	B'_f	D'_f	H'_f	$G' - G''$	B'_e	D'_e	H'_e	Ω
21113 <i>e</i> $G' - G''$	-0.8159	-0.6427	-0.5309	+0.3229	+0.2518	+0.2009	-0.1679	-0.0844	-0.0277	-0.0069	+0.5382
B'_e	x	+0.9280	+0.8306	-0.2683	-0.2095	-0.1671	+0.1321	+0.0703	+0.0214	+0.0031	-0.4441
D'_e	x	x	+0.9691	-0.2106	-0.1641	-0.1306	+0.1030	+0.0538	+0.0144	-0.0005	-0.3495
H'_e	x	x	x	-0.1732	-0.1348	-0.1071	+0.0845	+0.0440	+0.0112	-0.0012	-0.2883
21113 <i>f</i> B'_f	x	x	x	x	+0.9665	+0.8962	+0.0372	-0.3944	-0.2464	-0.1725	+0.9458
D'_f	x	x	x	x	x	+0.9757	+0.0546	-0.4130	-0.2912	-0.2247	+0.8605
H'_f	x	x	x	x	x	x	+0.0739	-0.4204	-0.3281	-0.2779	+0.7665
40002 $G' - G''$	x	x	x	x	x	x	x	-0.7773	-0.6819	-0.5930	-0.0082
B'_e	x	x	x	x	x	x	x	x	+0.9487	+0.8609	-0.3388
D'_e	x	x	x	x	x	x	x	x	x	+0.9685	-0.1820
H'_e	x	x	x	x	x	x	x	x	x	x	-0.1118

Notes: The *e* levels of 21113←01101 and the 40002←01101 bands are in Fermi resonance. The interaction parameter Ω is determined to be 0.019295(5).

Correlation coefficients for the intensity parameters of the interacting bands 21113←01101 and the 40002 ←10002 bands of $^{12}\text{C}^{16}\text{O}_2$

	21113←01101					40002←10002				
	S_v	a_1	a_2	a_3	a_4	a_1	a_2	a_3	a_4	Ω
21113←01101 S_v	x	-0.1183	-0.1100	+0.0545	+0.1004	+0.0155	-0.0675	-0.0095	+0.0651	-0.0126
a_1	x	x	+0.9098	-0.3407	-0.9098	+0.0060	-0.0179	-0.0166	+0.0180	-0.0023
a_2	x	x	x	-0.0116	-0.999904 ^a	-0.0029	-0.0263	+0.0003	+0.0249	-0.0035
a_3	x	x	x	x	+0.0114	-0.0715	-0.0154	+0.1410	+0.0089	+0.0021
a_4	x	x	x	x	x	+0.0024	+0.0269	-0.0002	-0.0254	+0.0034
40002←10002 a_1	x	x	x	x	x	x	+0.1939	-0.8419	-0.1993	+0.0053
a_2	x	x	x	x	x	x	x	+0.0012	-0.0059	+0.0060
a_3	x	x	x	x	x	x	x	x	-0.0014	-0.0059
a_4	x	x	x	x	x	x	x	x	x	-0.0080
Ω	x	x	x	x	x	x	x	x	x	x

Notes: Although separate ro-vibrational constants (B , D , H) were determined for the e and the f levels for the 21113←01101 band, the band strength and the Herman-Wallis parameters could not be determined for each level and hence only one value for both levels were determined (see **Table 6(a)**). The off-diagonal terms marked x are symmetric with those listed above the diagonal.

^a Due to the very large correlation between the a_2 and the a_4 terms, (21113←01101 band), more digits are provided to avoid any problems that could arise due to truncation while computing the error analysis.

Table 7

Comparisons of vibrational band strengths, S_v , (cm/molecule at 296 K) for select bands^a measured in the 2- μ m region of CO₂.

Iso.	Band	Band center (cm ⁻¹) ^b	Vibrational Band strength (S_v)		# lines and range in J	
			PS	Toth et al.	PS	Toth et al.
626	21113←01101	4807.694	$6.5488(6) \times 10^{-22}$	$6.558(10) \times 10^{-22}$	183; (P73-R72)	258; (P95-R96)
626	40002 ←01101 ^c	4808.174	1.23×10^{-26} (Fixed)	$5.24(72) \times 10^{-26}$	65; (P55-R55; Q2-Q20)	40; (P51-R53)
626	20013←00001	4853.623	$6.88420(2) \times 10^{-21}$	$6.897(6) \times 10^{-21}$	85; (P84-R84)	105; (P104-R104)
626	30013←10002 ^d	4942.508	$1.123(1) \times 10^{-22}$	$1.277(2) \times 10^{-22}$	29; (P68-P12)	93; (P92-R92)
626	21112←01101 ^d	4965.385	$1.686(2) \times 10^{-21}$	4.73×10^{-21}	42; (P77-P36)	268; (P98-R98)
626	30014←10002	4790.572	$3.331(4) \times 10^{-23}$	3.346×10^{-23}	65; (P64-R64)	89; (P88-R88)
636	20012←00001 ^e	4887.385	$2.6690(8) \times 10^{-22}$	2.61×10^{-22}	73; (P72-R72)	95; (P94-R94)
636	20013←00001 ^e	4848.066	$2.7080(2) \times 10^{-23}$	2.72×10^{-23}	82; (P60-R64)	89; (P88-R88)
628	20012←00001 ^f	4904.859	$1.2988(6) \times 10^{-22}$	1.25×10^{-22}	117; (P67-R49)	185; (P92-R92)
628	20013←00001 ^f	4791.259	$4.8692(4) \times 10^{-23}$	4.65×10^{-23}	129; P(64-R64)	182; (P90-R91)

^a Only those bands whose Vibrational band strengths (S_v) have been determined using theoretical quantum mechanical expressions (**Eqs.1-3**) are listed in this Table. For other bands (including a number of weaker bands) individual line positions and intensities were adjusted in the least squares fits when appropriate, and their values are given in the **Supplemental files**.

^b For purpose of identification only.

^c The band was weak and its vibrational band strength was fixed in the least squares fit (see **Table 6(a)**).

^d Transitions from only P branch were observed in the present study.

^e Only two ¹³C-enriched spectra were included in the fit (see the text for details).

^f One spectrum with natural CO₂ sample was included in the fit. All other spectra (including air-broadened) contained 99.99% ¹²C-enhancement where abundances of rarer isotopologues (*e.g.*, ¹³C¹⁶O₂, ¹²C¹⁶O¹⁸O, ¹²C¹⁶O¹⁸O) in each spectrum were determined. The differences observed between **PS** and Toth et al. [**11,15**] reflect those estimates and should be considered as only estimated vibrational band strengths. Because of the sample purity used, the intensities for 636 and 628 bands listed in [**11,15**] should be more accurate than from present study.

Table 8

A sample of measured line parameters for the P20-R20 transitions in the 20013←00001 band of $^{12}\text{C}^{16}\text{O}_2$.

Line	Position and unc. ^a	Intensity S ^b	S (% unc)	Lorentz half- width coefficients ^c	% unc	n_1 and n_2 ^d	% unc	Pressure shift (δ^0) and unc. ^c	T-dep. pressure shift (δ') and unc. ^e	Speed dependence ^f	% unc
P20	4837.243864(1)	2.376×10^{-22}	0.003	0.07341 0.10032	0.01 0.06	0.7353 0.6616	0.08 0.21	-0.005287(12) -0.006792(102)	+0.0198(22) -0.2100(122)	0.1061	0.5
P18	4838.955594(1)	2.471×10^{-22}	0.003	0.07462 0.10223	0.01 0.06	0.7257 0.6736	0.08 0.19	-0.005203(12) -0.006761(100)	+0.0151(22) -0.2350(118)	0.1125	0.5
P16	4840.650679(1)	2.502×10^{-22}	0.003	0.07599 0.10396	0.01 0.06	0.7202 0.6846	0.08 0.19	-0.005171(12) -0.006627(99)	+0.0082(22) -0.2342(115)	0.1178	0.4
P14	4842.329244(1)	2.456×10^{-22}	0.003	0.07754 0.10581	0.03 0.06	0.7155 0.6909	0.08 0.19	-0.005016(12) -0.006418(100)	+0.0013(22) -0.2492(115)	0.1224	0.4
P12	4843.991396(1)	2.328×10^{-22}	0.003	0.07922 0.10808	0.03 0.06	0.7135 0.6891	0.08 0.19	-0.004811(12) -0.006155(103)	-0.0110(23) -0.2434(117)	0.1250	0.4
P10	4845.637224(1)	2.114×10^{-22}	0.003	0.08109 0.11061	0.02 0.06	0.7134 0.6886	0.08 0.19	-0.004546(12) -0.006286(110)	-0.0205(23) -0.2901(124)	0.1260	0.4
P8	4847.266801(1)	1.816×10^{-22}	0.003	0.08302 0.11340	0.02 0.06	0.7169 0.6903	0.08 0.20	-0.004281(14) -0.006199(120)	-0.0394(24) -0.3165(134)	0.1231	0.4
P6	4848.880178(1)	1.441×10^{-22}	0.003	0.08505 0.11641	0.02 0.07	0.7237 0.6988	0.10 0.23	-0.003941(15) -0.006380(138)	-0.0504(26) -0.3529(153)	0.1159	0.5
P4	4850.477391(1)	1.002×10^{-22}	0.003	0.08735 0.11928	0.02 0.08	0.7275 0.7195	0.14 0.25	-0.003495(16) -0.006324(151)	-0.0618(24) -0.3935(163)	0.1031	0.7
P2	4852.058456(1)	5.146×10^{-22}	0.003	0.09099 0.12319	0.03 0.11	0.7210 0.7447	0.19 0.32	-0.002959(22) -0.006038(217)	-0.1046(34) -0.4302(224)	0.0843	1.3
R0	4854.399765(1)	2.607×10^{-22}	0.003	0.09529 0.12964	0.05 0.16	0.7116 0.7581	0.20 0.44	-0.002882(37) -0.005635(291)	-0.0682(62) -0.2994(272)	0.0558	4.1
R2	4855.940408(1)	7.746×10^{-22}	0.003	0.08826 0.12011	0.02 0.09	0.7251 0.7414	0.11 0.27	-0.003330(20) -0.006366(174)	-0.0756(33) -0.3900(185)	0.0757	1.2
R4	4857.464813(1)	1.260×10^{-22}	0.003	0.08578 0.11703	0.02 0.07	0.7204 0.7173	0.10 0.22	-0.003503(16) -0.006172(149)	-0.0902(27) -0.4195(165)	0.0951	0.7
R6	4858.972913(1)	1.696×10^{-22}	0.003	0.08378 0.11419	0.02 0.07	0.7129 0.7014	0.10 0.21	-0.003608(14) -0.005814(128)	-0.0985(25) -0.3453(141)	0.1128	0.5
R8	4860.464622(1)	2.067×10^{-22}	0.003	0.08182	0.02	0.7061	0.09	-0.003655(13)	-0.1059(23)	0.1226	0.4

				0.11150	0.06	0.6907	0.19	-0.006118(112)	-0.3410(125)		
R10	4861.939835(1)	2.359×10^{-22}	0.003	0.07978 0.10876	0.03 0.06	0.7053 0.6917	0.09 0.19	-0.003685(13) -0.006188(103)	-0.0977(23) -0.3093(116)	0.1248	0.4
R12	4863.398430(1)	2.566×10^{-22}	0.003	0.07799 0.10641	0.03 0.06	0.7045 0.6916	0.09 0.19	-0.003880(12) -0.006121(99)	-0.0979(22) -0.2675(113)	0.1246	0.4
R14	4864.840267(1)	2.685×10^{-22}	0.003	0.07628 0.10435	0.01 0.06	0.7095 0.6889	0.08 0.19	-0.004025(12) -0.006319(96)	-0.0886(22) -0.2596(130)	0.1214	0.4
R16	4866.265187(1)	2.718×10^{-22}	0.003	0.07483 0.10262	0.01 0.06	0.7147 0.6815	0.08 0.19	-0.004181(12) -0.006534(96)	-0.0804(22) -0.2351(111)	0.1188	0.4
R18	4867.673013(1)	2.675×10^{-22}	0.003	0.07360 0.10111	0.01 0.05	0.7231 0.6658	0.08 0.20	-0.004368(12) -0.006665(95)	-0.0718(22) -0.2059(112)	0.1147	0.5
R20	4869.063551(1)	2.566×10^{-22}	0.003	0.07251 0.09920	0.01 0.06	0.7344 0.6557	0.08 0.21	-0.004529(12) -0.006792(98)	-0.0656(22) -0.1828(116)	0.1096	0.5

The percent (%) uncertainties listed under various columns correspond to one sigma internal statistical errors obtained from least-squares fits.

^a Positions and uncertainties are in cm^{-1} .

^b Line intensities (S) are in $\text{cm}/\text{molecule}$ at 296 K.

^c Lorentz half-width coefficients (b_L^0) and pressure shift coefficients (δ^0) are in units of $\text{cm}^{-1} \text{atm}^{-1}$ at 296 K. The numbers in the top row in each column correspond to air-broadening and the bottom self-broadening.

^d n_1 and n_2 are the temperature dependence exponents of air- and self-width coefficients, respectively, and have no units.

^e Temperature dependences of pressure shift coefficients, $\delta'(\text{air})$ and $\delta'(\text{self})$, are in units of $\text{cm}^{-1} \text{atm}^{-1} \text{K}^{-1}$.

^f Quadratic speed dependence parameter has no units.

Table 9

Measured off-diagonal relaxation matrix element coefficients, W_{ij} , ($\text{cm}^{-1} \text{atm}^{-1}$ at 296 K), and their temperature dependence exponents (unitless) for $\text{CO}_2\text{-CO}_2$ and $\text{CO}_2\text{-air}$ for the $20013\leftarrow 00001$ band of $^{12}\text{C}^{16}\text{O}_2$.

Mixing between	RMEC ($\text{CO}_2\text{-CO}_2$) (W_{ij}) at 296 K	Temp. dep. Exponents for ($\text{CO}_2\text{-CO}_2$)	RMEC ($\text{CO}_2\text{-air}$) (W_{ij}) at 296 K	Temp. dep. exponents for $\text{CO}_2\text{-air}$
P2 & P4	0.00471 (32)	0.80 <i>fxd</i>	0.00637 (5)	0.80 <i>fxd</i>
P4 & P6	0.00830 (33)	0.80 <i>fxd</i>	0.01107 (5)	0.80 <i>fxd</i>
P6 & P8	0.01135 (43)	0.958 (81)	0.01450 (6)	0.860 (12)
P8 & P10	0.01427 (47)	1.060 (77)	0.01703 (7)	0.892 (13)
P10 & P12	0.01714 (50)	1.104 (71)	0.01896 (7)	0.917 (13)
P12 & P14	0.02092 (54)	0.975 (66)	0.02024 (7)	0.948 (13)
P14 & P16	0.02463 (59)	0.870 (64)	0.02111 (8)	0.948 (13)
P16 & P18	0.02674 (63)	0.850 (65)	0.02162 (9)	0.934(14)
P18 & P20	0.02789 (69)	0.809 (67)	0.02206 (9)	0.881 (15)
P20 & P22	0.02904 (69)	0.846 (70)	0.02226 (10)	0.766 (17)
P22 & P24	0.03056 (76)	0.780 (71)	0.02221 (11)	0.696 (18)
P24 & P26	0.03428 (84)	0.778 (73)	0.02193 (13)	0.599 (20)
P26 & P28	0.03673 (93)	0.647 (78)	0.02146 (14)	0.556 (21)
P28 & P30	0.04033 (103)	0.629 (75)	0.02084 (15)	0.623 (19)
P30 & P32	0.04295 (114)	0.580 (64)	0.01967 (17)	0.70 <i>fxd</i>
P32 & P34	0.04451 (119)	0.80 <i>fxd</i>	0.01841 (20)	0.70 <i>fxd</i>
P34 & P36	0.04412 (123)	0.80 <i>fxd</i>	0.01785 (23)	0.70 <i>fxd</i>
P36 & P38	0.04697 (140)	0.80 <i>fxd</i>	0.01663 (27)	0.70 <i>fxd</i>
P38 & P40	0.04270 (163)	0.80 <i>fxd</i>	0.01579 (33)	0.70 <i>fxd</i>
P40 & P42	0.03890 (190)	0.70 <i>fxd</i>	0.01431 (38)	0.70 <i>fxd</i>
P42 & P44	0.03162 (217)	0.70 <i>fxd</i>	0.01324 (45)	0.70 <i>fxd</i>
P44 & P46	0.02225 (242)	0.70 <i>fxd</i>	0.01132 (51)	0.70 <i>fxd</i>
P46 & P48	0.01363 (254)	0.70 <i>fxd</i>	0.00940(56)	0.70 <i>fxd</i>
P48 & P50	0.00810 (269)	0.70 <i>fxd</i>	0.00470(51)	0.70 <i>fxd</i>
P50 & P52	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
P52 & P54	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
P54 & P56	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
P56 & P58	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
P58 & P60	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
R2 & R4	0.00429 (22)	0.80 <i>fxd</i>	0.00253 (5)	1.126 (63)
R4 & R6	0.01554 (32)	0.80 <i>fxd</i>	0.00997 (7)	0.959 (25)
R6 & R8	0.02065 (41)	0.876 (44)	0.01453 (7)	0.962 (17)
R8 & R10	0.02344 (43)	0.998 (44)	0.01763 (7)	0.975 (14)
R10 & R12	0.02596 (44)	1.003 (42)	0.01986 (6)	0.965 (12)

R12 & R14	0.02744 (44)	0.981 (42)	0.02114 (7)	0.981 (11)
R14 & R16	0.02834 (45)	0.939 (43)	0.02197 (7)	0.981 (11)
R16 & R18	0.02802 (46)	0.945 (45)	0.02245 (7)	0.969 (11)
R18 & R20	0.02757 (47)	0.930 (48)	0.02260 (7)	0.949 (11)
R20 & R22	0.02679 (49)	0.917 (51)	0.02254 (7)	0.931 (11)
R22 & R24	0.02526 (51)	0.879 (57)	0.02227 (7)	0.877 (12)
R24 & R26	0.02314 (53)	0.785 (66)	0.02173 (8)	0.826 (12)
R26 & R28	0.02133 (54)	0.627 (74)	0.02097 (8)	0.780 (12)
R28 & R30	0.01855 (54)	0.557 (75)	0.01995 (8)	0.737 (11)
R30 & R32	0.01560 (49)	0.70 <i>fxd</i>	0.01905 (8)	0.70 <i>fxd</i>
R32 & R34	0.01131 (50)	0.70 <i>fxd</i>	0.01800 (9)	0.70 <i>fxd</i>
R34 & R36	0.00794 (50)	0.70 <i>fxd</i>	0.01686 (10)	0.70 <i>fxd</i>
R36 & R38	0.00602 (44)	0.70 <i>fxd</i>	0.01573 (11)	0.70 <i>fxd</i>
R38 & R40	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.01437 (12)	0.70 <i>fxd</i>
R40 & R42	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.01280 (13)	0.70 <i>fxd</i>
R42 & R44	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.01036 (13)	0.70 <i>fxd</i>
R44 & R46	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.00739 (12)	0.70 <i>fxd</i>
R46 & R48	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.004 <i>fxd</i>	0.70 <i>fxd</i>
R48 & R50	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.004 <i>fxd</i>	0.70 <i>fxd</i>
R50 & R52	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.004 <i>fxd</i>	0.70 <i>fxd</i>
R52 & R54	0.004 <i>fxd</i>	0.70 <i>fxd</i>	0.004 <i>fxd</i>	0.70 <i>fxd</i>

Measured off-diagonal relaxation matrix element coefficients, W_{ij} , for CO₂-CO₂ and CO₂-air for the Q branch lines in the 21113←01101 band of ¹²C¹⁶O₂.

Mixing between	RMEC CO ₂ -CO ₂ (W_{ij}) at 296 K	Temperature dependence exponent, Self-mixing	RMEC CO ₂ -air, (W_{ij}) at 296 K	Temperature dependence exponent, air mixing (W_{ij})
Q1 & Q3	0.00527 (59)	0.70 <i>fxd</i>	0.00090 (9)	0.70 <i>fxd</i>
Q3 & Q2	0.00471 (92)	0.70 <i>fxd</i>	0.00228 (24)	0.70 <i>fxd</i>
Q2 & Q5	0.00464 (87)	0.70 <i>fxd</i>	0.00293 (28)	0.70 <i>fxd</i>
Q5 & Q7	0.02636 (284)	0.70 <i>fxd</i>	0.01803 (54)	0.70 <i>fxd</i>
Q7 & Q4	0.0010 (223)	0.70 <i>fxd</i>	0.01877 (67)	0.70 <i>fxd</i>
Q4 & Q9	0.0042 (16)	0.70 <i>fxd</i>	0.00863 (44)	0.70 <i>fxd</i>
Q9 & Q6	0.01175 (410)	0.70 <i>fxd</i>	0.02363 (65)	0.70 <i>fxd</i>
Q6 & Q11	0.00723 (42)	0.70 <i>fxd</i>	0.00358 (38)	0.70 <i>fxd</i>
Q11 & Q13	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>
Q13 & Q8	0.005 <i>fxd</i>	0.70 <i>fxd</i>	0.005 <i>fxd</i>	0.70 <i>fxd</i>

The relaxation matrix element coefficients for only the Q lines were measured in this band. These parameter values could not be measured accurately; nevertheless needed adjustments to minimize the fit residuals. The relaxation matrix element coefficients for the nearest neighbor Q lines only were considered (regardless of their assignments) in this analysis.