High-accuracy $^{12}\text{C}^{16}\text{O}_2$ line intensities in the 2 $\mu$m wavelength region measured by frequency-stabilized cavity ring-down spectroscopy

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ABSTRACT: Reported here are highly accurate, experimentally measured ro-vibrational transition intensities for the R-branch of the (20012) - (00001) $^{12}\text{C}^{16}\text{O}_2$ band near $\lambda = 2 \mu$m. Measurements were performed by a frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) instrument designed to achieve precision molecular spectroscopy in this important region of the infrared. Through careful control and traceable characterization of CO$_2$ sample conditions, and through high-fidelity measurements spanning several months in time, we achieve relative standard uncertainties for the reported transition intensities between 0.15% and 0.46%. Such high accuracy spectroscopy is shown to provide a stringent test of calculated potential energy and $ab\ initio$ dipole moment surfaces, and therefore transition intensities calculated from first principles.

KEYWORDS: Precision molecular spectroscopy, line lists, carbon dioxide, cavity ring-down spectroscopy, infrared spectroscopy, dipole moment surfaces
1 Introduction

The remote sensing of atmospheric molecules relies upon first-principles, physics-based models that incorporate accurate and precise laboratory spectroscopic data. For example, current satellite-based measurements of atmospheric CO$_2$, such as the ongoing GOSAT (JAXA), and OCO-2 (NASA) missions and the upcoming MICROCARB (CNES) mission, as well as the worldwide terrestrial spectrometer campaign (TCCON), demand low uncertainty in the pressure, temperature and composition dependence of air-broadened O$_2$ and CO$_2$ absorption cross sections. These quantities can be calculated in terms of absolute transition frequencies and intensities, and line shape parameters that account for collisional broadening, pressure shifting, line mixing and collisional narrowing [1, 2]. In the context of NASA’s Earth-orbiting OCO-2 satellite mission which measures the column-integrated dry air mixing ratio of CO$_2$ [3], calculated cross-sections with relative uncertainties on the order of 0.3 % are required [4]. In order to meet this ambitious data target and therefore maximize the scientific achievements of this and other remote-sensing missions, reference-quality, laboratory measurements of CO$_2$ spectroscopic parameters are required.

Here we report a detailed description of the instrumentation and methodology used to perform low-uncertainty cavity ring-down spectroscopy (CRDS) measurements of relatively strong carbon dioxide line intensities in the wave number region 4 990 cm$^{-1}$ to 5 010 cm$^{-1}$. The resulting intensities are reproduced with high fidelity over a period of several months with relative combined standard uncertainties of 0.25 %. Comprehensive comparisons with existing database parameters as well as recent $ab$ $initio$ and experimental intensities are reported and discussed.

2 Description of Experiment

2.1 Survey of spectral region

The upper panel of Fig. 1 shows a simulated air-broadened absorption spectrum of carbon dioxide (with water vapor interferences) for the wave number region investigated here and for pressure, moisture, mole fraction and path length conditions representative of this study. The spectrum is dominated by 19 targeted transitions assigned to the (20012) - (00001) vibrational band of $^{12}$C$^{16}$O$_2$ lower-state rotational quantum numbers $J'' = 16, 18, \ldots 52$. The lower panel of Fig. 1 has the same calculated spectrum plotted with a logarithmic ordinate, showing that the
interferences associated with other $^{12}$C$i6$O$_2$, $^{13}$C$i6$O$_2$ and H$_2$O transitions are typically at most two orders of magnitude below the peak absorption of the target transitions. Although, the targeted transitions were relatively isolated, because of the high signal-to-noise ratio of the measured spectra, our analyses accounted for the wings of neighboring strong lines as well as residual contributions from some of the weak interferences.

2.2 FS-CRDS method

We acquired absorption spectra using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) method. This is an implementation of CRDS in which the optical resonator (i.e. ring-down cavity) is length-stabilized relative to a continuous-wave (CW), frequency-stabilized reference laser and pumped by a narrow line width CW probe laser [5, 6]. FS-CRDS results in high-fidelity spectra that are determined from precise measurements of optical frequency shifts and intensity decay times. The active locking scheme in FS-CRDS ensures that the cavity mode spacing provides a stable and linear frequency detuning axis, and the single-mode excitation of the resonator eliminates laser bandwidth effects that can lead to complicated multi-exponential decay signals [7]. At each frequency step, the probe laser beam is brought into resonance with a single cavity mode (designated by its mode order $q$) and subsequently switched off to cause single-exponential decay of the light intensity exiting the resonator. In this fashion, the spectrum detuning relative to the first mode order $q_0$ is equal to $(q-q_0)\nu_f = \Delta \nu_f$ where $\nu_f$ is the cavity free spectral range (FSR). Individual intensity decay signals are converted into photocurrent with a DC-coupled photodetector, amplified and recorded using a high-speed A/D board. The time constant $\tau$ for each decay event is obtained by fitting the three-parameter function $s(t) = Ae^{-t/\tau} + s_0$ to the time-dependent photocurrent signal $s(t)$, where $A$ and $s_0$ are the amplitude and time-independent offset, respectively. Multiple decays are obtained at each frequency detuning to provide an average decay time $\bar{\tau}$ and standard deviation $\sigma_\tau$. Measured spectra are given by the set of values $\alpha_{tot}(\Delta \nu_f) = (c\bar{\tau})^{-1}$ where $c$ is the speed of light. These data quantify the total (i.e. absorption plus baseline) intensity loss-per-unit length in the sample as a function of spectrum detuning.
2.3 *FS-CRDS spectrometer*

The FS-CRDS spectrometer used in this study is similar to other systems that were developed at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD [8-10]. This spectrometer comprises several component sub-systems, including a high-finesse optical resonator and gas cell, a reference laser and servo controller for active resonator length stabilization, gravimetrically prepared gas mixtures of CO₂ in N₂ and associated flow delivery system, a tunable CW probe laser, a photoreceiver and digitizer, and a personal computer with high-speed data acquisition, signal analysis and control software. Each instrument sub-system is discussed in detail in this Section.

The optical instrument is assembled on a 1 m by 1.3 m breadboard seated atop a mobile cart. A standard rack mount, also on wheels, houses the fiber laser amplifier, oscilloscope, power supplies, locking and system control electronics, and a personal computer. An additional rack mount is situated next to the optical table with a gas cylinder mount and flow delivery manifold.

2.4 *Optical resonator and gas cell*

The optical resonator and gas cell consist of two flexure mirror mounts supported by individual steel brackets, four 2.54 cm diameter invar rods 52 cm in length connecting the brackets, and a 1.27 cm diameter tube with formed bellows to connect the two mirror mounts and house the gas sample and optical cavity [5]. As shown in Fig. 2, each flexure mirror mount has a gas inlet (outlet) port used to exchange sample gas in a flowing configuration (see Section 2.5), with the gas sweeping past both ring-down mirrors to prevent the occurrence of dead volumes. Commercial dual-wavelength-coated, high-reflectivity low-loss mirrors (2.54 cm diameter, 6 m radius of curvature) with intensity reflection coefficients of 0.99964 and 0.95 at $\lambda = 2 \text{ μm}$ and $\lambda = 633 \text{ nm}$, respectively, are installed into each flexure mount. The distance between the ring-down cavity mirrors is nominally 75 cm and accurately determined by measurement of the cavity FSR as discussed below. The vacuum seal between the intra-cavity gas sample and the laboratory environment is made by anti-reflection-coated CaF₂ windows which are bonded to a standard knife-edge-seal flange. This design results in the low-loss, ring-down cavity mirrors experiencing zero pressure difference between their high-reflection and anti-reflection coated faces, thus mitigating potential stress-induced birefringence effects [11, 12].
The FSR of the evacuated optical cavity was measured using an infrared wavelength meter (1 μm to 5 μm operating wavelength range) with a frequency resolution of 40 MHz. While a software-based dither locking scheme [13] maintained probe laser transmission, a small portion of the probe laser beam was analyzed by the wavelength meter for up to 12 s. The probe laser frequency was sequentially locked to 750 successive longitudinal modes of the optical resonator and the probe laser frequency was measured at each step. From these data, linear regression analysis yielded the empty-cavity free spectral range $\nu_f = 200.806$ MHz with a standard uncertainty of 60 kHz. This value was in good agreement with $\nu_f$ obtained by fitting a spectral model with known $^{12}$C$^{16}$O$_2$ transition frequencies [14] to a measured absorption spectrum. Also, at each pressure and temperature condition, the $\nu_f$ was corrected to account for density-dependent changes in the refractive index of the sample gas. These corrections were found to be less than 0.02 % of the empty-cavity values for all conditions considered.

2.5 Active length stabilization of optical resonator

The mirror-to-mirror distance of the ring-down cavity was actively stabilized in order to provide a linear and stable relative frequency axis. To this end, a temperature-stabilized HeNe laser (100 kHz line width at 10 ms, long-term stability of 1 MHz), counter-propagating and co-linear with the probe laser, was simultaneously coupled to the optical resonator. A slow frequency dither was summed with a constant DC voltage and amplified to drive the free-space 633 nm acousto-optic modulator (AOM). The AOM was aligned in a double-pass configuration to minimize pointing changes associated with changes in frequency. A commercial photoreceiver measured the HeNe transmission as a function of the AOM dither waveform, and an error signal was generated using a lock-in amplifier. A servo controller was fed back to a cylindrical piezoelectric (PZT) actuator with 12 μm of travel range. The PZT was attached to the output mirror of the optical resonator in order to enable precise control of the ring-down cavity mirror-to-mirror distance. Slow drifts in cavity length associated with laboratory temperature were mitigated by the low-expansion invar rods in the cavity construction. Additionally, an insulated enclosure was placed around the optical resonator/sample cell assembly to further dampen temperature fluctuations during long-term data acquisition. All data were acquired at room temperature conditions (298.3 K ± 1.3 K).
2.6 Certified gas cylinders and flowing delivery system

Two gas cylinders of dilute CO\textsubscript{2} in a balance of dry N\textsubscript{2} were certified against gravimetrically prepared standards by the Gas Sensing Metrology Group at NIST. The certified CO\textsubscript{2} (all isotopologues) molar fractions were $\chi_{\text{CO}_2} = 49.826 \text{ mmol/mol} \pm 0.019 \text{ mmol/mol}$ (mixture A) and $\chi_{\text{CO}_2} = 100.474 \text{ mmol/mol} \pm 0.057 \text{ mmol/mol}$ (mixture B), respectively (uncertainties are calculated with a coverage factor of $k = 1$). Regulated flow from a chosen gas cylinder was throttled by a metering valve prior to entering the optical resonator via an inlet port located near the anti-reflection (AR) side of the input mirror. The sample gas flow rate and pressure could be adjusted to a range of conditions using a mass flow controller and diaphragm pump, respectively, located downstream of the optical cavity. Also, a proportional-integral controller located downstream of the optical resonator was used to maintain a constant gas pressure (less than 1.5 Pa variation) in the measurement volume. This arrangement used a high-precision capacitance diaphragm gauge and a solenoid-actuated flow needle valve to overcome pressure fluctuations caused by changes in pumping speed and upstream pressure. Experiments were performed on both certified gas cylinders at multiple steady-state pressures and at two distinct flow rates (10 cm\textsuperscript{3} min\textsuperscript{-1} and 20 cm\textsuperscript{3} min\textsuperscript{-1}, respectively).

The relative isotopic composition $\delta^{13}C_{\text{VPDB}} = \frac{^{13}C / ^{12}C}{[^{13}C / ^{12}C]_{\text{ref}}} - 1$ of both certified gas samples was determined here by Fourier-transform spectroscopy (FTS) measurements of $^{12}$C$^{16}$O\textsubscript{2} (R10 and R18 transitions of the (10012) - (00001) band) and $^{13}$C$^{16}$O\textsubscript{2} (P10, P14, and P22 transitions of the (00012) - (00001) band). The sample $\delta^{13}C_{\text{VPDB}}$ values were determined by reference to a previously characterized CO\textsubscript{2} sample with a known value of $\delta^{13}C_{\text{VPDB}}$, where VPDB indicates the Vienna Pee Dee Bee scale defined to have a reference value of $^{13}$C/$^{12}$C\textsubscript{ref} = 0.011 237 2. For both certified gas samples, the FTS measurements performed at NIST gave $\delta^{13}C_{\text{VPDB}} \approx -40 \text{ \%}$ which is typical of carbon dioxide that is of petrochemical origin. Assuming $\delta^{18}O_{\text{VPDB}} = -24 \text{ \%}$ which is typical of petroleum-derived carbon dioxide and a stochastic distribution of C and O isotopes, yields a relative abundance of the $^{12}$C$^{16}$O\textsubscript{2} (626) isotopologue equal to 0.984 7 ± 0.000 1 for the both sample gases. We note that this value is approximately 0.05 \% greater than the relative abundance $\chi_{626,HT} = 0.984 2$ assumed in the HITRAN database. Following this convention, all
measured intensities reported below are normalized to a $^{12}\text{C}^{16}\text{O}_2$ relative abundance corresponding to $\chi_{626,HT}$ using the multiplicative factor $\chi_{626,HT}/\chi_{626} = 0.999463$.

2.7 Measurement of sample temperature and pressure

Temperature and pressure measurements were performed using NIST-calibrated sensors and instruments with traceability to the SI. Sample gas conditions corresponded to five pressures ranging from 6 kPa to 34 kPa. The temperature was measured by a 100 Ω industrial-grade, platinum resistance thermometer (PRT) located at the mid-plane of the resonator (20 mK Type B standard uncertainty) and in direct contact with the outside surface of the stainless steel tubing (OD = 1.25 cm) forming the ring-down cavity enclosure. The PRT temperature was logged continuously yielding an average standard deviation of 40 mK during the time to acquire each spectrum. Temperature uniformity was confirmed to be better than $\Delta T < 30$ mK by making a series of Type-J thermocouple electromotive force measurements across the gas cell. The absolute pressure of the gas sample under flowing conditions was measured outside of the pressure control loop described in Section 2.6 by a resonant-Si gauge manometer with a full-scale range of 133 kPa. This gauge was calibrated against a NIST pressure standard, resulting in Type B standard relative uncertainties between 0.004 % and 0.002 % over the entire measurement range. Further, the pressure difference across the gas cell under flowing conditions was measured to be $< 0.008$ % of the mean value.

2.8 Probe laser and optical detection

Continuous spectral coverage from $4989 \text{ cm}^{-1}$ to $5009 \text{ cm}^{-1}$ was achieved by two fiber-coupled distributed feedback (DFB) laser diodes, each with a linewidth less than 2 MHz. An optical fiber amplifier increased the laser power to 20 mW before injection into an AOM operating at 55 MHz. The first-order output of this probe laser AOM was subsequently coupled into the optical resonator. Laser tuning and cavity resonance was achieved as described in [13], and cavity decays were initiated by switching off the RF power to the probe laser AOM.

Light decaying from the optical resonator was detected using a DC-coupled, photoreceiver comprising a liquid-N$_2$-cooled 0.5-mm-diameter InSb photodiode and a transimpedance amplifier. The manufacturer’s specifications included: photodiode responsivity of 1.45 A/W and noise-equivalent power (NEP) of 0.2 pW Hz$^{-1/2}$; amplifier bandwidth of 20 MHz and gain of $2\times10^4$ V/A.
Triggered signal levels (1 V) corresponded to about 35 μW of peak optical power. The photoreceiver output signal was digitized by a 16-bit acquisition card (1 MΩ input impedance) at a sampling rate of 200 MSamples/s. We measured integrated root-mean-square (RMS) noise levels (DC-100 MHz) equal to 0.3 mV and 1.3 mV for the digitizer board and photoreceiver, respectively. A detailed analysis of the noise power spectral density revealed non-white-noise behavior with a much lower spectral density in the frequency range relevant to the decay time measurement (0.08 mV at 1 MHz bandwidth).

Decay signals were fit in real time using a fast fitting algorithm [15], and at each spectrum detuning step 150 decay signals were averaged to provide \( \bar{\tau} \) and the ensemble standard deviation \( \sigma_\tau \). For the empty-cavity case, the relative decay time measurement precision \( \sigma_\tau / \bar{\tau} \) and decay signal acquisition rate were approximately 0.06 % and 10 Hz, respectively, corresponding to a minimum noise-equivalent absorption coefficient (NEA) of \( 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2} \). Allan deviation analysis of the decay time statistics resulted in a minimum detectable absorption coefficient of \( 10^{-10} \text{ cm}^{-1} \) when averaging 1 000 measured decay events.

In order to address possible systematic effects associated with our choice of detector/amplifier system, a limited number of spectra also were acquired with another detection system: a thermoelectrically cooled, DC-coupled, InGaAs photodiode (0.3 mm diameter, 0.9 V/A) coupled to a transimpedance amplifier (6.2×10⁴ V/A) with 10 MHz of bandwidth. The spectral noise density of this system exhibited a relatively white frequency distribution, with integrated values 3.5 to 2 times greater (over the ranges DC-100 kHz to DC-10 MHz, respectively) than those observed with the InSb photoreceiver. Most importantly, compared to the InSb photoreceiver system, the decay time measurement precision was degraded 7- to 10-fold.

### 3. Data Analysis

#### 3.1 Spectrum Model

All measured spectra (in dimensions of loss-per-unit length) were modeled as

\[
\frac{1}{c\tau(\Delta\nu_q)} = \alpha_b(\Delta\nu_q) + \sum_{n=1}^{n} \alpha_n(\Delta\nu_q) \tag{1}
\]

in which \( \Delta\nu_q = \Delta q \nu_f \) is the spectrum detuning, \( \alpha_b(\Delta\nu_q) \) represents the base cavity losses (mirror reflectivity, scattering losses and etalons etc.) and \( \alpha_n(\Delta\nu_q) \) corresponds to the absorption
coefficient of the \( n \)th observed molecular transition. For the limited spectral regions considered here no etalons in the spectrum baseline were observed and it was sufficient to model \( \alpha_n(\Delta \nu_q) \) as a linear function of \( \Delta \nu_q \). The summation over \( n \) absorption transitions accounts for blended spectra caused by spectral interferences such as those shown in Fig. 1, including both water vapor and relatively weak CO\(_2\) lines. The absorption coefficient from each line was modeled by

\[
\alpha_n(\Delta \nu_q) = A_n g_n(\nu_0 + \Delta \nu_q - \nu_n),
\]

(2)

where \( A_n \) is the line area, \( g_n \) is the area-normalized line profile (described below), \( \nu_0 \) is the absolute frequency of the first spectrum point, and \( \nu_0 + \Delta \nu_q - \nu_n \) is the spectrum detuning relative to transition \( n \) located at center frequency \( \nu_n \).

In order to minimize uncertainty in determining the areas of the target transitions, we chose to model these line shapes with the quadratic speed-dependent Nelkin-Ghatak line profile (qSDNGP) [16]. No attempt was made to determine physically meaningful line profile parameters from these data. This profile, also known as the quadratic speed dependent hard collision profile (qSDHC), accounts for both collisional (Dicke) narrowing and speed dependent effects in the quadratic approximation and is a limiting case of the recently recommended Hartmann-Tran profile (HTP) [17]. In addition to the line area \( A_n \) and line center \( \nu_n \), remaining parameters of the qSDNGP include: Doppler half-width, velocity-averaged Lorentzian half-width, speed dependent relaxation rate, velocity-averaged line shift, speed-dependent line shift, and frequency of velocity-changing collisions given by \((\Gamma_D, \Gamma_0, \Gamma_2, \Delta_0, \Delta_2, \nu_{vc})\), respectively. In this analysis, single spectrum fits were obtained at a given pressure by using the calculated Doppler width, setting the line shift parameters \( \Delta_0 = \Delta_2 = 0 \), and by floating the five parameters \( A, \nu_0, \Gamma_0, \Gamma_2, \) and \( \nu_{vc} \). We also investigated the extent to which the fitted area depended on either of two physical constraints for the parameters \( \Gamma_2 / \Gamma_0 \) and \( \nu_{vc} \). The two constraints are:

\[
\Gamma_2 / \Gamma_0 = (1-n) \frac{2}{3} \frac{m_p}{m_a} \frac{1}{1 + \frac{m_p}{m_a}} [18]
\]

\[
\nu_{vc} = k_B T / (2 \pi m_a D)
\]

where \( n \) is the temperature exponent for the broadening coefficient, \( m_p / m_a \) is the perturber-to-absorber mass ratio, \( k_B \) is the Boltzmann constant, and \( D \) is the mass diffusion coefficient of the CO\(_2\) in N\(_2\) (assumed to be proportional to pressure and equal to 0.16 cm\(^2\) s\(^{-1}\) at \( p = 101 \) kPa) [19]. We found essentially identical fitted areas (to within the fit uncertainties at the 0.05 % level) for all cases considered.
In addition to capturing more of the collisional physics as compared to the standard Voigt profile, our analysis is consistent with previous studies in which the qSDNGP yielded relatively small systematic fit residuals while introducing minimal uncertainty in the measured line areas [9]. The highest fit quality QF (defined below) was obtained for the R16 line at transition wave number $\tilde{\nu}_0 = 4,989,971,515$ cm$^{-1}$ (QF = 4200) at a pressure of $p = 26.8$ kPa using mixture A. This spectrum resulted in an individual relative fit uncertainty for the line area $A$ equal to 0.01 %. As expected, the fitted area obtained after setting $\Gamma_2 = v_{ec} = 0$ (which corresponds to the Voigt profile case) gave peak areas that were systematically low of those obtained using the qSDNGP by more than 0.5%.

CO$_2$ and background H$_2$O interferences were assigned based on tabulated positions given in HITRAN 2012, and their respective Voigt profiles were used by fixing the Doppler width to its calculated value and floating the peak area and Lorentzian width. Also, lines R16 through R28 were fitted using the constrained far-wing contributions of the neighboring target lines using the qSDNGP. However, we identified three cases of interferences which required more detailed analysis to optimize fit residuals, including: 1) weak $^{12}$C$^{16}$O$_2$ lines partially overlapping with the strong target lines and detuned by 2 GHz to 3 GHz (R16, R20 and R24), 2) overlapping $^{13}$C$^{16}$O$_2$ lines within 1 GHz of the target lines (R22, R32, R46 and R53), and 3) partially overlapping water vapor lines (intensities ranging from $10^{-25}$ cm/molec. to $10^{-23}$ cm/molec (R18, R24 and R42). In cases 1 and 3, the total area of the interferences plus the target lines was fit simultaneously to optimize the fit residuals. Subsequently, the model for total area was refit to the data by constraining the line intensity ratio ($S_{interference}/S_{target}$) using either HITRAN 2012 [14] values or those in the UCL database [20]. This two-step fitting procedure was necessary to ensure that the fitting algorithm converged to a result exhibiting minimal residual peak area, consistent with literature values for the interfering intensities. The choice of the database affected the resulting target intensity $S_{target}$ by less than 0.01 %. The same procedure was followed for case 2, although the first step (fitting the total area and then constraining) was omitted. The difference between constrained and unconstrained fits was biggest for case 2 ($^{13}$CO$_2$ interferences) and was approximately 0.5 % for the R46 and R52 lines.

We note that the level of background water vapor varied strongly with time in our experiment. Based on fitted areas and published water vapor line intensities, the molar fraction of water vapor in our samples decreased tenfold over a time of one week from nearly 300 μmol/mol
down to about 30 μmol/mol. We attribute this decrease to water vapor desorbing from the bounding surfaces of the ring-down cell after exposure to room air. Of the three target transitions where water vapor absorption was modeled, only the R42e line was significantly influenced by an overlapping water line. Representative spectra for this transition are given in Fig. 3. Moreover, this specific interference was problematic only for water vapor molar fractions greater than about 100 μmol/mol. In this case, only spectra acquired with water vapor concentrations below this level were considered in the final analysis.

3.2 Rescaling to account for temperature variations

Drift in the laboratory conditions during spectral acquisition led to changes in the temperature of the sample gas within the ring-down cell. During acquisition of individual spectra, these data exhibited an average standard deviation of 0.038 K and a maximum excursion of 0.15 K. In the absence of any temperature correction, this variability may compromise the measurement accuracy, especially for the high-\( J \) transitions which have a relatively strong temperature dependence to the line intensity (e.g. 1.34 % K\(^{-1}\) for \( J'' = 52 \)). In order to correct for this measured effect, we rescaled the spectra at each frequency step by accounting for the temperature dependence of the total gas number density, line intensity, and the Lorentzian half-width. Unlike the temperature, the measured total gas pressure was observed to be constant within a range of ±0.02 % of the mean value, and hence this quantity was treated as a constant during each spectrum acquisition.

Here we assume ideal gas law conditions (maximum relative uncertainty of 0.006 % at the sample conditions), where the sample number density at each frequency step is

\[
  n_q = \chi_{CO_2} \frac{p}{k_B T_q} \tag{3}
\]

in which the index \( q \) indicates the frequency step, \( \chi_{CO_2} \) is the molar fraction of CO\(_2\), and \( p \) and \( T_q \) are the measured pressure and temperature of the gas sample at each frequency step, respectively. Considering only the target line of intensity \( S(T_q) \), the uncorrected, measured absorption coefficient associated with this transition is

\[
  \alpha_q(\Delta\nu_q) = n_q c S(T_q) g \left( \delta\nu_q, \Gamma_0(T_q) \right) \tag{4}
\]

where we have dropped the transition index \( n \) used in Eq. 2 and where \( \delta\nu_q \) is the spectrum detuning relative to line center.
We assume that the rescaling of the data affects only the absorptive part of the measured spectrum, without altering the base losses of the ring-down cavity. It follows that it is sufficient to define an excess absorption \( \Delta \alpha_q = \alpha_q(T_q) - \alpha_q(\bar{T}) \) of the target transition relative to its expected value at the mean spectrum temperature \( \bar{T} \). At each frequency step \( q \) we can write,

\[
\Delta \alpha_q = \alpha_{\text{fit},q}(f_{\text{norm},q} - 1),
\]

with the normalization factor as the product of three temperature-dependent ratios,

\[
f_{\text{norm},q} = \frac{T_q}{\bar{T}} \frac{S(\bar{T})}{S(T_q)} \frac{g(\delta \nu_q, \Gamma_0(\bar{T}))}{g(\delta \nu_q, \Gamma_0(T_q))}.
\]

Here \( \alpha_{\text{fit},q} \) is the absorption coefficient obtained by fitting the assumed line profile (qSDNGP) and a linear baseline to the uncorrected data assuming a constant temperature of \( \bar{T} \).

The line intensity ratio in Eq. 6 depends upon the molecular partition function \( Q(T) \) as well as the energy of the lower-state rovibrational level \( E'' \) [21]. We used the partition function for \(^{12}\text{C}^{16}\text{O}_2\) which is calculated from direct summation and based on the variational calculations of \( E' \) given by Huang et al. [22]. This new partition function has been adopted by HITRAN 2016 [23] and differs by approximately \(-0.3\% \) from the previous calculation used in HITRAN 2012 at the standard reference temperature \( T_r = 296 \text{ K} \). We note however, that the old and new calculations for the ratio \( Q(T)/Q(T_r) \) differ by less than \( 0.003 \% \) over the temperature range of 290 K to 300 K.

In terms of the partition function and associated parameters, the scaling factor used in converting the line intensity from \( T \) to \( \bar{T} \) was modeled as

\[
\frac{S(\bar{T})}{S(T)} = \frac{Q(T_q)}{Q(T)} \exp[-\frac{\hbar E''}{k_B} (\frac{1}{\bar{T}} - \frac{1}{T_q})].
\]

The line profile ratio in Eq. 7 was evaluated assuming a standard power-law dependence for \( \Gamma_0(T_q) = \Gamma_0(\bar{T}) \left( \frac{T}{T_q} \right)^n \) where \( n \) is again the temperature exponent for the broadening coefficient (ranging from 0.69 to 0.76 for the measured lines) as specified in HITRAN 2012 for the case of air-broadening. For the purposes of this correction, all other qSDNGP line profile parameters (except for \( \Gamma_0 \) ) were assumed to be independent of temperature.

With the preceding definitions, the corrected total loss-per-unit length measured at each step \( q \) was evaluated as
We subsequently fit Eq. 8 to the corrected total losses by floating the five parameters $A, \nu_0, \Gamma_0, \Gamma_2$ and $\nu_\infty$, thereby providing a peak area $A(\bar{T})$ that corresponds to the spectrum-averaged temperature $\bar{T}$. Given the small correction, only one iteration of the algorithm was implemented in rescaling the spectrum.

3.3 Standard Line Intensity Determination

In order to determine the line intensity at $T_r = 296$ K we also normalized each measured peak area $A(\bar{T}) \equiv A_{296}$ using

$$A_{296} = \frac{\bar{T} \ S(T_r)}{T_r \ S(\bar{T})} = \frac{T_r \ Q(\bar{T})}{T_r \ Q(T_r)} \exp\left[-\frac{hcE''}{k_B} \left(\frac{1}{T_r} - \frac{1}{\bar{T}}\right)\right].$$

Using the relationship between peak area (in GHz/cm), absorber number density and intensity gives the following linear correspondence between $A_{296}$ and $p$,

$$A_{296} = S_{296} c n_{CO_2}(p, T_r),$$

in which $S_{296}$ and $n_{CO_2}(p, T_r)$ are the line intensity in units of $\text{cm}^{-1}/(\text{cm}^2 \text{molec.})$ and number density of CO$_2$, respectively at $T_r$. The linear correspondence assumed in Eq. 10, where we have integrated over the normalized line profile (i.e., $\int g(\nu) d\nu = 1$), was rigorously evaluated for all transition intensities reported herein (see Section 5).

The reported line intensities and standard uncertainties were obtained by weighted linear regression (with 0-intercept) of the $A_{296}$ vs. $n_{CO_2}(p, T_r)$ data using Eq. 10, thus yielding a slope equal to $S_{296} c$. In each linear regression, the weighting factors were given by $1/\sigma_A^2$ where $\sigma_A(p)$ is the standard error in the fitted peak area at pressure $p$. This uncertainty scales inversely with the observed quality-of-fit (QF) factor for the chosen line profile [24]. We note that this type of regression analysis is equivalent to a weighted average of the $S_{296}$ values obtained from Eq. 10 where the respective weighting factors are given by $1/(p \sigma_A^2(p))$. Figure 3 illustrates the linear regression analysis for the R36 transition. Because the derived line intensity depended upon multiple spectra which were measured over time intervals typically exceeding one week, the slope...
uncertainties determined above account for the majority of the Type A (statistical) uncertainty in $S_{296}$. As discussed below, this component of the overall uncertainty can be assigned to statistical variability in sample conditions and noise in the measured ring-down spectra.

4 Evaluations of Measurement Uncertainty

Combined uncertainties in $S_{296}$ reported herein include both the type A (statistical) and type B (systematic) experimental uncertainties. Apart from the transition-dependent uncertainty in the temperature renormalization and the slightly different uncertainties on the sample gases (0.04 % and 0.06 % for mixtures A and B, respectively), the Type B relative uncertainties in $S_{296}$ (for mixture B) are nearly the same for all measured transitions and range from 0.072 % to 0.092 %. An example calculation of combined Type B uncertainty for the R36 transition is shown in Table 1. The component relative standard uncertainties assigned to temperature, pressure, non-ideal gas effects, isotopologue relative abundance, spectrum detuning axis (FSR), choice of line profile, and CO$_2$ molar fraction are (0.003 %, 0.009 %, 0.006 %, 0.01 %, 0.03 %, 0.05 %, 0.06%), respectively, resulting in a relative combined standard Type B uncertainty of 0.084 %.

The most important contributors to the Type B uncertainty are the choice of line profile, FSR determination, and CO$_2$ molar fraction. Of these three quantities, the FSR could be reduced below 0.000 5 % (1 kHz) relative uncertainty with higher-precision methods that use a more stable cavity locking reference laser and/or optical frequency comb as described in Ref. [10]. However, substantial reduction in the uncertainty of the line profile awaits advanced theoretical treatments that will require experimental validation. Likewise, substantial reduction in the uncertainty of the sample gas CO$_2$ molar requires challenging technical advances in gravimetric preparation and mitigation of surface adsorption/desorption effects that alter the relative abundance of CO$_2$ within the sample chamber over time.

Also shown in Table 1 is the Type A uncertainty for the R36 transition. This value was estimated to be 0.075 % based on the slope uncertainty of the weighted linear regression for the $A_{296}$ vs. $p$ data. We note that these measurements spanned roughly one week and were subject to relatively long-term variations in the spectrometer performance. As expected, the measured Type A relative uncertainties tended to decrease as the line intensity and spectrum QF increased.
However, variations in the sample conditions achieved over long time scales likely dominated the Type A uncertainty for all cases considered. We found that measurements of $S_{296}$ which were repeated several months apart exhibited similar variation (0.15 %) as that resulting from a set of $A_{296}$ vs. $p$ data which was acquired over a much shorter (week-long) time scale.

The most likely source of irreproducibility in the measured intensity would be caused by temperature- and flow-dependent interactions of the CO$_2$ with the internal surfaces of the ring-down cell. Although the measurements were always done under flowing conditions to mitigate wall effects, the duty cycle of spectrum acquisition was well below 100 %. During the dormant times, we kept a static charge within the ring-down cell to conserve sample gas. Under these conditions, CO$_2$ tends to adsorb to the walls of the ring-down cell, and thereafter desorb as gas flow resumed prior to spectrum acquisition. In order to investigate this effect, we measured intensities of a several transitions at two flow rates and for two CO$_2$ molar fractions, by quantities varying by a factor of two. For all cases, measurement reproducibility was better than 0.15 %, and comparable to the long-term Type A measurement uncertainty.

Intensities for seven of the CO$_2$ transitions investigated here were measured using both photoreceivers described in Sec. 2.8. Relative differences between the measured intensities encompassing these transitions had a standard deviation of 0.43 % which was dominated by the higher noise level of the InGaAs photoreceiver. Also, because the average relative difference in line intensity was 0.35 % and comparable to the standard deviation, this comparison provided no evidence of systemic effects on measured line intensity associated with our choice of photoreceiver.

5 Results

As an illustrative example, we present the measurement of the R36 line intensity at $\tilde{V}_0 = 5\,001.49871$ cm$^{-1}$. Three representative spectra spanning 14 GHz of tuning range are plotted in the top panel of Fig. 4. Results are shown for mixture A at three constant pressure conditions: 6.78 kPa, 20.16 kPa, and 33.54 kPa, respectively. The measured spectra (colored markers) comprised a single CO$_2$ transition, centered at a frequency detuning of $\delta \nu_0 = 0$. The spectra were fit (solid lines) using the qSDNGP, and the fit residuals with a standard deviation of $8 \times 10^{-10}$ cm$^{-1}$.
are plotted in the bottom panel (solid lines with markers). For the R36 transition, the highest observed quality-of-fit factor was QF = 1 700 at ρ = 20.16 kPa.

Temperature-corrected fitted line areas for several transitions are plotted vs. number density in Fig. 5, along with the corresponding fit uncertainties and fit residuals. Continuing with the illustrative example, an unweighted linear regression of $A_{296}$ vs. number density for the R36 line yielded $S_{296} = 3.904 \times 10^{-22}$ cm/molec. with a combined standard uncertainty of $u_r(S_{296}) = 7 \times 10^{-25}$ cm/molec. (see Table 1, relative combined standard uncertainty of 0.18 %). The fit residuals plotted in the bottom panel, with a standard deviation of 0.005 kHz cm$^{-1}$, illustrate the observed high degree of linearity in the measured values of $A_{296}$ vs. number density.

A list of measured intensities for 19 transitions of the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band ranging from R16 to R52 can be found in Table 2. These data span the wave number range 4 989 cm$^{-1}$ to 5 009 cm$^{-1}$. Included for comparison are intensities from both HITRAN 2012 [14, 25] and the Carbon Dioxide Spectroscopic Databank (CDSD-296) [26]. We also compare the NIST data to rovibrational line intensities calculated by Zak et al. (UCL) using various semi-empirical and ab initio potential energy surfaces (PES) in combination with an ab initio dipole moment surface (DMS) for $^{12}$C$^{16}$O$_2$ [20] as well as those calculated by Huang et al. (Ames-2016) using a semi-empirically refined PES and an ab initio DMS [27].

6 Discussion

6.1 Comparison with the literature – databases

For comparison between existing databases and our highly accurate intensities we define the relative difference $\varepsilon = S_l/S_{NIST} - 1$, where $S_l$ are either the HITRAN 2012 [14, 25], CDSD-296 [26], Ames-2016 [27], or UCL [20, 23] intensities and $S_{NIST}$ the corresponding measured NIST intensities. Values of $\varepsilon$ are given in Table 2, and plotted in Fig. 6. The tabulated HITRAN 2012 line intensities, which originated from Ref. [25], differ from those reported here by as much as $-3\%$. The magnitude of this difference is larger for more intense lines, and changes sign at higher rotational quantum numbers ($m = J'' + 1$ for R-branch transitions). A systematic deviation of this magnitude is significantly larger than the target uncertainties of current and future remote sensing campaigns [1-4].
Smaller systematic deviations with magnitude of approximately 1% are also observed for CDSD-296 ($\bar{\epsilon} = -1.1\%$), where $\bar{\epsilon}$ is the mean value of all $\epsilon$ plotted in Fig. 6. Of the line list databases considered here, the recently reported ab initio intensities from UCL [20] and Ames-2016 [27] exhibit the best agreement with our measurements, with average relative differences of $\bar{\epsilon} = -0.20\% \pm 0.27\%$ and $\bar{\epsilon} = -0.26\% \pm 0.27\%$, respectively. This level of agreement between theoretical ab initio and experimental line intensities is similar to that demonstrated in a recent study of the (30013) - (00001) $^{12}\text{C}^{16}\text{O}_2$ band, where the UCL ab initio calculations and NIST FS-CRDS measurements yielded $\bar{\epsilon} = -0.33\%$ and $\sigma_\epsilon = 0.23\%$ [28].

The high-level agreement between rigorous experimental measurements of $^{12}\text{C}^{16}\text{O}_2$ transitions intensities and those calculated by UCL using ab initio quantum chemistry methods has, in large part, motivated the further integration of the UCL database into the most recent edition of HITRAN 2016 (see Section 2.2, including Fig. 7, of Ref [23]). The continued benchmarking of ab initio intensities against experimental measurements of the highly abundant isotopologues (i.e., $^{12}\text{C}^{16}\text{O}_2$) enables the confident inclusion of calculated line list parameters for hot-band lines, rare and clumped isotopologues and other low-abundance species that are difficult to measure experimentally with sufficient accuracy and precision.

6.2 Comparison with literature – individual experiments

In Fig. 7, intensity measurements reported by the French National Center for Scientific Research (CNRS, blue circles) [29] and the Seconda Università di Napoli (SUN, red diamonds and magenta inverted triangles) [30-32] are shown to be in modest agreement with the NIST values. However, the claimed uncertainty in the SUN intensities appears largely underestimated [30-32], especially for the R16e and R18e transitions [31, 32]. The underestimated uncertainties in the SUN data were eluded to by Wübbeler et al. in a detailed study of the R12 transition intensity [33]. Recent work by Odintsova et al. [34] revisited the R2, R4, and R6 rovibrational transitions using optical feedback cavity enhanced absorption spectroscopy (OF-CEAS) referenced to an optical frequency comb, multispectral fitting, and the HTP, and subsequently identified the source of the underestimated intensities and uncertainties as 1) the choice of line profile (GP and NGP [32] vs. HTP [34]) and 2) the use of low-accuracy pressure gauges in Ref. [31-32]. As state in Section 3.1, we note that the use of specific limiting cases of the HTP (such as the Voigt profile)
to fit spectra reported herein resulted in the systematic underestimation of the transition intensity on the order of 0.5 %.

Figure 7 also serves to illustrates the comprehensive nature (19 individual transitions measured with absolute accuracy between 0.15 % and 0.46 %) of this NIST experimental study of transitions intensities throughout the R-branch of the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band near $\lambda = 2 \mu$m.

6.3 Detailed comparison with the UCL ab initio DMS (HITRAN 2016)

Returning to the comparison with the UCL database, several experimental measurements of the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band, as well as the CDSD-296 values, are again plotted vs. $m$ in Fig. 8, but this time, relative to the UCL ab initio intensities. In Fig. 8, we define $\varepsilon_{UCL} = S_i / S_{UCL} - 1$, where $S_{UCL}$ are the intensities calculated by Zak et al. [20] and recently adopted by HITRAN 2016 [23], and $S_i$ are values from NIST (reported herein), University of Naples II (UniNA2) [34], Physikalisch-Technische Bundesanstalt (PTB) [33], and CDSD-296 [26], respectively. In the top panel, the range of lower-state rotational quantum numbers is expanded to include both P- and R-branch transitions of $|m| \leq 60$, currently outside of the tuning range of the NIST instrument. This overview of the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band reveals a subtle yet significant trend in $\varepsilon_{UCL}$ vs. $|m|$ for both the combined NIST + PTB + UniNA2 high-precision data set and CDSD-296.

Also plotted relative to the UCL database [20, 23] in the top panel of Fig. 8 are the Ames-2016 intensities [27]. An unphysical discontinuity appears in Ames-2016 as $|m| \rightarrow 0$, attributed to a known basis set convergence error [27]. An update to Ames-2016 which eliminates this so-called “J-jump” is promised [27]. Given the estimates in Section 3.1 of [27], the Ames-2016 update will most likely decrease slightly the level of agreement between NIST and Ames-2016 quantified in Section 6.1 of this manuscript by approximately 0.25 % to 0.3 %, or approximately half of the reported usual “J-jump” splitting of 0.5 % to 0.6 % observed in Ames-2016 for the symmetric CO$_2$ isotopologues.

A detailed look at the highly accurate R-branch data is shown in the bottom panel of Fig. 8. Superimposed upon the combined data set of NIST + PTB + UniNA2 is a quadratic regression (dotted black line) of the CDSD-296 intensities, shifted by $\delta_{\varepsilon_{UCL}} = +1.1 \%$ relative to the CDSD-296 values (open circles). The shift value $\delta_{\varepsilon_{UCL}}$ was estimated from the average relative deviation $S_i / S_{CDSD} - 1$, where $S_i$ are the individual transition intensities within the combined NIST + PTB...
+ UniNA2 data set (19 NIST transitions, 1 PTB transition, and 3 UniNA2 transitions, respectively) and $S_{CDD}$ are the corresponding CDSD-296 intensities.

Rationale for the magnitude and sign of the empirical shift parameter $\delta_{\varepsilon_{UCL}}$ is found by studying the origins of the $(20012) - (00001)$ $^{12}$C$^{16}$O$_2$ band intensities predicted by CDSD-296 [26]. In Section 4.2 of Ref. [26], Tashkun et al. reported a direct comparison between CDSD-296 predictions and the 9 transition intensities of Casa et al. [32], noting good agreement (within reported experimental error). It is now accepted, however, from Refs. [33-34] and from this work, that the intensity measurements of Casa et al. [31-32] were systematically low due to the choice of line profile, and that the quoted accuracy was overestimated [34]. For the R2, R4, R6, R12, R16, and R18 transitions, we find that $S_l$ from the combined NIST + PTB + UniNA2 data set are, on average, 1.6% greater than $S_l$ reported by Casa et al. [32]. We therefore postulate that the Casa et al. measurements influenced the systematic shift in the CDSD-296 intensities predicted for the $(20012) - (00001)$ $^{12}$C$^{16}$O$_2$ band, as evidenced by the empirical shifting factor $\delta_{\varepsilon_{UCL}} = 1.1\%$.

Beyond the systematic shift parameter $\delta_{\varepsilon_{UCL}}$ (which is independent of $m$), a subtle yet significant trend in $\varepsilon_{UCL}$ vs. $m$ was observed for the combined NIST + PTB + UniNA2 intensities. Inspection of the black dotted line in the bottom panel of Fig. 8 reveals that the magnitude and sign of the trend in $\varepsilon_{UCL}$ vs. $m$ observed for the combined NIST + PTB + UniNA2 experimental intensities agree with the quadratic trend predicted by CDSD-296 using an effective Hamiltonian and DMS. This trend in experimental and semi-empirical data sets, whether quadratic or otherwise, could indicate the limited accuracy with which quantum chemistry calculations of $S$ performed using a full $ab\ initial DMS [20]$ predict the $m$-dependence of the line intensity. Similar trends have also recently been observed in the high-resolution Fourier transform spectroscopy of the $(20013) - (00001)$ and $(30013) - (00001)$ $^{12}$C$^{16}$O$_2$ bands [35, 36]. Semi-classical spectroscopic expressions for $S_v$ (the total vibrational band intensity) generalized using perturbation theory to include vibration-rotation interactions via the $F$-factor often are used to fit residual $m$-dependence in the line intensity that is not captured by the standard Hönl-London factors. For the so-called parallel bands of CO$_2$ where $\Delta l = 0$, this factor is modeled as $F = (1 + a_1 m + a_2 m^2 + a_3 m^3)^2$ [36-39], where $F$, and $a_x$ are the Herman-Wallis coefficients which model perturbations to the standard rigid-rotor Hamiltonian (i.e., vibration-rotation interactions) [40]. Without corresponding accurate FS-CRDS measurements of numerous transitions intensities within the P-branch ($m < 0$) of the
(20012) - (00001) \(^{12}\text{C}^{16}\text{O}_2\) band, however, it is premature to fit the \(F\)-factor and definitively report updated, values of \(S_v\) and \(\alpha_\epsilon\) [39]. This is the focus of ongoing and future experiments at NIST.

7 Conclusion

We report experimentally determined line intensities throughout the R-branch of the (20012) - (00001) band of \(^{12}\text{C}^{16}\text{O}_2\) near \(\lambda = 2 \, \mu\text{m}\). These intensities, measured by frequency-stabilized cavity ring-down spectroscopy, provide the most stringent experimental test of \textit{ab initio} dipole moment and potential energy surfaces. Benchmarking \textit{ab initio} calculations at standard conditions is a prerequisite for establishing the validity of extrapolating calculated molecular reference data to extreme thermodynamic and exotic kinetic conditions [41]. As was the case for \(^{12}\text{C}^{16}\text{O}_2\) intensities at \(\lambda = 1.6 \, \mu\text{m}\) [28], \textit{ab initio} calculations of the line intensities are overall found to be in excellent agreement with our high-accuracy experimental values. The further validation of theory (both \textit{ab initio} and semi-empirical effective Hamiltonian approaches) by high-accuracy measurements of experimental reference data will undoubtedly expand our understanding of planetary and atmospheric sciences by enabling increasingly precise remote sensing missions.

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REFERENCES:


Table 1. Standard (1σ) uncertainty components contributing to uncertainty in the measured intensity of the (20012) - (00001) band R36 $^{12}$C$^{16}$O$_2$ transition located at $\tilde{v}_0 = 5001.49871\text{ cm}^{-1}$. The random (type A) relative standard uncertainty is dominated by the 0.15 % irreproducibility value in the intensities determined from repeating peak area vs. number density data sets. The systematic (type B) uncertainties are nearly identical for all transitions, the sole difference being caused by the transition-dependent sensitivity of the temperature correction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$u_r(S_{296})$ (%)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{296}/n$</td>
<td>0.04</td>
<td>$^a$from weighted regression of $A_{296}$ vs. $n$</td>
</tr>
<tr>
<td>$&lt;A_{296}/n&gt;$</td>
<td>0.15</td>
<td>long-term measurement repeatability</td>
</tr>
<tr>
<td><strong>Type B</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(S(T_i)/S(T))(T/T_i)$</td>
<td>0.01</td>
<td>transition-dependent $T$ correction</td>
</tr>
<tr>
<td>$p$</td>
<td>0.01</td>
<td>pressure and non-ideal gas effects</td>
</tr>
<tr>
<td>$\chi_{CO_2}$</td>
<td>0.06</td>
<td>$^b$sample molar fraction</td>
</tr>
<tr>
<td>$\chi_{626}$</td>
<td>0.01</td>
<td>isotopic abundance of $^{12}$C$^{16}$O$_2$</td>
</tr>
<tr>
<td>$\delta_{13c}$</td>
<td>0.04</td>
<td>$\delta_{13c}$ concentration</td>
</tr>
<tr>
<td>$A$ (line shape)</td>
<td>0.05</td>
<td>$^c$area uncertainty caused by choice of line profile</td>
</tr>
<tr>
<td>FSR</td>
<td>0.03</td>
<td>cavity free spectral range</td>
</tr>
<tr>
<td><strong>Combined Type B</strong></td>
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<td></td>
</tr>
<tr>
<td><strong>Combined Types A &amp; B</strong></td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Average value. Individual values for all lines range from 0.014 % to 0.14 %.

$^b$Uncertainty (k = 1) for gravimetrically prepared cylinder with $\chi_{CO_2} = 49.826 \text{ µmol/mol}$ (mixture A) the uncertainty is 0.04 %. For the cylinder with $\chi_{CO_2} = 100.474 \text{ µmol/mol}$ (mixture B), the uncertainty is 0.06 %.

$^c$Based on variation of fitted peak area with chosen line profile.
Table 2. Intensities for the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band measured in this study, along with the corresponding total combined uncertainties. For comparison, we also list the relative differences $\varepsilon = S/S_{NIST} - 1$ between literature values and the NIST intensities. All intensities are referenced to 296 K and to a relative abundance of 0.984 2 for the $^{12}$C$^{16}$O$_2$ isotopologue.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\bar{\nu}_0$ (cm$^{-1}$)</th>
<th>$S_{296}$ (10$^{-22}$ cm/molec.)</th>
<th>$u_r(S_{296})$ (10$^{-24}$ cm/molec.)</th>
<th>UCL $\varepsilon$ (%)</th>
<th>Ames $\varepsilon$ (%)</th>
<th>CDSD $\varepsilon$ (%)</th>
<th>HITRAN 2012 $\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R16e</td>
<td>4 989.971 52</td>
<td>13.27</td>
<td>2</td>
<td>-0.60</td>
<td>-0.69</td>
<td>-1.2</td>
<td>-3.0</td>
</tr>
<tr>
<td>R18e</td>
<td>4 991.258 51</td>
<td>12.98</td>
<td>2</td>
<td>-0.46</td>
<td>-0.52</td>
<td>-1.1</td>
<td>-2.8</td>
</tr>
<tr>
<td>R20e</td>
<td>4 992.515 74</td>
<td>12.37</td>
<td>2</td>
<td>-0.24</td>
<td>-0.31</td>
<td>-0.89</td>
<td>-2.5</td>
</tr>
<tr>
<td>R22e</td>
<td>4 993.743 17</td>
<td>11.542</td>
<td>1.9</td>
<td>-0.45</td>
<td>-0.49</td>
<td>-1.1</td>
<td>-2.5</td>
</tr>
<tr>
<td>R24e</td>
<td>4 994.940 78</td>
<td>10.529</td>
<td>1.8</td>
<td>-0.56</td>
<td>-0.64</td>
<td>-1.3</td>
<td>-2.6</td>
</tr>
<tr>
<td>R26e</td>
<td>4 996.108 54</td>
<td>9.387</td>
<td>1.6</td>
<td>-0.59</td>
<td>-0.65</td>
<td>-1.3</td>
<td>-2.6</td>
</tr>
<tr>
<td>R28e</td>
<td>4 997.246 41</td>
<td>8.178</td>
<td>1.4</td>
<td>-0.37</td>
<td>-0.42</td>
<td>-1.1</td>
<td>-2.2</td>
</tr>
<tr>
<td>R30e</td>
<td>4 998.354 39</td>
<td>6.961</td>
<td>1.2</td>
<td>0.19</td>
<td>0.13</td>
<td>-0.63</td>
<td>-1.6</td>
</tr>
<tr>
<td>R32e</td>
<td>4 999.432 44</td>
<td>5.853</td>
<td>1.0</td>
<td>0.034</td>
<td>-0.016</td>
<td>-0.82</td>
<td>-1.6</td>
</tr>
<tr>
<td>R34e</td>
<td>5 000.480 55</td>
<td>4.827</td>
<td>0.8</td>
<td>-0.062</td>
<td>-0.11</td>
<td>-0.97</td>
<td>-1.6</td>
</tr>
<tr>
<td>R36e</td>
<td>5 001.498 71</td>
<td>3.904</td>
<td>0.7</td>
<td>-0.051</td>
<td>-0.12</td>
<td>-1.0</td>
<td>-1.4</td>
</tr>
<tr>
<td>R38e</td>
<td>5 002.486 91</td>
<td>3.107</td>
<td>0.5</td>
<td>-0.23</td>
<td>-0.28</td>
<td>-1.2</td>
<td>-1.4</td>
</tr>
<tr>
<td>R40e</td>
<td>5 003.445 15</td>
<td>2.431</td>
<td>0.4</td>
<td>-0.49</td>
<td>-0.57</td>
<td>-1.5</td>
<td>-1.5</td>
</tr>
<tr>
<td>R42e</td>
<td>5 004.373 44</td>
<td>1.853</td>
<td>0.3</td>
<td>0.11</td>
<td>0.067</td>
<td>-1.0</td>
<td>-0.70</td>
</tr>
<tr>
<td>R44e</td>
<td>5 005.271 77</td>
<td>1.402</td>
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<td>-0.29</td>
<td>-0.32</td>
<td>-1.4</td>
<td>-0.93</td>
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<tr>
<td>R46e</td>
<td>5 006.140 19</td>
<td>1.0350</td>
<td>0.19</td>
<td>0.097</td>
<td>0.037</td>
<td>-1.2</td>
<td>-0.29</td>
</tr>
<tr>
<td>R48e</td>
<td>5 006.978 70</td>
<td>0.7542</td>
<td>0.14</td>
<td>0.053</td>
<td>-0.027</td>
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<tr>
<td>R50e</td>
<td>5 007.787 36</td>
<td>0.5402</td>
<td>0.10</td>
<td>0.056</td>
<td>-0.031</td>
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<tr>
<td>R52e</td>
<td>5 008.566 20</td>
<td>0.3804</td>
<td>0.08</td>
<td>0.079</td>
<td>-0.0018</td>
<td>-1.3</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Notes:

$a$[14, 25]

$b$[20, 23]

$c$Intensities at 296 K from Ames-2016 [27] were accessed online at http://huang.seti.org on 25 September 2017.

$d$[26]
Figure 1. Simulated absorption spectrum for the spectral region of interest revealing the dominant $^{12}\text{C}^{16}\text{O}_2$ band transitions and interferences from weaker carbon dioxide and water vapor transitions. Pressure and temperature of 133 kPa and 296 K, respectively, path length of 75 cm, and molar fractions of carbon dioxide and water vapor both equal to $10^{-4}$. Air-broadening is assumed and line parameters are based on HITRAN 2012. The lower-state angular momentum quantum number $J'$ is indicated above every other (20012) - (00001) $^{12}\text{C}^{16}\text{O}_2$ transition.
Figure 2. Schematic of the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) instrument. Free-space HeNe and DFB probe laser propagation is shown as solid red and blue lines/arrows, respectively. Electronics and radiofrequency cables are shown as solid black lines. Clockwise from the top left, acronyms and abbreviations used in the schematic are DFB, distributed feedback; FC, fiber-coupled; BS, beam splitter; OI, optical isolator, AOM, acousto-optic modulator, PBS, polarization beam splitter; L, lens; AV, valve; W, window; DM, dichoric mirror; LN, liquid nitrogen; PZT, piezo-electric transducer; PID proportional-integral-derivative; M, mirror; CCD, charge-coupled device; PC, personal computer; DDPG, digital delay pulse generator; DAQ, data acquisition; and ppm, parts-per-million.
Figure 3.  a) Spectrum of the (20012) - (00001) R42e $^{12}$C$^{16}$O$_2$ transition in the presence of two different trace amounts of H$_2$O. Plotted in blue squares is the measured spectrum at a total pressure of $P = 26.830$ kPa and a fitted H$_2$O mole fraction of $\chi_{H_2O} = 300$ $\mu$mol/mol. For comparison, the same spectrum with a significantly smaller $\chi_{H_2O}$ is plotted as red circles. Each spectrum was fitted to a sum of qSDNGPs (black lines), and broadening and transition frequency parameters for the H$_2$O interferences were held fixed to known values [14]. (b) Even in the presence of a large $\chi_{H_2O}$, the QF factor and noise on the residuals is for all intents and purposes identical for both spectra shown in (a).
Figure 4. (a) Absorption spectrum of the R36e transition within the (20012)-(00001) \(^{12}\text{C}^{16}\text{O}_2\) band recorded at pressures of \(P = 6.78\) kPa (red triangles), \(p = 20.2\) kPa (green circles), and \(p = 33.5\) kPa (blue squares), respectively. Fitted models using the quadratic speed-dependent Nelkin-Ghatak profile (qSDNGP) are plotted as solid black lines. (b) Fit residuals (observed minus calculated) for the three spectra shown in (a). The quality-of-fit (QF) is defined as \(QF = (\alpha_{\text{max}} - \alpha_{\text{min}}) / \sigma_f\), where \(\sigma_f\) is the standard deviation of the fit residuals given by \(\sigma_f = \sqrt{\frac{\sum_{q=1}^{M} [\alpha_{\text{exp}}(V_q) - \alpha_{\text{fit}}(V_q)]^2}{M - k}}\), in which \(\alpha_{\text{exp}}(V_q)\) and \(\alpha_{\text{fit}}(V_q)\) are the measured and fitted frequency-dependent absorption coefficients, respectively, \(M\) is the number of spectral points, and \(k\) is the number of adjustable line shape parameters in the fit model.
Figure 5. (a) Plot of temperature-corrected, fitted line areas ($A_{296}$) vs. CO$_2$ number density at $T_r = 296$ K for the R16, R36 and R42 (20012) - (00001) band $^{12}$C$^{16}$O$_2$ transitions. Error bars correspond to the standard uncertainty of the area reported by each spectrum fit, and the lines correspond to weighted linear regressions (with constrained 0-intercept) whose slopes yield the intensities of the respective transitions. Relative uncertainties for the fitted slopes were less than 0.03 % for all three lines. (b) Residuals from the multispectral fit illustrating the high degree of linearity of the fitted peak areas.
Figure 6. (a) Relative differences $\varepsilon = S_i/S_{NIST} - 1$, where $S_{NIST}$ are the NIST transition intensities (reported herein) and $S_i$ are the intensities from various CO$_2$ line list databases. For reference, the relative difference for the NIST intensities as compared with themselves are plotted as open black triangles with appropriate standard uncertainties. Values of $\varepsilon$ for comparisons with HITRAN 2012 (Fourier transform laser spectroscopy), CDSD-296 (calculated effective dipole moment surface (DMS)), Ames-2016 ($ab\ initio$ DMS), and UCL ($ab\ initio$ DMS) are also plotted as circles, diamonds, squares, and inverted triangles, respectively. The standard uncertainties for each database (not shown) are: HITRAN 2012, 1 % [14, 25]; CDSD-296, 1.6 % [26]; Ames-2016, 1-3 % [27]; UCL, 1 % [20, 23]. While HITRAN 2012 and CDSD-296 intensities show systematic deviations from the NIST values, the UCL and Ames-2016 $ab\ initio$ DMS intensities are in good agreement throughout the $R$-branch of the (20012) - (00001) $^{12}$C$^{16}$O$_2$ band.
Figure 7. (a) Relative differences $\varepsilon = S_i/S_{NIST} - 1$, where $S_{NIST}$ are the NIST transition intensities (reported herein) and $S_i$ are the intensities from various experiments in the literature. For reference, the relative difference for the NIST intensities as compared with themselves are plotted as open black triangles with appropriate standard uncertainties. Values of $\varepsilon$ for comparisons with CNRS [29], SUN03 [30], and SUN09 [32] are also plotted as circles, diamonds, and inverted triangles, respectively. Each experiment reported using tunable diode laser spectroscopy and/or Fourier transform infrared spectroscopy to measure (20012) - (00001)$^{12}$C$^{16}$O$_2$ intensities [29-32]. The standard uncertainty for the CNRS data (not shown) is 2% [29], while standard uncertainties for the SUN data set are plotted along with the reported values [30-32].
Figure 8. Top panel: Comparison of intensities relative to *ab initio* calculations (UCL line list) for P- and R-branches of the (20012) - (00001) $^{12}\text{C}^{16}\text{O}_2$ band. Here, $m = -J''$ and $m = J'' + 1$ for the P- and R- branches, respectively. Intensities are expressed as a relative difference with respect to the corresponding UCL [20, 23] line list value, $\epsilon_{\text{UCL}} = S_i/S_{\text{UCL}} - 1$. Relative uncertainties for the CDSD [26] data base (1.6 %) and the Ames-2016 [27] data base (1-3%) are large compared to recent high-precision measurements of NIST (reported herein), PTB [33], and UniNA2 [34], and therefore are not shown. Bottom panel: Comparison of $\epsilon_{\text{UCL}}$ vs. $m$ for only the R-branch of the (20012) - (00001) $^{12}\text{C}^{16}\text{O}_2$ band. Plotted in dotted black line is a quadratic regression curve of the CDSD data set fitted for $|m| \leq 60$ and shifted by $\delta_{\epsilon_{\text{UCL}}} = +1.1 \%$. 