Line intensities of the 30011e – 00001e band of $^{12}$C$^{16}$O$_2$ by laser-locked cavity ring-down spectroscopy

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**A R T I C L E   I N F O**

Article history:
Received 31 October 2017
Revised 18 December 2017
Accepted 18 December 2017
Available online 19 December 2017

Keywords:
Carbon dioxide
Cavity ring-down spectroscopy
Line intensities

**A B S T R A C T**

Thirty well isolated ro-vibrational transitions of the 30011e – 00001e band of $^{12}$C$^{16}$O$_2$ at 1.54 $\mu$m have been recorded with a laser-locked cavity ring-down spectrometer. The line intensities were obtained with accuracies better than 0.85%. Comparisons of the line intensities determined in this work with literature experimental values and those from HITRAN2016, AMES, UCL-IAO and CDSD-296 line lists are given.

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1. Introduction

As the second most abundant greenhouse gas in Earth’s atmosphere, carbon dioxide currently has a global average concentration of 404 parts per million by volume [1]. The terrestrial atmospheric concentration of carbon dioxide has increased almost 43 percent since pre-industrial times due to human activities. Its significant role in climate change impels several agencies to launch space-based observations of carbon dioxide, for example OCO-2 (USA) [2], GOSAT (Japan) [3], ASCENDS (USA) [4], Tan-Sat (China) [5], to monitor CO$_2$ global levels and their variations. These projects aim to retrieve the atmospheric column-averaged CO$_2$ dry air mole fraction (XCO$_2$) with precisions in the range of 0.25–1%. These remote sensing activities heavily depend on the molecular absorption model used within the retrievals, therefore the accuracy of the line parameters and line profiles. To fulfill the goals of the current missions, the accuracy of CO$_2$ line intensities are required to reach 0.3–0.5% [6].

Line intensities are much more difficult to be determined accurately than line positions. Along with the development of high-precision laser spectroscopy techniques and the significant progress of line profile models, the accuracy of CO$_2$ line intensities determined at the laboratory has fulfilled the requirements for modern atmospheric remote sensing experiments [7–13]. However, only several studies [10] accessed to obtain a few lines with a precision of 0.3–1%. In the meantime, attempts [12,14–20] have been made to provide high-accuracy theoretical line intensities for CO$_2$. For instance, Huang et al. [14–17] has performed a series of ab initio studies, obtained the most accurate potential energy surface (PES) of CO$_2$, and generated the infrared line lists for 13 CO$_2$ isotopologues denoted as AMES [16,17]. Tennyson’s group from University College London have shown that it is possible to derive computed line intensities using ab initio calculated dipole moment surface (DMS) with an accuracy comparable to available measurements for tri-atomic molecules such as the water molecule, hydrogen ion and carbon dioxide [12,21–24]. The agreement at the 0.3% level between ab initio computations and high-accuracy experiments [12] for $^{12}$C$^{16}$O$_2$ indicates the possibility of the atmospheric remote sensing research using ab initio calculations. Another set of calculated CO$_2$ line lists, named as UCL-IAO list, for 13 isotopologues of carbon dioxide has been produced by Zak et al. [19,25,26] with the combination of the high accuracy ab initio DMS [12] and the methodology used in Ref. [21]. Meanwhile, an empirical carbon dioxide spectroscopic databank (CDSD-296) [18,19] in the spectral range of 6–14,075 cm$^{-1}$ has been created by Tashkun et al. within the framework of effective operators and based on the global weighted fit of spectroscopic parameters to the observed data from more than 200 measured spectra with uncertainties varying between ~0.1% [8] and over 100% [27]. It leads to a high percentage of line intensities in CDSD databank with the stated un-
uncertainty of 20% or worse, which are still too high for remote sensing activities.

Recently, the widely-used molecular spectroscopic database HITRAN has been updated to the 2016 version [28]. The intensities of most lines in the 0-8000 cm$^{-1}$ region in the latest database have been provided by UCL-IAO since similar accuracy can be given for all isotopologues by using the variational approach in the UCL-IAO line-list. Recent high-precision near-IR spectroscopic measurements in the 1.6 μm [10,12] and 2.0 μm [13,29] have experimentally confirmed that the UCL-IAO line list is accurate to the sub-percent level. Some lines in the UCL-IAO list, the so-called “sensitive” bands involving vibrational states with strong resonances, have been replaced with the data from CDSD-296 [19], such as the 30011e – 00001e, 13311e – 13302e, 40011e – 00001e, 40011e – 00001e bands of the CO$_2$ isotopologue [20]. For the transitions with line intensity larger than $1 \times 10^{-27}$ cm$^{-1}$/ (molecule cm$^{-2}$) in the 30011e – 00001e band of 12C$^{16}$O$_2$, there is an average difference of 3.5% - 7.8% between UCL-IAO and CDSD-296. The CDSD-296 values agree well with Toth’s experimental values [30] within stated uncertainties of 2.4% for most observed lines, but are 5% weaker than the observed values retrieved by cavity ring-down spectroscopy (CRDS) in Grenoble [18] for the transitions of $J > 48$. However, the UCL-IAO data agree better with the observed values in Ref. [18] for the transitions with intensity weaker than $2 \times 10^{-26}$ cm$^{-1}$/ (molecule cm$^{-2}$). For this reason, an independent high-accuracy line intensity measurement is needed for the transitions of 30011e – 00001e band of 12C$^{16}$O$_2$.

In the present work, the line intensities of thirty transitions with no interference from other absorption lines have been recorded by a laser-locked cavity ring-down spectrometer with high precision as well as high sensitivity. This spectrometer is similar to the experimental set-ups developed in Refs. [31,32]. High-precision line intensities are retrieved from the recorded spectra with a relative uncertainty of 0.7% on average, which was considerably improved over our previous studies on CO$_2$ and N$_2$O around 780 nm [33,34]. Precise intensities of the lines in the 30011e – 00001e “sensitive” band will be useful for the evaluation of the HITRAN2016, CDSD-296, AMES and UCL-IAO database.

2. Experimental details

The diagram of the experimental setup is presented in Fig. 1, which consists of frequency locking and spectral probing. A tunable external-cavity diode laser (ECDL, Toptica DL Pro-1550) is split into two beams by a polarizing beam splitting cube. The s-polarization beam is locked to a temperature-stabilized ring-down (RD) cavity using the Pound–Drever–Hall (PDH) method. The RD cavity is composed of two high-reflectivity mirrors with a distance of 110.8 cm. Each mirror has a reflectivity of 99.996% at 1.5-1.7 μm (Layertec GmbH). Therefore, the RD cavity has a finesse of about 7.8 × 10$^4$ and a mode width of about 1.6 kHz. The RD cavity is made of Invar, located in a stainless-steel vacuum chamber. A feedback circuit controls the heating-current in a wire surrounding the stainless-steel chamber to stabilize the Invar cavity temperature at about 298.8 K which was measured with two calibrated platinum thermal sensors attached at two sides of the RD cavity. We used a frequency counter (Agilent 53181A) to monitor the beat frequency between the laser and a frequency comb, and the results are shown in Fig. 2(a). The comb is synthesized by an Er: fiber oscillator operated at 1.56 μm. The repetition frequency and carrier offset frequency of the comb are locked to precise radio-frequency sources referenced to a GPS-disciplined rubidium clock (SRS FS725). The beat signal has a long-term drift of about 1 MHz per h, which is consistent with the thermal expansion of the cavity under a temperature drift of 50 mK. The temperature uncertainty of the RD cavity was estimated to be 0.2 K at maximum taking into account the temperature non-uniformity along the RD cavity. The frequency calibration of the observed spectrum was based on the precise measurement of the RD cavity’s free spectral range (FSR). Fig. 2(b) shows FSR of the empty cavity obtained from the positions of two cavity modes. The FSR value was determined to be 13527263.7(5) Hz, with a maximum fluctuation of about 2 Hz within three hours. It is worth to mention that the dispersion due to sample absorption [35] have been considered in our measurements.

The p-polarization beam passes an acousto-optic modulator (AOM) and a fiber electro-optic modulator (EOM). The EOM modulation frequency is stepped in increments of the RD cavity’s free spectral range to record the spectrum. A single selected sideband of EOM is then coupled into the high-finesse cavity to produce the ring-down signal detected by an avalanche photodiode detector (APD) with a combination of polarization waveplates and Glan–Taylor prisms. When the signal reaches a steady level, it triggers an AOM to block the probe laser beam to initiate a ring-down event. The ring-down curve is fit by an exponential decay function to derive the decay time τ, and the sample absorption coefficient α is determined according to the equation $\alpha = (c r)^{-1} (c r_{L})^{-1}$, where $c$ is the speed of light and $r_{L}$ is the decay time of an empty cavity. Fig. 3(a) shows the recorded $(c r)^{-1}$ value of the empty cavity, and the corresponding Allan deviation is given in Fig. 3(b). The limit of detection, presented as the minimum detectable absorption coefficient, reaches about 4.8 × 10$^{-12}$ cm$^{-1}$ at an averaging time of about 30 s.

Natural carbon dioxide sample gas with a stated purity of 99.995% was bought from the Nanjing Special Gas Co. and further purified by a “freeze-pump-thaw” process before use. Three pressure series, listed in Table 1, were adopted to reduce the statisti-

![Diagram](image-url)
Fig. 2. The Free spectral range (FSR) precision. (a) Beat frequency between the probe laser and the frequency comb. Data are shifted for better illustration. (b) FSR values of the empty cavity determined by measuring the position difference of two cavity modes.

Fig. 3. The sensitivity of the CRDS instrument. (a) Absorption coefficient detected with an empty cavity. (b) Allan deviation of the data shown in (a).

cal uncertainty. Sample pressures were measured by capacitance gauges Pfeiffer Vacuum CCR364 (full range 1 Torr) and CCR 372 (full range 100 Torr) with stated accuracies of 0.2% and 0.15%, respectively. The pressure gauges were calibrated at National Institute of Metrology, China. The absolute relative uncertainties at different pressure series are also given in Table 1. To avoid the interference from neighbor absorptions of other molecules and isotopologues, only thirty well-isolated transitions in the 30011e – 00001e band were studied in this work. The absorption spectra of 30 lines were recorded at four different pressures of a respective series, and 30 times at each pressure.
3. Results

3.1. Line intensity retrieval

The spectra were recorded at sample pressures of 0.005 to 0.8 kPa, the ratio \( \Gamma_4/\Gamma_0 \) of the Lorentzian (calculated values with Hitran2016) to Doppler widths varies from 0.011 to 0.09 in a narrow pressure range. It is hard to remove the partial correlations between various parameters used in the partially-Correlated quadratic-Speed-Dependent Hard-Collision (pCqSDHC) profile [36]. Casa et al. [37] and Long et al. [38] have concluded that the line parameters including the integrated absorbance and Lorentzian widths obtained from fitting using the “hard” collision Rautian (RP) [39] profile are very close to those obtained from fitting the same spectrum using the speed-dependent Nelkin–Ghatak profile (SDNGP) [40]. In this case, the spectrum recorded with pressure series a and b were fitted with the Voigt profile, while the Rautian profile was adopted for the spectrum of transitions weaker than \( 4 \times 10^{-26} \text{ cm}^{-1} \) (molecule cm\(^{-2}\)). The Doppler width was fixed at the calculated value. The line center, intensity, collision broadening width, Dicke narrowing coefficient and the parameters for baseline were derived from the fit. Fig. 4(a) shows the spectra of the R (62) line recorded with sample pressures in the range between 100.18 and 800.60 Pa. The fitting residuals of the measured spectra at 800.60 Pa is also presented in Fig. 4(b).

The line intensity \( S(T_0) \) in \( \text{cm}^{-1} \) (molecule cm\(^{-2}\)) at the standard temperature \( T_0 = 296 \text{ K} \) can be given by the following equation:

\[
S(T_0) = \frac{1}{4\pi \varepsilon_0} \frac{8\pi^2 v_0}{3h^4 c^3} |R|^2 L(J) e^{-hcE_e/k_BT_0}[1 - e^{-hcE_e/k_BT_0}] \tag{1}
\]

In Eq. (1), \( 1/4\pi \varepsilon_0 = 10^{-36} \text{ erg cm}^3 \text{ D}^{-2} \); \( h \) is the Planck constant; \( c \) is the speed of light; \( v_0 \) is the transition wavenumber in \( \text{cm}^{-1} \); \( E_e \) is the lower level energy in \( \text{cm}^{-1} \); and \( k_B \) is the Boltzmann constant. The Hön–London factor \( L(J) \) is equal to \( |m| \), where \( m \) is \( -J \) for \( P \) branch transitions, and \( J+1 \) for \( R \) branch. The rotational dependence of the transition dipole moment squared \( |R|^2 \) can be expressed as:

\[
|R|^2 = |R_0|^2 (1 + A_1 m + A_2 m^2)^2 \tag{2}
\]

Where \( |R_0|^2 \) is the vibrational transition dipole moment squared, \( A_1 \) and \( A_2 \) are the Herman–Wallis coefficients. The calculated values of the total partition function, \( Q(T_0) \), is 286.094 at \( T_0 = 296 \text{ K} \), and \( Q(T) \) is 289.5 at \( T = 298.8 \text{ K} \) for \( ^{12}\text{C}_\text{O}_2 \) from TIPS_2017 [41].

The line intensities of thirty lines in the 30011e – 00001e band of \( ^{12}\text{C}_\text{O}_2 \) are given in Table 2 with natural abundance of 0.9842 and temperature at 296 K. The statistical uncertainty obtained from the fit, the rotational dipole moment squared \( |R|^2 \) and pressure series for each transition are also included in Table 2. The vibrational transition dipole moment \( |R_0|^2 \) and the Herman–Wallis coefficients are determined to be 2.076(41) \( \times 10^{-8} \text{ Debye}^2 \), 3.30(25) \( \times 10^{-4} \) and \( -3.809(76) \times 10^{-5} \) from the fit according to Eq. (2). The relative difference between the experimental line intensities and calculated values with the Herman–Wallis coefficients are also given in Table 2.

3.2. Estimated overall error budget

The uncertainty of the line intensity is composed of statistic and systematic uncertainties. The former one was determined from the least-squares fits. The systematic uncertainty sources include (i) isotopologue abundance, (ii) pressure, (iii) temperature, (iv) baseline polynomial fit, and (v) line profile model.

(i) In order to estimate the systematic uncertainty arising from the abundance of \(^{12}\text{C}_\text{O}_2 \), we determined other minor isotopologue abundance of carbon dioxide in the sample. The absorption spectrum of transitions located at 6264.707 cm\(^{-1} \) and 6447.248 cm\(^{-1} \) were recorded to obtain the isotopologue abundance of \(^{13}\text{C}_\text{O}_2 \) and \(^{12}\text{C}_\text{O}_1^{16}\text{O} \), respectively. They were determined to be 1.09% and 0.39% using the experimental line intensities given by Toth et al. [42] and Karlowsky et al. [43]. The ratio between these two abundances agrees well with the natural abundance ratio of 0.01106: 0.00395. On the other side, the isotopologue abundance of carbon dioxide in the sample were measured with a residual gas analyzer (Stanford Research System: RGA 100) based on mass spectrometry (MS) method. The measured abundances of carbon dioxide isotopologues with masses of 44 \(^{12}\text{C}_\text{O}_2 \), 45 \(^{13}\text{C}_\text{O}_2 \) and \(^{12}\text{C}_\text{O}_1^{16}\text{O} \), 46 \(^{12}\text{C}_\text{O}_1^{16}\text{O} \), \(^{13}\text{C}_\text{O}_1^{16}\text{O} \) and \(^{12}\text{C}_1^{17}\text{O}_2 \) are in the ratio of 0.9843: 0.0116: 0.0040, which also agree well with the
natural abundance ratio of 0.98420: 0.01179: 0.00395. Considering the line intensity uncertainties of these two transitions, the relative uncertainty introduced by the isotopologue abundance is assumed to be 3% for these two isotopologues. It causes less than 0.03% uncertainty for the abundance of $^{12}$C$^{16}$O$_2$. The determined $^{12}$C$^{16}$O$_2$ abundance agrees with the natural abundance within 1σ variation. Therefore, the natural value is adopted here, and the uncertainty of 0.03% contributes to the systematic errors.

(ii) The pressure uncertainties of 0.25% ~ 0.7% listed in Tables 1 and 2 are taken into account in the systematic errors.

(iii) The temperature relative uncertainty is at the level of 0.07%. It will introduce a systematic error of 0.07% ~ 0.61% for lines with lower level energies in the range of 7.804 ~ 1621.003 cm$^{-1}$ based upon the equation:

$$\frac{\Delta S}{S} \approx (1 + \frac{h c E''}{k_b T}) \Delta T.$$  \hspace{1cm} (3)

Eq. (3) can be derived from the following equation:

$$S(T_0) = \frac{k(T) \times T}{n_0 \times 273.15} \frac{Q(T)}{Q(T_0)} \left[ \frac{1 - e^{-\frac{h c E''}{k_b T}}}{1 - e^{-\frac{h c E''}{k_b T_0}}} \right] e^{-\frac{h c E''}{k_b T}} \frac{1}{T}.$$  \hspace{1cm} (4)

In Eq. (4), $k(T)$ is the line strength at the unit of cm$^{-1}$/cm atm, $n_0$ is the Loschmidt constant, and $T$ is the experimental temperature.

(iv) The difference between the integrated line absorbance obtained with linear and second-order polynomial baselines is about 0.05%.

(v) The systematic uncertainty caused by using different line profile models can be neglected for 24 lines with line intensities stronger than $4 \times 10^{-26}$ cm$^{-1}$(molecule cm$^{-2}$), since the spectra were recorded with pressures less than 60 Pa.

We notice that the Dicke narrowing coefficient derived from the fit using RP is one-third of the calculated value related to the mass diffusion coefficient $D$ by $\beta = k_b T/(2 \pi m C D)$ with $m$ the molecular mass, within the Lande-Jones interaction potential [44]. The quality of fit (QF) parameter based on the RP model reduces to 320 with calculated Dicke narrowing value from 1500 with adjustable Dicke-narrowing coefficient. This implies that the Dicke narrowing coefficient calculated by the diffusion theory is not suitable to describe the speed dependent frequency. The spectra recorded at a pressure of 800.6 Pa have also been simulated with speed-dependent Voigt profile (SDVP) and quadratic speed-dependent Rautian profile (qsDRP). Fig. 3(c) shows the fitting residuals with qSDRP. Less than 0.1% difference is found for the integrated absorbance from different line profile models.

The total systematic uncertainties for each line have been calculated, and given in Table 2 together with the statistical uncertainties. The main source of systematic uncertainties is from the pressure for strong line, and from the density population due to the temperature uncertainty for the transitions with high $J$. The relative uncertainty is less than 0.85% for all the lines.

### 4. Discussion and conclusion

The rotational lines of 30011e − 00001e band have been experimentally studied with Fourier-transform spectroscopy [30,45] and cavity ring-down spectroscopy [18] for the lines stronger than...
$1 \times 10^{-28} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$. The accuracy of the line intensity measured by FTS was assumed to be within 1% for most lines, while down to 4-7% in the CRDS-Grenoble measurement. However, there is a $-2.2\%$ deviation on average between the FTS-Toth [30] and FTS-Boudjaadar [45] measurements.

Fig. 5 compares FTS and CRDS-Grenoble experimental values with our measurements in the upper panel. The results are summarized as the relative intensity difference versus rotational quantum number $m$. Our measurements agree well with FTS-Toth values for the lines stronger than $2 \times 10^{-25} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$. The deviations of FTS-Boudjaadar values from this work vary from 1% to 4% with the increment of quantum number $j'$. The relative difference between two CRDS measurements is about 6% being within the claimed uncertainty of CRDS-Grenoble.

Comparisons of our experimental line intensities to values archived in HITRAN2016 and CFSD-296 database, AMES and UCL-IAO $ab$ initio calculations are presented in the lower panel of Fig. 5. The average relative difference between HITRAN2016 and the present measured values equals to 0.03% and has a standard deviation of 0.63%. The line intensities in CFSD-296 agree with our measurements within $1\sigma$ combined relative uncertainty, with a deviation of 1.7% on average. The calculated values from AMES line list also agree well with our values for most lines, while the deviations between AMES and our measurements increase to 3% for the transitions with high $j'$ values in the R branch. A much larger discrepancy is found for the UCL-IAO line list. For the transitions with quantum number $[m] \geq 36$, UCL-IAO values are 5.5% larger than our measurements on average. The relative difference goes up to 8.5% for the R (64) line. Our measurements show that the calculated line intensities of the 30011e – 00001e band from the UCL-IAO line list are “sensitive”, which was also mentioned to be used with caution [19]. High precision measurement of line intensities of other “sensitive” bands will be performed in the future.

**Acknowledgments**

This work is jointly supported by the NSFC (Nos. 21473172, 21427804 and 21688102), NBRPC(No. 2013CB834602), and CAS (No. XDB21020100).

**Supplementary materials**


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