Journal of Quantitative Spectroscopy & Radiative Transfer 207 (2018) 1–7

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Line intensities of the 30011e – 00001e band of $^{12}C^{16}O_2$ by laser-locked cavity ring-down spectroscopy

P. Kang[a], J. Wang[a], G.-L. Liu[a], Y.R. Sun[a,b], Z.-Y. Zhou[c], A.-W. Liu[a,b,*], S.-M. Hu[a,b]

[a] *Hefei National Laboratory for Physical Sciences at Microscale, iChem Center, University of Science and Technology of China, Hefei 230026, China*
[b] *CAS Center for Excellence and Synergetic Innovation Center in Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China*
[c] *National Institute of Metrology, Beijing 100013, China*

ARTICLE INFO

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

ABSTRACT

Thirty well isolated ro-vibrational transitions of the 30011e – 00001e band of $^{12}C^{16}O_2$ at 1.54 μm 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.

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-

* Corresponding author at: Hefei National Laboratory for Physical Sciences at Microscale, iChem Center, University of Science and Technology of China, Hefei 230026, China.
E-mail address: awliu@ustc.edu.cn (A.-W. Liu).

https://doi.org/10.1016/j.jqsrt.2017.12.013
0022-4073/

certainty 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, 40012e – 00001e, 40011e – 00001e bands of the key CO_2 isotopologue [20]. For the transitions with line intensity larger than 1×10^{-27} cm^{-1}/ (molecule cm^{-2}) in the 30011e – 00001e band of $^{12}C^{16}O_2$, 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 2×10^{-26} cm^{-1}/(molecule cm^{-2}). For this reason, an independent high-accuracy line intensity measurement is needed for the transitions of the 30011e – 00001e band of $^{12}C^{16}O_2$.

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_2O 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 135272623.7(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.

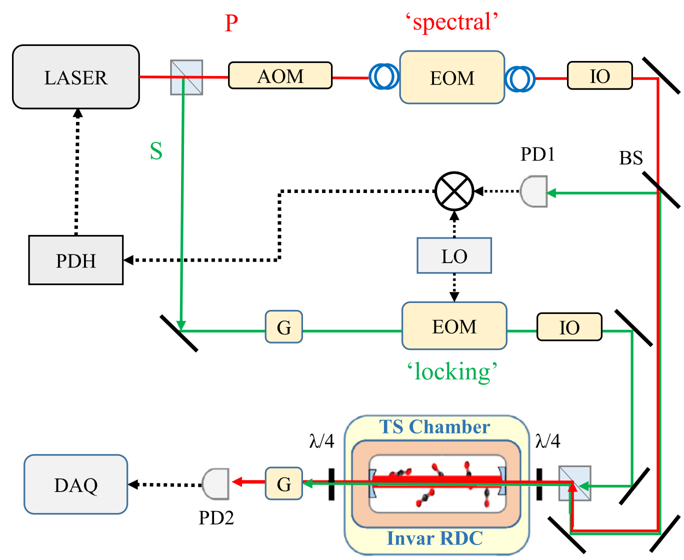

Fig. 1. Configuration of the experimental setup. AOM: acoustic-optical modulator; BS:50:50 beam splitter; DAQ: data acquisition system; EOM: electro-optical modulator; G:Glan-Taylor prism; LO: local oscillator; PBS: polarizing beam splitter; PD: photodiode detector; QWP: quarter- wave plate; SG: signal generator; TS: temperature stabilized.

Table 1
Pressure series list for line intensity measurements of 30011e - 00001e band of $^{12}C^{16}O_2$.

Series	1 (Pa)	2 (Pa)	3 (Pa)	4 (Pa)	Relative uncertainty
a	5.00	6.22	8.47	9.97	0.7%
b	22.88	31.51	37.49	59.01	0.3%
c	100.18	120.64	676.20	800.60	0.25%

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 polarizing waveplates and Glan–Tylor 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 $\alpha = (c\tau)^{-1}$-$(c\tau_0)^{-1}$, where c is the speed of light and τ_0 is the decay time of an empty cavity. Fig. 3(a) shows the recorded $(c\tau)^{-1}$ 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-