



## Notes

Cavity ring down spectroscopy of  $^{18}\text{O}$  and  $^{17}\text{O}$  enriched carbon dioxide near 795 nmH. Pan<sup>a</sup>, X.-F. Li<sup>a</sup>, Y. Lu<sup>a</sup>, A.-W. Liu<sup>a,\*</sup>, V.I. Perevalov<sup>b</sup>, S.A. Tashkun<sup>b</sup>, S.-M. Hu<sup>a</sup><sup>a</sup> Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China<sup>b</sup> Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB, Russian Academy of Science, 1 Akademian Zuev sq., 634021 Tomsk, Russia

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## ABSTRACT

The dyad bands of  $^{17}\text{O}$  and  $^{18}\text{O}$  enriched carbon dioxide near 795 nm have been recorded with a continuous-wave cavity ring-down spectrometer. Seven cold bands of four isotopologues:  $^{12}\text{C}^{18}\text{O}_2$ ,  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ ,  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$  and  $^{12}\text{C}^{17}\text{O}_2$  have been observed for the first time. The spectroscopic parameters  $G_v$ ,  $B_v$ , and centrifugal distortion constants, have been determined.

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## 1. Introduction

The infrared absorption spectroscopy of carbon dioxide is of great interest for many applications, such as monitoring the atmospheric  $\text{CO}_2$  concentration [1], the volcanic gases evaluation in geochemistry [2], and understanding of the biological activities in biochemistry [3]. The present work is the continuation of a series of studies [4,5] devoted to the systematic study of the infrared absorption spectrum of the overtone bands of the carbon dioxide isotopologues in our laboratory. In this paper we are concentrated on seven bands of the isotopologues containing  $^{18}\text{O}$  and  $^{17}\text{O}$  oxygen:  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}_2$ ,  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$  and  $^{12}\text{C}^{17}\text{O}_2$ . We will use the HITRAN [6] notation for the different isotopologues:  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ : 628;  $^{12}\text{C}^{18}\text{O}_2$ : 828;  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ : 627;  $^{12}\text{C}^{17}\text{O}_2$ : 727.

The present paper is organized as follows. In Section 2, we present briefly the experimental procedure and the analysis methodology. Section 3 is devoted to the band-by-band

analysis and the modeling of the spectra parameters. The conclusion is given in Section 4.

## 2. Experiment and data reduction

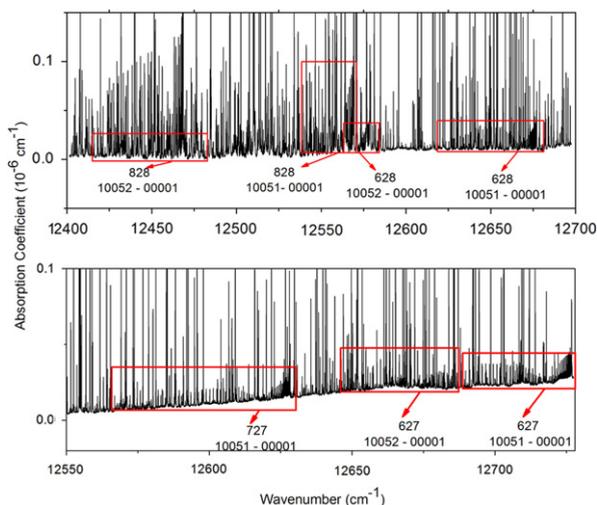
The spectrum of  $^{18}\text{O}$  and  $^{17}\text{O}$  enriched carbon dioxide samples in the 785–806 nm range was measured using a continuous wave cavity ring-down (cw-CRDS) spectrometer. The details of the spectrometer have been presented in Ref. [7]. The sample absorption coefficient  $\alpha(\nu)$  was obtained by measuring the ring-down time  $\tau(\nu)$  of the transmitted laser beam power:

$$\alpha(\nu) = \frac{1}{c} \left( \frac{1}{\tau(\nu)} - \frac{1}{\tau_0} \right) \quad (1)$$

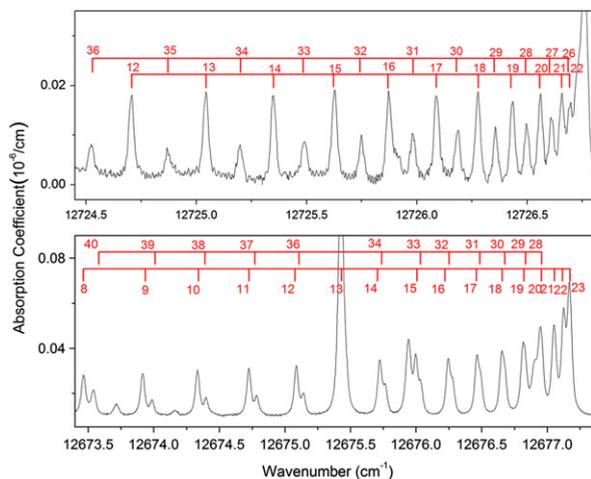
where  $c$  is the speed of light and  $\tau_0$  is the ring-down time of empty cavity. The noise-equivalent minimal detectable absorption coefficient  $\alpha_{\min}$  was about  $6 \times 10^{-10} \text{ cm}^{-1}$  in the measurement.

The  $^{18}\text{O}$  and  $^{17}\text{O}$  enriched carbon dioxide samples were purchased from Icon Services. The stated isotopic concentrations for the oxygen atom are 84.3% of  $^{18}\text{O}$  in the first sample and 49% of  $^{17}\text{O}$  in the second one. 26 Torr  $^{17}\text{O}$  enriched carbon dioxide sample was used in the

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**Fig. 1.** Overview of the CW-CRDS spectrum of  $^{18}\text{O}$  and  $^{17}\text{O}$  enriched carbon dioxide around 795 nm. Upper panel:  $^{18}\text{O}$  enriched carbon dioxide sample, 200 Torr. Lower panel:  $^{17}\text{O}$  enriched carbon dioxide sample; 26 Torr. Many strong lines presented in the figure are due to trace water vapor in the sample.



**Fig. 2.** R-branch of the 10051-00001 band of  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$  (upper panel) and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  (lower panel). The rotational assignments are presented.

**Table 1**

Spectroscopic parameters (in  $\text{cm}^{-1}$ ) of the rovibrational bands of  $^{17}\text{O}$  and  $^{18}\text{O}$  enriched carbon dioxide around 795nm.

Isotope	Abundance	$G_v$	$B_v$	$D_v \times 10^7$				
628	0.0039471	0.0	0.36818450	1.18647				
627	0.000734	0.0	0.378613504	1.25449				
828	0.0000039573	0.0	0.34681732	1.05549				
727	1.3685E-7	0.0	0.367194620	1.18053				
	<b>Bands</b>	$\Delta G_v^a$	$G_v$	$B_v$	$D_v \times 10^7$	$J_{\max}^{b,P/R}$	$n/N^c$	$RMS^d$
628	10051-00001	12668.13584(20)	12668.13584(20)	0.35377645(58)	0.9795(30)	44/46	67/71	0.9
628	10052-00001	12569.93703(29)	12569.93703(29)	0.35413165(79)	1.4022(39)	47/47	44/61	0.9
627	10051-00001	12717.59476(18)	12717.59476(18)	0.36360359(56)	1.0405(31)	36/44	68/71	0.8
627	10052-00001	12618.15561(16)	12618.15561(16)	0.36431337(50)	1.4915(26)	36/45	66/69	0.7
828	10051-00001	12560.67496(21)	12560.67496(21)	0.33359188(45)	0.8710(18)	52/52	39/44	0.7
828	10052-00001	12460.06885(31)	12460.06885(31)	0.33329156(79)	1.2227(36)	46/50	36/39	1.0
727	10051-00001	12561.95971(42)	12561.95971(42)	0.3531641(15)	1.3818(88)	40/41	42/51	1.4

Note: The lower state constants were fixed at the values of Refs. [11,12]. The uncertainties are given in parentheses in the unit of the last quoted digit.

<sup>a</sup> Difference between the upper and lower vibrational term values.

<sup>b</sup>  $J_{\max}$  is the maximum value of the angular momentum quantum number observed for P/R branches.

<sup>c</sup>  $n$ : number of transitions included in the fit;  $N$ : number of assigned rotational transitions.

<sup>d</sup> Root mean square deviation (in  $10^{-3}\text{cm}^{-1}$ ).

measurement, while two pressures at 100 and 200 Torr were adopted in the measurement of the  $^{18}\text{O}$  enriched carbon dioxide sample. The pressure was measured by a manometer with 1000 Torr full-scale range and 0.15% accuracy. The spectrum calibration is based on the readings given by a lambdameter (Burleigh WA-1500) with 60 MHz accuracy. Taking into account the self-induced pressure shift, the accuracy of the unblended and not-very-weak lines is estimated to be better than  $0.003\text{cm}^{-1}$ . An overview of the cw-CRDS spectra is presented in Fig. 1. A small part of the 628 and 627 spectrum is presented in Fig. 2 which illustrates R branch of the 10051-00001 band.

### 3. Ro-vibrational analysis

A total of 406 transitions have been observed for four carbon dioxide isotopologues: 628, 627, 828 and 727. Seven vibrational bands are rotationally identified with the help of the calculations performed within the framework of the effective operator method using the sets of effective Hamiltonian parameters published in Refs. [8–10]. The rotational analysis was performed using the standard equation for the vibration-rotation energy levels:

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

where  $G_v$  is the vibrational term value,  $B_v$  is the rotational constant,  $D_v$  and  $H_v$  are centrifugal distortion constants. The spectroscopic parameters for an upper state were fitted directly to the observed line positions of the respective band. The lower state rotational constants were constrained to their literature values [11,12]. The observed line positions together with the residuals are given in the Supplementary material of this paper. The spectroscopic parameters retrieved from the fitting are presented in Table 1. The rms values of the (obs.–calc.) deviations are generally  $1 \times 10^{-3}\text{cm}^{-1}$  which is consistent with the experimental accuracy.

### 4. Conclusion

The line positions of the dyad overtone bands 10051-00001 and 10052-00001 of four carbon dioxide isotopologues

(628, 627, 828 and 727) have been experimentally determined for the first time. The estimated accuracy of the obtained line positions is better than  $0.003 \text{ cm}^{-1}$ . The results will be used to improve the theoretical modeling of high resolution spectra of these isotopologues and also the CDSDB databank [13,14].

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jqsrt.2012.08.017>.

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