

# Highly sensitive diode laser absorption measurements of CO<sub>2</sub> near 1.57 μm at room temperature

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The absolute absorption spectrum intensities of carbon dioxide sample have been recorded with a tunable diode laser spectrometer in the spectral range 6350–6364 cm<sup>-1</sup>, which is suitable for the in situ sensing of carbon dioxide in the lower stratosphere using a commercial telecommunication -type diode laser. It was found that the typical uncertainty of experimental line intensities is about 1% compared with the values listed in the HITRAN database, which are calculated by direct numerical diagonalization (DND).

Keywords: wavelength modulation, diode lasers, absorption spectroscopy.

## 1. Introduction

Carbon dioxide is one of the most important minor components in the atmosphere and the second greenhouse gas after atmospheric water, and it contributes greatly to the global warming of the atmosphere [1]. As a result of human activity (in particular, combustion), its concentration has continuously increased during the last century [2]. In order to retrieve the concentration profiles of this minor constituent in the atmosphere, accurate line parameters (*i.e.*, positions, intensities and self-broadening coefficients) of carbon dioxide transitions are required [3, 4]. The improvement of these line parameters listed in the spectroscopic database is always the central interest in atmospheric spectroscopy [5]. Recently, we undertook an accurate line parameters measurement of CO<sub>2</sub> around 1.31 μm and found a few new spectroscopy lines not reported in HITRAN database. The ability of this set of parameters in predicting unmeasured transitions has been discussed and has been found to have high sensitivity and resolution in absorption spectroscopy research [6].

The line parameters of the prominent CO<sub>2</sub> absorption bands located near 1.57 μm are particularly useful for tropospheric studies. As a result, high-resolution laboratory investigations of both their intensities and pressure broadening have been pursued in

this region [6–8]. Given the high accuracy necessary to be in compliance with the scientific objective, a precise set of CO<sub>2</sub> molecular parameters is of particular importance for the retrieval process. In order to confirm the accuracies of the past results and provide guidance for future improvements to the HITRAN database, in this paper we revisit the line intensities of the CO<sub>2</sub> transitions available in the laser tunability range from 6350 to 6364 cm<sup>-1</sup>. Our results are compared with those in [9, 10], which were obtained using a Fourier-transform spectrometer, and also with those in the HITRAN database which are calculated by direct numerical diagonalization (DND) [11].

In the WM technique, the signal detected from the lock-in can be expressed as [9]

$$A_n(\nu) = -\frac{I_0 S \rho L 2^{1-n}}{n!} \delta^n \nu \left. \frac{d^n \chi(\nu)}{d\nu^n} \right|_{\nu=\nu_0} \quad (1)$$

where  $I_0$  is the incident power,  $\rho$  is the density of absorption species,  $S$  is the absorption line intensity,  $L$  is the optical path length,  $\nu$  is the frequency of laser emission and  $\chi$  refers to the absorption profile.

During the measurement of the absorption lines of gaseous molecules, there are two main broadening mechanisms, *i.e.*, the Doppler broadening and the colliding broadening. At low pressure, the mechanism of the Doppler broadening is dominant. The absorption line is then of the normalized Gaussian shape, which can be expressed as [9]

$$\chi_G(\nu) = \frac{1}{\gamma_D} \sqrt{\ln/\pi} \exp\left[-\ln 2 \left(\frac{\nu - \nu_0}{\gamma}\right)^2\right] \quad (2)$$

where  $\gamma_D$  is the half width of the Doppler broadening and  $\nu_0$  is the central frequency of absorption line. From Eq. (1), the second harmonic signal of the Gaussian lineshape function can be expressed as [9]

$$S_G^2(\nu) = -\eta \frac{I_0 S \rho L}{2\gamma_D^5} \ln 2 \exp\left[-\ln 2 \left(\frac{\nu - \nu_0}{\gamma_D}\right)^2\right] \left[\gamma_D^2 - 2\ln 2 (\nu - \nu_0)^2\right] \delta^2 \nu. \quad (3)$$

## 2. Experimental details

The experimental apparatus used in this work is schematically shown in Fig. 1. The mutipass cell is of the White-type with the base path length of 8 m. The total optic path length, which can be varied, ranges from 46 to 1159 m. In the experiment, a single-mode DFB diode laser was used, and the emission output of the pigtailed DFB InGaAs

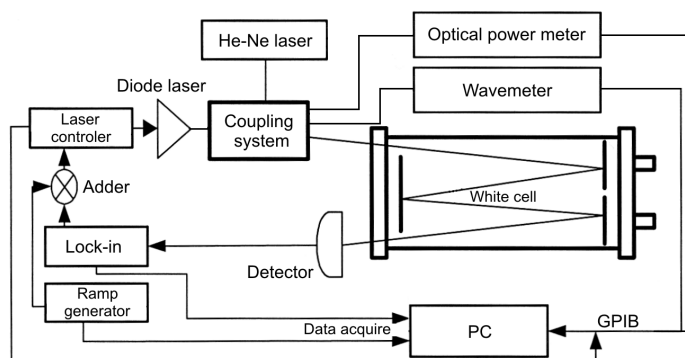


Fig. 1. Sketch of experimental apparatus for the WM spectroscopy.

laser diode, which is mounted in a butterfly package with a central emission wavelength of  $1.573\ \mu\text{m}$ , sweeps over  $6349\text{--}6365\ \text{cm}^{-1}$ , with the typical linewidth of about 2 MHz and a side mode suppression ratio greater than 30 dB. This linewidth is negligible when compared to that of gas absorption, which is over 1 GHz. The wavelength of laser, which is controlled by a laser-controller (TDS3724B, LightWave), varies with the laser current, whose magnitude and accuracy are about  $0.017\ \text{cm}^{-1}/\text{mA}$  and 0.01 mA, respectively. The output of the laser was directed to a  $1\times 3$  fiber coupler. Some 10% of the laser power was directed to optical power meter (1830C, Newport) for monitoring the power, and another 10% was directed to optical wavemeter (WA-1500 NIR, Buleigh) for monitoring the laser-frequency of the laser's emission. The remaining power from the diode laser was transmitted through a white-cell for absorption measurements. The transmitted laser intensity was monitored by an InGaAs detector. The transmission signals were then sent to a lock-in for demodulation, and the output signals of lock-in were sent to a PC-based data acquisition board (DAQ), which is capable of sampling at 20 kS/s with 16-bit resolution. Finally, the data were transferred to a personal computer and analyzed using LabWindows/CVI programs. Each measured spectrum was recorded in a single sweep of the laser without signal averaging.

### 3. Results and discussion

In this work, the  $\text{CO}_2$  spectra in the  $1.57\ \mu\text{m}$  region were recorded at high resolution in the laboratory with tunable diode laser absorption spectrometer (TDLAS). Direct absorption spectroscopy and wavelength modulation absorption spectroscopy (WMAS) techniques have been adopted here for the measurements of spectra intensities. A low-frequency ramp at 1 Hz was used to scan the DFB diode over the selected absorption lines by the driving current.

Figure 2 features the eleven absorption lines of the  $30012 \leftarrow 00001$  band of carbon dioxide, which are reachable in the tunability range. The signal was obtained from

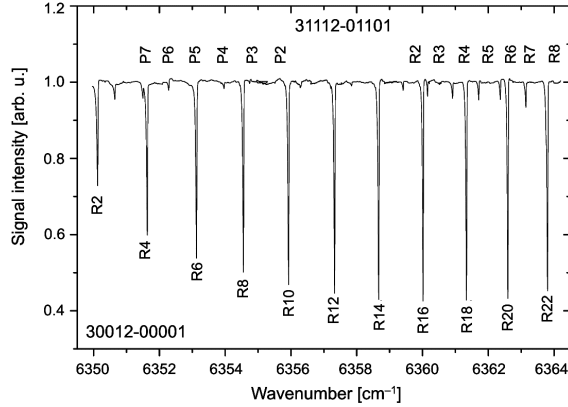


Fig. 2. Experimental spectrum of the CO<sub>2</sub> absorption lines of 31112 ← 01101 band around 1.57 μm. The pressure is 0.5 torr and the absorption path length is 540.82 m.

CO<sub>2</sub> with 99.99% purity, under the condition that the theoretical absorption length was 540.82 m and the CO<sub>2</sub> pressure in the white cell was 0.5 torr. Figure 2 consists of the juxtaposition of eleven experimental spectra. Each single spectrum was obtained by ramping the driving current at an appropriate temperature to scan the laser emission wavelength over the selected single CO<sub>2</sub> transition. Table 1 gives the list of the lines investigated in this work. The experimental results of absorption line transition, positions, and the corresponding line intensities, are listed in the first, second and fourth columns of Table 1, respectively. In this table, the values of the calculated line intensities from the HITRAN database are also listed in the third column. The experimental results are compared with those in [9, 10], which were obtained with a Fourier-transform spectrometer, and also with those in the HITRAN database, which are calculated by DND [11]. From the values of ratio between the calculated and

Table 1. List of the lines investigated in this work; the molecular parameters are from papers [9, 10].

Transition	Position [cm <sup>-1</sup> ]	S [10 <sup>-23</sup> .cm <sup>-1</sup> /(molecule.cm <sup>-2</sup> )]				
		S <sub>Hitran</sub>	S <sub>V&amp;S</sub> [9]	S <sub>H&amp;S</sub> [10]	S <sub>exp</sub>	S <sub>exp</sub> /S <sub>Hitran</sub>
R2	6350.1476	0.5137	0.559	0.483	0.45494	0.88561
R4	6351.64069	0.8381	0.839	0.852	0.84451	1.00765
R6	6353.10367	1.132	1.121	1.114	1.14288	1.00961
R8	6354.53653	1.384	1.363	1.321	1.37154	0.991
R10	6355.93933	1.585	1.550	1.492	1.57878	0.99608
R12	6357.3121	1.729	1.679	1.657	1.72602	0.99828
R14	6358.6549	1.816	1.750	1.697	1.82036	1.0024
R16	6359.9678	1.845	1.760	1.750	1.85249	1.00406
R18	6361.2509	1.823	1.734	1.689	1.82363	1.00035
R20	6362.5043	1.755	1.648	1.595	1.76253	1.00429
R22	6363.72812	1.65	1.529	1.505	1.64089	0.99448

experimental line intensities, which are listed in the fourth column, we can see that the typical uncertainty of line intensities is less than 1%.

The procedure of direct recording of the ratio of the transmitted signal with gas to that without gas in the cell becomes increasingly problematic as the signal gets weaker. It is shown that the weak bands of CO<sub>2</sub> (40012 ← 10001, 30011 ← 00001, 31112 ← 01101, 41101 ← 00001, 32212 ← 02201) were not identified from Fig. 2. In order to improve signal-to-noise ratio we adopt wavelength modulation absorption spectroscopy (WMAS) to detect the weak bands. An experimental result detected by WMAS is shown in Fig. 3. The signal was obtained from CO<sub>2</sub> with 99.99% purity, under the condition that the theoretical absorption length was 540.82 m and the CO<sub>2</sub> pressure in the white cell was 0.5 torr. The temperature and center current of diode laser were kept at 34°C and 70 mA, respectively. The modulation frequency and modulation amplitude of lock-in were kept at 1.78 kHz and 30 mV, respectively. The absorption lines are the P(5) line of the CO<sub>2</sub> (31112 ← 01101) band, the P(14) line of the CO<sub>2</sub> (30011 ← 00001) band and the P(9) line of the CO<sub>2</sub> (32212 ← 02201) band, respectively. The peak positions of these lines in the HITRAN2003 database are 6352.311279 cm<sup>-1</sup>, 6352.116329 cm<sup>-1</sup> and 6351.963537 cm<sup>-1</sup>, with corresponding intensities of 2.930×10<sup>-25</sup> cm<sup>-1</sup>/(molecule·cm<sup>-2</sup>), 4.864×10<sup>-26</sup> cm<sup>-1</sup>/(molecule·cm<sup>-2</sup>) and 1.748×10<sup>-26</sup> cm<sup>-1</sup>/(molecule·cm<sup>-2</sup>), respectively.

From Eq. (1), we can see that the harmonic signals are directly proportional to  $I_0$  and  $S$  for different absorption lines. Because  $I_0$  varies with the frequency of diode laser, in our experiment optical power meter was used to normalize it while detecting the harmonic signals. Thus, the harmonic signals are only proportional to  $S$ , and the intensities of absorption line can be obtained by using a nonlinear least-squares fit of them to Eq. (3). Compared with HITRAN database, all the positions of spectral lines derived in the experiment can be ascertained accurately.

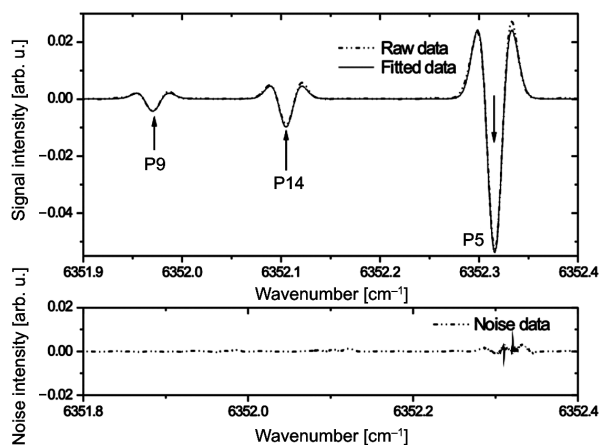


Fig. 3. Observed second harmonic signals of CO<sub>2</sub> using the WM technique at an absorber pressure of 0.5 torr and an absorption path length of 540.82 m.

T a b l e 2. List of the lines investigated in this work; the molecular parameters are from the HITRAN.

Band	Transition	Position	$S [10^{-25} \cdot \text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})]$		
			$S_{\text{Hitran}}$	$S_{\text{exp}}$	$S_{\text{exp}}/S_{\text{Hitran}}$
30011 ← 00001	P16	6350.3711	0.4925	0.528469	1.07303
30011 ← 00001	P14	6352.11633	0.4864	0.461417	0.94864
30011 ← 00001	P12	6353.83647	0.4632	0.423572	0.91445
30011 ← 00001	P10	6355.53137	0.422	0.426326	1.01025
30011 ← 00001	P8	6357.20093	0.3633	0.373311	1.02756
30011 ← 00001	P6	6358.84505	0.2886	0.301725	1.04548
30011 ← 00001	P4	6360.46364	0.2005	0.230656	1.1504
30011 ← 00001	P2	6362.05664	0.1028	0.116205	1.1304
31112 ← 01101	P7	6350.66329	3.984	4.455	1.11822
31112 ← 01101	P6	6351.50637	3.48	3.87	1.11207
31112 ← 01101	P5	6352.31128	2.93	3.2675	1.11519
31112 ← 01101	P4	6353.12775	2.333	2.55525	1.09526
31112 ← 01101	P3	6353.92823	1.685	1.843	1.09377
31112 ← 01101	P2	6354.7241	0.9583	1.102	1.14995
31112 ← 01101	Q1	6356.29035	0.9654	1.042	1.07935
31112 ← 01101	R1	6357.8346	0.9651	1.0385	1.07605
31112 ← 01101	R2	6358.60527	1.702	1.8035	1.05964
31112 ← 01101	R3	6359.34268	2.366	2.383	1.00719
31112 ← 01101	R4	6360.11378	2.982	3.244	1.08786
31112 ← 01101	R5	6360.8196	3.554	3.588	1.00957
31112 ← 01101	R6	6361.59718	4.081	4.132	1.0125

The dashed curve in Fig. 3 represents the experimental signals detected by WMAS. The solid one is the fitted signal derived from a nonlinear least-squares fit of the data to Eq. (3), and then used to retrieve line intensity from the spectra. The calculated intensities of the line are  $3.275 \times 10^{-25} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$ ,  $4.61417 \times 10^{-26} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$  and  $1.6423 \times 10^{-26} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$ . For  $P(9)$  line of the  $\text{CO}_2$  (32212 ← 02201) band, the absorption is  $1.46586 \times 10^{-7}$  and the signal-to-noise ratio (SNR), which is the ratio of the peak amplitude of the fitted signal to this RMS deviation shown in Fig. 3, is about 19.66.

WMAS can yield a large improvement in SNR, as illustrated in Fig. 3, in which the 2nd harmonic signals in the vicinity of  $6352 \text{ cm}^{-1}$  by WMAS are presented. Figure 4 shows the experimental results of  $\text{CO}_2$  over  $6350\text{--}6364 \text{ cm}^{-1}$  spectral region. The signal was obtained from  $\text{CO}_2$  with 99.99% purity, under the condition that the theoretical absorption length was 540.82 m and the  $\text{CO}_2$  pressure in the white cell was 0.5 torr. The modulation frequency and modulation amplitude of lock-in were kept at 1.24 kHz and 30 mV, respectively. In order to obtain higher sensitivity,

Table 2. Continued.

Band	Transition	Position	$S [10^{-25} \text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})]$		
			$S_{\text{Hitran}}$	$S_{\text{exp}}$	$S_{\text{exp}}/S_{\text{Hitran}}$
31112 ← 01101	R7	6362.26536	4.563	4.717	1.03375
31112 ← 01101	R8	6363.05544	4.992	4.9265	0.98688
31112 ← 01101	R9	6363.67995	5.372	5.315	0.98939
32212 ← 02201	P11	6350.26868	0.2006	0.20189	1.00643
32212 ← 02201	P10	6351.15357	0.1888	0.19661	1.04136
32212 ← 02201	P9	6351.96354	0.1748	0.16423	0.93953
32212 ← 02201	P8	6352.8224	0.1586	0.158522	0.99951
32212 ← 02201	P7	6353.63149	0.1402	0.145982	1.04124
32212 ← 02201	P6	6354.46702	0.1194	0.13317	1.11532
32212 ← 02201	P5	6355.2725	0.09624	0.102498	1.06502
40012 ← 10001	R4	6350.06973	0.2373	0.236752	0.99769
40012 ← 10001	R6	6351.54739	0.3187	0.320178	1.00464
40012 ← 10001	R8	6352.99945	0.3872	0.386997	0.99948
40012 ← 10001	R10	6354.42587	0.4404	0.439262	0.99741
40012 ← 10001	R12	6355.82663	0.4771	0.476416	0.99857
40012 ← 10001	R14	6357.20171	0.497	0.497417	1.00084
40012 ← 10001	R16	6358.55109	0.5009	0.501928	1.00205
40012 ← 10001	R18	6359.87474	0.4904	0.490975	1.00117
40012 ← 10001	R20	6361.17264	0.4676	0.467108	0.99895
40012 ← 10001	R22	6362.44476	0.4351	0.434105	0.99771
40012 ← 10001	R24	6363.69109	0.3958	0.396374	1.00145

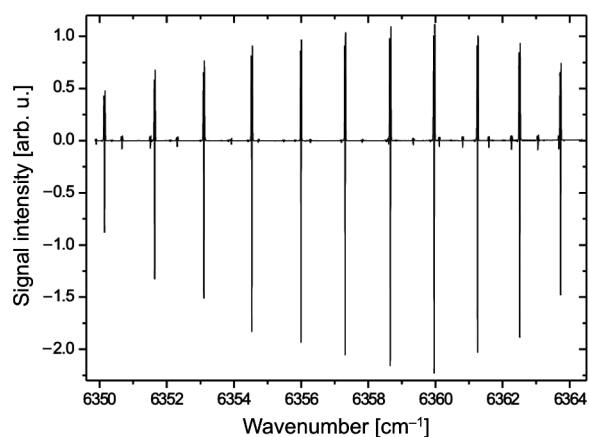


Fig. 4. Observed second harmonic signals of  $\text{CO}_2$  using the WM technique at an absorber pressure of 0.5 torr and an absorption path length of 540.82 m.

the 2nd harmonic signal was obtained by the average of 100 scans and the digital filter.

Table 2 shows the comparison of the spectral line positions and intensities from our experiments with those from HITRAN database in the region 6350–6364  $\text{cm}^{-1}$ . From this table, we can see that the weakest line observed in our experiment is P2 transition of 30011  $\leftarrow$  00001 band, whose intensity, absorbance and SNR are  $1.116 \times 10^{-26} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$ ,  $9.96 \times 10^{-8}$  and 4.53, respectively. The experimental results of absorption band, transition, line positions, and line intensities, are listed in the first, second, third and fifth columns of Tab. 2, respectively. In this table, the values of the calculated line intensities from the HITRAN database are also listed in the fourth column. In the sixth column of the table, the values of ratios between the calculated and experimental line intensities are listed, from which it is easily obtained that the standard uncertainty for the intensity varies from less than about 1% for the strongest lines to about 10% for the weakest lines.

#### 4. Conclusions

This work presents the spectroscopic intensity measurements of the  $\text{CO}_2$  around 1.57  $\mu\text{m}$  based on DFB lasers, which are of primary importance for atmospheric applications, and are helpful for further improvement of reliable retrievals of the concentration profiles of this minor constituent in the atmosphere. Overtone absorption lines of  $\text{CO}_2$  in the regions between 6350 and 6364  $\text{cm}^{-1}$  have been examined by means of tunable diode lasers in free-running mode. The diode laser emission wavelength was scanned around the gas resonances by simply sweeping its injection current, permitting a direct observation of the absorption line-shapes. Weak overtone absorption lines have been detected by using the wavelength modulation spectroscopy with the 2nd harmonic detection technique. The intensity of the weakest line detected in this experiment is  $1.116 \times 10^{-26} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$  at the pressure of 0.5 torr, and the corresponding absorption is  $9.96 \times 10^{-8}$  with SNR of 4.53.

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