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Highly sensitive tunable diode laser absorption spectroscopy of CO_2 around 1.53 μm

YONG LIU*, BAOSHENG LI, YUFENG ZHAI, AN WANG

Anhui Institute of Optics and Fine Mechanics, The Chinese Academy of Sciences, 230031 Hefei, China

*Corresponding author: Yong Liu, liuyong@aiofm.ac.cn

The absolute absorption spectrum intensities of carbon dioxide sample have been recorded with a tunable diode laser spectrometer in the spectral range 6506–6520 cm^{-1}, which is suitable for the *in situ* sensing of carbon dioxide in the lower stratosphere, and were studied using a commercial telecommunication-type diode laser. The intensity of the weakest line we detected in this experiment is 9.116×10^{-27} $cm^{-1}/(molecule\cdot cm^{-2})$ at a pressure of 0.35 torr, and the corresponding absorption is 1.96×10^{-6} with SNR of 2.67.

Keywords: wavelength modulation, diode lasers, absorption spectroscopy.

1. Introduction

Carbon dioxide is one of the most important minor components of 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]. This issue, of fundamental importance for the present and the future of mankind, constitutes the first climatic change of anthropogenic origin. Therefore, accurate line parameters (*i.e.*, positions, intensities and self-broadening coefficients) of carbon dioxide transitions are required in order to retrieve the concentration profiles of this minor constituent in the atmosphere from such experiments [3, 4]. The usability of this set of parameters in predicting unmeasured transitions has been discussed and found to have high sensitivity and resolution in absorption spectroscopy research [5].

The prominent CO_2 absorption bands located near 1.53 μm are particularly useful for troposphere studies. As a result, high-resolution laboratory investigations of both their intensities and pressure broadening have been pursued in this region. Given the high accuracy necessary to be in compliance with the scientific objective, a precise set of CO_2 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 database, in this paper we revisit the line intensities of the CO_2 transitions available in the laser tunability range from 6506 to 6520 cm^{-1}. Our results are compared with the HITRAN database which are calculated by direct numerical diagonalization (DND) [6].

In the wavelength modulation (WM) technique, the signal detected from the lock-in can be expressed as [7]

$$A_n(\upsilon) = -\frac{I_0 S \rho L 2^{1-n}}{n!} \delta^n \upsilon \frac{d^n \chi(\upsilon)}{d\upsilon^n}\bigg|_{\upsilon = \upsilon_0} \tag{1}$$

where I_0 is the incident power, ρ – the density of absorption species, S – the absorption line intensity, L – the optical path length, υ – the frequency of laser emission, and χ 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 [7]

$$\chi_G(\upsilon) = \frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}} \exp\left[-\ln 2\left(\frac{\upsilon - \upsilon_0}{\gamma}\right)^2\right] \tag{2}$$

where γ_D is the half-width of the Doppler broadening, υ_0 is the central frequency of absorption line. From Eq. (1), the second harmonic signal of the Gaussian line shape function can be expressed as [7]

$$S_G^2(\upsilon) = -\eta \frac{I_0 S \rho L}{2\gamma_D^5} \ln 2 \exp\left[-\ln 2\left(\frac{\upsilon - \upsilon_0}{\gamma_D}\right)\right]\left[\gamma_D^2 - 2\ln 2(\upsilon - \upsilon_0)^2\right]\delta^2 \upsilon \tag{3}$$

2. Experiment

The experimental apparatus used in this work is schematically shown in Fig. 1. The multipass 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 laser diode, which is mounted in a butterfly package with a central emission wavelength of 1.53 μm, sweeps over 6506–6520 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),

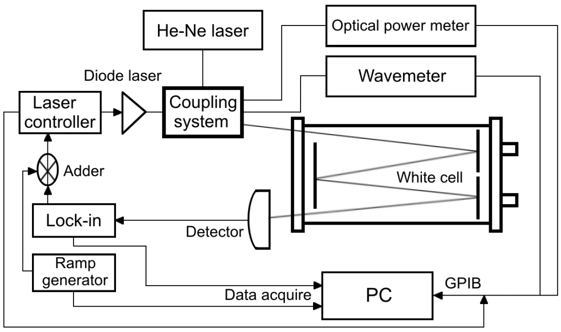

Fig. 1. Schematic of experimental apparatus for the WM spectroscopy.

varies with the laser current, whose magnitude and accuracy are about 0.017 cm^{-1}/mA and 0.01 mA, respectively. The output of the laser was directed to a 1×3 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 emission frequency. 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 paper, the CO_2 spectra in the 1.53 μm region are recorded at high resolution in the laboratory with a tunable diode laser absorption spectrometer (TDLAS). Direct absorption spectroscopy and wavelength modulation absorption spectroscopy (WMAS) techniques have been adopted here for measuring the intensities of spectra. In this experiment, the emission output of the pigtailed DFB InGaAs laser diode, which is mounted in a butterfly package with a central emission wavelength of 1.53 μm, sweeps over 6506–6520 cm^{-1}, with the typical linewidth of about 2 MHz and a side mode suppression ratio greater than 30 dB. A low-frequency ramp at 1 Hz is used to scan the DFB diode over the selected absorption lines by the driving current.

Figure 2 features the ten absorption lines of the around 1.53 μm, which are reachable in the tunability range. The signal was obtained from CO_2 with 99.99% purity, under the condition that the theoretical absorption length was 540.82 m and the CO_2 pressure in the white-cell was 10.5 torr. Figure 1 consists of the juxtaposition of ten experimental spectra. Each single spectrum was obtained by ramping the driving

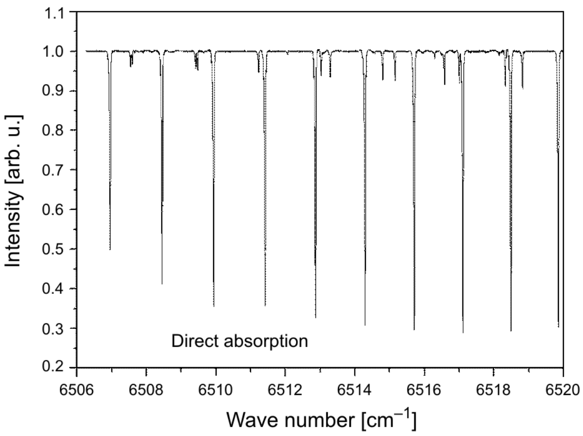

Fig. 2. Experimental spectrum of the CO_2 absorption lines around 1.53 μm. Pressure is 10.5 torr and an absorption path length is 540.82 m.

current at an appropriate temperature to scan the laser emission wavelength over the selected single CO_2 transition.

Figure 2, presents the 2nd harmonic signals, recordered in the vicinity of 1.53 μm (*i.e.*, 6506–6520 cm^{-1}) by WMAS. The implementation principle and experimental apparatus for WMAS have already been described in [5]. The signal was obtained from CO_2 with 99.99% purity, under the condition that the theoretical absorption length was 355.4 m and the CO_2 pressure in the white-cell was 0.35 torr. The modulation frequency and modulation amplitude of lock-in were kept at 1.2 kHz and 28 mV, respectively. In order to obtain higher sensitivity, the 2nd harmonic signal was obtained by the average of 100 scans and the digital filter.

The weakest line of experimental results detected by TDLAS in Fig. 3 is shown in Fig. 4. The absorption line is the P(28) line of the CO_2 (31111-01101) band, whose peak position is 6512.0261 cm^{-1} with the intensity of 9.116×10^{-27} cm^{-1}/(molecule·cm^{-2}) in the HITRAN2004 database. The dashed curve in Fig. 4**a** represents the experimental signals detected by TDLAS. The solid one is the fitted signal derived from a nonlinear least-squares fit of the data. The fitted intensity of the line is 9.75×10^{-27} cm^{-1}/(molecule·cm^{-2}) and the corresponding absorption is 1.96×10^{-6}. The SNR, which is the ratio of the peak amplitude of the fitted signal to the rms deviation shown in Fig. 4**b** is about 2.69.

As in [5], a multispectrum fitting procedure was used to retrieve line parameters from the spectra. This procedure was found very efficient to complete the previous results when treating weak bands of the spectrum. Additional experimental details and analysis techniques are given in [5]. The Table shows the comparison of the spectral line positions and intensities from our experiments with those from HITRAN database in the region 6506–6520 cm^{-1}. The experimental results of absorption band, transition,

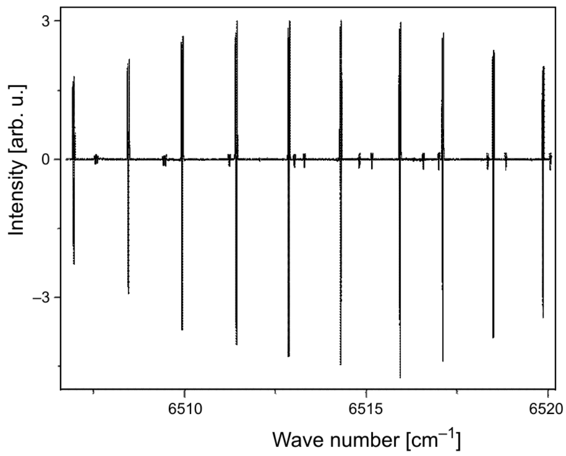

Fig. 3. Observed 2nd harmonic signals of CO_2 using the WM technique at an absorber pressure of 0.35 torr and an absorption path length of 355.4 m.

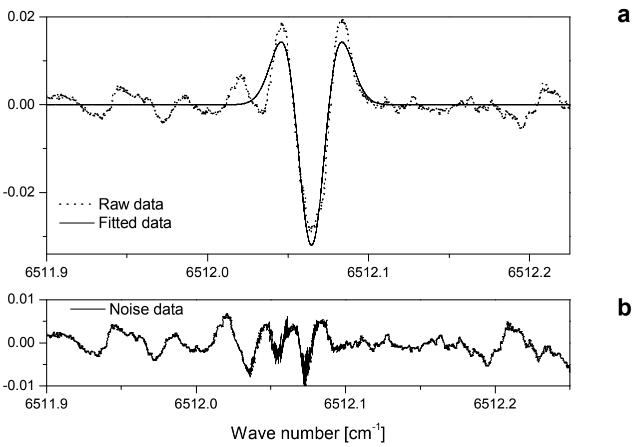

Fig. 4. Observed least absorption spectrum P28 transition of the CO_2 (31111-01101) band at an absorber pressure of 0.35 torr and an absorption path length of 355.4 m.

and line positions are listed in columns 1–3 of the Table, respectively. In this table, the values of the calculated line intensities from the HITRAN database are also listed in the column 4, the direct absorption signal intensities and the second harmonic signal intensities are listed in columns 5 and 6, respectively. From the values of the ratio between the calculated and the second harmonic signal line intensities, which are listed in the column 7, the standard uncertainty for the intensity varies from less than about 5% for the strongest lines to about 10% for the weakest lines.

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

Band	Transition	Position	S [10^{-26} cm^{-1}/(molecule·cm^{-2})]			$S_{Harmonic}/S_{HITRAN}$
			S_{HITRAN}	S_{DA}	$S_{Harmonic}$	
1	2	3	4	5	6	7
31111-01101	P34	6507.55738	4.587	—	4.405	0.960
30011-00001	R6	6508.41714	122.8	127.13	122.496	0.998
31111-01101	P32	6509.38043	5.603	—	5.369	0.958
31111-01101	P31	6509.44095	6.165	—	5.860	0.951
30011-00001	R8	6509.90186	149	153.35	156.603	1.051
31111-01101	P30	6511.18907	6.713	—	6.144	0.915
31111-01101	P29	6511.35236	7.31	—	7.723	1.056
30011-00001	R10	6511.36878	169.2	163.34	169.2	1.000
31111-01101	P28	6512.0261	0.9116	—	0.975	1.070
30011-00001	R12	6512.818	182.8	177.59	180.264	0.986
31111-01101	P28	6512.98305	7.882	—	6.997	0.888
31111-01101	P27	6513.24124	8.494	—	7.367	0.867
31111-01101	P26	6514.15935	1.115	—	1.169	1.048
30011-00001	R14	6514.24962	189.8	186.33	187.502	0.988
31111-01101	P26	6514.76211	9.066	—	8.609	0.950
31111-01101	P25	6515.10737	9.663	—	9.423	0.975
30011-00001	R16	6515.6638	190.6	189.34	191.258	1.003
31111-01101	P24	6516.52601	10.2	—	8.927	0.875
31111-01101	P23	6516.95054	10.75	—	9.380	0.873
30011-00001	R18	6517.06069	185.8	187.09	184.350	0.992
31111-01101	P22	6518.27453	11.23	—	11.780	1.049
30011-00001	R20	6518.44049	176.2	178.76	172.771	0.981
31111-01101	P21	6518.77055	11.69	—	10.610	0.908
30011-00001	R22	6519.80339	163.1	165.32	165.199	1.013
31111-01101	P20	6520.00746	12.07	—	11.859	0.983

Figure 5 shows a comparison of the spectral line positions and intensities from our experiments with those from HITRAN2004 database in the region 6506–6520 cm^{-1}. From this figure, we can see that there are many new absorption lines not reported in HITRAN2004 database.

4. Conclusions

This work represents the spectroscopic intensity of the CO_2 around 1.53 μm based on DFB lasers, and the intensity measurements which are of primary importance for atmospheric applications, and will be helpful for further improvement of reliable

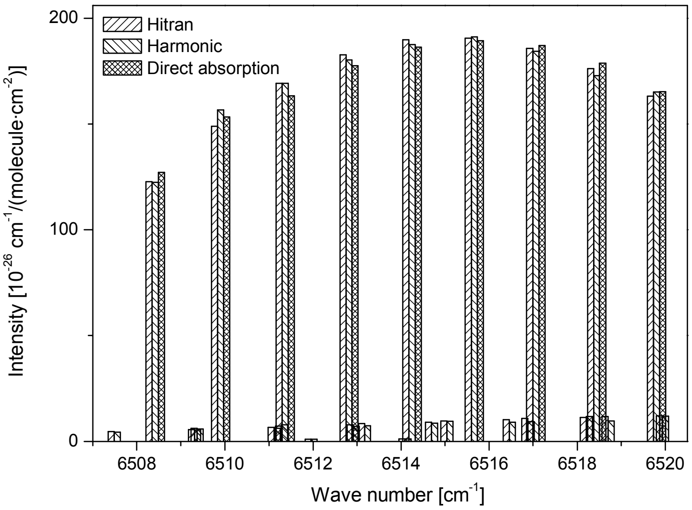

Fig. 5. Comparison of calculated (with the HITRAN database) and measured spectral line positions and line intensities of CO_2 at 296 K.

retrievals of the concentration profiles of this minor constituent in the atmosphere. Overtone absorption lines of CO_2 in the regions between 6506 and 6520 cm^{-1} have been examined using 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 we detected in this experiment is 9.116×10^{-27} $cm^{-1}/(molecule\cdot cm^{-2})$ at a pressure of 0.35 torr, and the corresponding absorption is 1.96×10^{-6} with SNR of 2.67.

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