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Absorption measurements for highly sensitive diode laser of CO_2 near 1.3μm at room temperature*

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Fifteen new absorption lines were observed when studying CO_2 absorption spectroscopy by wavelength modulation technique with a distributed feedback laser. The overtone spectra of CO_2 around 1.31μm and the corresponding spectral parameters (i.e. positions, intensities, self-broadening coefficients) are presented. The intensity of the weakest line detected is 2.25163×10^{-27}cm^{-1}/(molecule·cm^{-2}) at the pressure of 667Pa, with a corresponding absorption of 3.88×10^{-8}.

Keywords: absorption spectroscopy, wavelength modulation, harmonic detection
PACC: 0765G, 4225B, 4280,4260F

1. Introduction

Wavelength modulation absorption spectroscopy (WMAS) with tunable diode lasers has been used by many researchers to perform sensitive measurements on gaseous media. Tunable diode lasers absorption spectroscopy (TDLAS) usually scans over an isolated absorption line of the species under investigation by the use of a single narrow laser line. To achieve the highest selectivity, the analysis is usually made at low pressures, at which the absorption lines are not substantially broadened. This type of measurement was pioneered by Hinkley[1] and Reid *et al*[2], and has been developed into a very sensitive and general technique for monitoring most atmospheric trace species.[3−5] There are many advantages in using diode lasers for such measurements, including the relative ease with which modulation can be performed by a modulated injected current, the relatively modest capital cost, and the small weight of the apparatus. Moreover, because of the room-temperature operation and fibre-optic compatibility, near-infrared diode lasers have found increasing use in commercial spectroscopic sensors for trace gases in such application as atmospheric chemistry, combustion research, emission monitoring, and toxic gas detection. All these characteristics have made the technology developed into a very sensitive and general one to monitor atmospheric trace species, and become an advanced tool for optical sensor of polluting gases.[6,7]

Quantitative analysis of the trace chemical components in our atmosphere has received much attention in the last two decades. This is an urgent task concerned in the growing global environmental problem, such as the greenhouse effect and the destruction of ozone layer in the stratosphere. Demand for precise spectral line profile parameters is increasingly strong, since these parameters are essential to the correct retrieval of the trace gas compositions in our atmosphere from the spectroscopic observations using satellite- or ground-based sensors. A large number of data have been accumulated mainly in the infrared region as the databases.[8] Carbon dioxide (CO_2) is a special species of the trace gas components in our atmosphere, because it is one of those distributed commonly in the universe. The precise line parameters of CO_2 are thus required not only for the environmental chemistry and

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physics of our atmosphere, but for the studies of planetary and stellar atmosphere. The wavelength 1.31μm is a traditional window for atmospheric remote sensing, and is very popular for use in many current and planned atmospheric remote-sensing experiments. In these experiments, accurate spectroscopic parameters of the atmospheric species are essential to the analysis of the data.[9] Carbon dioxide, one of the most important minor components in the atmosphere, is always a subject attracting great interest. The improvement of its line parameters listed in the spectroscopic database around 1.31μm is always the central interest in atmospheric spectroscopy.[10] The purpose of these investigations is to obtain the precise spectral parameters (i.e. positions, intensities, linewidths) and to perform reliable retrievals of the concentration profiles of this minor constituent in the atmosphere.[11]

2. Experiments

The experimental apparatus used in this work are schematically shown in Fig.1. The multipass cell is of the white-type with the base path length of 8m. The total optic path length, which can be varied, ranges from 46 to 1159m. In the experiment, a single-mode distributed feedback (DFB) diode laser was used, and the emission output of the pigtailed DFB InGaAs laser diode, which was mounted in a butterfly package with a central emission wavelength of 1.31μm, swept over 7599–7617cm^{-1}, with a typical linewidth of about 2MHz and a side mode suppression ratio greater than 30dB. This linewidth is negligible when compared to that of gas absorption, which is above 1GHz. The wavelength of the laser, which was controlled by a laser-controller (TDS3724B, LightWave), varied with the laser current, whose magnitude and accuracy were about 0.017cm^{-1}/mA and 0.01mA, respectively. The output of the laser was directed to a 1×3 fibre 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 amplifier for demodulation, and the output signals of lock-in amplifier were sent to a PC-based data acquisition board (DAQ), which was capable of sampling at 20kS/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.

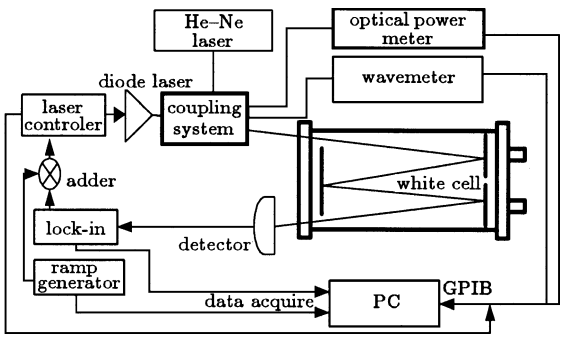


Fig.1. Sketch of experimental apparatus for the WM spectroscopy.

3. Results and discussion

The WMAS technique with diode laser can significantly reduce noises (e.g. the flicker $1/f$ noise), which allows improvements in the detectability by a few orders of magnitude, when compared with the unmodulated case. However, there are still various types of background signals that can and will appear in WMS.[12] In our experiment, an increase of one order of magnitude in signal-to-noise ratio was observed when using digital signal processing technique combined with WMAS technique. This experimental result detected by TDLAS is shown in Fig.2. The signal was obtained from CO_2 (99.99% purity) with the theoretical absorption length of 850m and the CO_2 pressure of 60Pa in the white cell. The temperature and central current of diode laser were kept at 36°C and 70mA, respectively. The modulation frequency and amplitude of lock-in amplifier were kept at 1.78kHz and 30mV, respectively, with the time constant of 1 ms. The absorption lines, shown in Fig.2, are the R(24) and R(25) lines of the CO_2 (41113-01101) band, whose peak positions are 7600.473738cm^{-1} and 7600.577018cm^{-1}, respectively, with the corresponding intensities of 1.018×10^{-26}cm^{-1}/(molecule·cm^{-2}) and 1.141×10^{-26}cm^{-1}/(molecule·cm^{-2}) in the HITRAN2003 database. The dashed curve in Fig.2(a) is the single experimental signal detected by TDLAS, and the solid one is the fitted signal derived from a nonlinear least squares fit of the data. The calculated intensities of the two lines are 1.12846×10^{-26} and 1.18294×10^{-26} cm^{-1}/(molecule·cm^{-2}). And the signal to noise ratio (SNR), which is the ratio of the

peak amplitude of the fitted signal to the rms deviation, as shown in Fig.2(b), is about 2. Then, in Fig.2(c), we show the spectrum of the same signal, as that shown in Fig.2(a), after applying the digital signal processing (DSP). This DSP includes multiple averages of 100 times and digital filter, which is a third order elliptic low-pass filter with the maximum frequency of 100. From Fig.2(c), we can see that the signal after DSP improves greatly with respect to the SNR, with the corresponding SNR of 62. Thus, by applying a combination of DSP with WMAS, the SNR can be increased by one order of magnitude.

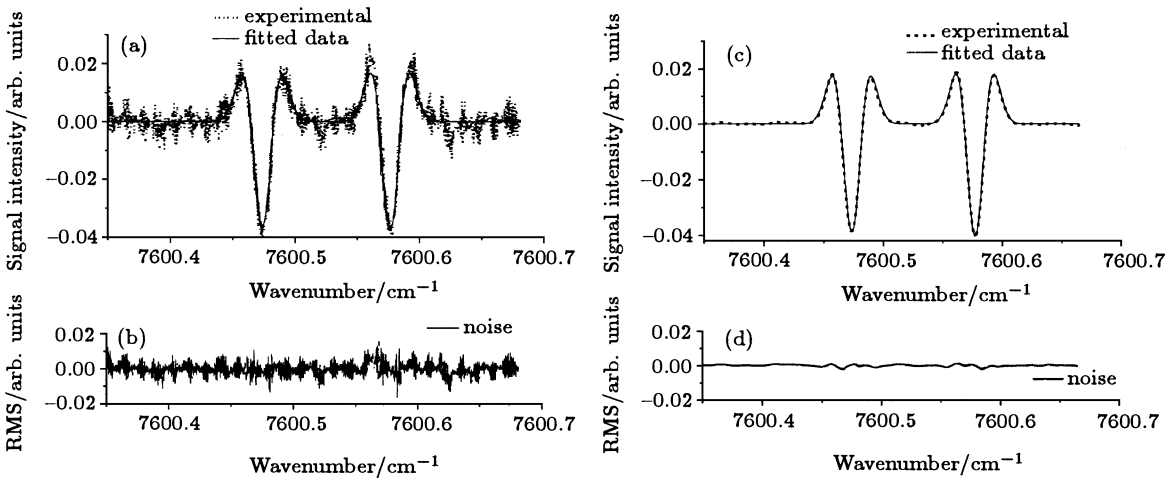


Fig.2. Two CO_2 absorption lines observed by WM spectroscopy and second harmonic detection technique at the gas pressure of 60Pa. Improvement in SNR due to digital signal process is illustrated by comparison between the spectrum in (a) and (c).

Figure 3 shows the experimental spectra of CO_2 around 1.31μm (i.e. 7599–7617cm^{-1}), which was measured within multipass cell using wavelength modulation absorption spectroscopy technique, with the temperature of diode laser varying from 8°C to 37°C. In the measurement, the sample pressure was 668Pa and the absorption path of 1097.092m. In addition, the second harmonic signal was obtained by the average of 50 scans.

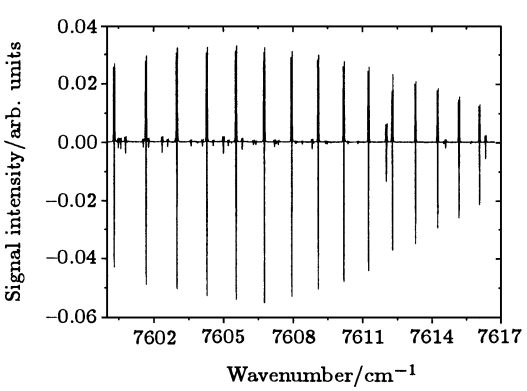


Fig.3. Observed second harmonic signals of CO_2 using the WM technique at an absorber pressure of 668Pa and an absorption path length of 1097m.

Figure 4 shows the comparison of the spectral line positions and intensities between our experiments and those from HITRAN 2003 database in the region 7599–7617cm^{-1}. The upper one is the spectra of CO_2 at 296K derived from HITRAN database, and the lower one is the spectra observed in our experiment. From this figure, we can see that there are 15 newly observed lines, which were not presented in HITRAN 2003 database. The intensity of the weakest line observed in our experiment is 2.25163×10^{-27}cm^{-1}/(molecule·cm^{-2}) and the corresponding absorption is 3.88 $\times10^{-8}$ with SNR=2.

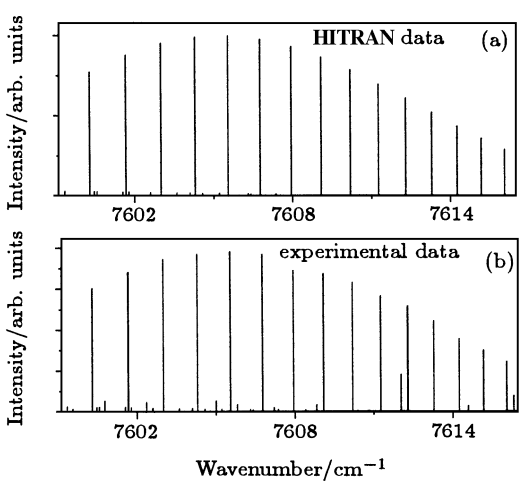


Fig.4. Comparison between (a) calculated (from the HITRAN database) and (b) measured spectral line positions and line intensities of CO_2 at 296K.

Moreover, the absorption signals of CO_2 around 1.31μm at different pressures (i.e. $2.65\times10^4 - 4.0\times$

10^{+1}Pa) have been detected using the TDLAS technique and analyzed using a nonlinear least squares fit technique. The linewidths and the self-broadening coefficients are derived for each absorption line observed in the experiment. The experimental results of absorption line positions, line intensities and the corresponding self-broadening coefficients, are listed in the first, second and fifth columns of Table 1, respectively. In this table, the values of the calculated line intensities and self-broadening coefficients from the HITRAN database are also listed in the third and sixth columns. From the values of ratio between the calculated and experimental line intensities, which are listed in the fourth column, we can see that the typical uncertainty of line intensities is about 5%.

Table 1. Compilation of the measured self-broadening coefficients and line intensities of CO_2. The line positions are taken from the HITRAN 2003. The superscript * denotes a new absorption line.

Position/cm^{-1}	[a]Line intensity		Res ($S_{Hitran}/S_{observed}$)	Self-broadening coefficients/$cm^{-1}\cdot atom^{-1}$	
	Observed	Hitran2003		Observed	Hitran2003
7599.36127	1.34599	1.254	0.93166	0.08345	0.0935
7599.57118*	0.71967	–	–	0.0876	–
7600.30145	30.1203	30.93	1.02688	0.094	0.1103
7600.47374	1.12846	1.081	0.95795	0.07247	0.0916
7600.57702	1.18284	1.141	0.96463	0.07693	0.0926
7600.77971*	2.67342	–	–	0.08845	–
7601.55069	1.03328	0.9552	0.92443	0.0937	0.0897
7601.55988*	1.15859	–	–	0.0854	–
7601.66744	34.0626	35.17	1.03251	0.09369	0.1079
7601.77639	1.04929	1.015	0.96732	0.0836	0.0906
7602.35552*	2.33653	–	–	0.08361	–
7602.59203	0.86334	0.822	0.95212	0.092	0.0878
7602.99631	37.1161	38.09	1.02624	0.09583	0.1055
7603.59774	0.71378	0.6957	0.97467	0.09465	0.086
7604.09188	0.77496	0.756	0.97553	0.09212	0.0869
7604.28806	38.4114	39.65	1.03225	0.09317	0.1032
7604.56775	0.61618	0.5778	0.93771	0.08836	0.0843
7604.99468*	2.59211	–	–	0.08519	–
7605.20794	0.63221	0.6336	1.0022	0.08747	0.0852
7605.54272	38.9929	39.93	1.02403	0.0933	0.1009
7605.80421*	1.71855	–	–	0.07874	–
7606.2962	0.56423	0.5211	0.92356	0.08714	0.0835
7606.40049	0.40951	0.3769	0.92036	0.06959	0.081
7606.7603	38.3478	39.06	1.01857	0.09141	0.0987
7607.20358*	0.95923	–	–	0.0864	–
7607.35664	0.46296	0.4207	0.90872	0.09412	0.0818
7607.94084	36.8725	37.21	1.00915	0.08934	0.0966
7608.39919*	0.45379	–	–	0.08152	–
7608.82175*	1.64768	–	–	0.08723	–
7609.08437	33.6682	34.58	1.02708	0.08687	0.0946
7610.19094	31.4189	31.42	1.00003	0.08432	0.0926
7610.37597*	0.31258	–	–	0.08445	–
7610.79943*	0.26877	–	–	0.0876	–
7611.26059	28.2078	27.93	0.99015	0.08116	0.0906
7612.03522*	8.62651	–	–	0.08634	–
7612.29338	25.7083	24.32	0.946	0.08133	0.0887
7613.28937	22.1612	20.75	0.93632	0.07809	0.0869
7614.24863	17.7018	17.37	0.98126	0.07225	0.0852
7614.59165*	1.32982	–	–	0.05526	–
7615.17122	14.9554	14.26	0.9535	0.07148	0.0835
7615.68236*	0.22516	–	–	0.08338	–
7616.05723	12.0867	11.5	0.95146	0.07098	0.0818
7616.32205*	3.73857	–	–	0.07694	–

[a] Intensities are reported in units of $10^{-26}\times cm^{-1}/(molecule\cdot cm^{-2})$ at 296K

4. Conclusions

Tunable diode laser absorption spectroscopy with wavelength modulation has been carried out. The CO_2 spectra around 1.31μm were recorded by wavelength modulation technique at different pressures, and analyzed using nonlinear least squares fit technique. The sensitivity of the wavelength modulation spectroscopy was improved by the use of digital signal processing.

The spectral line parameters of CO_2 near 1.31μm were derived, by using experimentally the TDLAS technique for the first time so far as we know and theoretically the nonlinear least squares fit technique. The results obtained are in good agreement with those in the HITRAN 2003 database. At the same time, 15 new spectral lines of CO_2 not reported in the HITRAN 2003 database were identified. Among them, the intensity of the weakest line we could detect is $2.25163\times10^{-27}\,\mathrm{cm}^{-1}/(\mathrm{molecule}\cdot\mathrm{cm}^{-2})$ at the pressure of 667Pa, with the corresponding absorption being 3.88×10^{-8} and the SNR=2.

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