Vol 14 No 9, September 2005
1009-1963/2005/14(09)/1904-06

Chinese Physics

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Influence of laser intensity in second-harmonic detection with tunable diode laser multi-pass absorption spectroscopy*

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(Received 28 December 2004; revised manuscript received 7 May 2005)

Tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in atmospheric trace gases detection. The ratio of the second-harmonic signal to the intensity of laser beam incident to the multi-pass cell is proved to be proportional to the product of the path length and the gas concentration under any condition. A new calibration method based on this relation in TDLAS system for the measurement of trace gas concentration is proposed for the first time. The detection limit and the sensitivity of the system are below 110 and 31ppbv (parts-per-billion in volume), respectively.

Keywords: tunable diode laser absorption spectroscopy, multi-pass cell, harmonic detection, wavelength modulation

PACC: 8670L, 0765G

1. Introduction

Tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in detecting atmospheric trace gases due to its high sensitivity, high selectivity, and fast time response.[1−7] The most important part in a standard TDLAS system is a tunable distributed feedback (DFB) diode laser. The key features of the DFB lasers are: 1) very narrow linewidth, typically less than 50MHz, much less than the linewidth of single rotational gas absorption line, and 2) capability of modulating the wavelength of the laser output through the injection current. High sensitivity detection has been obtained by wavelength or frequency modulation spectroscopy and by monitoring first, second, or higher order of the modulation frequency in the detected output signal.[7,8] In addition, increasing the absorption path length by adapting a multi-pass technique could also greatly enhance the detection sensitivity.[1−6]

Methane is a gas whose concentration in the atmosphere is strongly affected by human activities. It is the second most important greenhouse gas after CO_2. Methane concentration in the atmosphere is about 1.6 ppmv (parts-per-million in volume) and much lower than CO_2, yet it is responsible for 26% of the total greenhouse effect, as its effectiveness as a greenhouse gas is 22 times that of CO_2. Therefore monitoring methane concentration in the atmosphere is of particular importance for the study of radioactive process and climate trends. To achieve such high detection sensitivity, it is desirable to use as strong an absorption line as possible. Methane has strong absorption line in the $\nu 3$ and $\nu 4$ bands at around 3.3 and 7.7μm, respectively. At the present time, however, it is still difficult to get a tunable DFB laser operating at wavelength over 2.3μm at room temperature. The strongest absorption of methane below 2.3μm is

*Project supported by the National Natural Science Foundation of China (Grant No 10274080) and the National High Technology Research and Development Program of China (Grant No 2003AA641010).

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the $2\nu 3$ band located at 1.6–1.7μm. There are several lines labelled as P, Q, and R lines free of interference from other atmospheric gases in this band. Among these lines R (3) line at λ=1.65μm is selected for our measurements.

2. Theory of harmonic signal detection

Tunable diode laser absorption spectroscopy in conjunction with harmonic detection has been extensively used to measure many trace-gases. To achieve high detection sensitivity, the laser diode is frequency-modulated by a low frequency sawtooth wave and amplitude-modulated by a high frequency (f) sine wave, the laser wavelength is slowly scanned across an absorption line by the sawtooth, the signal from the detector is processed by a lock-in amplifier referenced to the modulation frequency (f). The intensity $I(\nu)$ of a laser beam at frequency of ν passes through a cell of length L filled with an absorption gas can be approximated as

$$I(\nu) = I_0(\nu)[1 - \alpha(\nu)CL], \tag{1}$$

where $I_0(\nu)$ and $I(\nu)$ are the laser beam intensities before and after passing through the absorption gas, respectively. $\alpha(\nu)$ is the absorption coefficient the gas at frequency ν, $\alpha(\nu) \approx \alpha_0$; C is the concentration of the absorption gas. For harmonic detection one is only concerned with weak absorption lines, i.e., we can assume that the value of $\alpha_0 L$ is confined to $\alpha_0 L \ll 0.05$. The second harmonic signal obtained by demodulation can be expressed as[8]

$$I_{2\mathrm{f}} \propto I_0(v)\alpha_0 CL. \tag{2}$$

3. Experimental apparatus and results

The experimental apparatus employed for the measurements is a portable ground-based TDLAS system developed by our group specifically for ambient methane detection. The diode laser employed for this study is a commercially available near-infrared DFB laser from NEL NTT Electronic Corporation. The diode laser is driven by a current controller and a temperature controller. These controllers are made by ILX Lightwave. The laser output wavelength can be tuned coarsely by the temperature controller and tuned finely by the current controller. In order to achieve the expected sensitivity a double modulation was applied to the laser diode. The laser wavelength is slowly scanned through the absorption line from 1653.61nm to 1653.83nm by a sawtooth waveform at frequency of 50Hz and simultaneously modulated by a sinusoidal waveform at frequency of 5kHz. A multi-pass white cell with base length of 43.5cm is used to lower the detection limit. The path length of multi-pass white cell can be altered from 12.18 meters to 60.90 meters by adjusting the reflection times in the cell. A schematic of the experimental system is shown in Fig.1. The laser beam was first divided into two parts with a 1×2 (50/50%) fibre coupler. One is connected to the reference cell; the other is connected to the multi-pass cell through a standard single-mode optical fibre with a self-focusing lens at the end. After multiple reflections in the cell the laser beam is focused onto a detector. The harmonic detection technique is used in this TDLAS system. The two modulation signals to the laser and the two reference signals to the lock-in amplifiers are produced by a signal generator. The optical outputs from the reference cell and multi-pass cell after passing through the detectors are then divided into two parts respectively. One is sent to the lock-in amplifier to get the 2f absorption signal and the other passes through the amplifier-filter to provide a caliber for the incident laser intensity at the detector. The data acquisition and processing system has four channels, channel 1 and 4 are used to collect the 2f signals from the two lock-in amplifiers, the other two channels are used to collect the signals from the two amplifier-filters. The gas used in the experiments is the mixture of methane and nitrogen generated by the 146C dynamic gas calibrator made by Thermo Environmental Instruments, USA.

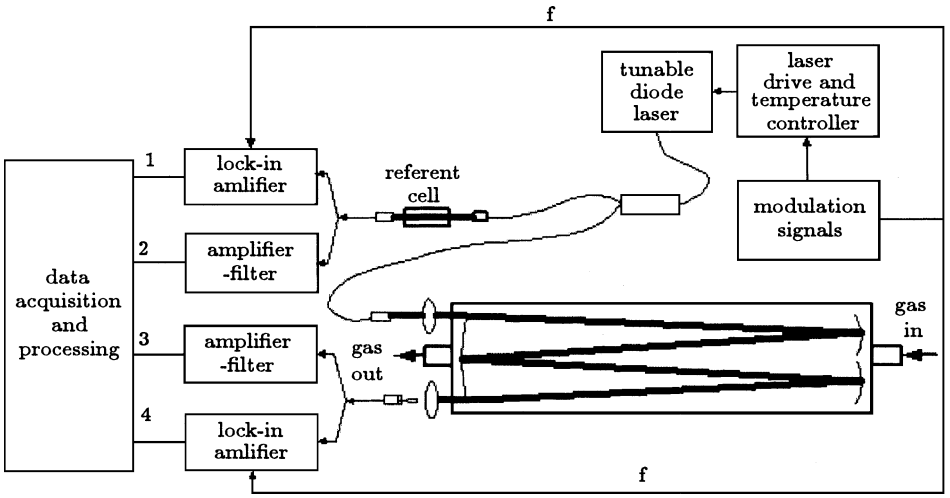


Fig.1. Schematic of TDL System, 1, 2, 3 and 4 are the data acquisition channels.

3.1. 2f detection with different path-length L

The two modulation waveforms are shown in Fig.2. The multi-pass white cell is filled with methane and nitrogen and sealed in the experiment; the concentration C of methane in the cell is about 10 ppmv.

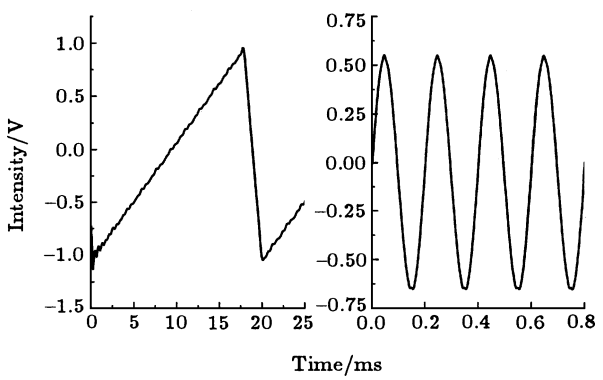


Fig.2. Waveforms of the modulation signals.

The signal output from the detector collected by channel 3 is shown in Fig.3. By carefully setting the amplitude of the sawtooth signal, the laser output wavelength scan range is made large enough to amply cover the absorption linewidth. If we assume the starting and ending scan wavelengths are λ_1 and λ_2, since the absorption happens only around λ_0, there would be no absorption at λ_1 and λ_2, therefore we have $I_0(\lambda_2) = I(\lambda_2)$ and $I_0(\lambda_1) = I(\lambda_1) = kI_0(\lambda_2)$, $I_0(\lambda_1)$ and $I_0(\lambda_2)$ are the incident laser intensities at the wavelengths λ_1 and λ_2, respectively. $I_0(\lambda_0)$ is the input laser intensity at the absorption line of λ_0 before the detector. k is a constant determined by the laser inject current–wavelength characteristics. As the semiconductor laser output wavelength has a good linear relation to the inject current, $I_0(\lambda_0)$ can be expressed as

$$I_0(\lambda_0) = I_0(\lambda_2)\left[(1-k)\frac{\lambda_2-\lambda_0}{\lambda_2-\lambda_1}+k\right], \tag{3}$$

$$I_0(\lambda_0) = k_0 I_0(\lambda_2), \tag{4}$$

where k_0 is a constant. The laser tuning range in the experiments was carefully set to make the methane absorption line in the middle of the scan, i.e., $\lambda_2 - \lambda_0 \approx \lambda_0 - \lambda_1$, thus we have $k_0 = (1-k)\frac{\lambda_2-\lambda_0}{\lambda_2-\lambda_1} + k \approx 0.5(1+k)$. We shorten $I_0(\lambda_0)$ as I_0 in the sections below.

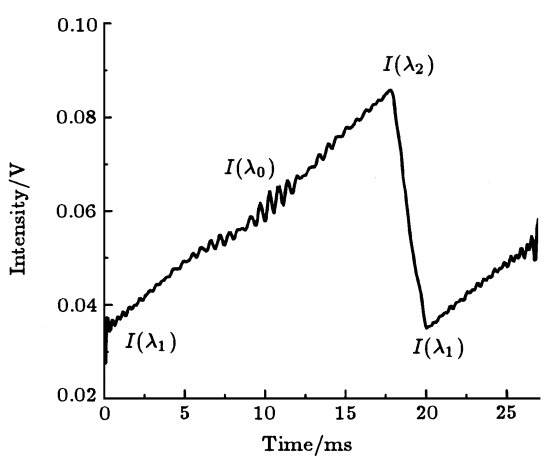


Fig.3. Waveforms of the signal from the detector after amplification and low-pass filtering.

We altered the path-length to 12.18m, 19.14m, 26.10m, 33.06m, 40.02m, 46.98m, 53.94m and 60.9m. For every path length, signals from two channels, the 2f absorption signal from the lock-in amplifier (Channel 4) and the incident laser intensity signal after the amplifier-filter (Channel 3), were recorded as shown in

Fig.4. The laser beam intensity after passing through multi-pass cell is attenuated as the total path length increases. This is due to the loss of the light intensity as a result of multiple reflections. Consequently the second harmonic signal 2f decreases as the path length increases. The coefficients of reflection for all three spherical mirrors in the white cell are measured about 98.133%. The values of laser transmission for difference path lengths were measured and calculated as shown in Fig.5. The normalized experimental and calculated I_{2f} values are also shown in this chart. Both experimental and calculated results shown in Fig.5 indicate that I_{2f}/I_0 is proportional to the path length when the gas concentration keeps constant.

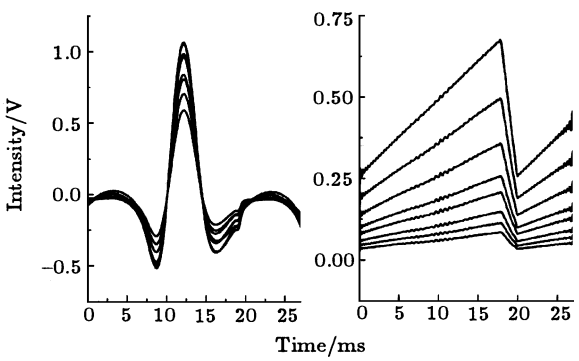


Fig.4. I_{2f} and I_0 as a function of sampling time.

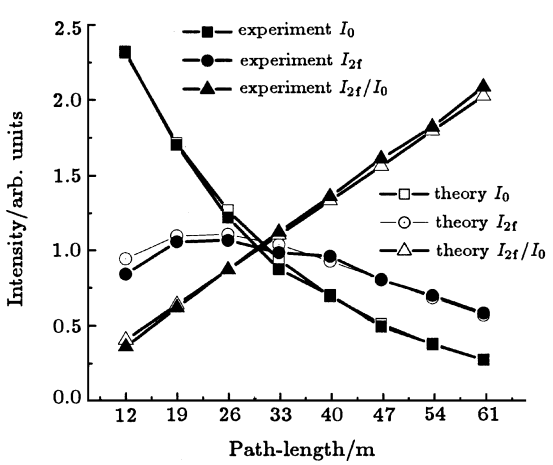


Fig.5. I_{2f}, I_0 and I_{2f} / I_0 as a function of path-length L with the same concentration C.

The correlation for the I_{2f}/I_0 between the experimental results and the theoretical simulation calculated with the least-square fitting method is 0.999, indicating an excellent agreement of the experiments with the theoretical calculation.

3.2. 2f detection with different concentration C

In the experiment below we alter the methane concentration C and keep the path length L fixed. The intensity of I_0 in the experiments varies slightly when the concentration changed, the maximum deviation 0.44% can be ignored. The curve of normalized experimental I_{2f} coincides with that of the normalized I_{2f} / I_0 very well as shown in Fig.6. Normalized theoretical I_{2f} is a straight line and points of normalized experiment I_{2f} lie almost on a line too. The coefficient calculated by least-square fitting with the line is 0.988, the experimental results agree with the theoretical calculation very well.

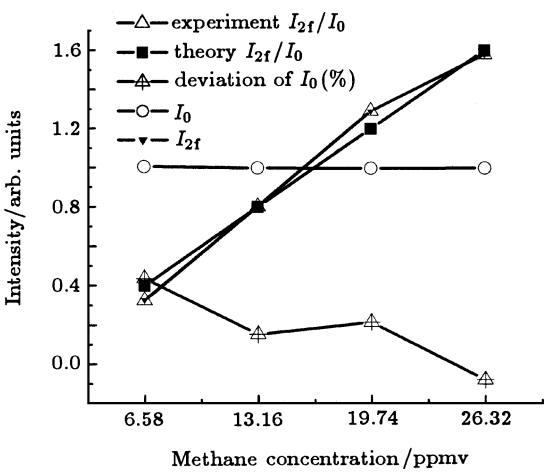


Fig.6. I_{2f}, $I_0$and I_{2f} / I_0 as a function of concentration C with the same L.

3.3. 2f detection with different C and L

In all the above experiments at least one condition was kept fixed, the experimental result agrees well with the theoretical calculation. We alter all the conditions in the following experiments; the concentration and path length are listed in Table 1.

Table 1. Gas concentration and path length used in this experiment.

Concentration/ppmv	13.16	19.74	26.32	32.9
Path-length/m	19.14	26.1	33.06	40.02
Product of C and L/(ppmv·m)	251.8824	515.214	870.1392	1280.64

The curves of I_0 and I_{2f} in Fig.7 are irregular, however, the I_{2f}/I_0 relation have an obvious regularity. They are almost straight lines as a function of the product CL. The correlation coefficient of I_{2f}/I_0 between the experimental results and the theoretical calculation is 0.998. This further proves that the I_{2f}/I_0 is proportional to the product of C and L.

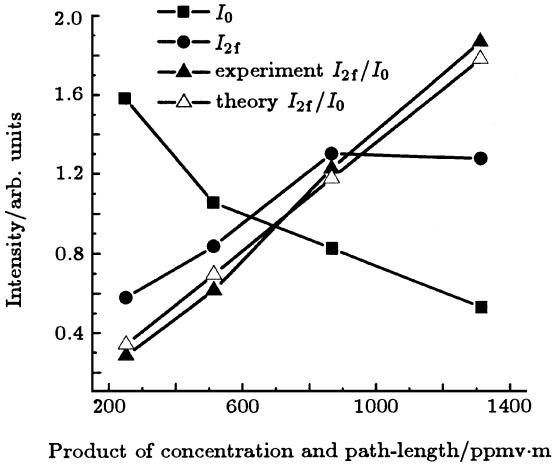


Fig.7. Normalized I_{2f}, I_0 and I_{2f} / I_0 as a function of the product CL.

3.4. Application

The results described above have proved that I_{2f}/I_0 is proportional to CL, which can be used as a caliber in the TDLAS system. In these systems a reference cell of known gas concentration should be used besides the multi-pass cell to calibrate the concentration of the detected gas. If all the detection devices, lock-ins and amplifier-filters for the reference channels and multi-pass signal channels are the same, the relationship of gas concentration in the reference cell and that in the multi-pass white cell is expressed as:

$$\frac{I_{2fR}/I_{0R}}{I_{2fD}/I_{0D}} = \frac{C_R L_R}{C_D L_D}. \tag{5}$$

Obviously if in the experiment I_{2fR}/I_{0R} is equal to I_{2fD}/I_{0D}, the absorption in the reference cell is equal to that in the multi-pass cell; one can have an even simpler expression:

$$C_D = \frac{C_R \times L_R}{L_D}, \tag{6}$$

where C_R, C_D and L_R, L_D are the gas concentrations and path lengths in the reference cell and the multi-pass cell, respectively.

The principle described in this paper has been applied to the TDLAS trace gas detection system developed by our group specially for monitoring trace of methane in the atmosphere. A number of experiments have been carried out. Figure 8 shows typical experimental results. In this experiment C_R=5010ppmv is the concentration of the reference gas, L_R=11cm is the path length of the reference cell, L_D=40.02m is the total path-length of propagation of the laser beam inside the multi-pass white cell. C_D is the equivalent concentration of methane in the multi-pass cell that will produce the same absorption as the reference cell. From the formula (6) we can then easily deduce that the methane concentration in the multi-pass cell is C_D=13.77ppmv. The coefficient of the linear fitting in Fig.8 is 0.999, indicating that the reference signal I_{2f}/I_0 fits very well with that of the multi-pass cell after the conversion.

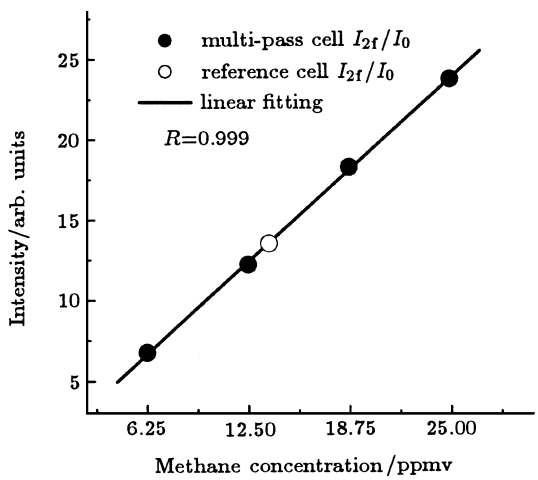


Fig.8. Reference signal and sample signal; note that the concentration of 5010ppmv in the reference cell corresponds to 13.77ppmv in the multi-pass cell.

4. Conclusion

In this paper a TDLAS system built in our laboratory for methane trace gas detection in the atmosphere was presented. Harmonic detection and multi-pass techniques were employed in this system. A number of experiments have been carried out on this system. The experimental results have proved that for weak absorption gas the ratio of the second harmonic signal and the incident laser intensity is proportional to the product of the gas concentration and the path length. From this a new calibration method is described in this paper. With this method the influence of the laser intensity fluctuation can be eliminated.

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