Applications of a tunable diode laser absorption spectrometer in monitoring greenhouse gases

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Tunable diode laser absorption spectroscopy (TDLAS) is a powerful technique to measure trace gas, which can provide high sensitivity, high selectivity, and fast time response. A brief description of our instruments with room-temperature near infrared tunable diode laser designed to measure greenhouse gas (i.e., CH_4, CO_2) in the ambient air is presented. A multiple-reflection cell and the second harmonic detection technique are used to lower the detection limit. The detection limit of the instrument is below 100 ppbv for CH_4 and 10 ppmv for CO_2, which is enough to the measurements of ambient CH_4 and CO_2. The instruments have been used to monitor the methane and carbon dioxide of the ambient air in a long time in Fengtai, Beijing. The results of measurement are shown and discussed in this paper.

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Tunable diode laser absorption spectroscopy (TDLAS) is a new trace gas detection technique with high sensitivity, high selectivity, and high precision[1−3]. This technique is universally applicable to some infrared active molecules and the same instrument can easily be converted from one to another by changing the laser and calibration gases. Distributed-feedback (DFB) InGaAs laser diode, the key element of the TDLAS system, emitting in the near-infrared between 1 and 2 μm is a promising tool for trace-gas sensing, such as CO, CO_2, O_3, CH_4, NO, NO_2, and HNO_3[4]. CH_4 and CO_2 are the two important greenhouse gases among these detectable species. CO_2 is the main product of combustion processes and human activities, its monitoring has far-reaching implications for globe control of the environment and for industrial, medical, and geophysical purposes[5]. CH_4 is the second most important greenhouse gas after CO_2, it is responsible for 26% of the total greenhouse effect, but its capability as a greenhouse gas is 22 times that of CO_2[6]. CH_4 and CO_2 are both of great interest for facilitating the understanding of the radioactive, chemical, and dynamic processes.

In this paper a diode laser spectrometer for measuring CH_4 and CO_2 gas concentrations is presented. The CH_4 absorption line at 6049 cm^{-1} with the line strength about 10^{-21} cm/molecule and the CO_2 absorption line at 6337 cm^{-1} with the line strength about 10^{-23} cm/molecule are found to be free of interference from other atmospheric gases and suitable for the high sensitive detection. The wavelength modulation spectroscopy (WMS) technique and multipass-cell were combined in our instruments. The principles and the structures of our two instruments are the same except for the laser and calibration gases.

The principle of TDLAS obeyed Beer's law

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

where $I_0(\nu)$ is the original laser power at the frequency of ν, $I(\nu)$ is the laser power after transmitted through the absorb gas, $\alpha(\nu)$ is the absorption coefficient of the gas at frequency of ν; C is the concentration of the absorption gas. Because the level of the greenhouse gas in the atmosphere is very low and its absorption in the near infrared region is very weak, the value of $\alpha_0 L$ is met the condition $\alpha_0 L \ll 1$. The second harmonic signal obtained by demodulation could be expressed approximately as

$$I_{2f} \propto I_0(\nu)\alpha_0 CL, \tag{2}$$

α_0 is the absorption coefficient at the center of the absorption line.

A schematic of the experimental setup is shown in Fig. 1, which consists of optical components, electronic circuits, and a gas sampling system. The temperature of

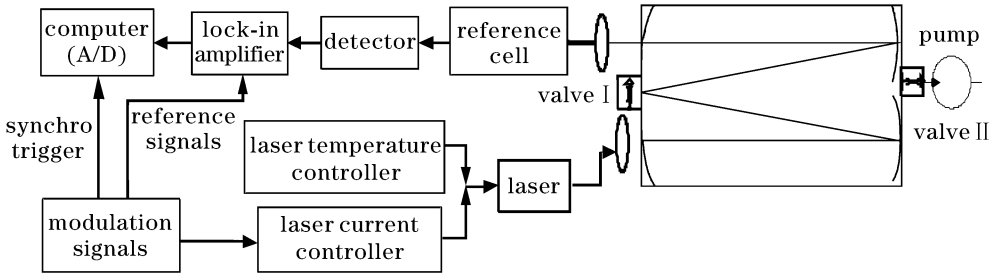

Fig. 1. Schematic of tunable diode laser.

the diode can be controlled with an accuracy of better than 0.005 k to stabilize the output wavelength of the laser. The laser transmitted to the multi-pass cell through a standard single-mode optical fiber with a self-focusing lens at the end. The multi-pass cell is based on White-type[7]. It has a base length of 22.8 cm and the total optical path is about 23 m with 102 times reflections. After multiple reflections in the cell the laser beam pass through a 10-cm-long reference cell which was filled with known high concentration sample gas used to calibrate the gas concentration in the cell, and then focused onto an InGaAs photodiode detector.

The electronics used in this instrument include a diode laser driver (include modulation signals generator, laser temperature, and current controller), a lock-in amplifier, and a data acquisition card. The experiment procedure requires that the wavelength of the laser be set close to absorption line of interest by adjusting the temperature. The laser is then slowly scan through the selected absorption line with a sawtooth current wave input (f = 50 Hz, voltage amplitude is 0.3 V), while a sine wave with frequency of 5 kHz is superimposed on the direct current simultaneously. The lock-in amplifier is used for phase-sensitive detection at the second-harmonic of the modulation frequency (f = 10 kHz, voltage amplitude is 10 V). The outputs from the lock-in amplifiers are digitized by the data acquisition card and then recorded using a personal computer.

The gas sampling system is composed of a mass flow controller, two electromagnetic valves, and a sampling pump. The two valves are connected to bottle filled with pure N_2 and ambient air respectively. Firstly open the valve I and fill the cell with pure N_2 (concentration is 99.999%) and obtain the standard spectrum with known concentration; Then close the valve I and open the valve II, pump the ambient air into the cell and obtain the gas concentration by fitting with the standard spectrum. The measurement results can be calibrated by filling the cell with different concentration gases. We have demonstrated that the detect limit is lower than 0.1 ppmv for CH_4 and 10 ppmv for CO_2, and the drift in 24 hours is lower than 0.1 ppmv. The detail can be found in Ref. [8].

Fengtai stadium (39°52′N, 116°17′E) in the southern Beijing was selected for the investigation. There are many heavy industries and the air pollution is very serious; which has brought the attention of Beijing government. It is the uptake of Beijing for the monsoon from south, so the control of air pollution in this region is very important to improve the air quality of Beijing.

Some of the monitoring results of CH_4 are shown in Figs. 2 and 3. From them we can see the range of the concentration during this period is between 1.85 and 12.68 ppmv. The general characteristic is that in the daytime, the CH_4 concentration is lower than that in the night. The maximum value was obtained in midnight which may be caused by the vehicles running on the expressway nearby. The second maximum value was obtained in wee hours. This is because that the CH_4 concentration is mainly affected by the atmosphere boundary layer. In midday, the troposphere moves violently, therefore the CH_4 emitted from its sources such as vehicles will transmit into the atmosphere in a short time and result

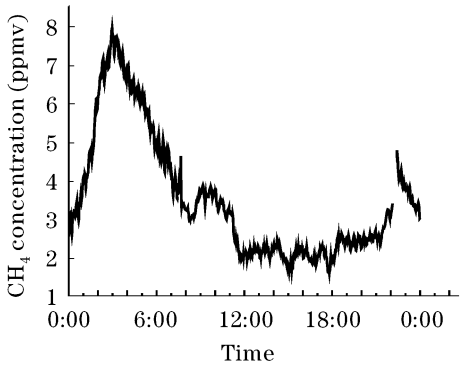

Fig. 2. CH_4 concentration (Aug. 23, 2005).

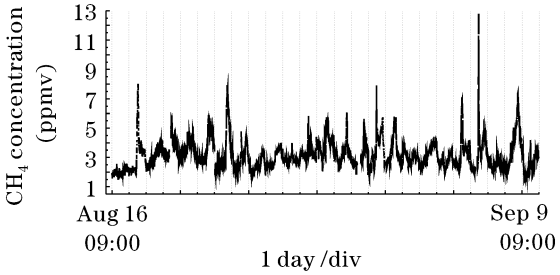

Fig. 3. Concentration of CH_4 as a function of time from Aug. 16 to Sep. 10, 2005.

in the lowest concentration. In evening the troposphere movement is steady, the concentration of CH_4 begins to increase. In a long-time measurement, the every-day CH_4 trend is almost the same. But there were four extraordinary values appeared in the night of 18 Aug., 23 Aug., 30 Aug., and 7 Sep., which probably were caused by emergency emissions. The true reason is under study.

Figure 4 displays the CO2 concentration trend in 24 hours time. From it we can see the maximum values were found at 9:00AM and 5:00PM. This mainly was caused by the vehicle emissions from the rush hour. Figure 5 shows the CO_2 concentration measurement data in a period of time. In contrast to the result of CH_4, the periodicity was not so obvious. As we know, too many factors can cause the CO_2 concentration fluctuation such as vehicle emissions, fuel burning, breath of human beings, and the emission from the chimneys near the experimental location.

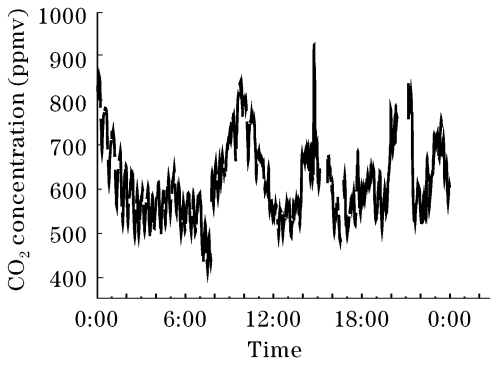

Fig. 4. CO_2 concentration (Aug. 23, 2005).

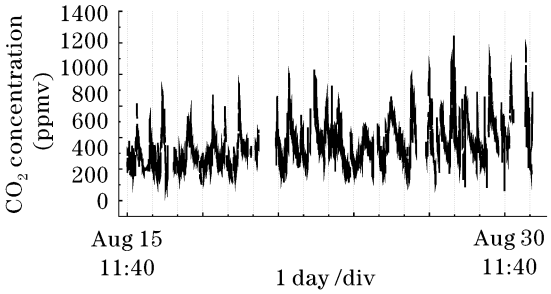

Fig. 5. Concentration of CO_2 as a function of time from Aug. 15 to 31, 2005.

This paper describes the design and monitoring results of TDLAS based green house gases (CO_2, CH_4) measurement instrument. This system is suitable for monitoring the greenhouse gases continuously with high sensitivity and stability. With the help of these measurement results, we can probably find and control the pollution sources and also provide a scientific evidence in atmosphere chemistry research.

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