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Development of a Stable Carbon Isotopes Analysis Instrument Based on Tunable Diode Laser Absorption Spectroscopy

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Abstract. A compact laser spectrometry instrument was developed for high precision measurements of isotope ratio of CO₂ by tunable diode laser absorption spectroscopy in the mid-infrared at 2.7 μm . The experimental spectrum of carbon isotopologues in the gas phase near 3641 cm^{-1} is very suitable for real-time analysis of these isotopologues. Simultaneous measurements of the mixing ratio and the corresponding $\delta^{13}\text{C}$ values of CO₂ in the atmosphere were performed. The achieved standard deviation (1σ) of $\delta^{13}\text{C}$ was 1.8‰. The Allan analysis of the time series of the mixing ratio of CO₂ shows a measurement precision of 0.2‰ for $\delta^{13}\text{C}$ with an optimum integration time of about 130 s. The spectrometer is capable of real-time measurements of stable carbon isotope ratios of CO₂ under ambient conditions.

1. Introduction

Carbon dioxide is one of the most important greenhouse gases and the arch-criminal of greenhouse effect. Its releasing must be controlled [1-3]. In order to search the sources and sinks of carbon dioxide, many studies on stable isotopes of atmospheric carbon dioxide have been performed [3,4]. Furthermore, ¹³C-breath gas analysis can be used to evaluate human's health condition, such as enzyme activities, organ functions, etc. [5].

Isotope ratio mass spectrometry (IRMS) has always been the main technology used by scientific researchers to analyze the isotopic ratio with high precision from 0.01‰ to 0.1‰ [6]. But the IRMS system is bulky and the samples to be analyzed must be pretreated which make it impossible to detect the isotopic ratio in-situ or on-line [7, 8]. The tunable diode laser absorption spectroscopy (TDLAS) system is very suitable for real-time on-line detection of the trace gases isotope ratio with the advantages of simple design, low cost and small size [9]. The isotope ratios can be easily calculated with high sensitivity and precision when temperature, pressure, optical path length and absorption line strength of gases are certain. The distributed feedback (DFB) laser was selected in the current experiment. The advantages of using DFB laser are better mode stability, room temperature operation, smaller size and cheaper price than the quantum cascade laser (QCL). Particularly, the tuning range of the DFB laser is fully satisfied with the experimental requirements.

In this paper, the development of a DFB laser based instrument for high precision measurement of isotope ratio of CO₂ in the mid-infrared at 2.7 μm is reported. The derived average value of CO₂ mixing ratio is 454 ppm. The corresponding $\delta^{13}\text{C}$ value is -98.75‰ with a 1σ standard deviation of 1.8‰. The measurement precision can reach to 0.2‰ in the light of the optimum integration time 130 s obtained by the Allan variance analysis.



2. Experimental Details

2.1. Experimental Setup

The carbon isotopes analysis instrument is displayed in Figure 1. The light source is a room temperature operated DFB laser (nanoplus GmbH) with a center wave number of 3641 cm^{-1} and a single mode output power of 6 mW. The tuning rates of the DFB laser are 0.02 nm/mA and 0.22 nm/K , respectively. The slope efficiency is 0.12 mW/mA . The DFB laser is driven by a homemade current and temperature controller. A red laser beam was used to calibrate the optical path on account of the light at $2.7\text{ }\mu\text{m}$ is not visible. The absolute wave number calibration was finished by applying the nearby water vapor absorption lines from the HITRAN 2012 database. The beam from the laser was passed to a homemade multi-pass absorption cell with an optical pathlength of 107 m after several reflections.

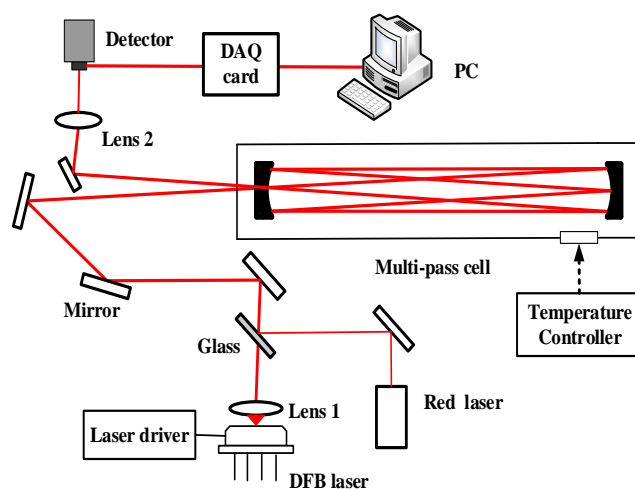


Figure 1. Experimental setup used for carbon isotope analysis

In order to improve the measurement accuracy and reduce the influence of the line strength with temperature variation, the temperature of the multi-pass absorption cell was maintained at $30\text{ }^{\circ}\text{C}$ by using a heater band and a temperature controller. The light signal from the multi-pass cell was focused onto a lens with a focal length of 5 cm , and then directed to a thermoelectrically cooled (TEC) photovoltaic detector (VIGO, PVI-4TE-3). The information from the detector was collected by a fast data acquisition card and then transmitted to a personal computer for further data processing and analysis.

2.2. Absorption Line Selection

It is very important to choose the suitable absorption lines for the design of an isotope ratio measurement system. The selection of appropriate absorption line has obvious impact on the performance of the spectral measurement system, including sensitivity, measurement accuracy and selectivity. Isotope ratio measurements usually have some requirements for the selection of absorption lines: (1) they should have identical absorption cross sections and ground state energy; (2) they should be detected in the single scanning range of the laser; (3) there is no cross interference with other gas molecules in the atmosphere, especially water vapor [10, 11].

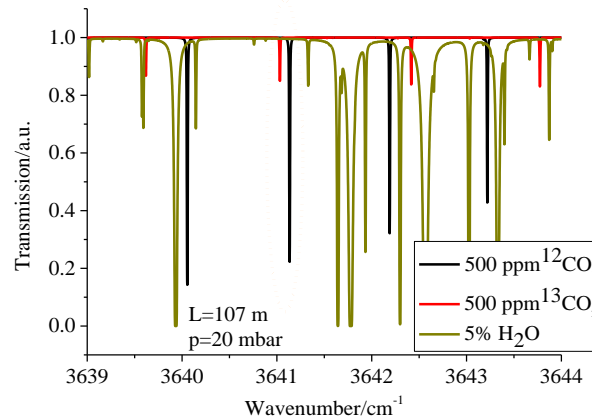


Figure 2. Signal simulation of 5% H₂O and 500 ppm CO₂ based on the HITRAN 2012 database with an optical path length of 107 m and the pressure of 20 mbar. ¹²CO₂, ¹³CO₂ and H₂O absorption lines are shown in black, red and dark yellow, respectively.

It is very simple to find appropriate spectral regions that may contain suitable absorption lines for the isotope ratio measurements using the above requirements. Signal simulation of 5% H₂O and 500 ppm CO₂ based on the HITRAN 2012 database in the spectral range of 3639-3644 cm⁻¹ is shown in Figure 2. Two absorption lines are selected for isotope analysis of CO₂, one is at 3641.0311 cm⁻¹ for ¹³CO₂ measurement, another is at 3641.1338 cm⁻¹ for ¹²CO₂ detection. They are free of interferences of water vapor absorption lines.

3. Results and Discussion

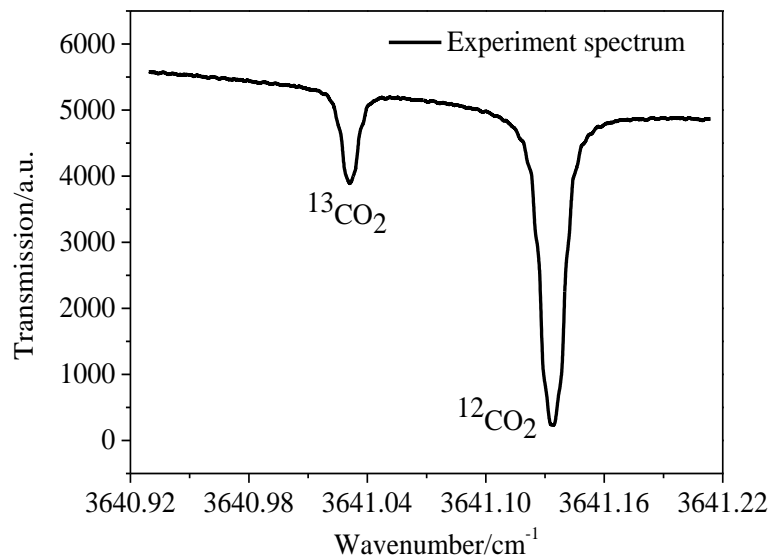


Figure 3. Experimental spectrum of ¹²CO₂ and ¹³CO₂ in the laboratory air

Figure 3 displays the direct absorption signals of ¹²CO₂ and ¹³CO₂ in the laboratory air at the pressure of 20 mbar and an optical path length of 107 m. The two absorption lines are located within a narrow scanned range of 0.1 cm⁻¹. The pressure of 20 mbar is sufficiently low to ensure a complete separation of the ¹²CO₂ and ¹³CO₂ absorption lines along with minimizing the influence of wing effects from the

nearby H₂O absorption lines. The parameters of the used ¹²CO₂ and ¹³CO₂ absorption lines for carbon isotope analysis based on the HITRAN 2012 database are provided in Table 1.

Table 1. The parameters of the used absorption lines of ¹²CO₂ and ¹³CO in this study

Isotopologue	Wavenumber (cm ⁻¹)	Line strength (10 ⁻²¹ cm ⁻¹ cm ² /molecule)	Ground state energy(cm ⁻¹)
¹⁶ O ¹² C ¹⁶ O	3641.1338	5.64	704.30
¹⁶ O ¹³ C ¹⁶ O	3641.0311	0.64	42.92

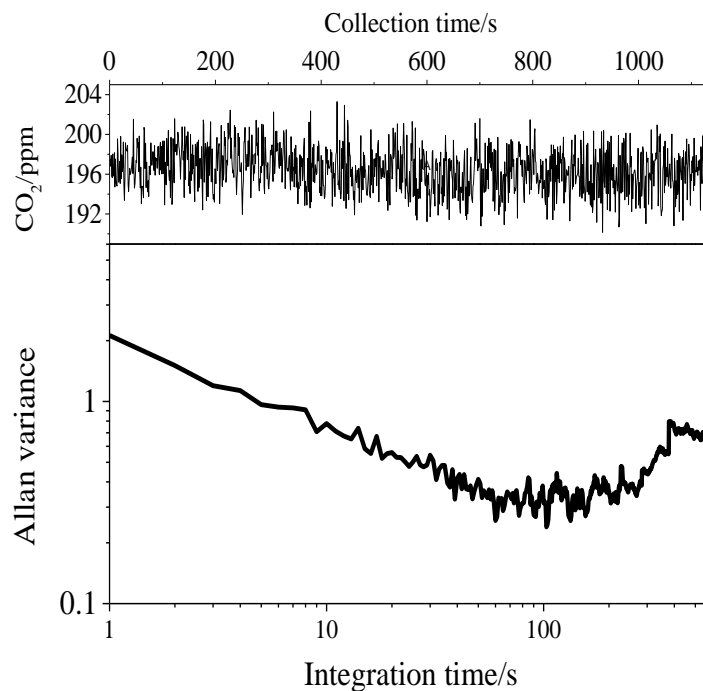


Figure 4. Allan variance analysis of 197 ppm CO₂ from a standard gas cylinder

In the absorption spectrum measurement experiment, the signal-to-noise ratio can be improved by selecting strong absorption lines or increasing the effective absorption path length (e.g using a multi-pass absorption cell or a high-precision optical cavity) in addition to reducing the internal noise of the spectrometer. In addition, for the normal white noise, it can be reduced to $N^{1/2}$ by averaging N laser scans in the stable time of the spectrometer. The optimum average time can usually be determined by Allan variance. In order to obtain the stable time of the system, the mixing ratios of CO₂ from a standard gas cylinder in the laboratory with 197 ppm CO₂ were detected. Figure 4 shows the time series and the corresponding Allan variance analysis. It can be seen that the optimum averaging time is 130 s from this figure. The room temperature was maintained at 30°C using air conditioning to dampen ambient temperatures variations during the measurement period.

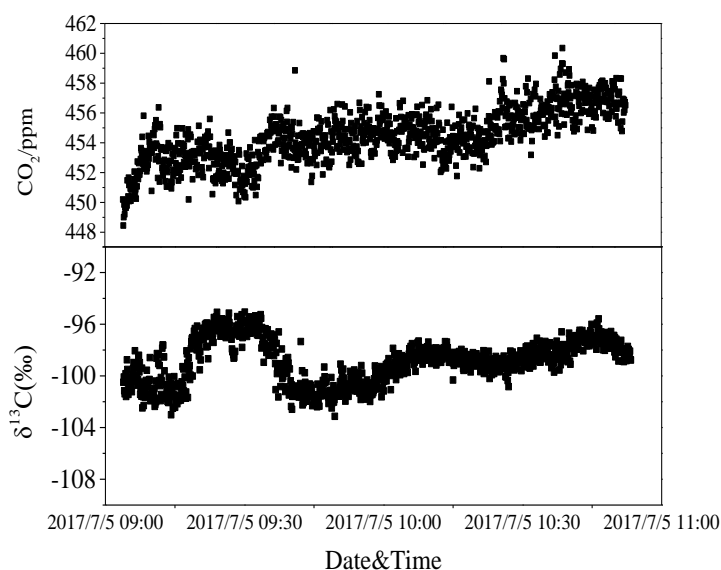


Figure 5. Time series of CO₂ in the laboratory air and the corresponding $\delta^{13}\text{C}$ values

We use this instrument to detect the isotope ratios of CO₂ in the atmosphere. The identical air in the laboratory were measured with a sample time of 1 s to obtain the reproducibility of the isotopic ratio measurements. In order to ensure the accuracy of sampling, the multi-pass cell was evacuated and purged with dry nitrogen every time before sampling and then refilled with the laboratory air. Figure 5 shows the reproducibility of the time series of CO₂ in the laboratory air profiles and the corresponding $\delta^{13}\text{C}$ values with 1 s sample time. The derived average value of CO₂ mixing ratio is 454 ppm. The corresponding $\delta^{13}\text{C}$ value is -98.75‰ with a 1 σ standard deviation of 1.8‰. The measurement precision can reach to 0.2‰ on the basis of the optimum integration time 130 s derived by the Allan variance analysis. In order to apply the CO₂ isotope ratio measurement system based on TDLAS technology to the medical and other fields, we need to further improve the long term stability of the system and perform calibration to get the correct isotope ratios.

4. Conclusions

In this paper, a high precision carbon isotopic ratio analysis of CO₂ at ambient level using TDLAS technique at 2.7 μm was demonstrated. The obtained results prove the feasibility to get real-time online carbon isotopic ratio at high time resolution of 1 s without any pretreatment of the samples. Experimental results explained that the system is able to measure $^{13}\text{C}/^{12}\text{C}$ isotopic ratios with a precision of 0.2‰ and is thus capable of in situ measurements of stable CO₂ isotope ratios under ambient conditions.

5. Acknowledgement

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