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

Xiaojuan Cui*, Zhirong Zhang, Tao Pang, Hua Xia, Pengshuai Sun, Bian Wu and Runqing Yu

Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 230031 Hefei, China.
* Email: cuixiaojuan@aifom.ac.cn

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 δ¹³C values of CO₂ in the atmosphere were performed. The achieved standard deviation (1σ) of δ¹³C was 1.8‰. The Allan analysis of the time series of the mixing ratio of CO₂ shows a measurement precision of 0.2‰ for δ¹³C 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 δ¹³C 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 \(\mu\)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.

![Experimental setup](image)

**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 °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% H$_2$O and 500 ppm CO$_2$ based on the HITRAN 2012 database with an optical path length of 107 m and the pressure of 20 mbar. $^{12}$CO$_2$, $^{13}$CO$_2$ and H$_2$O 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% H$_2$O and 500 ppm CO$_2$ 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 CO$_2$, one is at 3641.0311 cm$^{-1}$ for $^{13}$CO$_2$ measurement, another is at 3641.1338 cm$^{-1}$ for $^{12}$CO$_2$ detection. They are free of interferences of water vapor absorption lines.

3. Results and Discussion

Figure 3 displays the direct absorption signals of $^{12}$CO$_2$ and $^{13}$CO$_2$ 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 $^{12}$CO$_2$ and $^{13}$CO$_2$ absorption lines along with minimizing the influence of wing effects from the
nearby H₂O absorption lines. The parameters of the used $^{12}$CO₂ and $^{13}$CO₂ 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 $^{12}$CO₂ and $^{13}$CO in this study

| Isotopologue   | Wavenumber (cm⁻¹) | Line strength ($10^{21}$ cm⁻¹ cm²/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                      |

![Collection time/s vs CO₂/ppm](Image1)

**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.
We use this instrument to detect the isotope ratios of CO$_2$ 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 CO$_2$ in the laboratory air profiles and the corresponding $\delta^{13}$C values with 1 s sample time. The derived average value of CO$_2$ mixing ratio is 454 ppm. The corresponding $\delta^{13}$C value is -98.75‰ with a 1σ 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 CO$_2$ 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 CO$_2$ at ambient level using TDLAS technique at 2.7 um 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 $^{13}$C/$^{12}$C isotopic ratios with a precision of 0.2‰ and is thus capable of in situ measurements of stable CO$_2$ isotope ratios under ambient conditions.

5. Acknowledgement
We acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 41775128, 11204319), the External Cooperation Program of the Chinese Academy of Sciences (Grant No. GJHZ1726), and the Special Fund for Basic Research on Scientific Instruments of the Chinese Academy of Science (Grant No. YZ201315).

6. References
[1] G. V. Chilingar, O. G. Sorokhtin, L. Khilyuk, M. V. Gorfunkel, Greenhouse gases and greenhouse effect, Environ. Geol., 2009; 58:1207-1213.
[2] V.J. Hare, E. Loftus, A. Jeffrey, C. B. Ramsey, Atmospheric CO$_2$ effect on stable carbon isotope composition of terrestrial fossil archives, Nat. Commun., 2018; 9(252): 1-8.
[3] C. Yang, K. Jamison, L. Xue, Z. Dai, S.D. Hovorka, L. Fredin, R.H. Trevi, Quantitative assessment of soil CO$_2$ concentration and stable carbon isotope for leakage detection at geological carbon sequestration sites, Greenhouse Gas Sci. Technol. 2017; 7(4): 680–691, DOI: 10.1002/ghg

[4] C.T. Lai, J.R. Ehleringer, A.J. Schauer, P.P. Tans, D.Y. Hollinger, K.T. Pawu, J.W. Munger, S.C. Wofsy, Canopy-scale δ$^{13}$C of photosynthetic and respiratory CO$_2$ fluxes: observations in forest biomes across the United States, Global Change Biol., 2005; 11: 633-643.

[5] T. N. Lee, M. M. R, C.T. Williams, Ø Tøien, B. M. Barnes, D. M. O’Brien, C. L. Buck, Stable isotope analysis of CO$_2$ in breath indicates metabolic fuel shifts in torpid arctic ground squirrels, Comp. Biochem. Phys. A, 2017; (209): 10-15.

[6] D. Hofstetter, J.D. Francesco, L. Hvozdara, H.P. Herzig, M. Beck, CO$_2$ isotope sensor using a broadband infrared source, a spectrally narrow 4.4 μm quantum cascade detector, and a Fourier spectrometer, Appl. Phys. B, 2011; 103(4): 967-970. DOI: 10.1007/s00340-011-4532-1

[7] K. Tanaka, R. Kojima, K. Takahashi, K. Tonokura, Continuous measuring of stable carbon dioxide isotopes in CO$_2$ with a near-IR laser absorption spectrometer, Infrared Phys. Techn., 2013; 60: 281-287.

[8] R. Aguilera, T.E. Chapman, H. Pereira, G.C. Oliveira, R.P. Illanes, T.F. Fernandes, D. A. Azevedo, F. A. Neto, Drug testing data from the 2007 Pan American Games: δ$^{13}$C values of urinary androsterone, etiocholanolone and androstanediols determined by GC/C/IRMS, J. Steroid Biochem., 2009; 115: 107-114.

[9] Z. Muccio, G. P. Jackson, Isotope ratio mass spectrometry, Analyst, 2014; 134: 213-222.

[10] G. Gagliardi, A. Castrillo, R.Q. Iannone, E.R.T. Kerstel, L. Gianfrani, High-precision determination of the $^{13}$CO$_2$/$^{12}$CO$_2$ isotope ratio using a portable 2.008 μm diode-laser spectrometer, Appl. Phys. B, 2003; 77: 119-124.

[11] B. Tuzson, M.J. Zeeman, M.S. Zahniser, L. Emmenegger, Quantum cascade laser based spectrometer for in situ stable carbon dioxide isotope measurements. Infrared Phys. Techn., 2008; 51(3):198-206. DOI: 10.1016/j.infrared.2007.05.006