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Real-time measurements of CO2 stable carbon isotope ratio in the atmosphere using wavelength modulation spectroscopy

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1. Introduction

Measurements of the stable isotopes provide important information on the source and history of their compounds in many research areas. Since the isotope ratio changes in relation to the conditions, the real-time measurements are required. It is recognized that the standard measurement technique for the stable isotope ratio is isotope ratio mass spectroscopy (IRMS). The IRMS has high precision in the range from 0.01 to 0.1 per mill. Nevertheless, pre-treatment is needed when a gaseous sample is injected in the mass spectrometer. Therefore, it is difficult to perform the real-time measurements of the isotope ratio. Recently, the laser absorption spectroscopy has been applied to the measurements of the stable isotopes. The isotopomers are easily recognized without interference of other species, when the absorption line is selected appropriately. Using this technique, since the sample gas is just introduced into the sample gas cell without any pre-treatment, the real-time measurements are able to be performed. Several studies using a quantum cascade laser with the direct absorption technique and a DFB laser with wavelength modulation spectroscopy or cavity ring-down spectroscopy have been performed. However, the precision is insufficient. Therefore, in this paper, higher precision measurements of the CO_2 stable carbon isotopes have been performed using WMS with a 2008 nm DFB laser.

2. Experimental

A 2008-nm single-mode DFB laser diode with a typical output power of 10 mW was used as a light source. The beam was introduced into a wedged-window Herriott-type multi-pass cell. The cell had a path length of 29.91 m and a volume of 0.9 L. The transmitted laser beam was focused using an AR-coated CaF_2 lens on an InGaAs photodiode detector. The wavelength of the DFB laser was modulated sinusoidally at 11 kHz using the output of a digital lock-in amplifier. The laser was scanned at 0.77 Hz by changing the injection current, which was controlled using a function generator that supplied a triangle voltage wave. The detected line pairs were $^{12}CO_2$ at 4978.205 cm^{-1} and $^{13}CO_2$ at 4978.023 cm^{-1}. The stable isotope ratio was determined with comparing the measurements $^{13}C/^{12}C$ ratio to the international PDB-standard $^{13}C/^{12}C$. All experiments were performed at 313 K. The pressure in the cell is kept 10 kPa.

3. Results and Discussion

The second-harmonic WMS spectra of the sample CO_2 gas, 379 ppm and -30.5 per mill, are detected. The S/N (Signal to noise ratio) of $^{13}CO_2$ is approximately 66, even though the concentration of $^{13}CO_2$ is 100 times lower than that of $^{12}CO_2$. It was found that this line pair is favorable because of their clearly separated signals and comparable intensities. The continuous stable carbon isotope ratio measurements were performed using this apparatus to investigate long-term stability. The signal was measured during 10 hours with 5 minutes increment. The pressure and temperature were found to be controlled within 0.01 kPa and 0.1 K, respectively, during continuous measurements. In this long-term measurement, the precision ?was achieved to be 0.1 per mill. Then, the continuous stable carbon isotope ratio measurements in ambient air was performed. The CO_2 concentration was also measured with NDIR. The CO_2 concentration profile obtained by our constructed apparatus was good agreement with that obtained with NDIR. The stable carbon isotope ratio of CO_2 was also measured successfully using this system. It was found that its value decreased with increasing CO_2 concentration.

4. Conclusions

The stable carbon isotope ratios of CO_2 were measured using WMS with a 2008 nm DFB laser diode. The precision was achieved to be 0.1 per mill for long-term detection (10 h). The stable carbon isotope ratios of CO_2 was successfully measured using our constructed system.

Keywords: Measurements of carbon isotope ratio, Carbon dioxide, Wavelength modulation spectroscopy, Multi-pass cell, DFB laser