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Development of a near-infrared laser based spectrometer for measurements of CO2 stable oxygen isotopes

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1. Introduction

In recent years, due to human activities such as burning of fossil fuels and deforestation, the anthropogenic CO_2 in the atmosphere which causes global warming and environmental impacts is increasing. CO_2 originated in the various sources such as anthropogenic emissions, plant photosynthesis, and the ocean. Since CO_2 stable isotope ratio depends on the CO_2 sources, the continuous measurement of CO_2 stable isotope ratio in the atmosphere is a powerful method for investigating the sources of atmospheric CO_2. Recently, the laser absorption spectroscopy has been applied to the measurements of the stable isotopes. Using this technique, the isotopomers are easily recognized without interference of other species. Therefore, since the sample gas is just introduced into the sample gas cell, the real-time measurements are able to be performed. In the 2-um near infrared region, the continuous measurements of the stable carbon isotopes have been performed. However, the measurements of the stable oxygen isotopes are not performed in this wavelength region. Accordingly, we developed the new system that enables the sensitive measurements of atmospheric CO_2 stable oxygen isotope ratio in the 2-um near-infrared region.

2. Experimental

We applied wavelength modulation spectroscopy (WMS) to CO_2 stable oxygen isotope measurement. A 2.045-um distributed feed-back (DFB) diode laser was used as a light source. The laser wavelength was sinusoidally modulated at 11 kHz. After the beam was passed through a Herriott-type multi-pass cell, it was focused onto a photodiode detector. The second harmonic ($2f$) signal was demodulated by a digital lock-in amplifier, and the data was acquired to a personal computer. CO_2 stable oxygen isotope ratio was determined from the measurements of $^{12}C^{18}O^{16}O/^{12}C^{16}O^{16}O$ spectrum signal ratio. A premixed diluted gas of 424.5 ppm, $d^{18}O$ = 30.8 per mill in air was used as a sample gas.

3. Results and Discussion

The influence of a pressure, temperature, and the intensity of neighbor peaks on the stable oxygen isotope measurements were simulated. From the result of the spectrum simulation, it was found that the $^{12}C^{18}O^{16}O$ line, which is the 20012 - 00001 of the P(18) at 4890.586 cm^{-1}, and the $^{12}C^{16}O^{16}O$ line, which is the 20013 - 00001 of the R(56) at 4890.819 cm^{-1}, are suited for stable oxygen isotope measurement. The signal was averaged over 100 consecutive scans at 0.77 Hz for the continuous measurement of the stable oxygen isotopes. In 2-hours measurement, the obtained precision was 0.07 per mill. The limit of detection for CO_2 using our apparatus was 47.4 +- 16.1 ppb.

4. Conclusions

Using WMS with a 2.045-um DFB laser diode and a Herriott-type multi-pass cell, the CO_2 stable oxygen isotope ratio was measured. The precision of the 2-hours measurements and the limit of detection using our apparatus were achieved to be 0.07 per mill and 47.4 +- 16.1 ppb, respectively. It was showed that the measurements of the CO_2 stable oxygen isotopes ratio are able to be performed by using our apparatus.

Keywords: Measurements of stable oxygen isotope, Carbon dioxide, Wavelength modulation spectroscopy, Multi-pass, DFB laser