Continuous measurements of stable carbon isotopes in CO₂ with a near-IR laser absorption spectrometer

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Abstract

A near-IR laser absorption spectrometer using a technique of wavelength modulation spectroscopy is used to measure stable carbon isotope ratios of ambient CO₂ ($\delta^{13}\text{C}$) via the absorption lines ¹²CO₂ R(17) ($2\nu_1+\nu_2-\nu_2+\nu_3$) at 4978.205 cm⁻¹ and ¹³CO₂ P(16) ($\nu_1+2\nu_2+\nu_3$) at 4978.023 cm⁻¹. The isotope ratios are measured with a reproducibility of 0.02‰ (1 σ) in a 130-s integration time over a 12-hour period. The humidity effect on $\delta^{13}\text{C}$ values has been evaluated in laboratory experiments. The $\delta^{13}\text{C}$ values of CO₂ in ambient air were measured continuously over 8 days and agreed well with those from isotope ratio mass spectrometry of canister samples. The spectrometer is thus capable of real-time, *in situ* measurements of stable carbon isotope ratios of CO₂ under ambient conditions.

Keywords: CO₂ carbon isotopes, Wavelength modulation spectroscopy, Near-IR, Real-time measurement

1. Introduction

Precise measurements of the stable carbon isotopes of atmospheric carbon dioxide (CO_2) provide important information about carbon exchange processes. This is due to the differences in the isotope ratios among various sources and sinks of CO_2 , such as plant respiration, photosynthesis, anthropogenic and marine impacts [1], all of which are generated by chemical reactions and/or biogeochemical processes. The isotope ratio $^{13}\text{C}/^{12}\text{C}$ is typically expressed relative to a standard reference through the formula

$$\delta^{13}\text{C} = \left(\frac{R_{\text{sample}}^{13}}{R_{\text{reference}}^{13}} - 1 \right) \times 1000 \quad (1)$$

where R^{13} is the ratio $^{13}\text{C}/^{12}\text{C}$. The $\delta^{13}\text{C}$ value is usually reported in per mil (‰) relative to the international PDB-standard reference (Belemnite of the Pee Dee Formation in South Carolina, $[^{13}\text{C}] / [^{12}\text{C}] = 0.011237$) [2]. Isotope ratio mass spectrometry (IRMS) is the standard analytical method for the determination of isotope ratios [3], with a measurement precision from 0.01 to 0.1‰. In most cases, however, collected field samples must be analyzed in the laboratory. IRMS has other experimental drawbacks such as in the great care needed for sample preparation involving chemical processing or purification [4]. Thus high precision, *in situ* measurements of isotope ratios in the field would be advantageous.

Infrared absorption spectroscopy has been used to measure stable isotopes ratios for molecules having following three features: 1) The ro-vibronic absorption lines are well resolved to prevent spectral interference by own and other species absorption lines. 2) The absorption lines lie within a common scan window. 3) The intensities of the absorption lines of stable isotopes are almost identical and the linearity of the intensity is kept to avoid saturation and nonlinear effects by the detectors [5]; in these ways,

specific isotopes can be quantified. Mid-infrared and near-infrared spectroscopic techniques such as Fourier transform infrared (FT-IR) spectroscopy [6, 7] with a White-type multi-pass cell, and absorption spectroscopy with lead-salt tunable diode lasers (TDL) and an astigmatic Herriott-type multi-pass cell [8] have been applied to isotope ratio analysis. The FTIR measurements reached a maximum precision for $\delta^{13}\text{C}$ of 0.15‰ due to the optimization of FTIR spectra analysis [7]. However, since both FT-IR and mid-infrared TDL require cryogenic cooling, they are not suitable for long-term *in situ* measurements. A direct absorption technique with a light source at 4.3 μm , based on difference-frequency generation (DFG), was shown to achieve 0.8‰ precision for $\delta^{13}\text{C}$ at an ambient level of CO_2 [5]. An improvement of the mid-IR laser source will enable high precision measurement of stable carbon isotopes of CO_2 [5]. The quantum cascade laser (QCL), which requires thermoelectric cooling and has high spectral purity, has been used for detection of ambient CO_2 stable isotopes in the 4.3 μm region [9–15] with less than 0.1‰ precision [12]. In this wavelength region, measurements of stable oxygen isotopes were reported as well [12–15]. Thus QCL systems have been used for field measurements of both carbon and oxygen isotope ratios [13–15].

In the near-infrared region, relatively low-cost, compact-sized distributed feedback (DFB) lasers are available. Since they have a narrow bandwidth and a relatively high power output, they are well suited for a compact isotope analyzer. However, since absorption cross-sections of CO_2 at 1.6 μm are a factor of 10^4 smaller than those in the 4.3 μm region, highly sensitive spectroscopic techniques are required, such as wavelength modulation spectroscopy (WMS) and cavity ring-down spectroscopy (CRDS) [16–19]. In the 1.6 μm region, stable carbon isotopes of CO_2 were probed with

CRDS [16]. In the 2 μm region, where the CO_2 absorption cross-sections are 100 times larger than those in the 1.6 μm region, stable carbon isotopes were measured with WMS [17–19] and off-axis cavity-enhanced absorption spectroscopy [20]. In the 2 μm region, the best precision among the literature was 0.3‰ at 2% of CO_2 [17].

Although continuous field measurements of $\delta^{13}\text{C}$ in ambient CO_2 are becoming possible with the laser spectroscopic techniques mentioned above [12, 13, 14, 15], the effect of humidity on the data has not been evaluated in detail. Since ambient humidity varies significantly, there is a possibility that spectral overlap by H_2O lines and/or spectral broadening of CO_2 by H_2O can have an influence on the $\delta^{13}\text{C}$ results. Data on air, N_2 , and O_2 broadening parameters of CO_2 are available in the 1.42–2.32 μm region [21, 22]. H_2O broadening coefficients of some CO_2 absorption lines have been reported at 4.3 μm [23] and at 1.57 μm [24]. However, to our knowledge, there are no reported data for the 2 μm region.

Recently, our group has developed a near-IR laser absorption spectrometer that uses a 2.008 μm DFB laser [25]. The spectrometer made it possible to measure isotope ratios ($\delta^{13}\text{C}$) for 346.6 ppm CO_2 with a reproducibility of 0.24‰ (1σ) over a 130-s integration time for 10-hour period [25]. For the present work, we had two major objectives. First, we evaluated the humidity effect on $\delta^{13}\text{C}$ determination. Since there is no spectral overlap between H_2O lines and the CO_2 absorption line pair selected for the $\delta^{13}\text{C}$ determination [25], it was necessary to evaluate the effect of spectral broadening of the CO_2 lines by H_2O . This is especially important because $\delta^{13}\text{C}$ is determined by the WMS signal intensity, which is the difference between the peak intensity and the baseline [25]; thus pressure broadening of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ spectra by H_2O affects the $\delta^{13}\text{C}$ determination. The H_2O broadening coefficients of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ absorption line

pairs in the 2 μm region were obtained independently by direct absorption spectroscopy of pure $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ samples. The second objective was to provide continuous measurements of outside air at The University of Tokyo in central Tokyo. In order to assess the performance of our instruments, CO_2 mixing ratios in outside air were compared with those measured using a non-dispersed infrared spectrometer (NDIR). In addition, $\delta^{13}\text{C}$ values were compared with those from canister samplings analyzed by IRMS.

2. Experiments

2-1. Near-IR laser absorption spectrometer and H_2O broadening coefficient measurements

Our instrument is based on WMS using a 2.008 μm DFB laser and a Herriot-type multi-pass cell, as described previously [25]. The absorption line pair for the measurements of the stable carbon isotope ratio was $^{12}\text{CO}_2$ R(17) ($2\nu_1+\nu_2-\nu_2+\nu_3$, $4.47 \times 10^{-23} \text{ cm}^2\text{molecule}^{-1}\text{cm}^{-1}$) at 4978.205 cm^{-1} and $^{13}\text{CO}_2$ P(16) ($\nu_1+2\nu_2+\nu_3$, $7.07 \times 10^{-24} \text{ cm}^2\text{molecule}^{-1}\text{cm}^{-1}$) at 4978.023 cm^{-1} [25]. The injection current and the laser-chip temperature of the 10 mW, 2.008- μm single-mode DFB laser diode (NTT Electronics, Yokohama, Japan) were maintained with a diode laser control unit (ILX LDC3724C ILX Lightwave, Bozeman, MT, USA). The beam was collimated with an anti-reflection (AR) coated lens (Schäfter+Kirchhoff 60FC-4-A11-09, Hamburg, Germany) and introduced into a wedged-window, Herriott-type multi-pass cell. The laser beam was focused in the center of the cell with a 500 mm AR-coated CaF_2 lens. The optical path length in the cell was 29.91 m and the cell volume was 0.9 L. The transmitted laser beam was detected by an InGaAs photodiode (THORLABS PDA10DT, Newton, NJ,

USA).

The laser was scanned at 0.77 Hz, which was controlled by a triangle voltage wave supplied by a function generator (Agilent 33220A, Santa Clara, CA, USA). The modulation frequency was set to 11 kHz using the reference output of a digital lock-in amplifier (Stanford Research Systems SR810, Sunnyvale, CA, USA). The signal from the photodetector was processed by the lock-in with a time constant of 3-ms and 24-dB/oct digital filtering, corresponding to an equivalent noise bandwidth of 26 Hz. The modulation conditions were adjusted to obtain the highest signal-to-noise ratio (S/N) for the second harmonic of the WMS signals of $^{12}\text{CO}_2$. The data was acquired in a laptop PC through a 16-bit AD PCMCA card (CONTEC ADA16-8/2(CB)L, Osaka, Japan).

The multi-pass cell was evacuated either with a rotary pump through a liquid-nitrogen trap or with a dry pump. The pressure was monitored using a capacitance manometer (MKS Baratron 722B, Andover, MA, USA) and controlled to within 0.01 kPa by mass flow controllers (Kofloc 3660, Kyoto, Japan) positioned before and after the cell. The temperature was controlled to within ± 0.01 K. All experiments except for the measurements of H_2O broadening coefficients were performed at 313 K. The DFB laser, the optics and the cell were placed in an N_2 -purged box.

The standard gas used was (i) synthetic air (CO_2 366 ppm, $\delta^{13}\text{C}=-34.5\text{‰}$), (ii) compressed air (CO_2 393 ppm, $\delta^{13}\text{C}=-10.5\text{‰}$), (iii) compressed air (CO_2 424 ppm, $\delta^{13}\text{C}=-11.6\text{‰}$), (iv) compressed air (432 ppm CO_2 , $\delta^{13}\text{C}=-12.9\text{‰}$). The synthetic air cylinder was purchased from Taiyo Nippon Sanso Corp, Tokyo, Japan. The compressed air cylinders were purchased from Suzuki Shokan Corp, Tokyo, Japan.

The selected line pair meets the requirements for the quantitative measurements of

stable carbon isotopes of CO₂ shown in the introduction section. The signal intensities as a function of mixing ratio at ambient levels of CO₂ are shown in Fig. 1, suggesting that the linearity of the signal intensity is kept.

To assess signal stability, compressed air (393 ppm CO₂) was introduced into the WMS system with a flow rate of approximately 115 sccm (standard cc per minute). The pressure and the temperature were maintained at 10 kPa and 313 K, respectively. The instrument performance was tested using the Allan variance method [26]. The signal intensity ratio of $I(^{13}\text{CO}_2)/I(^{12}\text{CO}_2)$ was measured with 0.77 Hz resolution over 5 hours. Results are shown in Fig. 2, where the $I(^{13}\text{CO}_2)/I(^{12}\text{CO}_2)$ time series and the associated Allan variance (σ_A^2) are plotted. From the Allan variance plot, an optimum integration time of 100–200 s with $\sigma_A^2 = 1.4 \times 10^{-6}$ can be derived. However, the Allan variance plot starts to increase at 400 s, indicating that instrumental drift starts to dominate over white noise. Therefore, to assess the long-term stability of the instrument, measurements of $I(^{13}\text{CO}_2)/I(^{12}\text{CO}_2)$ using the same gas sample were continued over 12 hours. The reproducibility of the $\delta^{13}\text{C}$ is shown in Fig. 3, in which each point represents the mean value of 100 co-added signals with 0.77 Hz resolution. This result indicates that our instrument allows us to measure isotope ratios of ambient levels of CO₂ ($\delta^{13}\text{C}$) with a reproducibility of 0.02‰ (1 σ) without calibration for 12 hours. Thus the near-IR laser absorption spectrometer is able to provide convenient and reproducible ambient measurements.

For the H₂O broadening coefficient measurements, direct absorption spectra of ¹²CO₂ and ¹³CO₂ were measured. The total pressure in the cell was varied over the range 0.3–1.6 kPa. The CO₂ and N₂ pressures were kept at 0.08 and 0.2 kPa, respectively, and only the partial pressure of water vapor was changed over the range 0.02–1.32 kPa.

Pressure was measured using a capacitance manometer. A humidity and temperature transmitter (VAISALA, HMT334) was used to measure the partial pressure of H₂O in the cell. The partial pressure of H₂O was derived from the relative humidity at the measurement temperature. The values of partial pressures of H₂O obtained from the capacitance manometer were in agreement with those obtained from the humidity and temperature transmitter within $\pm 1\%$. The temperature was varied over the range 296–333 K. ¹²CO₂ (Cambridge Isotope Laboratory Inc., >99.9%), ¹³CO₂ (Cambridge Isotope Laboratory Inc., >99.9%) and N₂ (Taiyo Nippon Sanso Corp, >99.999%) were used in the measurements of the H₂O broadening coefficients.

2-2. Ambient air measurements

Measurements of outside air were conducted on the Hongo campus of The University of Tokyo (35.71°N, 139.76°E, central Tokyo) over February 3–10, 2012. The measurement site was located in the north of Tokyo, which is situated on the largest plain in Japan, the Kantō Plain. Several major industrial areas are situated close to the observation site, including Keihin about 20 km south, and Keiyo about 15–30 km east-southeast. Both areas are located on the coast of Tokyo Bay. They mainly include steel, machine, chemical, petrochemical and printing industries. The weather during the measurements was characterized by high pressure to the west and low pressure to the east, which provided cold and dry northerly winds associated with winter monsoon surges over Japan, except for February 6 and 7 where precipitation was observed at the measurement site. The temperature ranged from -1.0 to +10.8 °C, and the range of relative humidity was 15–52%. All dates and times are Japan Standard Time (JST; UTC + 09:00).

As depicted schematically in Fig. 4, ambient air was pulled from a height of 3.5 m above the ground and 20 m from the nearest road (Kototoi-Dori). The 12-hour traffic volume of Kototoi-Dori is about 10100 in the daytime and about 4400 at night [27]. Air was introduced through an aluminum-coated polymer tube (4 mm i.d.) at a constant flow rate of 6 L·min⁻¹ controlled by a diaphragm pump (ULVAC KIKO Inc, DAP-6D). The distance from the air sampling point to the inlet of the measurement instrument in the lab room was 40 m. Beforehand, we evaluated the effect of the aluminum-coated polymer tube and the diaphragm pump on the $\delta^{13}\text{C}$ determination. Compressed air was introduced into the WMS system with or without the 40-m long aluminum-coated polymer tube and the diaphragm pump. We confirmed that, under our experimental conditions, the aluminum-coated polymer tube and the diaphragm pump did not alter the $\delta^{13}\text{C}$ values significantly within the measurement uncertainty of the WMS system. A polytetrafluoroethylene membrane filter (Advantec MFS Inc., PF-020) was installed at the sample inlet. In order to reduce the humidity and to mitigate particulates, the air was also passed through a high efficiency particulate air (HEPA) filter (TSI, 99.97% > 0.3 μm) and a Nafion dryer (PERMA PURE, PD-100T-72E-M) before entering separate lines for the WMS instrument and the NDIR analyzer (LI-COR Ltd., LI-840). Such filters and dryer were used in the previous studies of the $\delta^{13}\text{C}$ measurements in ambient CO_2 [13 – 15]. Nevertheless, to check if the filters and dryer affect significantly on the $\delta^{13}\text{C}$ determinations, we performed the experiments in which compressed air was flowed into the WMS system with or without the filters and dryer. We confirmed that neither the filters nor dryer altered the $\delta^{13}\text{C}$ value within the measurement uncertainty of our WMS instrument under our experimental conditions. The CO_2 mixing ratios were measured with the NDIR analyzer and the WMS system, which were connected in

parallel. For the outside air measurement, the pressure in the cell of WMS instruments was kept at 10 kPa.

The calibration was done by diluting CO₂ standard sample. The signal intensities of ¹²CO₂ and ¹³CO₂ were kept linear against CO₂ concentration as shown in Fig. 1, indicating a weak linear dependence of the measured isotopic ratios on the CO₂ concentration, with a slope of +1‰/+20ppmv CO₂ at ambient levels. Such concentration dependence in the δ¹³C determination by the laser absorption spectroscopy was reported by Tuzson et al. [12] and Wada et al. [15]. During the measurements of ambient air, the sampling line was periodically switched between the air samples and the calibration gas. A 6-hour cycle was used during which the calibration gases were measured for 20 minutes, and the outside air was measured for 5 hours and 40 minutes. During calibration, synthetic air (366ppm CO₂) was measured for 10 minutes and compressed air (424ppm CO₂) was measured for 10 minutes. CO₂ was introduced into the NDIR at the flow rate of 1 standard L-min⁻¹ and into the WMS system at the flow rate of 680 standard cc-min⁻¹.

3. Results and Discussion

3-1. Measurements of the H₂O broadening coefficient of CO₂

To investigate the humidity effect on δ¹³C determination accurately, the H₂O broadening coefficients of CO₂ were measured. A direct absorption spectrum of ¹²CO₂ at a total pressure of 0.88 kPa (¹²CO₂; 0.08 kPa, N₂; 0.2 kPa, H₂O; 0.6 kPa) is shown in Fig. 5. In order to avoid H₂O condensation, the sample lines were kept at 333 K. Direct absorption spectra of ¹²CO₂ and ¹³CO₂ were obtained without WMS owing to the relatively high sample mixing ratios. Voigt profiles were fitted to the experimental

spectra (Fig. 5) using a nonlinear least-squares fit. The Gaussian half-widths of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ were fixed to the Doppler half-widths at each temperature, which were calculated using the following expression:

$$\gamma_D = 3.581 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}} \quad (2)$$

where γ_D is the Doppler half-widths, ν_0 is the position of the center of the line in cm^{-1} , T is the gas temperature in degree Kelvin and M is the molecular weight of the gas in atomic mass units [28]. As shown at the top of Fig. 5, the residuals between the experimental and fitting profiles show no systematic deviation. The half-width at half-maximum (HWHM) of the Lorentzian component of the $^{12}\text{CO}_2$ R(17) $2\nu_1 + \nu_2 - \nu_2 + \nu_3$ absorption line as a function of H_2O pressure is plotted in Fig. 6. The error bars are standard deviations (2σ) derived from the experimental variables, such as partial pressures or signal noise. The slope of the linear fit is the 0.126 ± 0.003 $\text{cm}^{-1}\text{atm}^{-1}$ H_2O broadening coefficient of $^{12}\text{CO}_2$, $\gamma_{\text{H}_2\text{O}}^{^{12}\text{CO}_2}$ at 313K. The same procedure is used to determine the 0.127 ± 0.009 $\text{cm}^{-1}\text{atm}^{-1}$ coefficient for $^{13}\text{CO}_2$. When the temperature dependence n is known for a selected line, the broadening coefficient at temperature T can be found from known values at T_0 :

$$\gamma(T) = \gamma(T_0) \times (T_0 / T)^n \quad (3).$$

To obtain n , the H_2O broadening coefficients of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ were measured at 296 K, 303 K, and 333 K using the same procedures as those at 313 K. The results are summarized in Table 1. The coefficients at 296 K are consistent with those obtained at the same rotational quantum number at $\nu_2 + \nu_3 - \nu_2$ of $^{12}\text{CO}_2$ and ν_3 of $^{13}\text{CO}_2$, respectively, in the $4.3 \mu\text{m}$ region [23]. The n of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ analyzed by least-squares fitting of Eq. (3) are 0.711 ± 0.044 and 0.754 ± 0.080 , respectively.

To evaluate the effect of humidity on the determination of $\delta^{13}\text{C}$, spectra were calculated using the parameters obtained for the various humidity conditions. The absorption peak shape was assumed to be a Voigt function and the total pressure and the cell temperature was given as 10 kPa and 313 K, respectively. The abundances of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ were assumed to be 0.984 and 0.011, which were given in HITRAN database [29]. In general, collisional broadening coefficients of $^{12}\text{CO}_2$ in air including water vapor, $\gamma_e^{12\text{CO}_2}$ is expressed as a function of partial pressures of air and water vapor as follows;

$$\gamma_e^{12\text{CO}_2} = P_{\text{air}}\gamma_{\text{air}}^{12\text{CO}_2} + P_{\text{H}_2\text{O}}\gamma_{\text{H}_2\text{O}}^{12\text{CO}_2} \quad (4)$$

where, $\gamma_{\text{air}}^{12\text{CO}_2}$ are air broadening coefficients for $^{12}\text{CO}_2$. P_{air} and $P_{\text{H}_2\text{O}}$ are the partial pressures of air and water vapor, respectively. The collisional broadening coefficients for of $^{13}\text{CO}_2$ in air including water vapor, $\gamma_e^{13\text{CO}_2}$ are expressed in the same way as Eq. 4. Absorption spectra including collisional broadening were simulated with changing water vapor mixing ratio. The peak intensity ratios ($I(^{13}\text{CO}_2) / I(^{12}\text{CO}_2)$) of simulated spectra were compared with those without water vapor whose differences were shown in per mill (‰).

Figure 7 shows the effect of humidity on $\delta^{13}\text{C}$ determination in the water vapor mixing ratio range of 0–7.3% at 313 K that corresponds to a relative humidity change from 0 to 100% at atmospheric pressure. This result suggests that the difference in the $\delta^{13}\text{C}$ values was +0.24‰ at the 0% and 7.3% water vapor mixing ratios.

3-2 Ambient air measurements

Outside air measurements were conducted over February 3–10, 2012. On February

9, samples were collected in 6-L canisters for IRMS analysis (Thermo Fischer Scientific, DELTA plus XL). The schedule of canister sampling is listed in Table 2. WMS signals were calibrated every 6 hours using the standard CO₂ sample as discussed in Section 2-2. The calibration was performed every 12 hours during the nighttime over February 3–7, which differed less than 0.8% from the 6-hour calibrations. The WMS instrument thus kept constant measurement conditions over 12-hour periods.

The WMS time series of CO₂ mixing ratios in outside air, the $\delta^{13}\text{C}$ values determined by online WMS, and the IRMS canister analyses are shown in Fig. 8. The $\delta^{13}\text{C}$ values determined by IRMS and WMS are listed in Table 2. Three-minute averages of the $\delta^{13}\text{C}$ values obtained by WMS are listed because it took 3 minutes to collect outside air into the canisters. The mixing ratio of water vapor in the Herriott cell was kept at 0.2%, resulting in less than 0.01‰ effect on the $\delta^{13}\text{C}$ determination, as estimated in Fig. 7. In this measurement, the difference in the $\delta^{13}\text{C}$ values induced from the water vapor was corrected. The results indicate that differences between the WMS and IRMS measurements were within 0.11‰, suggesting that the WMS instrument is capable of accurately determining $\delta^{13}\text{C}$ in ambient CO₂ *in situ* and in real-time. CO₂ mixing ratios determined by NDIR were in good agreement with those obtained by WMS. A linear regression yielded $R^2=0.98$, with a slope of 0.9 ± 0.01 .

During the observations, the CO₂ mixing ratio ranged over 420–600 ppm and $\delta^{13}\text{C}$ ranged from -18‰ to -9‰. On February 8 and in the afternoon on February 4, the surface wind was characterized as light and gentle, with northerly breeze. Such a condition may have caused an efficient vertical mixing between the atmospheric boundary layer and the free troposphere; therefore the CO₂ mixing ratios were relatively low and the $\delta^{13}\text{C}$ values were close to those in a free troposphere. February 3, 9 and 10

had calm or light air conditions, resulting in high CO₂ mixing ratios and relatively low $\delta^{13}\text{C}$ values. Those results might be owing to CO₂ accumulation emitted anthropogenically within the surface layer. In Fig. 9, a Keeling plot [30] is shown for an event where drastic changes in the CO₂ mixing ratio and $\delta^{13}\text{C}$ were observed during the nighttime on February 3 (20:00 LT to 23:30 LT). According to the simple Keeling two-end-member mixing model [30], a plot of $\delta^{13}\text{C}$ as a function of the reciprocal of the CO₂ mixing ratio is linear, with the intercept representing the isotopic composition of the CO₂ emitted by a source:

$$\delta^{13}\text{C}_s = \delta^{13}\text{C}_t - \left\{ [\text{CO}_2]_b (\delta^{13}\text{C}_b - \delta^{13}\text{C}_s) \times \frac{1}{[\text{CO}_2]_t} \right\} \quad (5)$$

In Eq. 5, $[\text{CO}_2]_t$ is the total CO₂ mixing ratio (measured) and $[\text{CO}_2]_b$ is the background CO₂ mixing ratio. $\delta^{13}\text{C}_t$, $\delta^{13}\text{C}_b$, and $\delta^{13}\text{C}_s$ are the isotope ratios of the total CO₂, the background CO₂, and the CO₂ emitted from local sources, respectively. The intercept in Fig. 9 is -40.1‰, which is closer to the value of $\delta^{13}\text{C}$ in CO₂ from natural gas combustion (-41 ‰) [31, 32] than it is for $\delta^{13}\text{C}$ in plant and soil respiration (-25.7 ‰ as a mean for both processes) or for $\delta^{13}\text{C}$ in gasoline combustion (-27 ‰) [32]. Thus, it is likely that air mass containing a significant amount of CO₂ from natural gas combustion passed over the site during the nighttime on February 3.

4. Conclusions

We performed *in situ* measurements of CO₂ mixing ratios and $\delta^{13}\text{C}$ in ambient air with a near-IR laser absorption spectrometer using WMS. In order to measure $\delta^{13}\text{C}$ values accurately, the H₂O broadening parameters of lines selected for $\delta^{13}\text{C}$ determinations were obtained. Although the maximum humidity effect on $\delta^{13}\text{C}$ was

+0.24‰, humidity did not significantly affect outside air $\delta^{13}\text{C}$ measurements owing to pre-drying. The variation of $\delta^{13}\text{C}$ in ambient CO_2 was the same for both the WMS measurements and the IRMS analysis. Thus the instrument is capable of obtaining accurate values of CO_2 mixing ratios and $\delta^{13}\text{C}$ in ambient air *in situ* and in continuous real time.

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Table 1: H₂O broadening coefficients for ¹²CO₂ and ¹³CO₂ at 296, 303, 313 and 333 K, with 2σ uncertainties.

T (K)	$\gamma_{\text{H}_2\text{O}}^{^{12}\text{CO}_2}$ (cm ⁻¹ atm ⁻¹)	$\gamma_{\text{H}_2\text{O}}^{^{13}\text{CO}_2}$ (cm ⁻¹ atm ⁻¹)
296	0.132 ± 0.004	0.132 ± 0.007
303	0.131 ± 0.001	0.129 ± 0.001
313	0.126 ± 0.003	0.127 ± 0.009
333	0.122 ± 0.005	0.121 ± 0.008

Table 2 Comparison of $\delta^{13}\text{C}$ obtained from WMS and IRMS. The IRMS $\delta^{13}\text{C}$ values were determined from canister samplings. The WMS $\delta^{13}\text{C}$ are three-minute averages to match the duration for canister sampling. The CO_2 mixing ratio measured with WMS is also presented at right.

Sample time ^a	$\delta^{13}\text{C}_{\text{WMS}} (\text{‰})$	$\delta^{13}\text{C}_{\text{IRMS}} (\text{‰})$	$[\text{CO}_2] (\text{ppm})$
6:30	-10.31	-10.3	426.9
7:00	-11.31	-11.4	448.2
9:45	-10.34	-10.3	428.8
12:45	-9.82	-9.9	415.2
17:20	-10.27	-10.3	427.0
17:55	-10.61	-10.5	427.3
23:00	-11.39	-11.3	445.0

^a Local time on February 9.

Figure captions

Fig. 1 The signal intensities of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ as a function of mixing ratios at ambient levels of CO_2 .

Fig. 2 *Top*: Time profiles of the signal intensity ratio $I(^{13}\text{CO}_2)/I(^{12}\text{CO}_2)$. *Bottom*: Allan variance plot. The broken line shows the white noise. Compressed air containing 393 ppm of CO_2 ($\delta^{13}\text{C}=-10.5\text{‰}$) was used.

Fig. 3 12-hour continuous measurements of $\delta^{13}\text{C}$ for a 393 ppm CO_2 sample gas ($\delta^{13}\text{C}$ of -10.5‰). Signals were measured every 130 seconds, and each point represents 100 averaged signals with 0.77 Hz resolution. The 1σ standard deviation of each point over the 12-hour period was 0.02‰.

Fig. 4 Schematic of the ambient air measurement system.

Fig. 5 Absorption spectrum of $^{12}\text{CO}_2$ R(17) ($2\nu_1+\nu_2-\nu_2+\nu_3$) at a total pressure of 0.88 kPa and a H_2O partial pressure of 0.6 kPa at 313 K. The gray line is the experimental spectrum and the black line is the fitted Voigt profile. The dots in the upper graph are the residuals between the experimental and fitted profiles.

Fig. 6 HWHM of the $^{12}\text{CO}_2$ R(17) $2\nu_1+\nu_2-\nu_2+\nu_3$ absorption line as a function of H_2O pressure. The error bars are two standard deviations derived from experimental errors such as in partial pressure measurements and noise. The line is the least-squares fit whose slope is the H_2O broadening coefficient.

Fig. 7 Humidity effect on $\delta^{13}\text{C}$ determination. The horizontal axis is the mixing ratio of water vapor in ambient air and the vertical axis is the difference of the $\delta^{13}\text{C}$ value between the conditions where the H_2O pressure broadening effect is included in the estimation and where it is not.

Fig. 8 Time series of (a) $\delta^{13}\text{C}$ determined by WMS spectroscopy and (b) CO_2 mixing ratio as analyzed by WMS. The symbols in panel (a) indicate the $\delta^{13}\text{C}$ values determined by IRMS analysis of canister sampling. Portion of the data (February 3, 2012 (20:00 LT to 23:30 LT)) shown by asterisk mark is used in the Keeling plot (Fig. 9).

Fig. 9 Keeling plot shown for an event where drastic changes in the CO_2 mixing ratio and $\delta^{13}\text{C}$ were observed during the nighttime on February 3, 2012 (20:00 LT to 23:30 LT). The intercept and slope of the least-squares linear regression are given.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9