High-precision CO_2 isotopologue spectrometer with a difference-frequency-generation laser source

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A precision laser spectrometer for the detection of CO_2 isotopes is reported. The spectrometer measures the fundamental absorption signatures of ^{13}C and ^{12}C isotopes in CO_2 at 4.32 μm using a tunable mid-IR laser source based on difference-frequency generation. The spectrometer attains a precision of up to 0.02% for 150 s of averaging. An overall accuracy of 0.05% was obtained when sampling various calibrated reference gases. © 2009 Optical Society of America

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The U.S. Carbon Cycle Science Plan aims to understand the distribution, contribution, and evolution of regional and local CO_2 source and sink processes. One goal that has not been attained relates to *in situ* measurements of the stable isotope (^{12}C, ^{13}C) content of CO_2. To accurately characterize and distinguish contributions from C4 carbon fixation in plants, oceanic, and industrial sources, a measurement precision of the order 0.1‰ or better is needed [1]. Other applications that may utilize high-precision isotopic detection include volcanic activity monitoring and breath analysis. A number of mid-IR laser-based isotopic ratio measurement techniques employing lead-salt [2], quantum cascade [3], and laser sources based upon difference-frequency generation (DFG) [4] have been reported. The high spectral resolution of tunable mid-IR laser spectroscopy is particularly attractive in field applications and complements laboratory-bound isotope ratio mass spectrometers (IRMS) [5]. Recently reported measurements of $\delta^{13}C$ in CO_2 using a lead-salt diode, and quantum cascade laser sources yielded precisions (sampling time) of 0.2‰ (20 s) [6] and 0.03‰ (400 s) [3], respectively. To attain optimal precision, a selection of ^{12}C and ^{13}C absorption lines of equal absorbance that can be accessed by a single laser source are desirable. Using different path lengths for ^{12}C and ^{13}C, one can select absorption lines with similar Boltzman factors and thus minimize temperature effects on the precision [7]. For absorption lines measured with equal path lengths, a temperature dependence of 19‰/K (value for the absorption lines chosen here) may be removed by good thermal engineering, accurate temperature measurements, and data analysis [3]. The spectrometer reported here (Fig. 1), consists of a fiber optically pumped DFG source employing a 40-mm-long $\times$ 1-mm-thick periodically poled lithium niobate crystal [8]. A DFB fiber and diode laser are employed as pump and signal sources, respectively. The pump laser output ~10 mW is amplified up to 1.5 W with a Yb fiber amplifier. Both beams are combined with a wavelength division multiplexer and focused into the crystal using a two-lens imaging design [8]. The plane-parallel polarized DFG beam is then directed onto a 10-mm-thick CaF_2 window at Brewster's angle [9].

The first half of the surface is dielectrically coated to provide 50% reflection, while the second back surface is dielectrically coated to reflect 100% and reflecting the idler beam back to the (uncoated part) of the first surface at Brewster's angle. This arrangement provides accurate splitting of the DFG beam into two parallel beams separated by 15 mm while avoiding etalon effects. The two parallel beams are directed through a thermally insulated dual two-pass absorption cell (diameter = 11 mm, volume = 0.04 liter), providing an effective round-trip path length of 80 cm for each cell. Gas lines leading to the absorption cell are in close contact and thermally insulated to provide equilibrium between the two cells to better than 1 mK. Absorption signals from both cells are continuously acquired by two thermoelectrically cooled photovoltaic HgCdTe detectors. A maximum idler power of 9 μW was obtained with a measured conversion efficiency of 70 μW W^{-1} cm^{-1}, which is about half of the theoretically possible value

Fig. 1. Optical setup.

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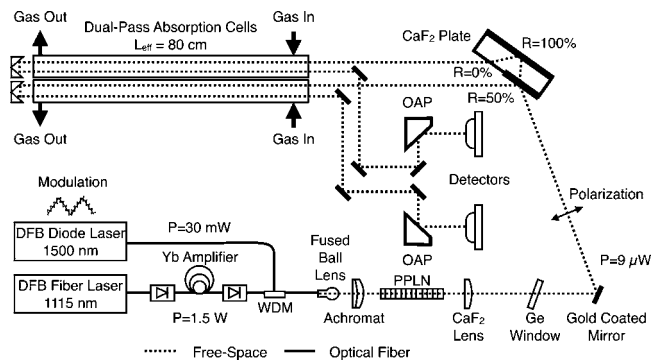
and consistent with published efficiencies. The system was operated at a slightly reduced power owing to fiber amplifier intensity noise at higher diode-laser pump powers, providing 4 μW of power for each channel. Even at lower pump powers common mode intensity noise was present but was captured and removed by continuously monitoring the reference and signal channels with two detectors. Each channel could be flushed with ambient or two different reference gases from a calibrated cylinder attached to the instrument, as shown in Fig. 2. The entire inlet and absorption cells were designed to minimize possible fractionation effects and included electro-formed nickel tubing, stainless mass-flow meters and controllers, and electropolished stainless absorption cells. The pressure in both channels is balanced to within 0.01 Torr using a differential pressure control servo valve and held at a sampling pressure of 50 Torr. A matched gas flow of 10 SCCM (SCCM denotes cubic centimeters per minute at standard temperature and pressure) per channel was used for measurements. The optical enclosure was temperature controlled to within 0.05 K using a 193 W thermoelectric air conditioner. The optical compartment containing free space optics was flushed with CO_2 free nitrogen to avoid residual absorption in the free space between the DFG source and the absorption cells. The signal laser was scanned and modulated with triangular waveforms at 9 Hz and 22.5 kHz, respectively, and the absorption signals were acquired using a 24 bit acquisition card with a sampling rate of 204.8 k samples per second. LabVIEW software based lock-in detection was used to detect and demodulate the absorption signals at their second-harmonic frequency. Isotopic ratios were determined by measuring the wavelength-modulated absorption of $^{13}CO_2$ (2299.7955 cm^{-1}) and $^{12}CO_2$ (2299.6426 cm^{-1}). Following the approach published by Erdelyi *et al.* [4], the absorbance for both isotopes was plotted for the sample and reference gas and fitted to a linear fit function. The ratio of the slopes determined the δ value as follows:

$$^{13}\delta = \left\{ \frac{^{13}\text{Slope}}{^{12}\text{Slope}} - 1 \right\} \times 1000. \qquad (1)$$

An Allan variance shown in Fig. 3 was derived from a 45 min time series in which the same calibrated reference gas was sampled in each channel. Allan variance performances such as shown in Fig. 3 were repeatable, providing a precision of 0.02‰ for averaging times of 150 or more seconds. A precision of 0.15‰–0.25‰ was obtained for 1 s averages. These performances are among the highest reported and compare well with performances recently reported by Nelson *et al.* [3]. This high performance is attributed to the high DFG source performance and beam quality, optical design, and carefully designed sampling inlet.

Small differences in the optical background between the two optical paths resulted in an offset (~1‰–5‰) in the measured $^{13}\delta$. These differences can slowly drift over time and cannot automatically be distinguished from changes in the $^{13}\delta_{\text{sample}}$ value. To capture this optical noise and to ensure continuous calibration to a known standard, the reference and sample gas flows are switched over to the opposite channel periodically. The δ value of the sample gas is then computed by dividing the difference of the maximum and minimum value of the gas modulated signal by two. By knowing the sign and value of the $^{13}\delta_{\text{reference}}$, the offset can be removed to determine the $^{13}\delta_{\text{sample}}$ value. The optimal frequency and duty cycle for a field measurement depends on the cell flow rate (in our case 10 SCCM), overhead for flush time (20 s), and should be limited by the instrument stability time as determined by an Allan variance. Consumption of calibrated reference gases are modest owing to the very small sampling volumes afforded by the high beam quality and *f*-number of the DFG laser source and is significantly smaller than long-path-length multipass absorption cells.
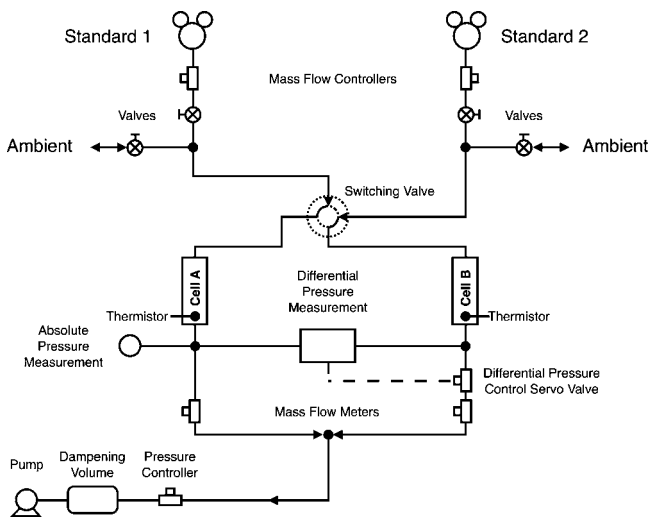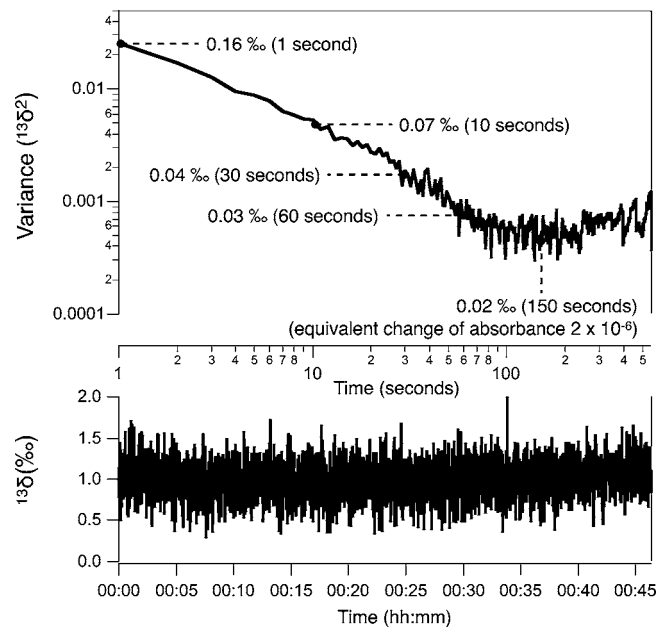

Fig. 2.   Gas sample inlet.

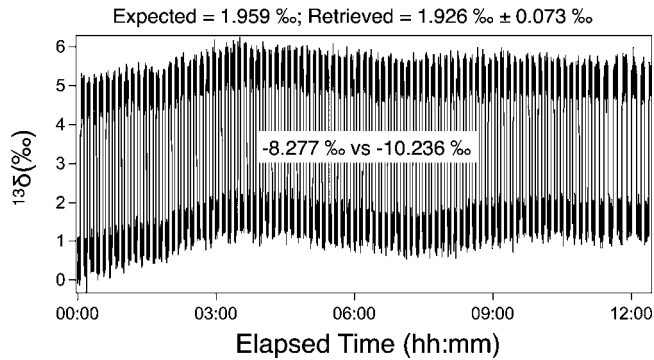Fig. 3.   Allan variance plot and corresponding time series.

Fig. 4.   12 h continuous sampling of two calibrated samples. The sample and reference channels were averaged for 180 s, followed by 20 s of flushing time in which the gas flows were switched between the channels.

Figure 4 shows a long term measurement in which two calibrated gas samples of $\Delta\delta^{13} = 1.959‰$ difference are sampled using the gas modulation technique described above. In this 12 h measurement period, optical drifts changed the offset over 1‰, and these were captured and subtracted with the gas modulation sampling. For analysis, the dataset was arbitrarily divided into 17 periods, each 36 min long, for which the δ^{13} value was computed. The average of these 17 periods yielded the expected $^{13}\delta$ value to within 0.033‰ with a standard deviation of 0.073‰. Figure 5 shows another measurement of the same reference gas at a higher resolution and period of high discernible precision based on instrument performance for which the δ^{13} is retrieved with an accuracy of 0.004‰ from the expected value. From this measurement, all 1 s data (high–low cycles) exhibit a standard deviation of 0.224‰. If binned to 60 s, a standard deviation of 0.046‰ is obtained, closely matching the performance indicated by the Allan variance measurement. The precision determined from the measurements displayed in Figs. 4 and 5 was further evaluated with the analysis of a suite of reference gases (375 parts per million CO_2) calibrated by IRMS [5], thus emulating the measurement of gas samples with different isotopic composition. Three of these reference gases with $\delta^{13}C$ values (cylinder number) of $-8.272‰$ (5617), $-8.277‰$ (5649), and $-10.236‰$ (1789) were compared with each other. Table 1 lists the deviation to the reference
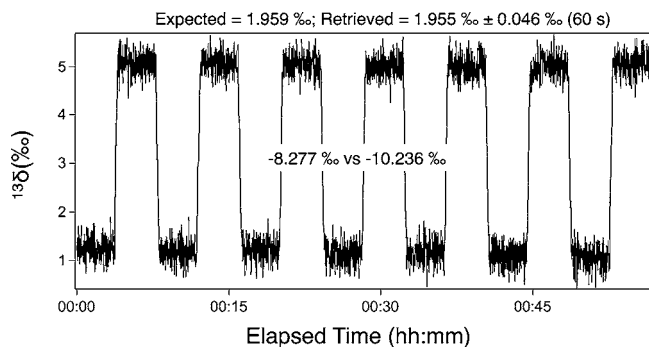

Fig. 5.   Measurement cycles of two calibrated samples.

Table 1. Cylinder Comparison and Measured Deviations Compared to IRMS Values (DFG-IRMS)

$\Delta‰$	5617	5649	1789	Average	n^a
5617		−0.039	0.061	0.051	5
5649	−0.039		−0.038	0.039	24

[a]Number of measurements of 36 min each.

values measured by IRMS (standard deviation $\leqslant 0.02‰$), which may also serve as an estimate of accuracy that can be achieved with this instrument. Further validation and assessment of the accuracy for this spectrometer are necessary to determine the dependence of sample humidity and its effect of line broadening of the absorption lines of wet ambient sample versus dry reference gases. In addition, a more stable and higher-power fiber-optic amplifier may further increase the signal to noise ratio. The precision and accuracy of the reported compact and field-deployable instrument are approaching the performance of laboratory-based IRMS systems and will enable critical field measurement capabilities that are difficult to obtain with flask-sampled IRMS analysis.

In summary, we have reported a compact DFG based laser spectrometer at 4.3 μm for the detection of the $\delta^{13}C$ isotopic ratio of CO_2 with a precision of 0.02‰ (150 s averaging). Comparison with different isotopic ratio mass spectrometer-calibrated references gases demonstrated a measurement accuracy of ∼0.05‰ when compared to measurements obtained with IRMS.

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