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A high precision pulsed quantum cascade laser spectrometer for measurements of stable isotopes of carbon dioxide

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We describe a prototype instrument using a Peltier cooled quantum cascade laser for precise measurement of stable carbon ($^{13}C/^{12}C$) isotopologue ratios in atmospheric CO_2. Using novel optics and signal processing techniques in a compact instrument, we are able to detect the difference between sample and reference with a precision of 0.1‰ (2σ standard error of mean of 11 samples) in 10 min of analysis time. The standard deviation of 0.18‰ for individual 30 s measurements shows that this prototype instrument already approaches the best reported literature values using continuous wave lead alloy tunable diode lasers. The application of pulsed near room-temperature quantum cascade lasers to this demanding problem opens the possibility of field worthy rapid response isotopic instrumentation and attests to the maturity of these lasers as spectroscopic sources.

1. Introduction

The measurement of isotopic ratios in the natural environment is a challenging problem that can be addressed with high resolution laser spectroscopic techniques [1–9]. Most of the prior work in laser spectroscopic measurement of isotopic ratios has been with continuous wave (CW) cryogenically cooled lasers (especially mid-infrared lead alloy semiconductor lasers) [1–7]. The advent of pulsed near room-temperature quantum cascade lasers (QCLs) [10, 11] opens the possibility of field worthy rapid response instrumentation for measurement of stable isotopologues. New isotopic measurement modes may be implemented, such as eddy covariance flux determination. The successful application of QCLs to isotopic measurements also attests to their maturity as spectroscopic sources.

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Measurement of the ratios of atomic isotopes in the molecules that participate in environmental exchange processes is an important tool for understanding those processes and the natural environment [12–15]. This is because there are characteristic isotopic enrichments or depletions generated by the chemical reactions or biochemical processes leading to sources and sinks of atmospheric trace gases. Stable isotope abundances are typically expressed in terms of delta units (δ, ‰), which are a comparison of the ratio of two isotopes in a sample (e.g. $R_x = {}^{13}C/{}^{12}C$), to the same ratio in a standard, R_{std}. The delta unit is defined as: $\delta_x = [(R_x - R_{std})/R_{std}] \times 1000$. Isotopic deltas of interest in the natural environment may be 1‰ or less, and the desired measurement precision is ~0.1‰.

Isotopic ratio measurements are difficult because the ratio variations are small, the minor isotopes are relatively rare, and the molecules of interest may be quite dilute in the natural environment. As an example, consider one of the stronger isotopic enhancements due to biological processes, the fixing of carbon in photosynthesis [12, 13]. Different classes of plants discriminate differently against uptake of ${}^{13}CO_2$ relative to ${}^{12}CO_2$, so that woody plants ('C3' photosynthesis) have $\delta^{13}C \approx -16$‰ and grasses ('C4' photosynthesis) have $\delta^{13}C \approx -4$‰, relative to atmospheric CO_2. One can measure the ratio ${}^{13}C/{}^{12}C$ to identify the class of plants involved in atmospheric sources and sinks of CO_2 [14, 15]. In atmospheric sampling, the average concentration of CO_2 is ~380 ppm and the concentration of ${}^{13}CO_2$ is ~3.8 ppm. The difference in concentration of ${}^{13}CO_2$ produced by burning C3 versus C4 plants (with the resulting CO_2 diluted to near background levels) would be 0.05 ppm. The standard method for determining trace gas stable isotope ratios is isotope ratio mass spectrometry (IRMS) [12, 13], which provides $\delta^{13}C$ with precision of ~0.01–0.05‰. However, IRMS has a number of experimental drawbacks, especially in the great care needed in sample preparation (often involving chemical processing or purification). Commercial IRMS units require permanent installation for reliable operation, so that field samples are normally returned to the laboratory and analysed long after they are taken.

Real time continuous isotopic measurements would greatly facilitate the investigation of environmental exchange processes, allowing guidance of sampling by real time analysis and enabling new techniques. If isotopic measurements can be made with sufficient accuracy at a rate of ~10 Hz, then the correlation of upward wind velocity with concentration yields area flux, a technique called eddy covariance flux measurement. Recently, lead alloy tunable diode lasers (TDLs) have been applied to continuous *in situ* atmospheric isotope ratio measurements [1–7]. Several of these systems have been reported with precisions on the order of 0.1‰ [1, 4–6]. Lead alloy TDLs represent an advance in isotope measurement methods but they are far from ideal, due to the need for liquid nitrogen (LN2) cooling, and the lasers often change characteristics after cooling cycles.

Quantum cascade lasers (QCLs) provide alternative sources of high resolution mid-infrared radiation that have overcome some of the difficulties associated with lead alloy TDLs. QCLs can operate in the mid-infrared, where many molecules display their strongest fundamental vibrational bands, for the highest sensitivity. QCLs can operate near room temperature, and offer single-mode continuous tuning and good power output. Since QC lasers were first demonstrated [16], they have

undergone rapid development [10, 11] and been used for atmospheric trace gas measurements, in CW operation with LN2 cooling [17] and pulsed with thermo-electric cooling [8, 9, 18–22].

In this paper we describe an instrument based on a pulsed quantum cascade laser for precise measurement of carbon isotope ratios (^{13}C/^{12}C) and present laboratory results. The new QC laser spectrometer employs a dual path length optical absorption cell [1] and improved signal processing techniques. The precision and minimal detectable absorbance we obtain with pulsed QC lasers is comparable to that achieved with LN2 cooled CW TDLs, despite the broader linewidths inherent to pulsed operation.

2. Instrument design

In the design of this instrument we have addressed problems that are specific to isotopes and general problems for precision measurements with pulsed QC lasers. At the needed level of precision (of $\sim 10^{-4}$, or 0.1‰) a number of subtle effects can limit the ultimate performance, such as the method of operation of the laser, or choices of spectral features and the method of deriving concentrations. The isotopic specific measurement problems include the large difference in abundances of the minor and major isotopes, and the temperature dependence of absorption strengths. Our group at Aerodyne Research, Inc. has worked over the past several years improving the precision of pulsed QCL spectrometers for several applications, resulting in many of the general approaches described here [20–22]. The QCL spectrometer combines commercially available QC lasers, an optical system, and a computer-controlled electronic system for driving the laser and data processing. The spectrometer is designed for simultaneous measurement of sample, pulse normalization and frequency-lock spectra. We have used commercially available distributed feedback InGaAs–AlInAs/InP QC lasers designed for pulsed operation (Alpes Lasers, Neuchâtel, Switzerland). An essential aspect of this work is that it has been possible to select a QC laser that covers the frequency range from 2310 to 2314 cm^{-1}, which meets the line selection criteria described below.

Pulsed laser operation presents two main problems for high precision measurements, noise due to pulse-to-pulse energy variations and the increase in laser linewidth. We have greatly reduced the problem of pulse-to-pulse variations by normalizing [20–22]. By taking advantage of the time delay of light propagation through the multipass cell, we can use a single infrared detector for both the absorption signal and pulse normalization. The problem of laser linewidth and the associated problem of lineshape stability remain precision limiting issues. Even though we minimize the linewidth by using short pulses ($\sim$10 ns) and operate the laser close to threshold, the laser width is greater than the molecular (Doppler) absorption linewidth.

Stability against temperature changes is a key factor in precision measurements and the basic thermal stability may be improved by careful selection of the two absorption lines. Infrared linestrengths vary with temperature, so drift in the instrument temperature can mask small isotopic deltas [5–7]. However, if the transitions

for both isotopes have similar lower state energy levels, the temperature variation of the two line strengths are closely matched. If the instrument temperature is to within 0.1 K, the lower state energy level separated can be only 100 to 300 cm^{-1} to maintain a precision of 0.2 to 0.5‰ [6]. We have previously reported surveys of thermal sensitivity for lines for the isotopes of CO_2 and CH_4 [1]. The line pairs around 2314 cm^{-1} require a temperature stability of only 0.2 K to obtain a precision of 0.1‰ [1]. The temperature stability requirement is negligible using the line pairs at 2311 cm^{-1} suggested by Weidmann *et al.* [8], which we have used extensively in this study. The choice of spectral features to reduce thermal sensitivity may be less optimal for gases other than CO_2, since the following factors also need consideration.

1. When using a single laser, lines from the major and minor isotopes must be within the frequency scanning range of the laser.
2. The lines should have large transition moments, for maximum sensitivity.
3. The lines should be free of interference from other atmospheric gases.

A key design feature of our laser spectrometer is a dual-path multipass cell used to compensate for the large difference in concentration between major and minor isotopologues of CO_2, an effect limiting precision. When long path lengths are used to increase the absorption depth due to the minor constituent, then the major constituent absorption depth may be excessive, giving essentially no transmission at line centre. Our approach uses two different paths through the same measurement volume for the major and minor isotope, where the ratio of path lengths is similar to the abundance ratio, yielding a similar absorption depth for both isotopologues [1]. The dual path-length cell is based on an astigmatic Herriott cell [23], with the two paths corresponding to either 174 or 2 traverses of the 0.32 m base length [23]. A diagram of the cell coupling arrangement is shown in figure 1. The beam for the 174 pass pattern (for $^{13}CO_2$) is injected at an angle to the centre axis and it exits on the opposite side of the axis. The 2 pass pattern is generated by placing a beamsplitter (BaF_2) on the centre axis, reflecting ~8% of the light straight into the cell. The 2-pass beam then returns on the same axis after reflecting from the back mirror. The resulting optical path lengths of 56.08 and 0.753 m have a ratio of 74:1, nearly balancing the $^{12}CO_2/^{13}CO_2$ isotopomer ratio of 91:1. The dual pathlength concept also greatly lessens the effect of temperature and pressure variations since both isotopomers are measured in the same volume.

The instrument optical system, shown in figure 2, collects light from the QC laser and directs it along four different paths: two paths through the absorption cell, plus the pulse normalization and frequency-locking reference paths. The highly divergent QC laser beam is collected by a reflecting microscope objective and imaged at a pinhole (used only for initial alignment). After the first focus, the beam passes through a wedged BaF_2 beamsplitter. The front reflection beam is used for the pulse normalization spectrum, which defines the wavelength dependence of the laser power, along with its temporal variability. The optical path length of the pulse normalization beam is matched to the sample path length outside the absorption cell, insuring that residual atmospheric absorption in that path is cancelled. The second reflection from the beamsplitter is directed through a short
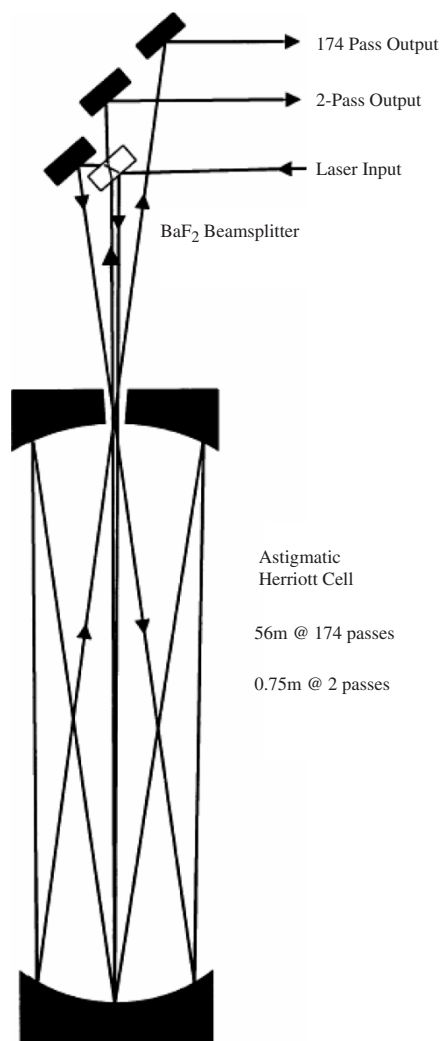
174 Pass Output

2-Pass Output

Laser Input

BaF_2 Beamsplitter

Astigmatic
Herriott Cell

56m @ 174 passes

0.75m @ 2 passes

Figure 1. Optical arrangement to produce dual pathlength optical absorption cell.

absorption cell with low pressure CO_2, and its spectrum is used to actively control the average frequency of the laser by changing the Peltier temperature. The beam transmitted through the beam splitter is re-imaged into the astigmatic Herriott multipass cell [23]. In this study, we sample at a relatively low pressure ($\sim$7 torr), which serves to reduce consumption of sample gas, minimize overlap of adjacent lines and reduce optical depth at ambient concentrations. The optical board is thermally controlled to better than ± 1 K and the instrument enclosure is purged with CO_2 free dry air.

The spectral measurement is based on rapidly sweeping the laser across the selected absorption lines, digitizing the direct-absorption signals and quantitatively
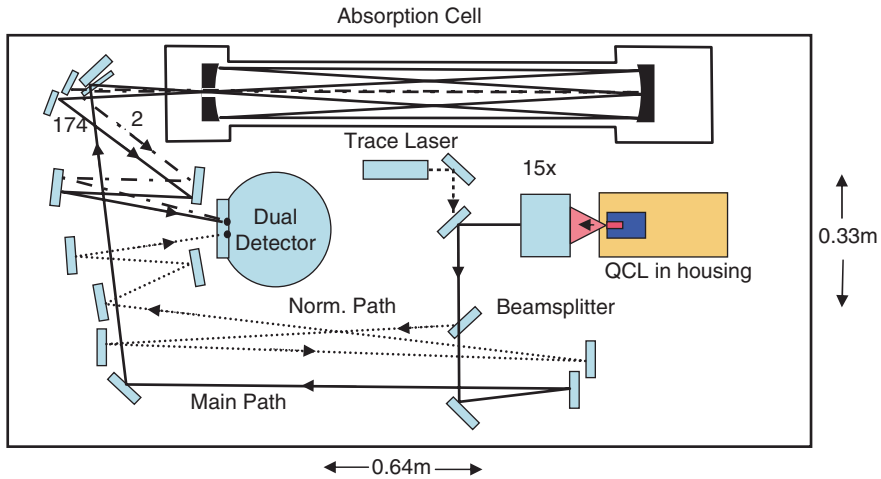
Figure 2. Optical layout of single quantum cascade laser instrument. The optical base measures 0.33×0.64 m.
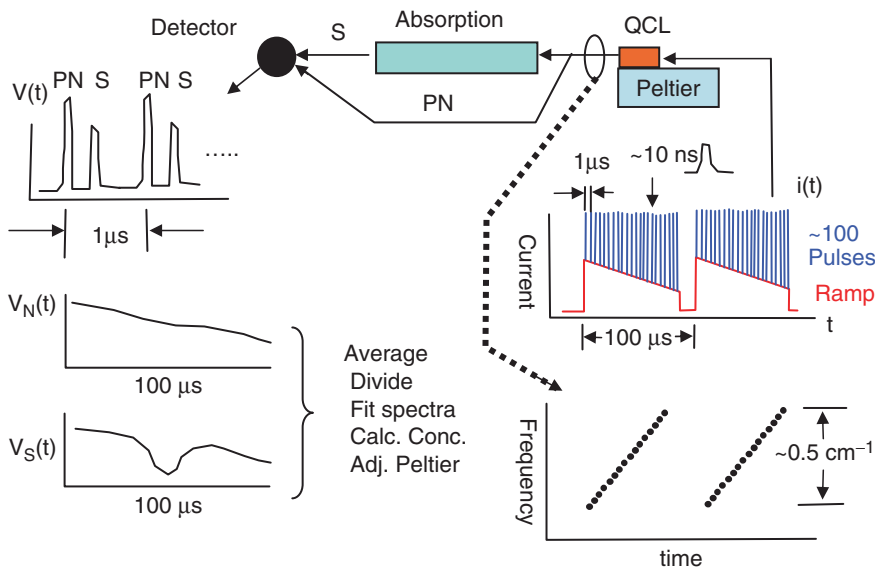

Figure 3. Laser control and signal processing schematic.

fitting the spectra to derive absolute concentrations. A unified computer system, using 'TDL Wintel' software developed at Aerodyne Research, Inc., drives the laser and synchronously analyses data in real time. A diagram of the signal processing system is shown in figure 3. The laser is excited just above threshold with $\sim$10–20 ns electrical pulses at 1 MHz. Spectral scans (over $0.5\,\text{cm}^{-1}$) are

obtained by simultaneously applying a sub-threshold current ramp, which modulates the laser temperature and thus its spectral frequency. Fast (5 MHz) DAC/ADC boards synchronously trigger the pulse electronics and integrate the resulting signals from LN2-cooled InSb photodiodes. The DAC board also generates a TTL gate that defines the ramp duration, including a short laser-off period at the end of each sweep to measure the detector offset. Since this instrument employs separate beam paths and detectors to monitor each isotope simultaneously, we employ dual data acquisition processes operating in parallel, to collect data through separate acquisition boards. We run two instances of TDL Wintel with processes that are precisely synchronized by operating the instances as 'master and slave'. The master instance controls the laser and sends timing signals to the slave, which then constructs appropriate timing gates for its detector. A typical spectral sweep consists of 100–400 pulses, giving a spectral sweep rate of $\sim$2.5–10 kHz. Concentrations and laser linewidths are determined in real time from the spectra through a nonlinear least-squares fitting algorithm (Levenberg-Marquardt) that uses fitting functions composed from Voigt [24] molecular profiles (based on the HITRAN [25] database plus measured pressure and temperature), convolved with a (Gaussian) laser line-shape and added to a polynomial baseline. Derived mixing ratios are typically accurate to $\sim$5% without calibration.

3. Laboratory data

The basic data produced by the instrument are the two absorption spectra, for $^{13}CO_2$ using the long path (56 m) and $^{12}CO_2$ using the short path (0.74 m). The spectral pair near 2311 cm^{-1} is shown in figure 4, for a sample with CO_2 concentration $\sim$350 ppm at a pressure of 7.5 torr. The data here are reported at 1 Hz, where the concentration noise is $\sim$150 ppb. Each panel in figure 4 displays three curves, (1) the experimental absorption spectrum, (2) a spectral fit to the data, a convolution of the Voigt molecular lineshape with the laser lineshape, and (3) a spectral simulation of only the molecular lineshape. We employ a simple Gaussian instrument profile in the convolution, which does a good job of capturing the measured lineshape and area, even though some details of the observed shape are missed by using a symmetrical profile. Comparing the molecular line to the data shows the degradation in resolution due to the significant laser linewidth. For the $^{13}CO_2$ absorption line the apparent peak absorbance is ~ 0.1, but the actual peak absorbance is three times greater. The $^{12}CO_2$ line at 2311.105 cm^{-1} (figure 4(a)) is optically black at centre even though that is not apparent from the experimental spectrum. Nevertheless, the analysis does a good job of reproducing the experimental $^{12}CO_2$ spectrum. These lines are strong enough that the absorbance area is not conserved and accurate results can only be obtained by doing a convolution of the molecular spectrum with the instrumental width.

In figure 5 we show in more detail the contributions to the spectrum in the long absorption path for $^{13}CO_2$. The underlying $^{12}CO_2$ lines contribute significantly to the absorption area in the wings of the $^{13}CO_2$ absorption region, despite the low pressure and good separation. To compensate for this effect, the fitting procedure is
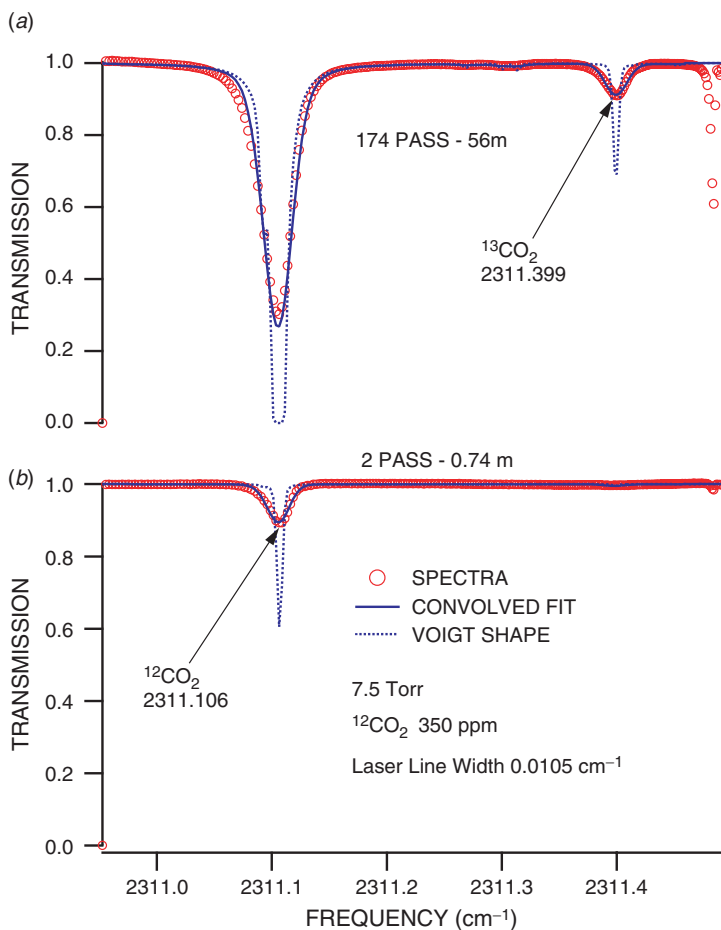
Figure 4. CO_2 isotopologue spectra with pulsed QC laser. The cell contains 350 ppm CO_2 in air at 7.5 torr. The laser linewidth is $0.0105 \, cm^{-1}$ hwhm. The graphs show recorded spectra (large dots), fit functions (solid lines) and simulated Voigt absorption lines (dashed lines), for the long path (upper panel, (*a*)) and short path (lower panel, (*b*)).

done for the two isotopomers simultaneously. Although it would be possible to vary both species in the fit, there is insufficient $^{12}CO_2$ absorption in the $^{13}CO_2$ region to accurately retrieve its concentration. Instead, the $^{12}CO_2$ concentration is set to the more accurate value determined from the short path absorption spectrum. This greatly reduces the dependence of the $^{13}CO_2/^{12}CO_2$ ratio determination on variations in the $^{12}CO_2$ concentration.

The long term stability of the instrument is evaluated using the Allan variance technique, which distinguishes high frequency random noise from drifts at longer time scales [26]. The contributions of random noise to the variance (σ^2) decrease as t^{-1}, so a plot of variance with increasing integration time is expected to have a (log-log) slope of -1 at short times, while at longer times the variance curve levels off and rises due to drifts. In figure 6 we show time series data and an Allan
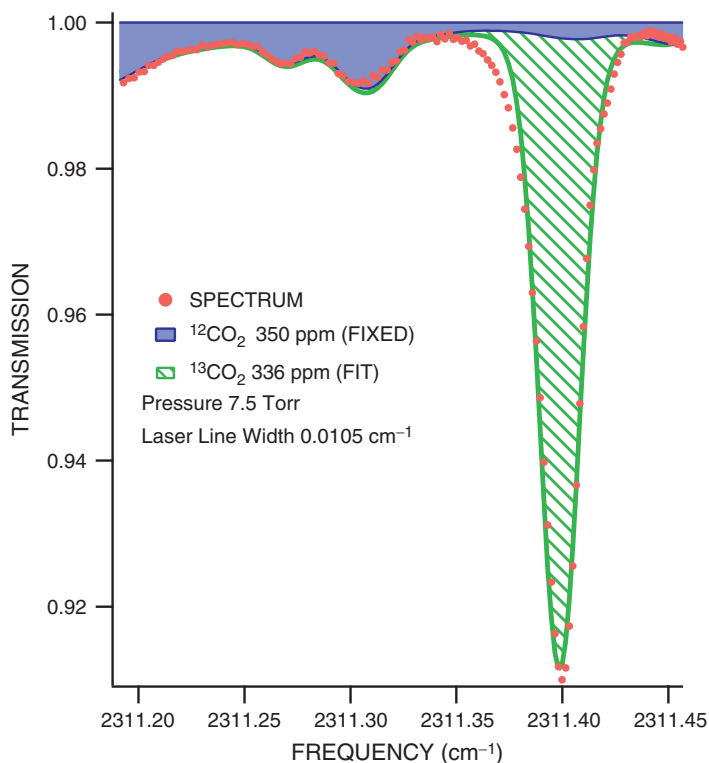
Figure 5. Detail of the contributions to the fit spectrum in the long absorption path. There are small contributions from a weak $^{12}CO_2$ line that is nearly coincident with the $^{13}CO_2$ line.

plot of both isotopologues and their ratio for a 10 h period. The $^{13}CO_2/^{12}CO_2$ ratio has a 1 s standard deviation of 0.5‰. However, the variance does not decrease with $t-1$ as would be expected for random (white) noise, but rather behaves as $f^{-0.5}$ 'pink' noise, indicating that that there are correlations in noise sources at time scales of 1–100 s. The variance minimum at 200 s corresponds to a minimum σ_{Allan} of 0.1‰.

The precision of an isotopic ratio measurement can be improved by alternating between a sample and reference, with the time for each measurement less than the averaging at which the Allan variance begins to increase. We present an alternating measurement in figure 7, sampling gases from two tanks: the 'sample' containing 350 ppm total $^{12}CO_2$ and unknown $\delta^{13}C$, was compared with a 'reference' mixture of CO_2 with $\delta^{13}CPDB = -49.4‰$ (determined by mass spectrometry courtesy of Professor Dan Schrag at Harvard University). For the data in figure 7, the averaging time for each sample was 25 s, with 5 s between samples for gas flushing. For this experiment we observe that the sample air has $\delta^{13}C_{CO_2} = -14.9‰$, relative to PDB. The difference between sample and reference is obtained with a precision of 0.1‰ (2σ standard error of mean of 11 samples) in 10 min of analysis time. The standard deviation of 0.18‰ in individual 30 s intervals shows that this prototype instrument already approaches the best reported literature values using
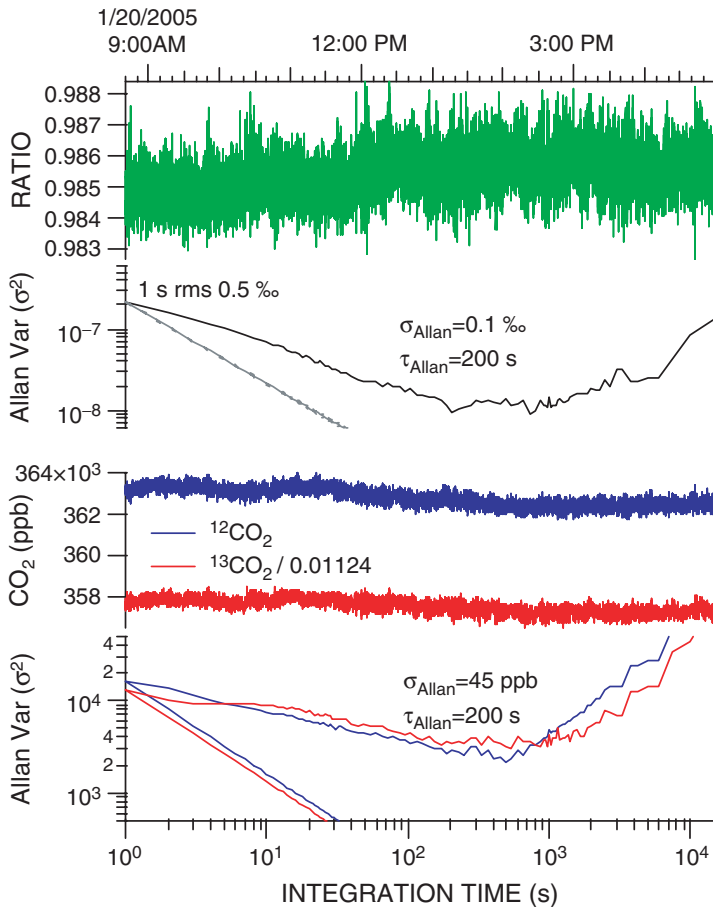
Figure 6.   Noise in isotope ratio and Allan plot showing long term drift behaviour.

continuous lead-alloy TDLs [4]. While the averaged data yields a best precision in delta of 0.1‰, the large-signal accuracy of the spectroscopically derived delta is substantially less ($\sim$10%). The spectroscopic accuracy is limited by uncertainty in the tabulated HITRAN line strengths, and by uncertainty in the spectral baseline, which relates to uncertainty in the laser lineshape. To achieve higher accuracy it is necessary to calibrate with standards.

4. Discussion

In the prototype instrument described above, we achieve a precision in isotopic ratio measurements of 0.18‰ in 30 s (1σ) and 0.1‰ in 600 s (2σ). This result is achieved by carefully controlling numerous system parameters, especially laser base temperature and average centre wavelength, as well as the temperature of the optical
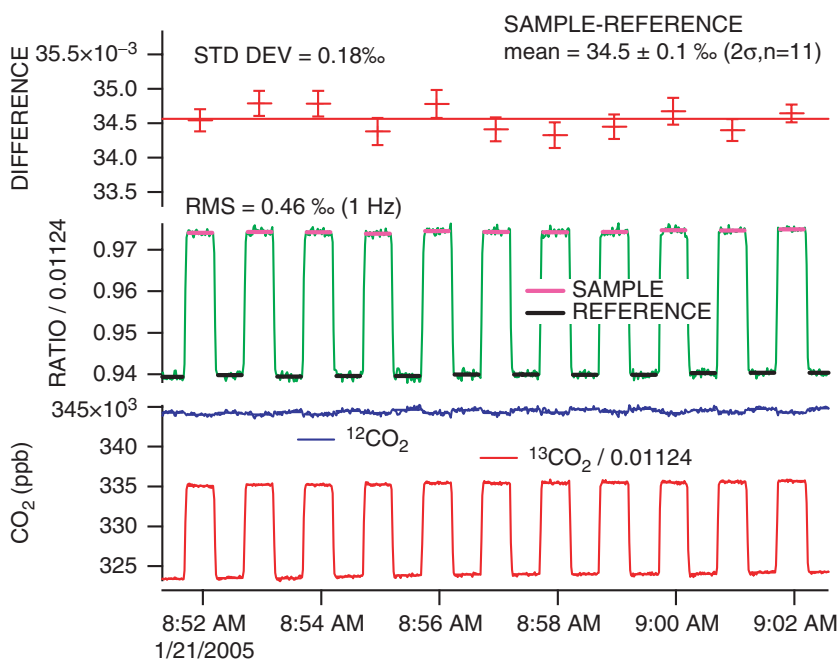
Figure 7. Alternating measurements of $^{13}CO_2/^{12}CO_2$ in sample and reference air from tanks. Reference was made by diluting pure CO_2 ($\delta^{13}C$PDB $= -49.4‰$) with dry N_2 to match sample gas $[^{12}CO_2]$ of $\sim$350 ppm. Reference gas $[^{12}CO_2]$ of $\sim$345 ppm (bottom panel) and isotope ratio of $0.940 = -60‰$ (middle panel) are directly retrieved (uncalibrated) values. The flow rate of 0.5 SLPM in a cell volume of 0.51 at pressure of 7 torr corresponds to a cell flushing (1/e) time of 0.6 s. The first 5 s of each 30 s interval were discarded.

table and the pulse electronics. We believe the largest source of noise and drift in the 1 to 100 s time scale is residual laser frequency fluctuations, affecting both the peak position and the laser linewidth. Another significant drift effect is variation in the residual CO_2 in the optical enclosure.

The success to date of our QC laser spectrometer for isotopic measurements provides the opportunity to comment on the utility of these lasers as spectroscopic sources. The measurement method presented is possible because a high-quality QCL was available at the desired wavelength, a significant factor given the current scarcity of QC laser manufacturers. The laser is very well behaved in tuning with temperature and current. The reproducibility of the output as we ramp and pulse the current contributes to the final precision performance of the instrument. Pulse energy noise can be divided out with our 'pulse normalization' approach, greatly reducing multiplicative noise. With careful system control, we can achieve noise performance approaching the best reported literature values using CW TDLs [4]. The laser used in this study has operated continuously for more than three months with negligible change in characteristics.

There are several directions available to improve the performance of this instrument. We continue to improve stabilization and control of the laser and

instrument overall, which has been a key element of the performance achieved to date. While we have focused to date on $^{13}CO_2$ and $^{12}CO_2$, we could also apply these techniques to, e.g. $^{13}CH_4/^{12}CH_4$ or $^{12}C^{18}O^{16}O/^{12}C^{16}O_2$. If we can achieve sufficient precision with fast response time then we could measure isotopic fluxes by eddy covariance. We have previously presented a dual QCL instrument [22] and we plan to modify that design to include the isotope dual-path optics. The instrument presented here has a LN2 cooled detector, but with continued improvement in thermoelectrically cooled infrared detectors a fully non-cryogenic instrument is possible. This would allow completely unattended long term operation and greatly advance the application of infrared spectroscopy to isotope analysis.

5. Summary and conclusions

A high precision pulsed-quantum cascade laser spectrometer operating in the mid-infrared ($2311\,cm^{-1}$) has been demonstrated to determine isotopic abundances by measuring $^{13}CO_2/^{12}CO_2$ in atmospheric air. The instrument uses a dual path-length absorption cell with a longer path ($56\,m$) for the minor isotope and a shorter path for the major isotope ($0.74\,m$), with absorption lines selected for similar lower state energies to negate the effects of sample temperature variation. By stabilizing the pulse electronics and normalizing pulse-to-pulse intensity variations, measurement precision for each isotopologue of 5×10^{-4} (1 s rms) relative to their ambient mixing ratios may be achieved. The difference in the isotopologue ratio between two samples of ambient air can be determined by alternating between sample and reference with a replicate precision of 0.18‰ (1σ) standard deviation for 30 s averaging intervals. This corresponds to a standard error of mean over 11 cycles of 0.1‰ (2σ) in 10 min of measurement time alternating between sample and reference in a flowing system.

References

[1] J.B. McManus, M.S. Zahniser, D.D. Nelson, *et al.*, Spectrochim. Acta A **58** 2465 (2002).
[2] K. Uehara, K. Yamamoto, K. Kikugawa, *et al.*, Sens. Actuators B **74** 173 (2001).

[3] T.J. Griffis, J.M. Baker, S.D. Sargent, *et al.*, Agric. Forest Meteorol. **124** 15 (2004).
[4] D.R. Bowling, S.D. Sargent, B.D. Tanner, *et al.*, Agric. Forest Meteorol. **118** 1 (2003).
[5] P. Bergamaschi, A.M. Brenninkmeijer, M. Hahn, *et al.*, J. Geophys. Res. **103** 8227 (1998).
[6] P. Bergamaschi, M. Schupp and G.W. Harris, Appl. Opt. **33** 7704 (1994).
[7] J.F. Becker, T.B. Sauke and M. Loewenstein, Appl. Opt. **31** 1921 (1992).
[8] D. Weidmann, G. Wysocki, C. Oppenheimer, *et al.*, Appl. Phys. B Lasers Opt. **80** 255 (2005).
[9] A.A. Kosterev, R.F. Curl, F.K. Tittel, *et al.*, Opt. Lett. **24** 1764 (1999).
[10] J. Faist, F. Capasso, C. Sirtori, *et al.*, Electron. Lett. **32** 560 (1996)
[11] F. Capasso, R. Paiella, R. Martini, *et al.*, IEEE J. Quantum Electron. **38** 511 (2002).
[12] P. Ghosh and W.A. Brand, Int. J. Mass Spectrom. **228** 1 (2003).
[13] S.E. Trumbore, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson and R. C. Harriss (Blackwell Science Ltd, Oxford, 1995).
[14] C.-T. Lai, A.J. Schauer, C. Owensby, *et al.*, J. Geophys. Res. **108**(D18) 4566 (2003).
[15] S.R. Saleska, S.D. Miller, D.M. Matross, *et al.*, Science **302** 1554 (2003).
[16] J. Faist, F. Capasso, D.L. Sivco, *et al.*, Science **264** 553 (1994).
[17] C.R. Webster, G.J. Flesch, D.C. Scott, *et al.*, Appl. Opt. **40** 321 (2001).
[18] A.A. Kosterev and F.K. Tittel, IEEE J. Quantum Electron. **38** 582 (2002).
[19] A.A. Kosterev, F.K. Tittel, R. Kohler, *et al.*, Appl. Opt. **41** 1169 (2002).
[20] D.D. Nelson, J.H. Shorter, J.B. McManus, *et al.*, Appl. Phys. B Lasers Opt. **75** 343 (2002).
[21] D.D. Nelson, J.B. McManus, S. Urbanski, *et al.*, Spectrochim. Acta A **60** 3325 (2004).
[22] R. Jimenez, S. Herndon, J.H. Shorter, *et al.*, SPIE Proc. **5738** 37 (2005).
[23] J.B. McManus, P.L. Kebabian and M.S. Zahniser, Appl. Opt. **34** 3336 (1995).
[24] J. Humlícek, JQSRT **27** 437 (1982).
[25] L.S. Rothman, A. Barbe, D.C. Benner, *et al.*, JQSRT **82** 5 (2003).
[26] D.W. Allan, Proc. IEEE **54** 221 (1966).