Taylor & Francis
Taylor & Francis Group

Carbon isotopomers measurement using mid-IR tunable laser sources

DAMIEN WEIDMANN*†, CHAD B. ROLLER‡, CLIVE OPPENHEIMER§,
ALAN FRIED¶ and FRANK K. TITTEL‡

†Space Science Department, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot,
Oxfordshire, OX11 0QX, UK
‡Rice Quantum Institute, Rice University, 6100 Main Street, Houston, TX 77251, USA
§Department of Geography, University of Cambridge, Downing Place, Cambridge, CB2 3EN, UK
¶Earth Observatory Laboratory, National Center for Atmospheric Research,
3540 Mitchell Lane, Boulder, CO 80301, USA

Recent developments of two mid-infrared tunable laser spectrometers dedicated to carbon isotope ratio determination are presented. First, a field deployable quantum cascade laser-based sensor is described, along with line selection strategy for $^{13/12}CO_2$ ratio measurements. Secondly, an instrument architecture based on difference frequency generation is presented. The analyses of fundamental limitations, specifically temperature and pressure stability, and water vapor collision broadening, are detailed.

Keywords: Carbon dioxide; Carbon-13; *In situ* laser sensors; IR spectrometry; Natural isotope ratios; Volcanoes

1. Introduction

Tunable laser absorption spectroscopy is an attractive method for real-time *in situ* monitoring of stable isotopes [1]. It therefore has potential applications in many fields including geochemistry, atmospheric chemistry, life sciences and medicine. In particular, the availability of advanced laser sources emitting in the mid-infrared (IR) 'fingerprint' region allows the development of isotopic ratio instrumentation capable of sub per mil precision and accuracy by targeting intense ro-vibrational absorption lines. The spectroscopic tunable laser source must fulfil the following requirements.

- A high power source that allows increased sensitivity for the detection of low gas concentration levels by improving the signal-to-noise ratio of the spectrometer. This also permits the use of thermoelectric cooled detectors rather than cryogenic detectors, greatly facilitating field deployment.

---

*Corresponding author. Tel.: +44-1235-445-804; Fax: +44-1235-445-848; Email: d.weidmann@rl.ac.uk

- A narrow spectral laser linewidth is critical to measurement accuracy and discrimination of closely spaced adjacent absorption lines. It also facilitates retrievals by obviating the need to account for the instrument apparatus function.
- A wide spectral tuning range is needed to span well-separated isotopic lines and to allow multi-species monitoring.
- The beam quality is important, in particular, for long range beam transport and coupling to a multipass cell or resonant cavity used for sensitivity enhancement.
- Fast response of both the laser source and the detection system allows real-time monitoring of isotopic gas species.

Isotopic sensors based on quantum cascade lasers (QCLs) and on difference frequency generation (DFG) have been developed and presented at the IAEA SIRIS 2004 conference. QCLs can emit between 4 and 24 μm [2], whereas DFG-based coherent sources using periodically poled LiNbO$_3$ (PPLN) emit in the range of 3–5 μm [3–5]. Antimonide semiconductor lasers [6, 7] and interband cascade lasers (ICL) [8, 9] are promising for applications in the 2–5 μm range, covering the gap in availability of compact semiconductor laser sources between the telecommunication bands in the near IR and QCLs in the mid-IR.

In this article, we focus mainly on recent research undertaken at Rice University, Houston, and NCAR, Boulder, on carbon isotopomer concentration measurements, in the context of volcanology and atmospheric science studies, respectively. We first describe a QCL-based sensor relevant to carbon isotopomer measurement for volcanic gas studies. Line selection and the use of advanced semiconductor laser sources are discussed. Furthermore, some design issues pertinent to the development of a DFG-based carbon isotopomer sensor in development at NCAR are presented. This discussion emphasizes different fundamental limitations affecting measurement accuracy and precision, such as temperature and pressure variations and the effect of humidity on collision lineshape broadening.

2.   QCL-based sensor for carbon isotopes measurements of volcanic gases

2.1 *Motivation*

Identification and measurement of gases released by volcanoes provide information on magmatic sources and so aid interpretation of volcanic behaviour and eruption forecasting [10]. As well as information on real-time trace gas concentrations in volcanic emissions, isotopic ratio measurements of species including carbon, hydrogen, nitrogen, oxygen and sulphur provide additional information concerning the gas sources and their geochemical history. Stable carbon isotopomers, especially $^{12}CO_2$ and $^{13}CO_2$, are of particular interest. Carbon dioxide is typically the most abundant gas released by volcanoes after H$_2$O. $^{13/12}CO_2$ monitoring can be used as a tracer to discriminate the sources contributing to observed CO$_2$ emissions. Figure 1 illustrates the variations in $^{12}C/^{13}C$ in terms of delta values ($\delta^{13}C$) that may be expected from various carbon sources [11, 12]. These differences enable the potential identification of, say, an increased magmatic input into observed emissions, which might imply intrusion of magma beneath the volcano with important implications for hazard assessment.

Real-time continuous monitoring in a volcanic environment presents considerable challenges that must be addressed. The atmosphere surrounding the sensor is often extremely corrosive due to high temperatures and the presence of acid species including SO$_2$, HCl and HF. Optimized and reliable sampling methods must also be investigated to ensure that the sampling itself does not affect the chemistry of the collected samples or introduce kinetic fractionation of the isotopic species. Hence, robust, compact and autonomously operating
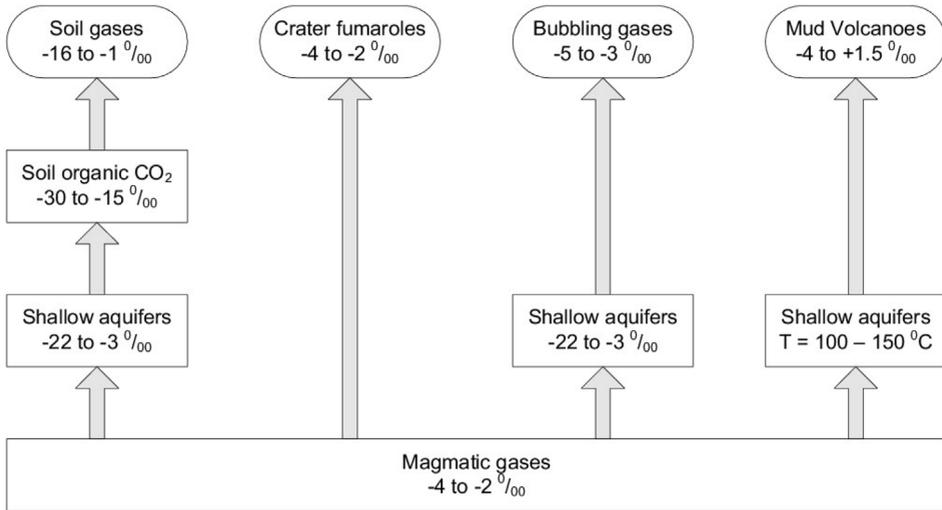
Figure 1. Illustration of potential sources of CO_2 in volcanic emissions and their typical $\delta^{13}C$ values.

sensors are preferable [13]. DFG-based sensors have already been demonstrated for measurements of volcanic CO_2 emissions [14, 15]. Recently Castrillo *et al.* [16] reported the first volcanic carbon isotopic ratio measurements using a spectroscopic ratiometer equipped with a distributed feedback (DFB) diode laser emitting at 2 μm [16, 17].

2.2 *QCL-based sensor for carbon isotopomers*

A QCL-based two channel spectrometer was developed for $\delta^{13}C$ measurements [18] based on an earlier sensor using a DFG source [19]. The identified target lines for this sensor were located at 2311.105566 cm^{-1} ($^{12}CO_2$, ν_3) and 2311.398738 cm^{-1} ($^{13}CO_2$, ν_3), respectively. With this selection, the $\delta^{13}C$ measurements are insensitive to gas temperature variations. However, the line intensities differ by a factor of about 100, and therefore a dual path length absorption cell was required. A schematic of the sensor head is depicted in figure 2. The sensor has already been described in ref. [18]. In brief, the spectroscopic source is a pulsed, thermoelectrically cooled, DFB QC laser excited by 25 ns current pulses. The dual path length absorption cell is an astigmatic Herriott cell modified to incorporate an additional short path. After exiting the cells, the two beams are directed to two thermoelectrically cooled HgCdZnTe detectors. The complete optical subsystem is housed inside a sealed Delrin case and purged with dry nitrogen to avoid contamination from atmospheric CO_2 or corrosive gases. The associated sensor electronics are located below the optical platform, as seen in figure 3, which shows the complete CO_2 isotopic ratiometer. A gas control subsystem alternating the flow of sample and calibration gases into the absorption cell is connected to the instrument.

The operating wavelength of the QCL obtained for this system was unfortunately found to be $\sim$8 cm^{-1} distant from the selected frequencies. Also, an unusually large threshold current (9 A) prevented the use of a fast ($\sim$400 Hz) subthreshold current ramp to rapidly tune the laser wavelength. Consequently, the sensor could not be deployed for field evaluation of $\delta^{13}C$ measurements to date. However, a $^{12}CO_2$ line at 2320.7501 cm^{-1} and a $^{16}O^{12}C^{18}O$ line at 2320.4599 cm^{-1} could be targeted. As the intensity ratio of these lines is $\sim$20, the basic principle of the CO_2 ratiometer could be demonstrated.
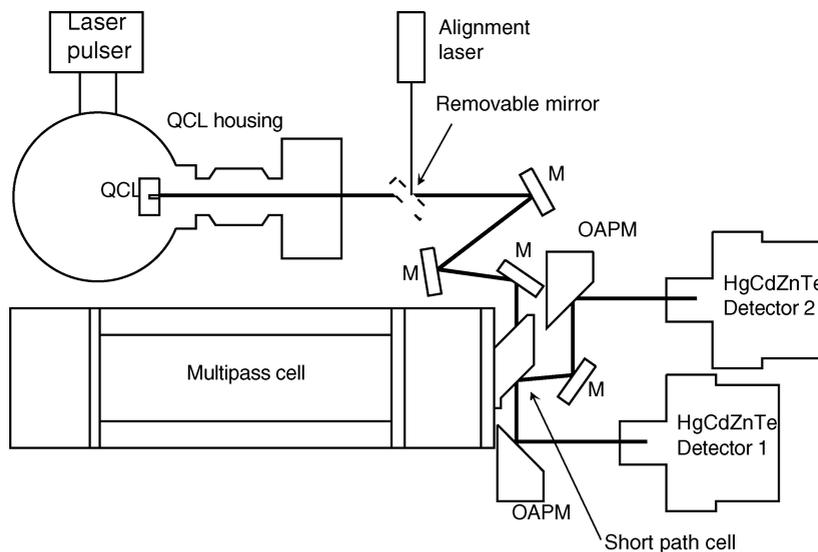
Figure 2.   Diagram of the QCL-based CO_2 isotopic ratiometer.

The performance of the QCL sensor was limited by pulse-to-pulse amplitude fluctuations (the current design does not include a pulse-to-pulse normalization procedure) and the intrinsic broad, and asymmetric, laser linewidth inherent with pulsed QCL excitation. The extrapolated precision of $\delta^{13}C$ is ~ 1 ‰. The application of intrapulse spectroscopy using longer laser excitation pulses [20, 21] to monitor $^{13/12}CO_2$ ratios could be a promising approach to limit linewidth and pulse-to-pulse variations. Alternatively, the use of room temperature CW DFB QCLs and ICLs would obviate this issue [22, 23].

2.3   *Optimum line selection: towards a dual laser system*

The line selection strategy, which consists of choosing optimum absorption lines for the two isotopomers under study, involves the consideration of several issues.

- The line intensities have to be considered. Ideally, similar intensities would be sought so that the same cell can be used (*i.e.* same path length), and to limit potential non-linearities in the detection system. Hence, the use of a single detector to monitor both reference and
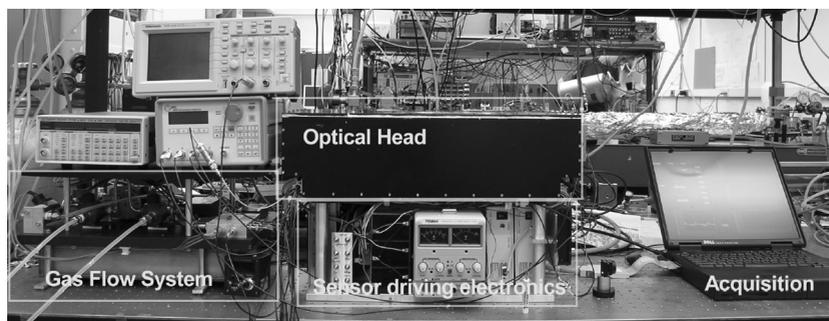

Figure 3.   Photograph of the complete CO_2 isotopic ratiometer system.

signal beams would be optimum. The line intensities have also to be high enough to ensure the best sensor sensitivity and to allow the use of a compact absorption cell.

- The temperature stability requirement depends on the Boltzmann distribution of the two respective isotopic transitions. A similar evolution of the two line intensities with temperature is crucial to limit sensitivity to temperature fluctuations. This condition is expressed by [24]:

$$\Delta T \cdot \Delta E = \Delta \delta \cdot k \cdot T^2, \tag{1}$$

where $\Delta \delta$ is the target accuracy on δ, k the Boltzmann constant, T the temperature, ΔE the energy difference between the lower levels of the two transitions and ΔT the temperature variation. Hence, in terms of spectroscopic parameters to obtain temperature insensitivity, the lower energy levels must be identical.

- The potential spectral and collisional interferences by other species have to be considered.
- Well isolated lines are preferred, making concentration retrievals easier.
- Other parameters may be dictated by the spectroscopic source to be used. For example, ensuring that the two lines are within the available tuning range and that the source linewidth matches the absorption widths of the selected isotopic line pair.

To implement line selection for any pair of isotopomers of any molecules, we developed an algorithm based on the aforementioned two first conditions using data from HITRAN 2004 [25]. First, depending on the experimental condition, the minimum line intensities to be considered have to be defined (cutoff intensity, S_{min}). Then, precision parameters are entered into the algorithm: the minimum acceptable temperature stability ΔT, the relative difference allowed between the two line intensities ΔS and the minimum frequency separation required between the two lines $\Delta \nu$. All the possible line pairs of the two selected isotopomers within the available database are then processed. The identified line pairs then have to be critically examined, taking into account the other aforementioned selection criteria.

The algorithm was applied to potential $^{12}CO_2$, $^{13}CO_2$ line pairs. First, the minimum intensity was set to 10^{-21} cm^{-1}/molec cm^{-2}. This intensity criterion is low for atmospheric studies, but sufficient for volcanic environments where CO_2 concentrations can exceed several percent. The parameters were chosen as follows: a target delta value accuracy of 0.1 ‰, a temperature stability of better than 0.5 K, a relative difference in intensities of $<$10 % and line separation of at least 0.05 cm^{-1}. A stringent condition on line intensities is required to achieve the expected accuracy on the delta value. The currently available thermoelectrically cooled detectors have been found to have a non-linear response. One hundred and eighty-eight pairs of transitions satisfy these criteria (figure 4). The points are located in three regions, detailed in the lower part of figure 4, corresponding to the intersection of the $^{12}CO_2$ and $^{13}CO_2$ bands indicated on the upper graph.

Figure 4 indicates that the optimum selection would involve two lines from two different bands, which would require two laser sources. With the parameters used to establish this selection, only two pairs belong to the same band (ν_3) and the smallest frequency separation is found to be ~25 cm^{-1} for 2336.5590 cm^{-1} ($^{13}CO_2$) and 2311.3990 cm^{-1} ($^{12}CO_2$). Such a tuning range is not yet accessible with existing semiconductor mid-IR sources.

By choosing more stringent parameters such as $S_{min} = 10^{-20}$ cm^{-1}/molec cm^{-2}, $\Delta T = 10$ K, $\Delta S = 1\%$, only three line pairs are found. They are listed in table 1. These three line pairs appear to offer the best strategy to achieve a high accuracy for $\delta^{13}C$ measurements. An alternative strategy would be to consider dual laser sources for isotopic ratio monitoring.
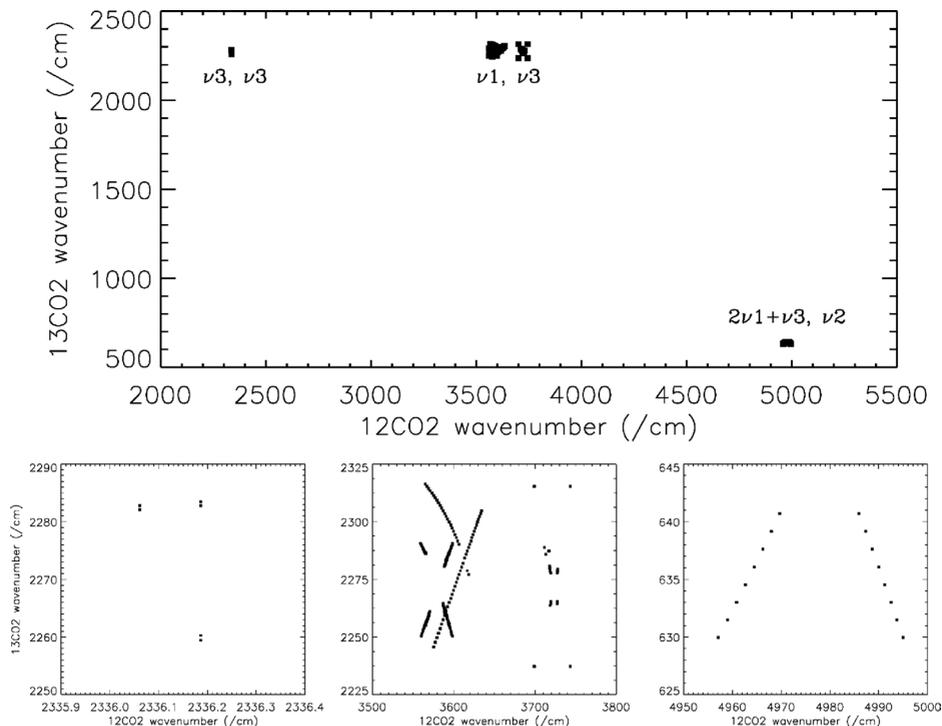
Figure 4. Plot depicting the line pairs satisfying the following criteria: intensity $>10^{-21}$ cm^{-1}/molec cm^{-2}, $\Delta T > 0.5$ K, relative intensity difference $<10\%$ and spectral separation >0.05 cm^{-1}. The lower graph provides details of the three ro-vibrational band intersections appearing in the main graph: (ν_3, ν_3), (ν_1, ν_3), $(2\nu_1 + \nu_3, \nu_2)$, from left to right.

Table 1. Optimum line selection for $^{13/12}CO_2$ ratio measurements.

$^{12}CO_2$			$^{13}CO_2$		
Frequency (cm^{-1})	Strength (cm^{-1}/molec cm^{-2})	Band	Frequency (cm^{-1})	Strength (cm^{-1}/molec cm^{-2})	Band
3601.4210	3.513e−020	$\nu_1 + \nu_3$	2294.4811	3.547e−020	ν_3
3599.7027	3.573e−020	$\nu_1 + \nu_3$	2295.8456	3.574e−020	ν_3
3597.9626	3.525e−020	$\nu_1 + \nu_3$	2297.1862	3.499e−020	ν_3

3. DFG-based sensor for carbon isotope measurements in atmospheric CO_2

3.1 *Motivation*

The monitoring of carbon isotopic ratios is an effective method to investigate the global carbon cycle and characterize anthropogenic perturbation effects. While atmospheric concentrations of CO_2 have been slowly increasing over the past 100 years, absolute concentrations are lower than predicted, using most current global carbon budget models. It has been hypothesized that a missing CO_2 sink exists in the Northern Hemisphere [26]. Identification of CO_2 sources and sinks is possible by discriminating $^{13}CO_2$ to $^{12}CO_2$ stable isotopic ratios [27]. CO_2 fluxes can be partitioned into subfluxes, such as CO_2 uptake and release from plants, soil and oceans (called assimilation and respiration, respectively) and from combustion. Because carbon harvested from deep below the Earth's crust is highly depleted in ^{13}C, it is easy to discriminate from oceanic and terrestrial assimilation and respiration.

3.2 *DFG-based $^{12}CO_2/^{13}CO_2$ ratiometer*

A DFG-based CO_2 spectrometer [28, 29] is currently under development at NCAR in Boulder. As an *in situ* sensor, it will permit rapid, repeat measurements and improve the estimates of land disequilibria and discrimination. To achieve these goals, a precision and accuracy of better than 0.1 ‰ for $\delta^{13}C$ is required. The spectrometer consists of two side-by-side dual pass cells with an 80 cm optical pathlength and a novel DFG collection approach, which uses a single detector and optical chopper to alternate between measurements of the two cells.

The source consists of two seed lasers: a telecom DFB diode laser emitting at 1500 nm and an optically pumped ytterbium fiber laser operating at 1115 nm. The instrument operates at 4.3 μm, targeting the ν_3 fundamental band of CO_2. The lines selected are at 2299.642 cm^{-1} ($^{12}CO_2$, P41) and 2299.795 cm^{-1} ($^{13}CO_2$, R22). The main advantage of this particular selection is that the line intensities are almost equal. On the other hand, temperature stability of the sample is critical to achieve a 0.1 ‰ precision of the delta value, which is challenging especially during field deployments.

3.3 *Fundamental limitations*

The line pair selection was made so that the two intensities were close, allowing the design of a simple cell using only one probe beam to measure both $^{13/12}CO_2$ lines. Inherently, the lower state energies of the selected line pair are different, $\Delta E \sim 1160$ cm^{-1}. The expected required temperature stability, calculated with equation (1), is 6 mK.

The frequency span between the two lines is small. As a consequence, pressure change has a strong effect on the peak amplitude and overlapping wing contributions from one line to the other. The theoretical effect of pressure change was investigated for direct absorption and second harmonic detection. The variation of $\delta^{13}C$ was calculated as a function of the pressure change for three different concentration retrieval procedures: peak amplitude estimation, line profile integration and retrieval based on a least square fitting procedure (reference fitting) [30]. The results are shown in figure 5.
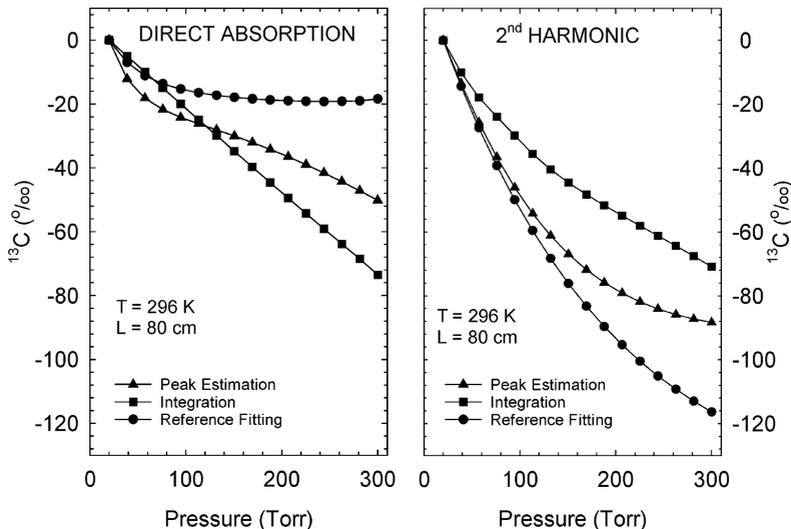

Figure 5. Calculation of the error induced on $\delta^{13}C$ by pressure change for three different concentration calculation methods.

2f detection is far more sensitive to pressure changes due to the relationship of the modulation depth and the half-width of the absorption profile. The integration area technique was not immune to changes in the absorption profile primarily due to a wing contribution from neighbouring absorption profiles, contributions of underlying weaker CO_2 absorption profiles, and the finite area of integration across the absorption profile relative to the fitting windows.

The results for the analysis of pressure instability at 40 Torr are given in the left hand part of table 2. Reference fitting using direct absorption spectra had the greatest tolerance for pressure changes, requiring a pressure stability of 620 mTorr to achieve isotopic discrimination of 0.1 ‰. 2f detection techniques were more vulnerable to pressure perturbations requiring pressure stabilities of 150 mTorr to achieve the same precision.

A fundamental limiting factor not previously considered is the effect of line broadening from CO_2–H_2O collisions. Self-, air-, and H_2O-collisional broadening were considered to determine the effect of changing humidity on measured $^{13/12}CO_2$ ratios. This is particularly relevant when one considers a reference standard in dry air and a sample gas in humid air, *e.g.*, volcanic fumaroles, which typically emit steam. The CO_2-H_2O collision broadened coefficients for $^{12}C^{16}O_2$ in the ν_3 band have been experimentally measured with line-by-line resolution by Rosenmann *et al.* [31]. Results for the R42 and R54 lines yielded collision-broadening coefficients of 0.146 and 0.144 cm^{-1}/atm, respectively.

For the theoretical analysis presented here, we will assume a $\gamma_{CO_2-H_2O}$ value of 0.145 cm^{-1}/atm. However, for the specific CO_2 absorption lines used in the isotopic measurements, the appropriate Lorentzian-broadening coefficient for CO_2–H_2O collisions should be determined. Figure 6 shows the per-mil change in $\delta^{13}C$ values for $^{13/12}CO_2$ lines of interest for both direct absorption and 2f spectra using integrated absorbance, peak intensities and reference fitting as a function of the relative humidity (RH) from 0 % ($P_{H_2O} = 0$ Torr) to 100 % ($P_{H_2O} = 31.8$ Torr at a temperature of 303.2 K). The right hand part of table 2 gives the maximum allowable changes in RH to maintain ± 0.1‰ $\delta^{13}C$ precision.

Another way of looking at the results shown in the RH side in table 2 is that it gives the required measurement precision needed to correct the results so that the water-broadening error is ≤ 0.1‰. In all cases, if one can measure the RH of the sample to an accuracy of 2.5 % or better, one can correct the data to achieve ratio errors of <0.1 ‰. At low RH differences of less than ~2.5 %, this correction is not needed to obtain this tolerance in the measured ratio. Most studies have not considered the importance of this effect before, and hence neglecting the effects of H_2O–CO_2 collisions could result in relatively large errors in the CO_2 isotopic ratio. Removal of water vapor from sampled gases risks introducing kinetic fractionation of $^{13/12}CO_2$ isotopes.

Table 2. Required pressure and relative humidity stability to achieve 0.1 ‰ accuracy of the $\delta^{13}C$ value.

	Pressure stability[†]		RH stability	
	Direct absorption (Torr)	2f detection (Torr)	Direct absorption (%)	2f detection (%)
Peak absorbance	±0.237	±0.145	±3.1	±2.6
Integrated absorption	±0.375	±0.202	±11.9	±3.0
Reference fitting	±0.620	±0.149	±3.8	±2.5

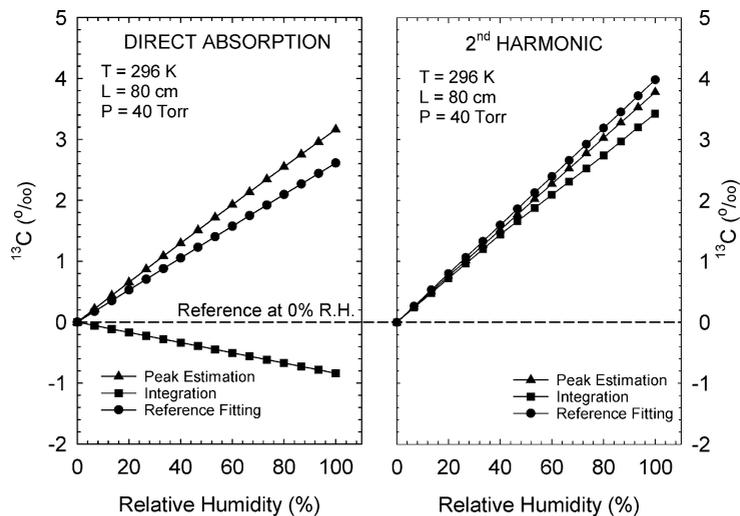[†]Pressure stability obtained for a 40 Torr operating pressure.

Figure 6. Calculation of the error induced on $\delta^{13}C$ by relative humidity change for three different concentration calculation methods.

4. Conclusion

Our current efforts to achieve accurate measurements of the stable carbon isotopic ratio, $^{13/12}CO_2$, using mid-IR tunable laser sources have been described. Two sensor architectures were presented for volcanic and atmospheric field applications.

A laser source availability problem prevented the QCL sensor from being tested in the field as initially planned. A further global analysis of isotopic line selection demonstrated that a dual laser source system is likely to achieve the best result in terms of $\delta^{13}C$ precision measurements. Fundamental limitations for a DFG-based isotopic ratiometer have been investigated. Temperature, pressure and RH stability requirements to achieve a $0.1\,\text{‰}\ \delta^{13}C$ accuracy were determined and showed that the effect of water vapor collisional broadening is not negligible.

References

[1] E.R.T. Kerstel. Isotope ratio infrared spectrometry. In *Handbook of Stable Isotope Analytical Techniques*, Vol. I, P.A. de Groot (Ed), pp. 759–787, Elsevier (2004).

[2] F. Capasso, C. Gmachl, R. Paiella, A. Tredicucci, A.L. Hutchinson, D.L. Sivco, J.N. Baillargeon, A.Y. Cho. New frontiers in quantum cascade lasers and applications. *IEEE J. Sel. Top. Quant.*, **6**, 931–947 (2000).

[3] D. Richter, D.G. Lancaster, F. Tittel. Development of an automated diode-laser-based multicomponent gas sensor. *Appl. Optics*, **39**, 4444–4450 (2000).

[4] A. Khorsandi, U. Willer, L. Wondraczek, W. Schade. *In situ* and on-line monitoring of CO in an industrial glass furnace by mid-infrared difference-frequency generation laser spectroscopy. *Appl. Optics*, **43**, 6481–6486 (2004).

[5] P. Maddaloni, G. Gagliardi, P. Malara, P. De Natale. A 3.5-mW continuous-wave difference-frequency source around 3 μm for sub-Doppler molecular spectroscopy. *Appl. Phys. B*, **80**, 141–145 (2005).

[6] P. Werle, A. Popov. Application of antimonide lasers for gas sensing in the 3–4 μm range. *Appl. Optics*, **38**, 1494–1501 (1999).

[7] S. Schilt, A. Vicet, R. Werner, M. Mattiello, L. Thévenaz, A. Salhi, Y. Rouillard, J. Koeth. Application of antimonide diode lasers in photoacoustic spectroscopy. *Spectrochim. Acta A*, **60**, 3431–3436 (2004).

[8] R.Q. Yang, C.J. Hill, B.H. Yang, C.M. Wong, R.E. Muller, P.M. Echternach. Continuous-wave operation of distributed feedback interband cascade lasers. *Appl. Phys. Lett.*, **84**, 3699–3701 (2004).

[9] J.L. Bradshaw, N.P. Breznay, J.D. Bruno, J.M. Gomes, J.T. Pham, F.J. Towner, D.E. Wortman, R.L. Tober, C.J. Monroy, K.A. Olver. Recent progress in the development of type II interband cascade lasers. *Physica E*, **20**, 479–485 (2004).

[10] C. Oppenheimer, P. Francis, M. Burton, A.J.H. Maciejewski, L. Boardman. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. *Appl. Phys. B*, **67**, 505–515 (1998).

[11] J.G. Blank, R.A. Brooker. Experimental studies of carbon dioxide in silicate melts: solubility, speciation, and stable carbon isotope behaviour. *Rev. Mineral.*, **30**, 157–186 (1994).

[12] J.W. Valley, D. Cole (Eds), *Stable Isotope Geochemistry*, Reviews in Mineralogy 43, Mineralogical Society of America, Washington D.C. (2001).

[13] P. De Natale, L. Gianfrani, G. De Natale. Optical methods for monitoring of volcanoes: techniques and new perspectives. *J. Volcanol. Geoth. Res.*, **109**, 235–245 (2001).

[14] D. Richter, M. Erdelyi, R.F. Curl, F.K. Tittel, C. Oppenheimer, H.J. Duffell, M. Burton. Field measurements of volcanic gases using tunable diode laser based mid-infrared and Fourier transform infrared spectrometers. *Opt. Laser Eng.*, **37**, 171–186 (2002).

[15] U. Willer, C. Bohling, P. Geiser, W. Schade. Infrared evanescent-field fiber sensor for in situ mapping of volcano gases. In *SPIE Proceedings of the Second European Workshop on Optical Fibre Sensors*, J.M. Lopez-Higuera, B. Culshaw (Eds), pp. 504–507, International Society for Optical Engeneering, Bellingham WA (2004).

[16] A. Castrillo, G. Casa, M. van Burgel, D. Tedesco, L. Gianfrani. First field determination of the $^{13}C/^{12}C$ isotope ratio in volcanic CO_2 by diode-laser spectrometry. *Opt. Express*, **12**, 6515–6523 (2004).

[17] G. Gagliardi, A. Castrillo, R.Q. Iannone, E.R.T. Kerstel, L. Gianfrani. High-precision determination of the $^{13}CO_2/^{12}CO_2$ isotope ratio using a portable 2.008-μm diode-laser spectrometer. *Appl. Phys. B*, **77**, 119–124 (2003).

[18] D. Weidmann, G. Wysocki, C. Oppenheimer, F.K. Tittel. Development of a compact quantum cascade laser spectrometer for field measurements of CO_2 isotopes. *Appl. Phys. B*, **80**, 255–260 (2005).

[19] M. Erdelyi, D. Richter, F.K. Tittel. $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements using a difference frequency-based sensor operating at 4.3 μm. *Appl. Phys. B*, **75**, 289–295 (2002).

[20] E. Normand, M. McCulloch, G. Duxbury, N. Langford. Fast, real-time spectrometer based on a pulsed quantum-cascade laser. *Opt. Lett.*, **28**, 16–18 (2003).

[21] T. Beyer, M. Braun, A. Lambrecht. Fast gas spectroscopy using pulsed quantum cascade lasers. *J. Appl. Phys.*, **93**, 3158–3160 (2003).

[22] D. Weidmann, F.K. Tittel, T. Aellen, M. Beck, D. Hofstetter, J. Faist, S. Blaser. Mid-infrared trace gas sensing with a quasi-continuous wave Peltier-cooled distributed feedback quantum cascade laser. *Appl. Phys. B*, **79**, 907–913 (2004).

[23] M. Troccoli, D. Bour, S. Corzine, G. Hofler, A. Tandon, D. Mars, D.J. Smith, L. Diehl, F. Capasso. Low-threshold continuous-wave operation of quantum-cascade lasers grown by metal organic vapor phase epitaxy. *Appl. Phys. Lett.*, **85**, 5842–5844 (2004).

[24] P. Bergamaschi, M. Schupp, G.W. Harris. High-precision direct measurements of $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$ ratios in atmospheric methane sources by means of a long-path tunable diode laser absorption spectrometer. *Appl. Optics*, **33**, 7704–7716 (1994).

[25] L.S. Rothman, D. Jacquemart, A. Barbe, D.C. Benner, M. Birk, L.R. Browne, M.R. Carleer, C. Chackerian, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner. The HITRAN 2004 Molecular Spectroscopic Database. *J. Quant. Spectrosc. Ra.*, **96**, 139–204 (2005).

[26] J.L. Sarmiento, N. Gruber. Sinks for anthropogenic carbon. *Phys. Today*, **55**, 30–36 (2002).

[27] G.D. Farquhar, J.R. Ehleringer, K.T. Hubick. Carbon isotopes discrimination and photosynthesis. *Ann. Rev. Plant Physiol. Mol. Biol.*, **40**, 503–537 (1989).

[28] D. Richter, A. Fried, B.P. Wert, J.G. Walega, F.K. Tittel. Development of tunable mid-IR difference frequency laser source for highly sensitive airborne trace gas detection. *Appl. Phys. B*, **75**, 281–288 (2002).

[29] D. Richter, A. Fried, C. Dyroff, J. Walega. Spectroscopic performance evaluation of optical fiber amplified coherent diode and fiber laser sources for difference frequency generation. Paper presented at the LACEA conference – Laser Applications in Chemical and Environmental Analysis, Annapolis, MD, 11 February (2004).

[30] Article online at: http://www.aerodyne.com/products/tdlwintel.html

[31] L. Rosenmann, M.Y. Perrin, J.M. Hartman, J. Taine. Diode-laser measurements and calculations of CO_2-line-broadening by H_2O from 416 to 805 K and by N_2 from 296 to 803 K. *J. Quant. Spectrosc. Radiat. Transfer*, **40**, 569–576 (1988).