Development of a 4.3 μm Quantum Cascade Laser based $^{13}CO_2/^{12}CO_2$ Isotopic Ratio Sensor

Damien Weidmann, Chad B. Roller, Frank K. Tittel, Robert F. Curl
Rice University, 6100 Main Street, Houston, TX, 77005, USA

Kiyoji Uehara
Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa, 223-8522, Japan, and
SORST project, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

Clive Oppenheimer
Department of Geography, Downing Place, Cambridge CB2 3EN, U.K.

Paolo DeNatale
Istituto Nazionale di Ottica Applicata (INOA), LENS, Via N. Carrara, 1, Sesto Fiorentino (FI), Italy

Abstract: High precision measurements of $^{13}CO_2/^{12}CO_2$ are needed in a wide range of fields that includes: atmospheric chemistry, volcano emission studies, combustion diagnostics, medical diagnostics and biology. Currently we are developing a compact, field deployable quantum cascade laser based sensor to perform real time measurements with a precision of $\delta \sim 0.1\,^0/_{00}$, using two channels absorption spectroscopy. The initial design of this analyser will target the prediction of potential volcanic activities, but can be useful in other applications.

A quantum cascade laser based $^{13}CO_2/^{12}CO_2$ isotopic ratio sensor can offer a valid alternative to the current standard technique for measuring isotopic ratios which is the Isotope Ratio Mass Spectrometry (IRMS). IRMS suffers from several drawbacks for specific applications: it is not field deployable, it does not perform real time measurements, it requires complex sample preparation and the sample destruction. Mid-infrared laser based spectrometers are attractive to measure $^{13}CO_2$ and $^{12}CO_2$ concentrations since they can target the strong fundamental vibrational absorption band of these two isotopes and thus provide high sensitivity. Lead salt laser based spectroscopy has already been demonstrated for $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements (Mc Mannus et al., 2002), but this instrument requires liquid nitrogen cooling. The application of a Difference Frequency Generation (DFG) based sensor has also been reported (Richter et al., 2002 ; Erdélyi et al., 2002). The development of a pulsed quantum cascade laser instrument would take advantage of a compact and robust spectroscopic source that can be operated at quasi-room temperature. QCL based sensors provide also the high selectivity needed in isotope absorption line discrimination, as well as high sensitivity and real time measurements capabilities (Kosterev et al., 2002).

For this work, a thermoelectrically cooled pulsed single frequency quantum cascade laser will be used. This laser operates at 4.3 μm, where the P-branch of $^{12}CO_2$ overlaps the R-

branch of $^{13}CO_2$ of the 00^01-00^00 transition. The instrument sensitivity depends on the judicious choice of appropriate absorption lines. The criteria for this selection are: 1) two similar intense absorption lines are needed. Different intensities in absorption can be compensated by using a dual path length absorption spectrometer. 2) The intensity of the two selected transitions must have nearly the same temperature dependence. The closer the two transition low energy levels correspond, the more insensitive to temperature the measurements will be. 3) Spectral interference effects by other atmospheric compounds must be avoided and 4) the two selected lines must be close enough in frequency to be resolved by the available scan range of the laser frequency. *Erdélyi et al.* (2002) chose to work with a pair of lines at 2299.642 cm^{-1} for $^{12}CO_2$, and 2299.795 cm^{-1} for $^{13}CO_2$, respectively. These two lines have nearly the same intensity and the needed temperature stability for a $0.01^0/_{00}$ delta precision is ~ 6 mK. *McMannus et al.* (2002) chose the line pair at 2314.304 cm^{-1} and 2314.408 cm^{-1} requiring a less stringent condition for the temperature stability (0.250 mK) and used a two different pathlengths approach (Uehara et al., 2001) because of a ratio of 46 between the two intensities. Our choice for the optimum line pair is 2311.105 cm^{-1} for $^{12}CO_2$ and 2311.399 cm^{-1} for $^{13}CO_2$. The intensity ratio is 97, so that a two different path lengths approach is necessary. But the unique advantage of this line pair is that concentration measurements will be insensitive to temperature because the two lower state energy levels of the transitions are nearly equal.

To realize an absorption cell that can provide conveniently two different path lengths with a 1 to100 ratio, a 36 m astigmatic Herriott cell (Mc Mannus et al., 1995) will be modified. The entrance window is removed and a short path length cell is added instead. The exit window of the short path length cell is also the coupling beamsplitter of the long path cell, as depicted on Fig.1.

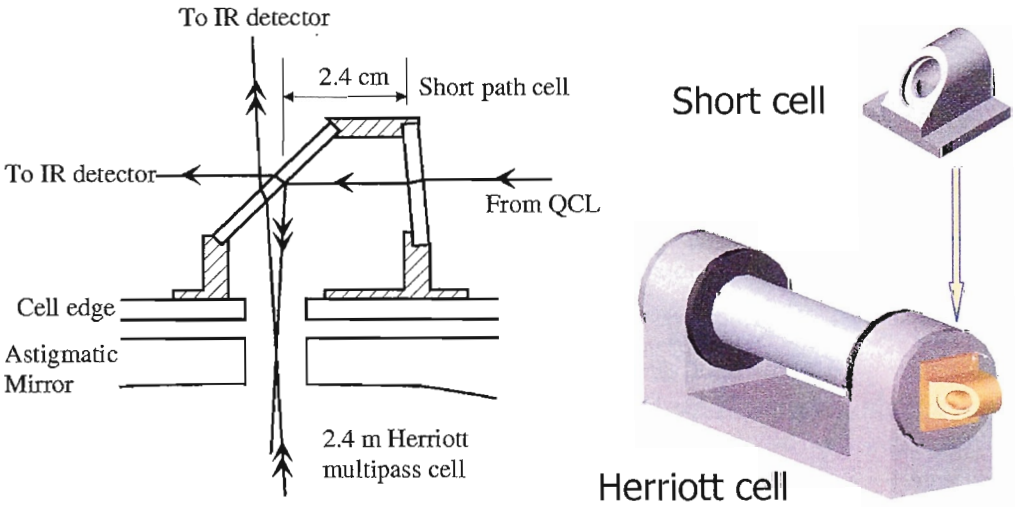

Figure 1: Implementation of a short path length cell to an astigmatic Herriott cell to provide a two unequal path length absorption system is shown. The QCL beam coming goes through the short path cell. The exit window of the short path cell serves also the Herriott multipass cell coupling beamsplitter. The reflected beam is sent to the Herriott and exits from it after 10 passes.

The proposed sensor design with a footprint of 30x45 cm is depicted in the Fig.2. It will be placed in an enclosure so that the sensor can operate under a dry nitrogen atmosphere. The QCL is in a vacuum tight housing with an internal lens for beam collection (Kosterev et al., 2002). Two thermoelectrically cooled mid-infrared detectors available from Vigo Systems are used so that the complete isotopic ratio instrument can be operated non-cryogenically.

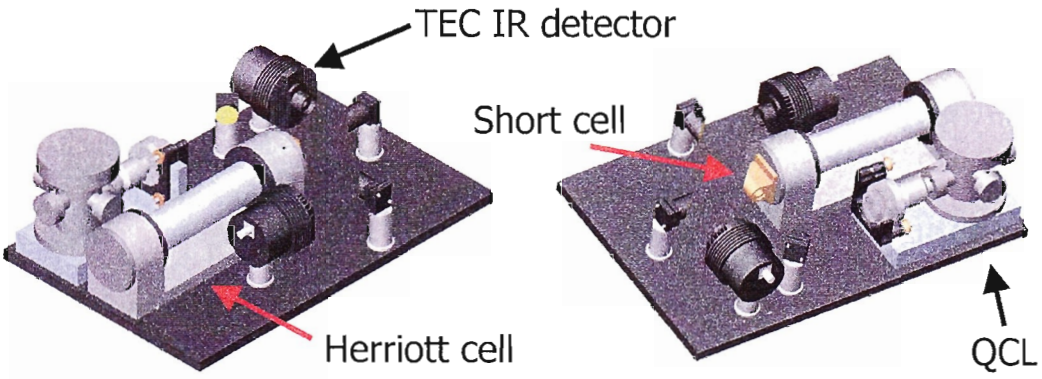

Figure 2: Schematic of the QCL based $^{12}CO_2/^{13}CO_2$ isotopic ratio sensor.

We reported the design issues and development of new quantum cascade based sensor architecture which benefits from previous feasibility studies performed with a DFG based isotopic ratio analyser. (Richter et al., 2002 ; Erdélyi et al., 2002). The line selection allowing temperature insensitive field measurements of carbon dioxide isotopic ratios to be made was discussed.. The instrument is compact and does not require liquid nitrogen cooling to operate. It is specifically designed for volcanic gas emission studies..

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