

Measurement of ^{13}C and ^{18}O Ratio in CO_2 using Quantum Cascade Laser based Tunable Absorption Spectroscopy

Ponkanok Nitzsche¹, Cem Dinc¹, Jürgen Wöllenstein^{1,2}, Katrin Schmitt^{1,2}

1 Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Köhler-Allee 102, 79110 Freiburg, Germany

*2 Fraunhofer Institute for Physical Measurement Techniques (IPM), 79110 Freiburg, Germany
Tel.-Nr.: +49 761 203-96808, E-Mail: ponkanok.nitzsche@imtek.uni-freiburg.de*

Summary:

We present a spectroscopic approach for measurements of ^{13}C and ^{18}O isotopic ratio in carbon dioxide (CO_2) gas using a quantum cascade laser (QCL). A narrow linewidth mid-infrared QCL is continuously scanned across three absorption lines of CO_2 near 2310 cm^{-1} including $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ isotopes. The simultaneous detection of three spectral lines permits the determination of simple concentration ratios (R^{13} and R^{18}) in atmospheric CO_2 . With an averaging time of about 10 s both R^{13} and R^{18} reach a precision of 0.2 ‰ and 0.1 ‰, respectively.

Keywords: Gas Sensors, Isotopic Composition Analysis, Optical Measuring System, Absorption Spectroscopy, Quantum Cascade Laser

Motivation

Since atmospheric CO_2 is an important indicator for many climate change researches, an attention focusing on fluxes of CO_2 between the different sources and sinks have been growing. The studies of stable CO_2 isotope ratios offer the possibilities to identify such CO_2 pools via isotopic fingerprint [1]. Traditionally, the stable isotopes are measured by means of sample preparation and isotope ratio mass spectrometry (IRMS). An alternative method for this measurement is tunable laser absorption spectroscopy (TLAS). In contrast to IRMS, TLAS permits a real-time measurement of the isotopic ratio with sufficient precision down to $<0.3\text{ ‰}$ at 1 s averaging time for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ [2].

Spectral Absorption Lines

A mid-infrared, tunable QCL near 2310 cm^{-1} is continuously tuned across three spectral absorption lines of CO_2 isotopes. These spectral lines are chosen in such a way that there is a sufficiently high absorption line strength and low interference with other atmospheric gases. Moreover, there must be at least one absorption line of each isotopes of interest within the laser tuning range and all measuring isotopes should possess a similar absorption line intensity to avoid any detector saturation.

The spectroscopic information, including the vacuum wavenumber ($\tilde{\nu}_0$), Low-state energy (E_L), spectral line intensity ($S(T_0)$), of the selected $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ isotopes

are shown in Table 1. The simulated absorption spectrum of these lines using the HITRAN database [3] shows that the measurement must be performed in a negative pressure chamber to minimize line overlapping caused by pressure broadening. In addition, the low state energies of these spectral lines are considerably different, which implies that the isotope ratio measurement is sensitive to temperature variation [4].

Tab. 1: Spectroscopic data of the selected lines

Isotopes	$\tilde{\nu}_0$ in cm^{-1}	E_L in cm^{-1}	$S(T_0)$ in $\text{cm}^{-1}/\text{mol}\cdot\text{cm}^{-2}$
$^{12}\text{C}^{16}\text{O}_2$	2310.002	1454.97	$4.86\cdot 10^{-21}$
$^{13}\text{C}^{16}\text{O}_2$	2310.347	639.63	$6.72\cdot 10^{-21}$
$^{16}\text{O}^{12}\text{C}^{18}\text{O}$	2310.206	278.28	$4.52\cdot 10^{-21}$

Experimental Setup

Figure 1 depicts a schematic of an optical configuration of the system. A temperature controller and current driver (PTC5K-CH and QCL1000 Lab, *Wavelength-Electronic*) are used with a function generator to control the QCL (HHL680, *AlpesLaser*) and tune the laser with a frequency of $f_{\text{mod}} = 1\text{ Hz}$. An optical isolator is employed to protect the QCL from back-reflected light. The first split beam is steered into a 10 cm-long hermetically sealed spectroscopic cell filled with a known concentration of CO_2 , which is applied for the calibration of QCL-wavelength. The second beam propagates into

the measurement chamber with an optical path length of $L_{\text{cham}} = 109 \pm 1$ cm. Two photodetectors (PVI-3TE-5, *Vigo System*) are used to detect the optical signal, simultaneously.

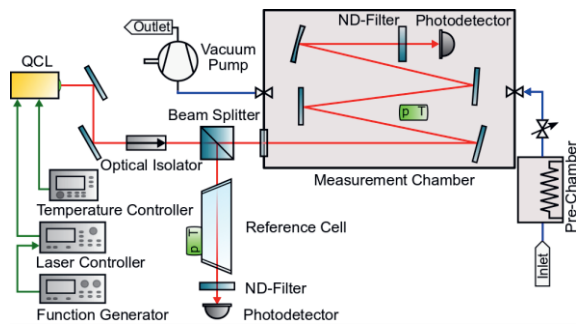


Fig. 1: Schematic sketch of the experimental set-up.

With a diaphragm vacuum pump and a fine-metering valve, the pressure inside the chamber can be reduced and regulated to $p_{\text{cham}} = 100$ mbar. A pre-chamber and measurement chamber are temperature-regulated and heat isolated. A temperature and pressure sensor are integrated inside the measurement chamber.

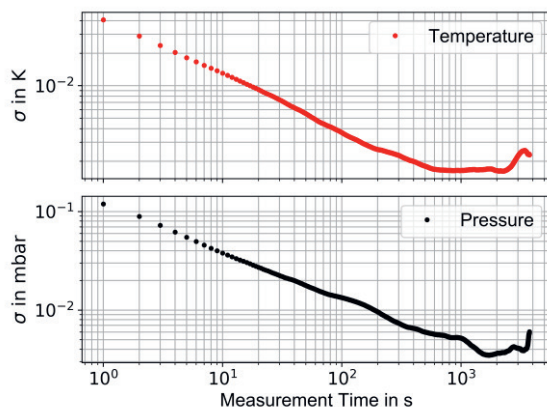


Fig. 2: Allan plots for temperature and pressure measured inside the measurement chamber.

The Allan plot of the time series of the recorded temperature and pressure inside the chamber are shown in Figure 2. The chamber conditions can be controlled with a precision of $\Delta T \sim 13$ mK and $\Delta p \sim 0.04$ mbar after an integration time of 10 s.

Measurement Results

To verify the feasibility and stability of the system, measurement with a constant 396 ppm CO_2 concentration in synthetic air was performed over 1000 s. With a piecewise baseline-correction and curve fitting of Voigt profile, the transmitted spectrum was defined thus, each isotope ratio as $R^{13} = [^{13}\text{C}^{16}\text{O}_2]/[^{12}\text{C}^{16}\text{O}_2]$ and $R^{18} = [^{16}\text{O}^{12}\text{C}^{18}\text{O}]/[^{12}\text{C}^{16}\text{O}_2]$. Employing the Allan Deviation method, the minimum deviation was reached after ~ 10 s, which is illustrated in Figure 3. With this averaging time, the system can achieve a precision of 0.2 ‰ and 0.1 ‰ for R^{13}

and R^{18} , respectively. In order to determine the accurate concentrations and isotopic ratios of CO_2 , the system must be calibrated.

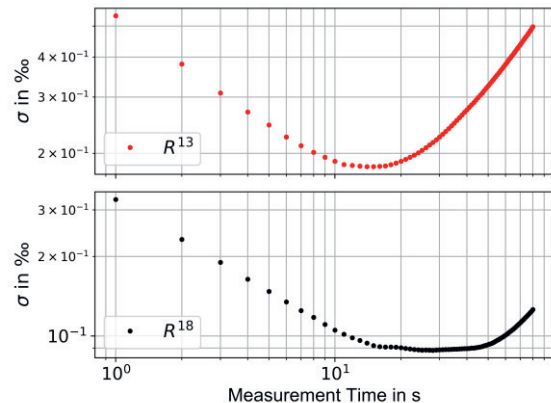


Fig. 3: Allan plot for both concentration ratios R^{13} (above) and R^{18} (below).

Conclusion

In this letter, we present the design and construction of QCL-based tunable absorption spectroscopy for an analysis of CO_2 isotopic compositions. A precise control of temperature and pressure is achieved to 13 mK and 0.04 mbar, respectively. At an integration time of about 10 s the detection limits for R^{13} and R^{18} were estimated by the Allan method as 0.2 ‰ and 0.1 ‰, respectively.

Acknowledgements

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