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Detection of Stable Isotopes of CO_2 using Quantum Cascade Laser based Absorption Spectroscopy

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Summary:
A spectroscopic approach to measure ^{13}C and ^{18}O isotopic ratios in carbon dioxide (CO_2) gas using a quantum cascade laser (QCL) is presented. The measurement was performed near 2310 cm^{-1}, where three absorption lines of CO_2 including $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$ isotopes are located. 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 20 s both R^{13} and R^{18} reached a precision (1σ) of 0.08 ‰ and 0.01 ‰, 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, the 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 possibility to identify such CO_2 pools via the 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. Tuzson et al. showed a precision of 0.03 ‰ and 0.05 ‰ for R^{13} and R^{18} after an integration time beyond 100 s [2].

Spectral Absorption Lines

A mid-infrared, tunable QCL was continuously tuned across three spectral absorption lines of CO_2 isotopes. These spectral lines were 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 isotope of interest within the laser tuning range. All measured 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) and spectral line intensity ($S(T_0)$) of the selected $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$ isotopes are shown in Table 1 [3]. To minimize line overlapping caused by pressure broadening, the measurement must be performed in a negative pressure condition. 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 [3].

Isotopes	$\tilde{\nu}_0$ in cm^{-1}	E_L in cm^{-1}	$S(T_0)$ in $cm^{-1}/mol\cdot cm^{-2}$
$^{12}C^{16}O_2$	2310.002	1454.97	$4.86\cdot 10^{-21}$
$^{13}C^{16}O_2$	2310.347	639.63	$6.72\cdot 10^{-21}$
$^{16}O^{12}C^{18}O$	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 are used with a function generator to control the QCL (HHL680, AlpesLaser) and tune the laser with a frequency of f_{mod} = 100 Hz. An optical isolator is employed to protect the QCL from back-reflected light. A 10 cm long, hermetically sealed spectroscopic cell filled with a known concentration of CO_2 was applied for the calibration of QCL wavelength. The optical path length of the measurement chamber was L_{cham} = 109±1 cm. Two photodetectors (PVI-3TE-5, Vigo System) were used to detect the optical signals simultaneously. With a diaphragm vacuum pump and a fine-metering valve, the pressure inside the chamber can be reduced and regulated to about

100 mbar. Pre-chamber and measurement chamber were temperature-regulated and heat isolated. A temperature and pressure sensor were integrated inside the measurement chamber.

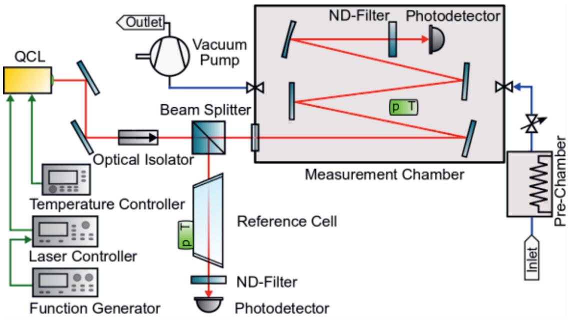

Fig. 1: Scheme of the experimental set-up.

Time series of temperature and pressure inside the chamber were measured. The Allan-deviation of the recorded temperature and pressure were calculated. A precision (1σ) of 9 mK and 0.03 mbar after an integration time of 20 s were achieved.

Measurement Results

396±8 ppm CO_2 gas in synthetic air was measured over 500 s. The transmission spectrum was defined as shown in Figure 2 (top). The black line represents the measured data after baseline correction. A HITRAN simulation [3] with the defined concentration and measured ambient conditions is illustrated with the red line. Figure 2 (bottom) shows their residual.

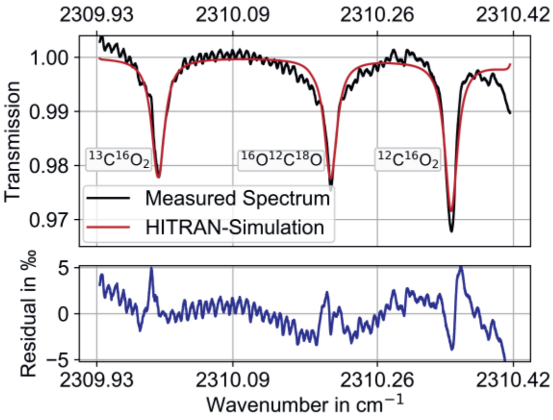

Fig. 2: Transmission spectrum of measured and simulated data and their residual.

The concentration of each isotope was calculated thus, the ratio as $R^{13} = [^{13}C^{16}O_2]/[^{12}C^{16}O_2]$ and $R^{18} = [^{16}O^{12}C^{18}O]/[^{12}C^{16}O_2]$. By employing the Allan deviation method, an optimum averaging time of 20 s can be derived, as illustrated in Figure 3. With this integration time, the system can achieve a precision (1σ) of ~0.08 ‰ and ~0.01 ‰ for R^{13} and R^{18}, respectively. However, in order to determine the actual and accurate concentrations and isotopic ratios of CO_2, the system must be calibrated.

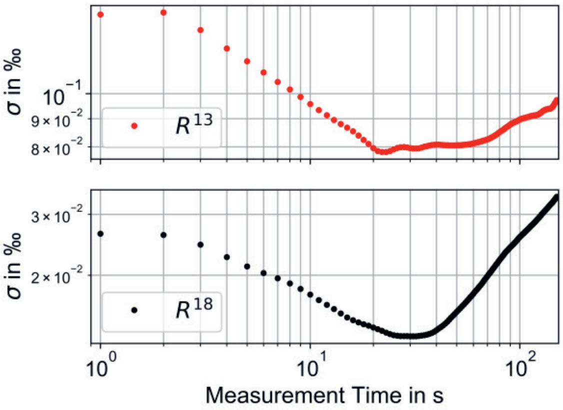

Fig. 3: Allan plot for both concentration ratios R^{13} (above) and R^{18} (below).

Conclusion

In this study, we present the design and construction of QCL-based tunable absorption spectroscopy for an analysis of CO_2 isotopic compositions. After an integration time of 20 s the temperature and pressure inside the measurement chamber show a sufficient stability. The detection limits (1σ) for R^{13} and R^{18} were estimated by the Allan deviation method as ~0.08 ‰ and ~0.01 ‰, respectively.

Acknowledgements

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