Quantum cascade laser-based tunable laser absorption spectroscopy for the detection of stable isotopes of CO$_2$

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Abstract

We present a conceptual design and results on the determination of three stable carbon dioxide (CO$_2$) isotopologues. The isotopic analyses have been performed using a quantum cascade laser (QCL)-based tunable laser absorption spectroscopy (TLAS) setup. A mid-infrared (MIR), tunable and narrow linewidth QCL is used as a light source to probe absorption lines at around 4.3 µm. Tuning the QCL in this selected region permits the simultaneous detection of three absorption lines of CO$_2$ isotopologues including $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{16}O^{12}C^{18}O$. The result shows that the wavelength conversion method using the reference gas cell is well-suited for this technique.

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

Motivation

Measuring and monitoring of stable isotopic compositions of carbon dioxide (CO$_2$) play a crucial role in many research and industry fields such as in ecology [1], atmospheric sciences [2], breathe gas analysis [3] and combustion processes [4]. Since every photosynthesis and respiration processes of any biological systems in this planet influence unique changes in isotopic compositions, analysis of the stable isotopic fractionation of CO$_2$ in atmosphere provides information about this biosphere-atmosphere exchange process. This could help us to understand more about the photosynthesis process and the discrimination against the heavier isotopes such as ^{13}C- or ^{18}O-isotope by all plants [5].

Due mainly to anthropogenic activities including land use change, burning of biomass and fossil fuel, and modern industrial structure, large amount of greenhouse gases has been emitted into the atmosphere in last few decade [6]. This causes a shift in the balance of biogeochemical processes which are closely associated with an effect of global warming [7]. The study of stable isotope ratios of carbon in CO$_2$ enable the investigation of the climate in the past and understanding the effects of the external forcing to the climatic system [8], thus allow an improvement of the climate model and prediction of future climate conditions [9], [10]. Moreover, studying of currently change of the natural isotopic ratio can help to identify and quantify sources and sinks for atmospheric trace gases [8].

In this contribution, an optical spectroscopic sensing technology based on the so-called tunable laser absorption spectroscopy (TLAS) [11] using a quantum cascade laser (QCL) as a light source is proposed in order to measure the isotopic ratio of atmospheric CO$_2$. The underlying theoretical principle is presented. The criteria and methods considering for the line selection will be discussed. Based on the selected absorption lines the mid-infrared, tunable QCL around 4.3 µm is chosen. The experimental setup for the detection of CO$_2$-isotopic compositions is built and characterized. At last the detected signal and evaluated results are discussed.

Theoretical background

In convention, the expression of an isotopic signature or a ratio of stable isotopes is given in parts per thousand (per mil, ‰). The delta δ notation is often used to describe the isotopic abundance obtaining by comparison of isotope ratio of a sample (R_{sample}) and a standard or reference material ($R_{standard}$) [12]. As example, the abundance of ^{13}C-isotope in CO$_2$ gas yields as:

$$\delta^{13}C(CO_2) = \left(\frac{^{13}R(CO_2)_{sample}}{^{13}R(CO_2)_{standard}} - 1 \right) \cdot 1000‰ \quad (1),$$

where

$$^{13C}R(CO_2) = \frac{[^{13}CO_2]}{[^{12}CO_2]}$$
$$= \frac{\text{abundance of rare isotope}}{\text{abundance of abundant isotope}} \quad (2).$$

The reference material or isotopic standard is referred to VPBD-(Vienna Pee Dee Belemnite) scale. The standard value of ^{13}C-isotopic ratio is given as $^{13}R(CO_2)_{standard\,(VPDB)} = 0.01180$, as determined from the measurement of NBS 19 calcite [13].

Due to an individual structure and composition of each isotopologue of any molecules their absorption spectrum shows a specific profile. Since the variation of isotopic ratio in atmospheric surrounding is very small, mid-infrared laser absorption spectroscopy is an appropriate technique used to determine the stable isotope abundances of atmospheric CO_2. By ramping the injected laser current with a sawtooth or triangle signal, the laser's wavelength is probed over one or more absorption lines of interest, thus adequate absorption lines of CO_2 isotopologues must be carefully selected. The transmitted laser intensity is detected with a photodetector after passing through the measuring gas as a signal. The Lambert-Beer law, Eq. (3) describes the relationship between the transmitted light, $I_T(\lambda)$ after propagating through the medium with an optical path length of L and the material properties including the absorption coefficient, $\alpha(\lambda)$

$$I_T(\lambda) = I_0(\lambda) \cdot e^{-\alpha(\lambda) \cdot L} \quad (3).$$

Here, λ denotes the wavelength and $I_0(\lambda)$ the initial light intensity at particular wavelength. Since the measurement sensitivity depends on the absorption path length, a long gas cell or a multi-pass cell can be used to improve the limit of detection of the setup. However, the well-known limitation of this TLAS-technique is optical interference fringes rising from the Fabry-Pérot etalons between reflecting and scattering surfaces of the optical components [14].

Lines selection

Since we would like to spectroscopically measure the ratio of CO_2-isotopologues, well-separated absorption lines of each isotope must be selected. In the experimental design the

selection of absorption lines detected by TLAS is typically based on two main criteria: (1) high absorption line strength and (2) a minimal interference with other gas lines in the measuring environment. In mid-infrared the absorption line strength of CO_2 is almost two orders of magnitude larger than in near-infrared range, as illustrated in Figure 1. The abundance weighted line intensity of four CO_2 isotopologues from 1.5 µm to 5 µm is simulated applying an appropriated line list from HITRAN2016-database [15] and the simulation is depicted in Figure 1.

In order to reach a sufficient absorption line strength, especially for the less abundant isotopologues, a mid-infrared light source in 4.3 µm range is used in this TLAS-measurement. Moreover, there is sufficiently low interference with bother atmospheric gas spectra in this wavelength range, since the measurement should be performed in the atmospheric surrounding.
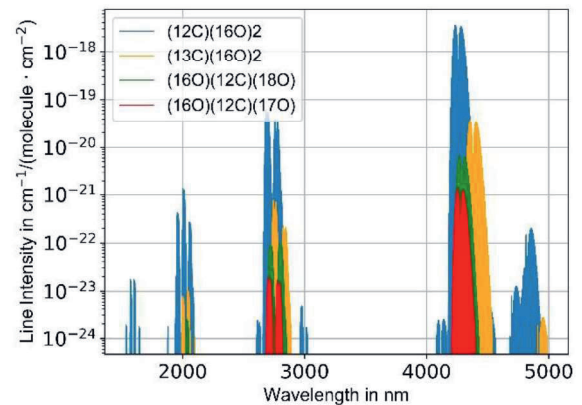

Fig. 2: The simulated line strength S_0 from 1.5 µm to 5 µm of four different isotopic compositions of CO_2 using HITRAN2016-database [15]. Blue, yellow, green and red lines represent the weighted line strength of $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{18}O$ and $^{16}O^{12}C^{17}O$, respectively.

However, further criteria must be considered when selecting the absorption lines for the spectroscopic detection of the isotopologues. In one tuning range of the laser's wavelength, there must be at least one absorption line for each isotopologue of interest so that one can simultaneously quantify their concentration and thus the ratio. As the weighted line strength of the most abundance isotope, Figure 2: blue line, is considerably higher than those with minority abundance, the absorption line of all measuring isotopologues should possess a similar line strength to avoid any detector saturation.

A suitable tuning range have been found, in which the spectrum of at least three different CO_2-isotopologues with comparable absorption line strength are located. The absorption spectra of four CO_2-isotopologues from 4328.1 nm to 4329.3 nm with 407 ppm CO_2 concentration which comprises 98.4204% $^{16}O^{12}C^{16}O$ (blue), 1.1057% $^{16}O^{13}C^{16}O$ (yellow), 0.39471% $^{16}O^{12}C^{18}O$ (green) and 0.0734% $^{16}O^{12}C^{17}O$ (red) are simulated and illustrated in Figure 2. According to HITRAN-database [15], this composition is referring to the natural abundance of CO_2 isotope in atmosphere.
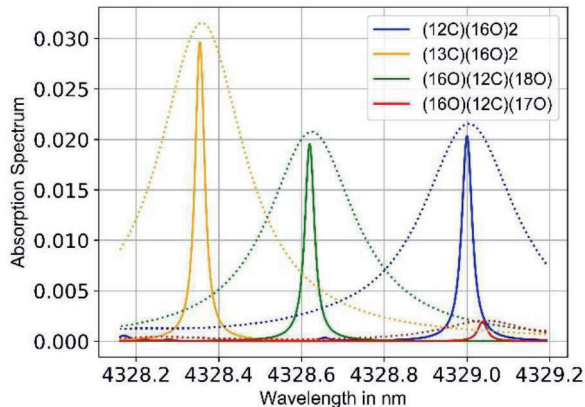

Fig. 2: *The simulated absorption lines of four CO_2-isotopologues from 4328.1 nm to 4329.3 nm. The solid lines and dashed lines represent the simulation with gas pressure of 100 mbar and 1 bar, respectively [15].*

The absorption path length is set to 100 cm and a temperature of 298 K. The absorption spectra are simulated with two gas pressures 100 mbar and 1 bar represented by solid and dashed lines, respectively. To minimize problems caused by pressure broadening and h the absorption line overlap, the measurement must be performed in a negative pressure chamber of 100 mbar. The absorption line of $^{16}O^{12}C^{17}O$ (red line) is however completely overlapped with the line of $^{12}CO_2$, thus the spectrum of $^{16}O^{12}C^{17}O$ in the measurement is not expected to be detected under this condition. In the selected spectral region, one can simultaneously measure three absorption lines with line center positions at 4328.354 nm, 4328.619 nm and 4329.000 nm corresponding to isotopologues $^{13}CO_2$, $^{16}O^{12}C^{18}O$ and $^{12}CO_2$, where $^{13}CO_2$ and $^{12}CO_2$ are $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$, respectively.

Experimental Setup

Figure 3 (Top) depicts a scheme of experimental setup consisting of an optical system, control modules, signal acquisition module and gas flow systems. The image of the experimental setup is shown in Figure 3 (Bottom).
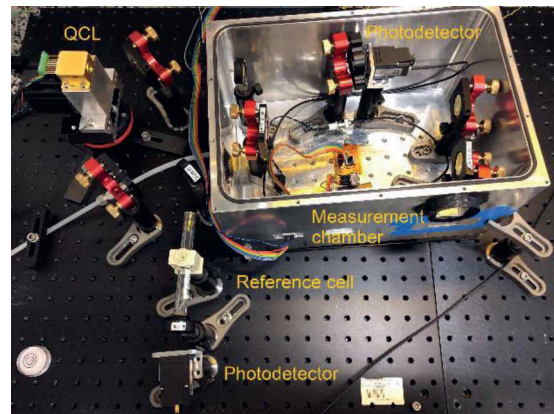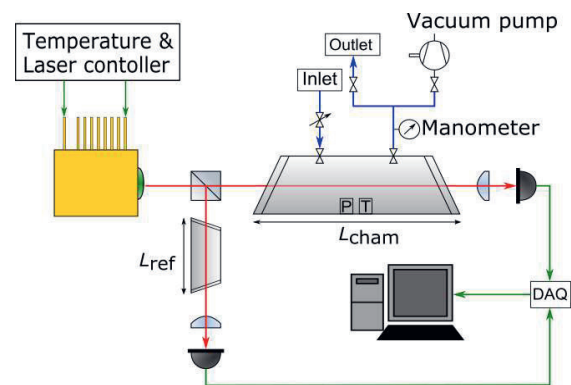

Fig. 3: *Top: a schematic sketch of the experimental set-up for the QCL-based TLAS measurement. Bottom: photograph of the optical configuration of the setup.*

The QCL (HHL680) from *Alpes Lasers* in HHL-package with a collimation lens and a TEC-cooling unit is controlled by a laser driver (QCL1000LAB) and a temperature controller (PTC5K-CH) from *Wavelength Electronics*. Connecting a function generator (WaveStation2012) from *LeCroy* with the laser driver enables the laser's wavelength to be tuned around 4.32 µm with a sawtooth signal and a ramp frequency of f_{ramp} = 1 Hz. The beam splitter (BSW510) from *Thorlabs* splits the laser beam in two beams, where the first beam propagates through a hermetically sealed spectroscopic gas cell filled with 98.4 % $^{16}O^{12}C^{16}O$, 1.1 % $^{16}O^{13}C^{16}O$ and 0.5 % N_2 with a total pressure of p_{ref} = 10 Torr or 13.332 mbar which acts as a reference cell. The concentration of the filled gases and the condition in the reference cell are specified from the manufacturer, *Wavelength References*. The cell has an optical path length of 10 cm. The reference signal is detected using a photodetector (PVI-3TE-5) from *Vigo System*

with a neutral density filter from *Thorlabs* (NDIR20B).

The second beam propagates through the measured gas chamber, which tilted in two dimensions reducing the interference fringes. With three gold coated mirrors (PF10-03-M01) and a concave mirror (CM254-150-M01) with focal point of 150 mm from *Thorlabs* the laser beam is directed and reflected back and forth inside the chamber to obtain a total optical path of L_{cham} = 107±2.5 cm. The absorption signal is likewise detected with Vigo-photodetector and a neutral density filter (NDIR30B). To reduce the gas pressure inside the chamber to $p_{cham} \approx$ 100 mbar, a diaphragm vacuum pump (N840.3 FT.18) from *KNF* with a turn valve at the gas outlet and a fine-metering valve at the gas inlet are connected with the chamber to regulate the gas flow and pressure. Inside the measuring chamber a temperature sensor (SHT31-ARP-B) from *Sensirion* and pressure sensor (HSCMAND001BAAA5) from *Honeywell* are integrated. The detected signals including applied laser current and temperature, gas pressure and temperature in the chamber, photodetector signals and the modulation signal from the function generator are acquired using *National Instrument* DAQ cards (NI9205 and NI9239) with a sampling rate of 1 k and 25 k samples per second, respectively.

Results and discussion

According to the QCL's data sheet, the laser's temperature should be set to - 15 °C in order to reach the selected tuning range from 4328.1 nm to 4329.3 nm. In the experiment, we use the function generator to periodically change the laser's current at the chosen temperature. To ensure that the laser's wavelength alters in the desired range, we firstly observe the signal from the reference cell with an oscilloscope and compare it with the simulated spectrum to define the accordant voltage range for the sawtooth ramp. The frequency of the ramp is set to 1 Hz.

The reference signal is used not only for the determination of the set-modulation voltage but also for the calibration of laser's emitted wavelength. However, the reference signal must be recorded synchronously with the TLAS-signal so that the frequency calibration is likewise valid for the TLAS-signal. The reference signal as a function of counts is illustrated in Figure 4. The blue line is an averaged signal using a set of 20 time-series raw data corresponding to 20 s. The red curve refers to the curve fit using a self-written algorithm in Python-program.
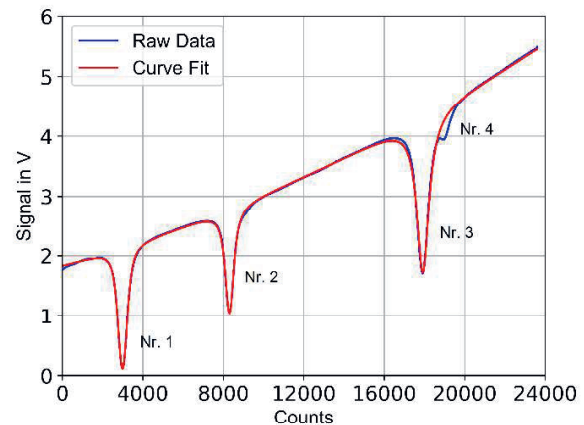

Fig. 4: *The measured reference signal as a function of counts. The blue and red curves represent the average raw data and the curve-fit of it, respectively.*

For the comparison, the reference signal has been simulated. The gas mixture inside the reference cell consisting of 98.4 % $^{16}O^{12}C^{16}O$, 1.1 % $^{16}O^{13}C^{16}O$, as told in the data sheet and the natural abundance for another two isotopologues is applied for the simulation. The simulated absorption spectrum is shown in Figure 5. The temperature is set to the averaged room temperature measured during the experiment T = 298.09±0.01 K and the pressure is set to p_{ref} =10 Torr.
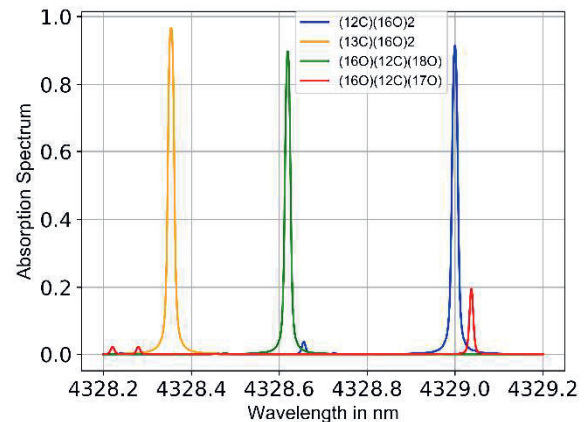

Fig. 5: *The simulated reference signal of four isotopes using the HITRAN-database [10]. The temperature is set to the averaged room temperature T = 298.09±0.01 K.*

Comparing the measured reference signal and those from the simulation, four absorption spectra of four different isotopologues can be identified. The spectrum of $^{12}CO_2$ and $^{13}CO_2$ masked as Nr.1 and Nr.3 can be clearly detected. The spectrum of $^{16}O^{12}C^{18}O$ (Nr.2) and $^{16}O^{12}C^{17}O$ (Nr.4) are not expected, however both spectra are detected in the measured signal. Even though the manufacturer can only confirm the filling of two isotopes with specific

concentrations, using this spectroscopic method another isotope of CO_2 in this reference gas cell can be identified.

Three center positions from the fitting parameters of the Nr.1 to Nr.3-spectrum have been taken for the calibration of the laser's wavelength. The center positions of the same spectra are likewise taken from the simulation in the unit of nm. Employing these two sets of data, a conversion-function is calculated as:

$$\lambda = a \cdot \text{counts}^2 + b \cdot \text{counts} + c \qquad (4).$$

Here, λ is the wavelength in nm and a, b, c-coefficients are - 7.0058×10^{-13}, 5.7956×10^{-5} and 4.3282×10^3, respectively. To gain a higher accuracy in frequency conversion a polynomial with higher degree can be used. For this application a quadratic polynomial is sufficient.

In order to measure the isotopes of atmospheric CO_2, the pressure in the measuring chamber is reduced to about 100 mbar using the diaphragm vacuum pump. In this measurement, we use the laboratory-air as a test gas. The parallel TLAS-signal is detected with the sampling rate of 25 k samples per second. To calculate the averaged signal, 20 periodical data-series are employed and the averaged signal against the number of counts is illustrated in Figure 6.
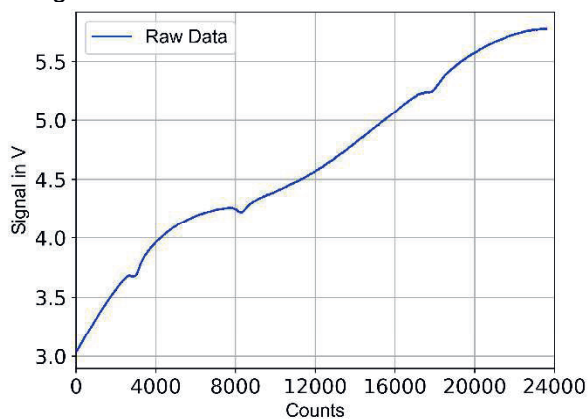

Fig. 6: *The averaging of 20 data-series of TLAS-signal as a function of counts. The gas pressure and temperature in the measuring chamber is measured as* p_{cham} = 99.5±0.3 mbar and T = 298.09±0.01 K.

The pressure and temperature inside the chamber is monitored using the integrated sensors during the measurement. The average values of the pressure and temperature over the 20 s is determined as p_{cham} = 99.5±0.3 mbar and T = 298.09±0.01 K, respectively.

The signal shows three absorption spectra of the isotopes as expected, however the baseline comprises strong interference fringes, which causing a difficulty in determination of the baseline. The signal around the position of absorption lines has been masked in order to determine a best-fit baseline function with a high-order polynomial function. Divided the averaged signal with this baseline function to remove the baseline from the signal, we obtained the transmittance. The negative natural logarithm of the transmittance, $-\ln(I/I_0)$ is calculated and shown in Figure 7 as a blue line. Employing the conversion-function Eq. (5) to convert the counts number to wavelength, the transmittance can be plotted as a function of wavelength.
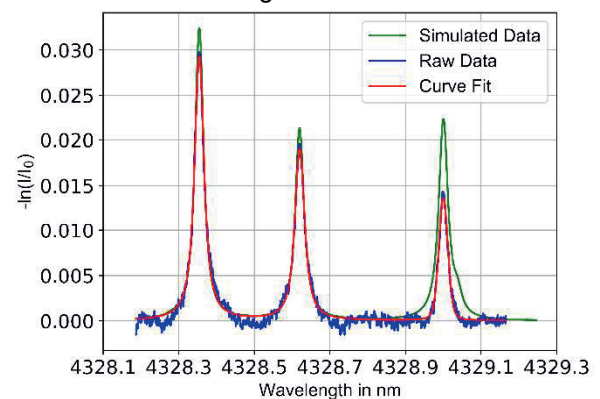

Fig. 7: *The negative natural logarithm of the transmittance as a function of wavelength. Green, blue and red lines represent the simulated, raw data and the curve fit of the raw data.*

A best fit-function of the transmittance spectrum has been computed using Voigt-profiles and illustrated as red line in Figure 7. The simulation of the negative logarithm of transmittance is likewise depicted as the green curve. The results show that the wavelength conversion method using information from the reference spectrum and simulation is sufficiently accurate for the calibration of the laser's frequency.

The first two spectra of the curve-fit corresponding to $^{13}CO_2$ and $^{16}O^{12}C^{18}O$ are in a well agreement with the simulation spectrum. However, the spectrum of $^{12}CO_2$ shows a deviation from the simulation. The calculated concentration obtained from this spectrum is thus not matching with the expected value, likewise the isotopic ratio. We suppose that the non-linearity of the detector could be a reason for this deviation. Further investigation of the system is required.

Summary and outlook

In this letter, the conceptual design and construction of an analysis of CO_2-isotopic

compositions using the so-called QCL-based tunable absorption spectroscopy have been presented. Three absorption lines of stable isotopologues, $^{13}CO_2$, $^{16}O^{12}C^{18}O$ and $^{12}CO_2$ in 4.3 μm range is selected. To reduce the pressure broadening effect, the measurement is performed in an under-pressure gas chamber. For the calibration of the laser's frequency, the reference gas cell is employed. The result confirms that the wavelength conversion for the TLAS-signal using the reference cell is well-matched with the simulation.

However, further works must be undertaken. These include the calculation of the CO_2-isotopic ratio, the evaluation of the long-term stability such as the thermal and pressure stabilities, and a measurement with a well-known CO_2-concentration and its isotopic compositions.

Acknowledgements

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