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Line strength measurements and relative isotopic ratio $^{13}\text{C}/^{12}\text{C}$ measurements in carbon dioxide using cavity ring down spectroscopy



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ABSTRACT

Accurate intensity measurements were performed for several lines of the two main isotopologues of carbon dioxide, using cavity ring down spectroscopy. Absorption spectra of the R52e line at 6112.8902 cm^{-1} ($30014\leftarrow 00001$ band) of $^{12}\text{CO}_2$ and the P6e line at 6114.8580 cm^{-1} ($30013\leftarrow 00001$ band) of $^{13}\text{CO}_2$ were recorded at pressures between 15 and 50 mbar at 298 K. Line shape analysis shows that Galatry profile, taking into account Dicke narrowing of spectral lines, better describes the measured spectra at all pressures than the Voigt profile. The values of Dicke narrowing parameter for both lines were found to be significantly smaller than those predicted based on the mass diffusion constant. The values of the line strength for R52e line of $^{12}\text{CO}_2$ and P6e line of $^{13}\text{CO}_2$ were determined with an uncertainty of 0.5%. These values were found to be in good agreement with the corresponding data available in literature, in particular with the most recent ab initio calculations. The results of relative isotopic ratio $^{13}\text{CO}_2/^{12}\text{CO}_2$ measurements are also presented in pure carbon dioxide samples and in 400 $\mu\text{mol/mol}$ carbon dioxide in air samples, using cavity ring down spectroscopy.

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1. Introduction

Being an important greenhouse gas, carbon dioxide in the Earth's atmosphere is carefully monitored by numerous space and ground-based missions, measuring CO_2 concentration as well as isotopic ratios of different isotopologues of CO_2 [1–3]. The latter is important for a detailed understanding of sources and sinks of CO_2 in the Earth's atmosphere. Spectroscopic methods play an important role in these measurements. In order to determine precisely the column concentration of CO_2 in the Earth's atmosphere, accurate data on spectral line parameters such as line positions, line intensities and broadening coefficients are needed. The needed high accuracy of atmospheric monitoring of CO_2 concentration imposes strict requirements for the quality of spectroscopic line data [4,5]. In particular, the intensities of the lines should be known with the accuracy better than 0.5% [4].

In the recent years many laboratory studies were carried out to determine CO_2 absorption spectra in various spectral regions. Measurements with carbon dioxide including different isotopologues were performed, using various spectroscopic methods such as Fourier Transform Spectroscopy, Cavity Ring Down Spectroscopy (CRDS) and other laser-based spectroscopic methods [6–14]. In the

majority of these studies the values of line intensities were determined with an uncertainty between 2–10%, and only a few publications, mostly concentrated on measurements of several individual spectral lines, presented the line strength data with uncertainty of 1% or less [11–14]. However, the high accuracy values of line intensities reported in these publications often do not agree with each other within the given uncertainties. Next to experimental laboratory studies, theoretical calculations on CO_2 line parameters were carried out. A Carbon Dioxide Spectroscopic Databank (CSDS) was created within the framework of the method of effective operators, containing line parameters for more than 500,000 CO_2 lines [15]. Data from the CSDS are used in the HITRAN 2012 database [16]. Within the HITRAN database, most of the line strength values are given with 10–20% uncertainty. Recently, several papers were published using ab initio calculations of line positions and line intensities for several isotopologues of CO_2 [17,18]. Within these publications line intensity values can be found with the uncertainty of 1%. To support the theoretical ab-initio calculations new accurate laboratory measurements of line intensities in CO_2 are needed.

Laser-based spectroscopic methods are widely used for isotopic ratio measurements. The advantages of these methods over conventional isotope ratio mass spectrometry are well-known [19]. Although for most laser absorption spectroscopic methods it is hard to achieve the accuracy typical for mass spectrometry measurements (better than 0.05‰ for $^{13}\text{C}/^{12}\text{C}$ isotopic ratio in CO_2), laser-

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based spectrometers can be compact, inexpensive and convenient to use for on-site measurements. In the recent years advanced instrumentation was developed, including frequency-stabilized CRD spectrometers and spectrometers based on quantum cascade lasers [20–22], which allowed significant improvement in the accuracy of isotopic ratio measurements in carbon dioxide.

In this work, we present the results of accurate line strength measurements for several lines of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in the 1.64 μm wavelength region, using CRDS. Next to this, the results of isotopic ratio $^{13}\text{C}/^{12}\text{C}$ measurements in pure CO_2 samples and in 400 $\mu\text{mol/mol}$ CO_2 in air samples are presented.

2. Experimental

2.1. Cavity ring down spectroscopy at 1.64 μm

To perform line strength and relative isotopic ratio measurements in pure CO_2 , a cavity ring down spectrometer was used operating around 1.64 μm . For this, a continuous wave external cavity diode laser (Sacher Lasertechnik, TEC-500-1650-020) was used, operating in the spectral region 5800–6250 cm^{-1} with an output power 20 mW. The laser was equipped with an optical isolator (35 dB) and connected to a single-mode optical fiber. The isolator suppresses optical feedback into the laser. From the fiber, the laser beam is divided in 50/50% beam splitter. One beam was sent to the wavelength meter (Bristol Instruments, 621 Wavelength Meter) to monitor the wavelength while recording spectra. The second beam went through an acousto-optical modulator (NEOS Technologies, 26027-2-1.55-LTD) to the CRD cell. The acousto-optical modulator (AOM) allows to quickly intermit the beam for measurements of the decay curves. In between the AOM and the CRD cell, a lens was mounted on a translational stage. This lens was used for mode matching the laser beam to the fundamental transverse electromagnetic mode (TEM₀₀) of the cavity. The CRD cell consists of a 50-cm long stainless steel cell with two highly reflective mirrors (Layertec, reflectivity $\sim 99.97\%$). The decay time in the empty cell is around 5 μs corresponding to an optical path length of ~ 1.5 km. One of the mirrors of the cell was mounted on a piezo to match the laser frequency to the main cavity modes of the cell. For relative isotopic ratio measurements the CRD cell was temperature-stabilized. The cell was equipped with 4 thermistors, a temperature sensor and was well-isolated. Spectral measurements were performed at 298 K, a temperature slightly higher than the lab temperature of 295 K. The temperature stability of the cell could be maintained within 0.1 K. The cell was equipped with a pressure gauge, a gas inlet for the gas mixture sample and a gas outlet towards the pump. The pressure gauge (Compact Capacitance Gauge Pfeiffer Vacuum) could be used for pressures up to 100 mbar. The gauge was calibrated; its uncertainty in pressure reading did not exceed 0.2%. The light leaking out of the CRD cell was focused onto an avalanche photodetector (Thorlabs, APD110C/M). The signal from the detector was sent to a computer, at which the decay time was calculated with LabVIEW.

The piezo of the external cavity diode laser was used to scan the laser frequency over a spectral absorption line. Data analysis showed that small shifts in frequency could occur in successive scans over a spectral line. These shifts were attributed to poor reproducibility of the initial frequency of the spectrum, corresponding to the initial voltage of the laser piezo. To account for this problem the following averaging procedure was used. The values of the line area determined from successive recordings of a spectral line were averaged, instead of averaging individual points of the line profile and determining the line area from an averaged profile. During the first recordings of the baseline signal using the CRD spectrometer oscillations (fringes) were observed. High frequency fringes were removed by tilting and shifting the focusing

optics and adjusting the distance between the cavity ring down cell and the detector [23]. Low frequency oscillations were reduced by alignment of the cell and adjusting the position of the mode-matching lens. During the measurements of the relative isotopic ratio, spectra of pure N_2 , at pressures corresponding to the pressure of CO_2 samples, were used as baseline spectra to account for low frequency oscillations.

2.2. Cavity ring down spectroscopy at 2.82 μm

For relative isotopic ratio measurements in 400 $\mu\text{mol/mol}$ CO_2/air samples, a CRD spectrometer operating at 2.82 μm was built. This spectrometer was based on a distributed feedback laser diode optimized for 2.818 μm (Nanoplus, DFB-260290 in a TO-66 housing and equipped with collimating lens). Within its operational temperature (30–40 $^\circ\text{C}$) and operational current (150–200 mA) an output power up to 6 mW was achieved. Changing temperature and current allowed scanning the laser frequency over ~ 5 cm^{-1} around 3549 cm^{-1} . At this wavelength an AOM (Isomet, 1210-G80L-2-MIR) was used with an efficiency of 80–90% and the CRD cell was equipped with high reflective mirrors of reflectivity $\geq 99.97\%$ at 2.8 μm (Lohnstar). Careful alignment of all optical elements taking into account mode matching provided decay times in the empty cell of the order of 9–10 μs . The ring down signal was recorded with a thermoelectrically-cooled infrared detector (VIGO System, PVI-4TE-5). Absorption of water vapor and CO_2 from the lab air can significantly influence measured spectra in this wavelength region. Special attention was paid to eliminate any leakages in the CRD cell and gas system.

3. Results

3.1. Relative isotopic ratio measurements in the spectral region around 1.64 μm

The absolute isotopic ratio R for two main isotopologues of CO_2 is determined by the ratio of amount of substance fractions x of these isotopologues in the sample:

$$R = \frac{x^{13\text{CO}_2}}{x^{12\text{CO}_2}} \quad (1)$$

Taking into account the Lambert–Beer law describing absorption strength of a spectral line, this relation can be written as follows:

$$R = \frac{A^{13\text{CO}_2}}{A^{12\text{CO}_2}} \cdot \frac{S^{12\text{CO}_2}(T)}{S^{13\text{CO}_2}(T)} \quad (2)$$

in which A is the line area of an absorption line for that specific isotopologue and S the corresponding line strength. Since the values of the line strength depend on temperature, the temperature of the samples should be constant during spectroscopic measurements. To determine the absolute isotopic ratio one needs data on the line strength for both isotopologues, which can be found in spectral databases, e.g. in the HITRAN database. Unfortunately, within this database the accuracy of line strength data is not better than 2–5% and for most values is within the range of 10–20%, which does not allow accurate determination of the absolute isotopic ratio. An alternative approach is to measure the Relative Isotopic Ratio (RIR) using a reference mixture with a well-known isotopic ratio. As such, the relative isotopic ratio can be determined from line area values for two lines (for each isotope one) measured both in the sample and in the reference mixture. In case all absorption spectra were recorded at the same temperature, the following equation can be used:

$$RIR = \frac{A_{\text{sample}}^{13\text{CO}_2}}{A_{\text{sample}}^{12\text{CO}_2}} \cdot \frac{A_{\text{ref}}^{12\text{CO}_2}}{A_{\text{ref}}^{13\text{CO}_2}} \quad (3)$$

Here we performed the measurements of the Relative Isotopic Ratio using three pure CO₂ samples, with different well-known amount ratios of ¹³CO₂/¹²CO₂. These samples were prepared at National Physical Laboratory (NPL) using mass spectrometry and gravimetry. We used three pairs of these samples to measure three values of relative isotopic ratio. For accurate determination of the *RIR* spectral lines of two isotopologues should meet several requirements [19]. These lines should have comparable strength, taking into account the natural abundances of the isotopologues. This will allow spectral measurements of two lines with the same signal/noise ratio. At the same time the lines should lie close to each other for quick and convenient scanning. It is well-known [24] that the accuracy of the relative isotopic ratio ΔRIR depends on the temperature stability of the sample:

$$\Delta RIR \sim \frac{\Delta E}{k_B T^2} \Delta T \quad (4)$$

in which ΔE is the difference between the lower state energies of ¹²CO₂ and ¹³CO₂ transitions, ΔT is the temperature variation during the measurement, k_B is the Boltzmann constant and T is the temperature of the sample. Therefore to minimize the temperature sensitivity one has to choose the lines of two isotopologues that do not differ much in lower state energy. Next to that, care should be taken to avoid overlapping of the lines with each other and with lines of other isotopologues or other molecules. In this work absorption lines R52e of ¹²CO₂ at 6112.8902 cm⁻¹ and P6e of ¹³CO₂ at 6114.8580 cm⁻¹ [16] were used for the *RIR* measurements and for line strength measurements. These lines belong to the ($3\nu_1 + \nu_3$) absorption band of carbon dioxide (30014←00001 band of ¹²CO₂ and 30013←00001 band of ¹³CO₂, respectively). For the chosen CO₂ lines, the possible variation of the sample temperature (within 0.1 K) leads to the uncertainty in the relative isotopic ratio ΔRIR of ~1.5%.

For the *RIR* measurements we used the following procedure. Firstly, the spectrum of nitrogen at appropriate pressure was recorded within the spectral range of the ¹²CO₂ line. Then the cell was filled with CO₂ sample 1 and the absorption strength of the ¹²CO₂ line was recorded. Then the cell was carefully pumped out and filled with CO₂ sample 2. The absorption strength of the ¹²CO₂ line was recorded. After that the laser frequency was shifted to the wavelength around the line of ¹³CO₂ and its absorption strength in CO₂ sample 2 was recorded. Then the cell was again carefully pumped out and the absorption strength of the ¹³CO₂ line in CO₂ sample 1 was recorded. At the end the spectrum of nitrogen at appropriate pressure was recorded within the spectral range of the ¹³CO₂ line. During all these measurements care was taken about the stability of pressure and temperature of the samples. Using this procedure we performed series of spectral measurements at different pressures 15, 30 and 50 mbar at 298 K.

Within CRD spectroscopy the absorption spectrum of a line is given in terms of the decay time - time dependence of the intensity of laser light leaking out of the cavity. Decay time τ_ν of the laser pulse with frequency ν (in this article ν is the wavenumber, cm⁻¹) contains all information about the loss processes in the CRD cell and can be written as [25]:

$$\tau_\nu = \frac{d}{c} \cdot \frac{1}{|\ln(r)| + \varepsilon_\nu d} \quad (5)$$

in which d is the length of the cavity, c the speed of light, r the intensity reflectivity of the cavity mirrors and ε_ν the extinction coefficient of the molecules at that frequency. Here, it is assumed that the entire cavity with the length d is filled with gas. Extinction of the light in the cell is determined by absorption and scattering processes. In the infrared region the contribution of light scattering is very small, and is therefore not taken into account. Thus, the measured decay time is totally determined by light absorption.

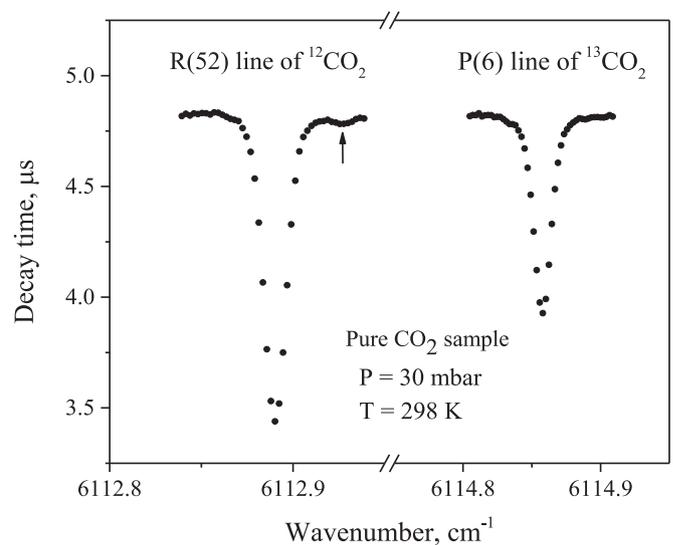


Fig. 1. Spectra of ¹²CO₂ and ¹³CO₂ absorption lines at 6112.8902 and 6114.8580 cm⁻¹, using CRD spectrometry. The weak ¹⁶O¹²C¹⁸O isotopologue line is shown with the arrow.

Having measured the decaying signal and determined the decay time, one can obtain the absorption coefficient of the molecules k_ν :

$$k_\nu = \frac{1}{\tau_\nu c} - \frac{|\ln(r)|}{d} \equiv \frac{1}{\tau_\nu c} - \frac{1}{\tau_\nu^0 c} \quad (6)$$

In the last equation, the second term represents the losses in the empty cavity and can be determined by measuring the decay time of the laser intensity in the empty cell τ_ν^0 . A typical CRD spectrum of the chosen ¹²CO₂ and ¹³CO₂ absorption lines in one of the CO₂ samples is shown in Fig. 1.

In every series of measurements CRD spectra $\tau(\nu)$ for two isotope lines in two pure CO₂ samples were recorded. Since, there were three pure CO₂ samples with different isotopic ratios, we repeated the measurements three times for three pairs of samples. For each line the absorption coefficient $k(\nu)$ was determined using the spectrum of pure nitrogen, transparent in this spectral region as a baseline $\tau_0(\nu)$. From the known absorption spectra $k(\nu)$ the values of the line area A were determined. The line area data were used to calculate the value of the relative isotopic ratio according to Eq. (3). For each pair of pure CO₂ samples, a series of measurements were performed at three different pressures. It was found that the values of the relative isotopic ratio do not depend on the pressure of the samples. The averaged values of the *RIR* for three pairs of pure CO₂ samples determined are given in the second column of Table 1. For comparison the corresponding values of the relative isotopic ratio recalculated from the amount ratios ¹³CO₂/¹²CO₂ determined by NPL are given in the last column of the table. It can be seen that there is good agreement between the measured and the reference values.

3.2. Line strength measurements for ¹²CO₂ and ¹³CO₂ lines

Line shape analysis was performed for recorded absorption spectra of R52e line of ¹²CO₂ at 6112.8902 cm⁻¹ and P6e line of ¹³CO₂ at 6114.8580 cm⁻¹. While fitting the ¹²CO₂ line a contribution from the weak line of ¹⁶O¹²C¹⁸O isotopologue at 6112.9296 cm⁻¹ [16] was taken into account (see Fig. 1). Absorption lines were fitted with Voigt and Galatry profiles. Compared to the widely used Voigt profile, the Galatry profile takes into account Dicke narrowing of spectral lines resulting from velocity changing collisions. Within the Galatry profile these collisions are described

Table 1
Results of the relative isotopic ratio measurements in pure CO₂ samples.

	Relative isotopic ratio ¹³ CO ₂ / ¹² CO ₂	
	Cavity ring down spectroscopy (this work)	Mass spectrometry and gravimetry (NPL)
sample 1/sample 2	(1.495 ± 0.008)	(1.502 ± 0.002)
sample 3/sample 2	(1.244 ± 0.006)	(1.247 ± 0.001)
sample 1/sample 3	(1.205 ± 0.006)	(1.204 ± 0.001)

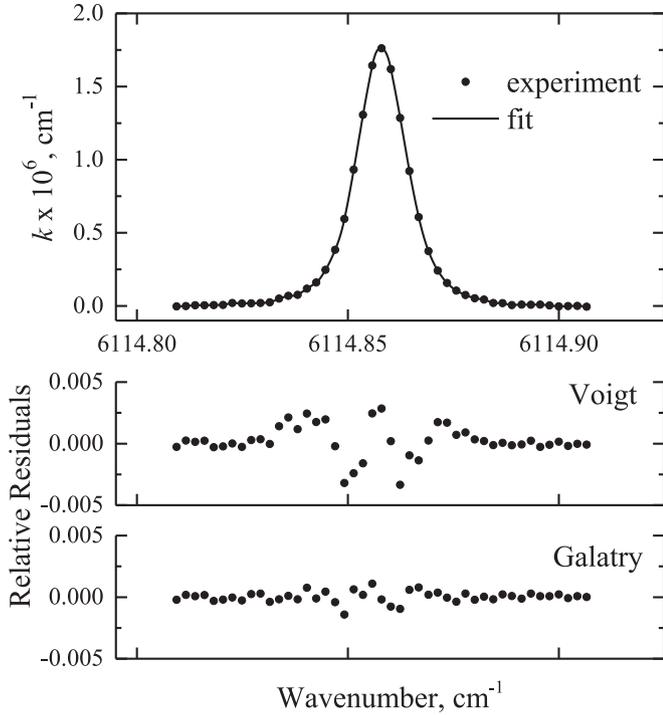


Fig. 2. Measured values of absorption coefficient and the fitting profile for the P6e line of ¹³CO₂ recorded at 30 mbar and 298 K (top panel), and relative residuals corresponding to the fitting of the experimental points with Voigt profile (middle panel) and Galatry profile (lower panel).

using the soft collisions approximation where the motion of the molecules is considered as diffusive. Software, based on the generalized non-linear method of least squares [26], allows fitting the experimental spectral points with Voigt or Galatry profile and calculating the optimal values of the parameters for these profiles, as well as calculating the relative residuals between the experimental data points and their adjusted values. During the fitting procedure the uncertainties of the measured values of the decay time, frequency and temperature of the sample are taken into account. The value of the temperature is used to calculate the Doppler profile, as the Doppler width is constrained to the theoretical value. An example of line shape analysis is shown in Fig. 2 for the P6e line of ¹³CO₂ (30 mbar, 298 K). Comparison of the relative residuals for two profiles clearly shows that Galatry profile provides a better description of the absorption line than Voigt profile and allows more accurate determination of the line area.

Fitting spectra with Galatry profile allows determination of the Dicke narrowing parameter z_{exp} . For both CO₂ lines, parameter z_{exp} showed a linear dependence with pressure within the uncertainty in the pressure range 15–50 mbar (see Fig. 3).

Experimental value of the Dicke narrowing parameter can be compared with z_{dif} , calculated using gas diffusion theory [e.g. 12]:

$$z_{dif} = \frac{k_B T}{m D \Delta \nu_D c} \quad (7)$$

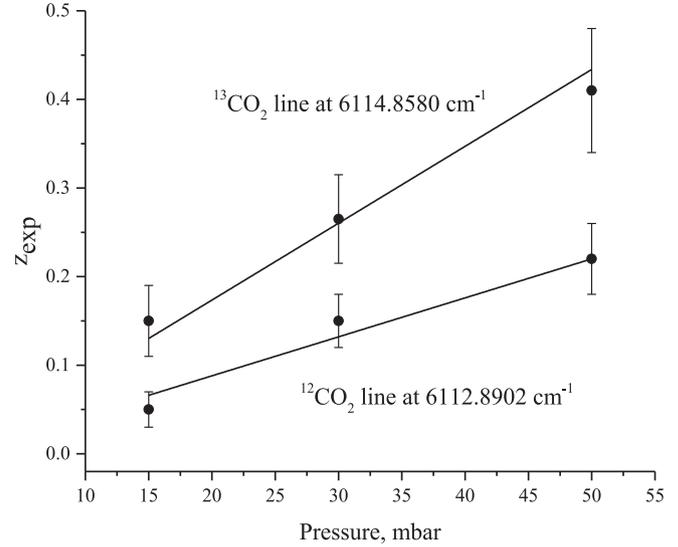


Fig. 3. Measured values of the Dicke narrowing parameter z_{exp} for R52e line of ¹²CO₂ at 6112.8902 cm⁻¹ and P6e line of ¹³CO₂ at 6114.8580 cm⁻¹ at different pressures. Solid lines show corresponding linear fits through the origin.

where $k_B = 1.38065 \times 10^{-23}$ J/K is the Boltzmann constant, T (K) temperature of the sample, m (kg/molec) mass of the molecule, D (m²/s) mass diffusion constant, $\Delta \nu_D$ (cm⁻¹) Doppler broadening (HWHM) and $c = 2.99792 \times 10^{10}$ cm/s speed of light. For both CO₂ lines the experimental Dicke narrowing parameter was found to be much smaller than the one predicted by theory: ~3.5 times smaller for ¹²CO₂ line and ~1.8 times smaller for ¹³CO₂ line. The reason for such difference can be attributed to the overestimation of velocity changing collisions resulting in Dicke narrowing given by (7). Within Eq. (7) it is assumed that all velocity changing collisions contribute to the narrowing of the spectral line. At the same time Dicke narrowing is determined only by elastic velocity changing collisions which do not change the internal state of the molecule [27]. Similar results for different molecules were reported in other publications [28 and references therein]. It is worth noting that the ratio between the experimental and theoretical values of the Dicke narrowing parameter found in this work is at odds with the results reported in [29]. At the same time the experimental value of the Dicke narrowing parameter determined in [29] (Fig. 5 therein at small pressures) is very close to that obtained here. Therefore the discrepancy in the ratio most probably results from different ways of calculating theoretical value of the Dicke narrowing parameter using mass diffusion constant.

Line shape analysis was performed for absorption spectra of carbon dioxide recorded in three samples with different mole fractions of ¹²CO₂ and ¹³CO₂. Compositions of CO₂ samples determined at NPL with uncertainty 0.2% are given in Table 2. For each line about 150 spectra were analyzed at three different pressures (15, 30 and 50 mbar). The values of the line area corresponding to the fitted Galatry profiles were used to determine the line strength. Typical uncertainties of the values of the line area for two lines were between 0.4 and 1% increasing towards lower pressures. It

Table 2
Composition of pure CO₂ samples used for line strength measurements (NPL).

	Mole fraction of ¹² CO ₂	Mole fraction of ¹³ CO ₂
Sample 1	0.983(2)	0.01652(4)
Sample 2	0.988(2)	0.01106(3)
Sample 3	0.986(2)	0.01375(3)

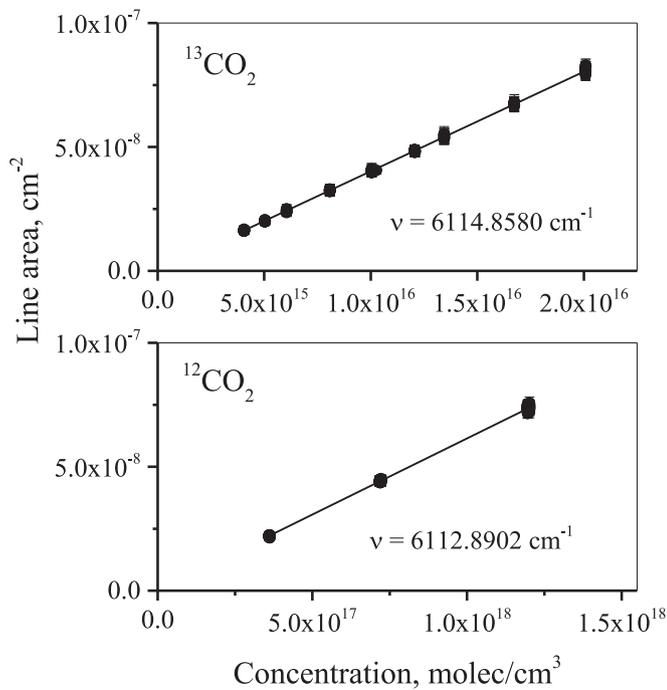


Fig. 4. Determination of the line strength for P6e line of ¹³CO₂ and R52e line of ¹²CO₂.

should be noted that the values of the line area determined with Galatry profile are larger than those determined using the Voigt profile: on the average 0.5% for the ¹²CO₂ line and 2% for the ¹³CO₂ line. This result is in agreement with [20], in which a difference was found of 2 to 4% between the line areas of the Voigt and Galatry profiles, for the different CO₂ lines at 1.6 μm measured by frequency-stabilized CRD spectroscopy.

The relation between the line area A (cm⁻²) and the line strength S (cm/molec) is given by the following equation:

$$S = \frac{A}{n} \cdot 10^6 \quad (8)$$

where n (molec/m³) is the concentration of absorbing molecules. For the experimental conditions used here the concentration can be calculated using the ideal gas equation:

$$n = \frac{p \cdot x}{k_B \cdot T} \quad (9)$$

where p (Pa) is the pressure of the sample, x is the mole fraction of absorbing molecules. Therefore, the line strength values can be determined from the slope of a straight line fitted to the plotted values of A over n . The corresponding fits for two measured lines of carbon dioxide are shown in Fig. 4. During the fitting procedure the uncertainties of the values of the line area (0.4–1%), pressure (0.2%) and temperature (0.15%) of the sample, and mole fractions of absorbing molecules (0.2%) were taken into account.

From these fits the values of the line strength for two CO₂ lines at 298 K were determined with the uncertainty 0.5%. To our knowledge these are the first intensity measurements for these spectral lines with uncertainty better than 1%. For comparison with

the corresponding data available in literature, the values of the line strength were recalculated for 296 K using the equation for the temperature dependence of the line intensity and the values of the total internal partition function for CO₂ isotopologues given on HITRAN database website [30]. The results are collected together with the corresponding values from HITRAN 2012 database in Table 3. The HITRAN 2012 values originate from theoretical calculations within the model of effective operators - effective Hamiltonian and effective dipole moment function [15]. The parameters of these functions were determined using the experimental data on line positions and line intensities measured by means of Fourier Transform Spectroscopy as well as CRD Spectroscopy, diode laser absorption spectroscopy and intracavity laser absorption spectroscopy (see ref. in [15]). The uncertainty code of these values in HITRAN 2012 is 3, which corresponds to the relative uncertainty of 20%. The values of the line strength from ab initio calculations [17,18] and from Fourier Transform Spectroscopy measurements [6] are shown in the last two columns of Table 3. It could be seen that for both isotopes the values of the line strength measured in this work agree with the corresponding experimental and theoretical values within the given uncertainties. The best agreement within 0.5% was found for the most recent ab initio values [17,18].

Devi et al. [7] recently presented accurate measurements of line parameters of carbon dioxide around 1.6 μm using Fourier Transform Spectroscopy. In this publication the line strength of the P6e line of ¹³CO₂ has the value of 4.088×10^{-26} cm/molec, which is almost 10% lower than the value presented here.

3.3. Relative isotopic ratio measurements in the spectral region around 2.82 μm

Relative isotopic ratio measurements in the spectral region around 2.82 μm were performed using two 400 μmol/mol carbon dioxide in air samples with well-determined amount ratios of ¹³CO₂/¹²CO₂ (NPL): sample 1: 0.011214, sample 2: 0.010856. The samples were prepared using whole air which contained argon in atmospheric amount fraction (~0.9%). Absorption lines P22e of ¹²CO₂ at 3549.9797 cm⁻¹ and R32e of ¹³CO₂ at 3550.9746 cm⁻¹ [16] were used for these RIR measurements. The lines belong to ($\nu_1 + \nu_3$) absorption band of carbon dioxide: 20013←10002 band of ¹²CO₂ and 10012←00001 band of ¹³CO₂, respectively. A somewhat modified measurement procedure was followed as compared to the procedure described above in Section 3.1. For the RIR measurements, cell and gas system were evacuated to exclude water vapor and carbon dioxide absorption from lab air. Then spectra of the two selected absorption lines in sample 1 were recorded. Scanning was implemented by changing the laser current. After that the cell and the gas system were evacuated and filled with sample 2, from which spectra of the same absorption lines were recorded. All measurements were performed at 298 K, using a low gas flow (2.5 L/h), keeping 10 mbar pressure in the cell. Working with low gas flows allowed to improve the reproducibility of the recorded spectra of the samples with low CO₂ concentrations. Using this procedure 15 series of measurements of the relative isotopic ratio were performed during the period of three weeks. Typical spectra of P22e absorption line of ¹²CO₂ and R32e absorption line of ¹³CO₂ are given in Fig. 5.

From the measured spectra in each series the values of the line area for the lines of two CO₂ isotopologues in two samples were determined. For this the same fitting procedure as described in Section 3.2 for spectra of pure CO₂ samples was used. It was found that the largest contribution to the uncertainty of the line area results from instability of the base line. The values of the line area determined using Voigt and Galatry profiles were found to be the same within the uncertainties. Using four values of the line area,

Table 3
Line strength values for the R52e line of $^{12}\text{CO}_2$ and the P6e line of $^{13}\text{CO}_2$.

Lines	Present work Line strengths (T = 296 K), cm/molec	HITRAN 2012 [16]	Zak et al. [17,18]	Toth et al. [6]
$^{12}\text{CO}_2$ R52e 6112.8902 cm^{-1}	6.008×10^{-26}	5.97×10^{-26}	6.018×10^{-26}	5.977×10^{-26}
$^{13}\text{CO}_2$ P6e 6114.8580 cm^{-1}	4.481×10^{-26}	4.49×10^{-26}	4.500×10^{-26}	4.570×10^{-26}
Uncertainty	(0.5%)	(20%)	(1%)	(<5%)

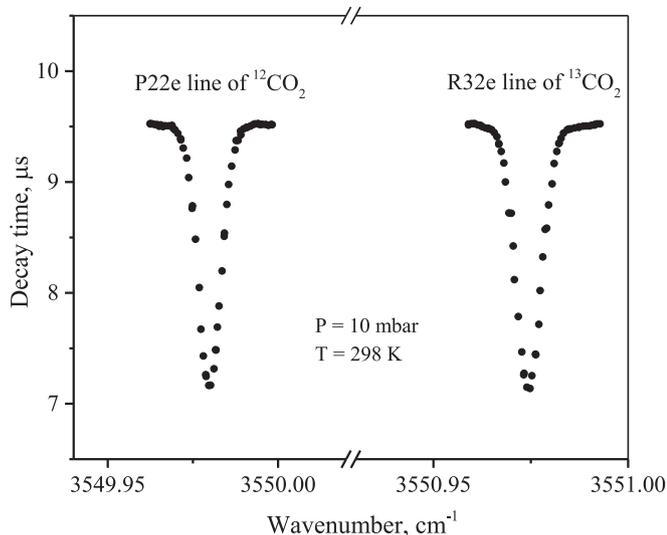


Fig. 5. Spectra of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ absorption lines at 3549.9797 and 3550.9746 cm^{-1} in 400 $\mu\text{mol/mol}$ carbon dioxide in air sample, using CRD spectrometry.

the value of the relative isotopic ratio can be calculated according to Eq. (3). After averaging the results of all series, the value of the relative isotopic ratio was determined (1.030 ± 0.008). This measured value of the relative isotopic ratio was found to be in good agreement with the one recalculated from the known amount ratios $^{13}\text{C}/^{12}\text{C}$ for two samples – 1.033 (NPL).

4. Conclusion

In the present work accurate line intensity measurements were performed for CO_2 using CRD spectroscopy in the wavelength region around 1.64 μm . The following absorption lines were studied: R52e at 6112.8902 cm^{-1} (30014←00001 band) of $^{12}\text{CO}_2$ and P6e at 6114.8580 cm^{-1} (30013←00001 band) of $^{13}\text{CO}_2$. Line shape analysis showed that the shape of CO_2 absorption lines measured in the pressure range from 15 to 50 mbar at T = 298 K can be better described with Galatry profile taking into account speed changing collisions, than with Voigt profile. The experimental values of the Dicke narrowing parameter for both CO_2 lines were found to be 50–70% less than those, calculated with the mass diffusion constant. This result supports theoretical predictions that only elastic velocity changing collisions which do not change the internal state of the molecule, lead to Dicke narrowing of individual spectral lines. The values of the line area determined using Galatry profile were found to be 0.5–2% higher than those from Voigt profile depending on the line. This result should be taken into account during accurate spectroscopic measurements of isotopic ratios in CO_2 , since the difference in the values of the line area given by two profiles can be different for spectral lines of two isotopologues.

The values of the line strength for two CO_2 lines around 1.64 μm were determined with uncertainty 0.5%. To our knowledge this is the most accurate laboratory data for these lines. Line strength values for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lines determined in this work

are in good agreement with those from HITRAN 2012 [16] and with Fourier Transform Spectroscopy measurements [6]. It should be noted that present data on line intensities agree with the most recent accurate ab initio calculations within 0.17% for $^{12}\text{CO}_2$ [17] and within 0.43% for $^{13}\text{CO}_2$ [18]. These ab initio values for CO_2 line intensities [17,18] will be included in the latest edition of the HITRAN database HITRAN 2016 [31].

Next to line intensity measurements CRD spectrometry was used for relative isotopic ratio measurements in pure CO_2 samples (measurements around 1.64 μm) and in 400 $\mu\text{mol/mol}$ CO_2/air samples (measurements around 2.82 μm). Good agreement was found between these values and the values of the relative isotopic ratio determined independently using mass spectrometry and gravimetry. We conclude that classical CRD spectrometer based on compact and easy-to-use distributed feedback laser diode and equipped with temperature-isolated cell allows determination of the relative isotopic ratio $^{13}\text{C}/^{12}\text{C}$ in natural CO_2/air samples with uncertainty less than 1%.

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