

Measurement of the concentration ratio for ^{13}C and ^{12}C isotopes at atmospheric pressure by carbon dioxide absorption of diode laser radiation at $\sim 2\ \mu\text{m}$

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Abstract. The ratio of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations in the human exhaled air is measured by the method of diode laser spectroscopy using a three-channel optical scheme and multipass cell. Unlike the previous measurements in the spectral range of $\sim 4.3\ \mu\text{m}$ with a resolved rotational structure at low pressure of selected samples, the present measurements are performed in the range of $\sim 2\ \mu\text{m}$, in which weaker absorption bands of CO_2 reside. In this case, it is possible to employ lasers and photodetectors operating at room temperature. The thorough simulation of the spectrum with collisional broadening of lines and employment of regression analysis allow one to take measurements at atmospheric pressure with the accuracy of $\sim 0.04\%$, which satisfies the requirements to medical diagnostics of ulcers.

Keywords: absorption spectroscopy, diode lasers, carbon isotopes, linear regression.

1. Introduction

The ratio concentrations of stable carbon isotopes ^{12}C and ^{13}C in carbon dioxide is interesting for many applications such as geological ecology, prediction of volcanic explosions [1], and medicine (in respiratory tests for predicting gastroenterological diseases [2]). These applications require a high accuracy and reproducibility of measurement results, because minor variations in the isotope concentration ratio under influence of various factors should be detected. In medical applications the required accuracy is 0.05% .

The absorption spectroscopy methods are mainly used for measuring the ratio of carbon isotope concentrations in carbon dioxide in three spectral ranges (~ 4.3 , ~ 2 , and $\sim 1.6\ \mu\text{m}$), which are relatively free of water vapor absorption bands. In the range of $\sim 4.3\ \mu\text{m}$ the cross section of CO_2 absorption is maximal and falls by two and five orders

of magnitude in the ranges of ~ 2 and $\sim 1.6\ \mu\text{m}$, respectively. In the most sensitive spectral range ($\sim 4.3\ \mu\text{m}$) the error of measuring the ratio of carbon isotope concentrations reported recently is 0.003% [3]. However, measurements in this range necessitate cryogenic cooling of setups or unique quantum-cascade lasers operating at room temperature but still with cooled detectors. In the spectral range of $\sim 1.6\ \mu\text{m}$ the sensitivity noticeably falls and a long optical path in high- Q cavities is needed. In [4], the measurement error of 0.18% was obtained in detecting the integral intensity of radiation from a cavity. Interest in the spectral range of $\sim 1.6\ \mu\text{m}$ is related to a possible employment of fibre optics. In the range of $\sim 2\ \mu\text{m}$, which is intermediate by the cross-section value, diode lasers and detectors operating at room temperature are used. The accuracy of measuring the isotope concentration ratio in this range is 0.05% [5].

Almost all known experiments are carried out at low pressures, when the rotational structure of absorption spectrum is resolved. Without overlapping spectral lines the accuracy of concentration measurements can be substantially increased [6]. In this paper, the method for measuring carbon isotope concentrations and their ratio is suggested based on a comparison of measured and calculated CO_2 absorption spectra in the range of $\sim 2\ \mu\text{m}$. The experiments were performed at atmospheric pressure and room temperature. Human exhaled air and mixtures of air with CO_2 (3%) were studied.

2. Experimental

The principal scheme of the experimental setup shown in Fig. 1 is similar to that described in [7]. Here we only mention the characteristics of its elements and specific features of the measurement method.

A $\sim 2\text{-}\mu\text{m}$, 1-mW vertical-cavity A_3B_5 (InGaAlAs/InP) laser (Vertilas Co.) continuously tuned in the frequency range $7\text{--}15\ \text{cm}^{-1}$ was employed. The diode laser was mounted on a Peltier thermal element in an airtight case. The laser temperature was stabilised at the level $2 \times 10^{-4}\ \text{K}$ with the help of an input–output NI-PCI-6120 interface card and control unit. The laser was fed by current pulses of special form with the duration of 20 ms and pulse repetition frequency of $10\text{--}15\ \text{Hz}$ [7]. The radiation frequency was tuned by varying gradually the injection current. The injection current amplitude was $3\text{--}7\ \text{mA}$. A measurement scheme has three optical channels:

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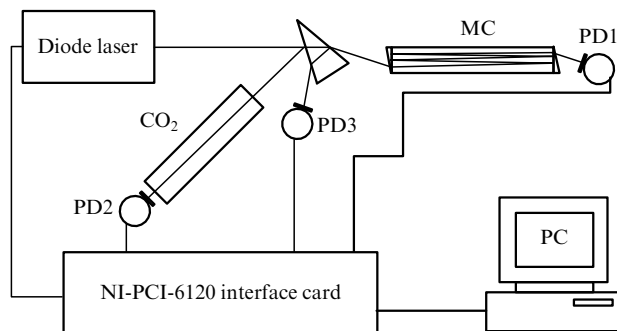


Figure 1. Scheme of the experimental setup.

an analytical channel with a multipass cell (MC) and photodetector PD1, frequency calibration channel (photodetector PD2), and baseline detection channel (photodetector PD3). All the photodetectors were of the G-8372-01 type produced by Hamamatsu. The laser radiation, temperature stabilisation, and signal detection systems were controlled by the input–output interface card from a PC with a LabView software package.

A multipass cell of the Herriott cell type [8] placed in the analytical channel had two aluminum-coated mirrors with holes for radiation coupling in and out. The radius of the mirror curvature was 1 m and the separation between the mirrors was ~ 40 cm. The vacuum-tight mirrors were mounted on a quartz tube of diameter ~ 2.2 cm. The total cell volume was ~ 150 cm³. After performing ten double reflections inside the cell, laser radiation passed to photodetector PD1. The effective optical path length was ~ 8 m. Near the ends of the cell there were two vacuum valves for connecting to vacuum and gas puffing systems. The system was filled with CO₂-enriched air mixture or human exhaled air by blowing the gases through the cell.

Laser radiation reflected from two surfaces of a splitting wedge passed to the second and third channels. The second channel with photodetector PD2 had a cell filled with pure CO₂ at a pressure of 70 Torr, which was used for calibrating the laser radiation frequency.

The concentrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ molecules were measured by comparing the measured spectrum with the spectra calculated for known molecule concentrations. This procedure requires the measured spectrum to be identified and frequency calibrated. For this purpose the intensities and positions of allowed transitions of $^{12}\text{CO}_2$ were measured at a reduced pressure of 70 Torr. At the first calibration stage, assuming the increment ν in the laser generation frequency to be strongly proportional to that of the injection current j ($\Delta\nu \sim \Delta j$) and knowing the approximate (average) proportionality coefficient b between them, we assigned to each value of the injection current the relative frequency of laser generation

$$\nu_{\text{rel}}(j) = (j - j_0)b,$$

where j_0 is the initial injection current. Then, the frequencies $\nu_{\text{rel}n}$ and intensities A_n of line maxima in the absorption spectrum were determined, where n is the absorption line number corresponding to the line position in a frequency scale relative to other detected lines in the spectrum under study. This procedure forms the frequency and amplitude arrays $[\nu_{\text{rel}}]$ and $[A]$ in the HITRAN

database format [9] with the number of data reduced to the number of the detected spectral absorption lines for faster calculation. To simplify the calculations, the frequency array was later normalised in the following way

$$\nu_{\text{rel}n}^{(1)} = \nu_{\text{rel}n} - \nu_{\text{rel}0}.$$

After this normalisation, the zero frequency corresponds to a first line in the array.

At the next stage, the frequencies of the absorption lines were more exactly bound to the HITRAN database. For this purpose, the first line from the array having the frequency $\nu_{\text{rel}0}^{(1)}$ was identified with a line of the frequency ν_H from the HITRAN database. Thus, the frequencies of all the rest lines from the array are determined by the expression

$$\nu_{\text{rel}n}^{(2)} = \nu_{\text{rel}n}^{(1)} + \nu_H.$$

Then, the elements of array $[\nu_{\text{rel}}^{(2)}]$ were juxtaposed with the frequencies of nearest spectral lines from the HITRAN database. The intensities of these lines form the array $[A_H]$, which is equal to $[A]$ in size and is used for comparing the amplitudes of lines from HITRAN with those of our spectra. Model experiments show that if the white noise (with the intensity 20% of the average intensity of the calculated spectrum) is added to the calculated spectrum, the correlation comparison of arrays $[A]$ and $[A_H]$ may result in wrong calibration. For the optimal characteristic of the correlation analysis we chose the amplitude ratio of adjacent spectral lines. Then, we transfer from arrays $[A]$ and $[A_H]$ to their characteristic arrays $[B]$ and $[B_H]$ and calculate the correlation factor $\text{corr}\{[B], [B_H]\}$ for this pair of arrays. The elements of the characteristic arrays and the correlation factor were determined by the relations:

$$B_n = A_{n+1}/A_n,$$

$$B_{Hn} = A_{Hn+1}/A_{Hn},$$

$$\text{corr}\{[B], [B_H]\} = \frac{\sum_n (B_n - \bar{B})(B_{Hn} - \bar{B}_H)}{\left[\sum_n (B_n - \bar{B})^2 \sum_n (B_{Hn} - \bar{B}_H)^2 \right]^{1/2}},$$

where n is the number of the array element. Similar operations were performed for all lines from the HITRAN database close to the laser generation spectral range. The frequency binding of the absorption lines was performed by the maximal correlation between the positions of the measured lines and the lines from the HITRAN database.

After the line positions in the calibrated spectrum are bound to the absolute frequencies, we performed a polynomial interpolation of the entire frequency scale over the frequency range of laser generation. All the procedure was performed automatically in the LabView software. An estimated accuracy of the laser radiation frequency binding was ~ 0.0001 cm⁻¹. A typical laser tuning curve is presented in Fig. 2.

The third measurement channel controls the baseline (the laser radiation intensity in the absence of absorption lines). The distance from PD3 to the wedge was chosen equal to that from the wedge to PD1 in open atmosphere (i.e., excluding the MC) in order to avoid the influence of radiation absorption in atmosphere on the measurement accuracy.

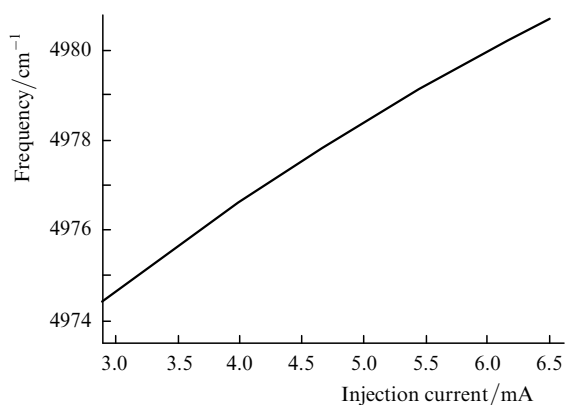


Figure 2. Dependence of the laser radiation frequency on the injection current obtained from frequency calibration.

Spectra obtained in the analytical channel were processed by the linear regression method [7]. According to the Lambert–Beer law, the expression for the laser intensity I_1 in the analytical channel can be written in the form:

$$I_1(\nu) = I_0(\nu) \exp \left[-\sum_i \alpha_i(\nu)L \right], \quad (1)$$

where I_0 is the intensity of laser radiation at the input to the MC; α_i is the absorption coefficient for i th component of gas mixture; and L is the optical path length. In measurements, the intensity I_0 is substituted by the intensity I_3 from the third channel. In the general case, the baselines in different channels do not coincide [7], which limits the measurement accuracy. For correcting these differences and taking into account the proportionality coefficient between I_0 and I_3 , a third-order polynomial $P^{(3)}$ is introduced. Then, Eqn (1) is reduced to the form

$$\ln I_1(\nu) = \ln I_3(\nu) - \sum_i k_i \alpha_{i0}(\nu)L + P^{(3)}(\nu), \quad (2)$$

where α_{i0} are the absorption coefficients of various gas mixture components at known concentrations, which are synthesised by using the HITRAN database. By using the method of signal processing given above, we calculated the regression coefficients k_i from which the measured concentrations of gas components are determined.

3. Results and discussion

Figure 3 shows an example absorption spectrum of human exhaled air detected in the analytical cell in the range of $\sim 4980 \text{ cm}^{-1}$ at atmospheric pressure. The cell with the exhaled air sample was leakproof and the measurements were performed in 20–30 minutes after puffing the gas when its temperature became equal to room temperature. Apart from the absorption lines of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ molecules, the absorption lines of H_2O and N_2O molecules fit into the frequency tuning range of laser generation. Their spectra were also simulated using the HITRAN database. It was experimentally found that the concentration of N_2O molecules was below the sensitivity threshold and did not affect the results of regression. For this reason, the spectrum of N_2O was neglected.

Figure 4 presents the synthesised spectra of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and H_2O molecules at the pressure of 1 atm and temperature $T = 296 \text{ K}$. The spectral lines have Voigt

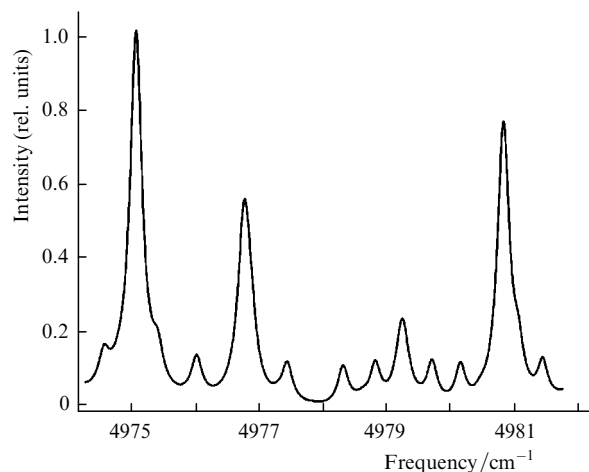


Figure 3. Example of the detected absorption spectrum of human exhaled air.

profiles. The linear regression of the measured spectra was performed by means of the modified General LS Linear Fit program included in the LabView software. The calculated regression coefficients allow one to determine the ratio of isotope concentrations. The concentration of the water vapour in air in various experiments was 1%–1.5% of the total molecule concentration. The concentration ratios for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ molecules were 89.6 and 91.8 in atmospheric air and human exhaled air, respectively.

The measurement accuracy of the isotope concentration ratio was tested by the Allan variance [7]. Figure 5 shows the time dependence of the square of the Alan variance for the

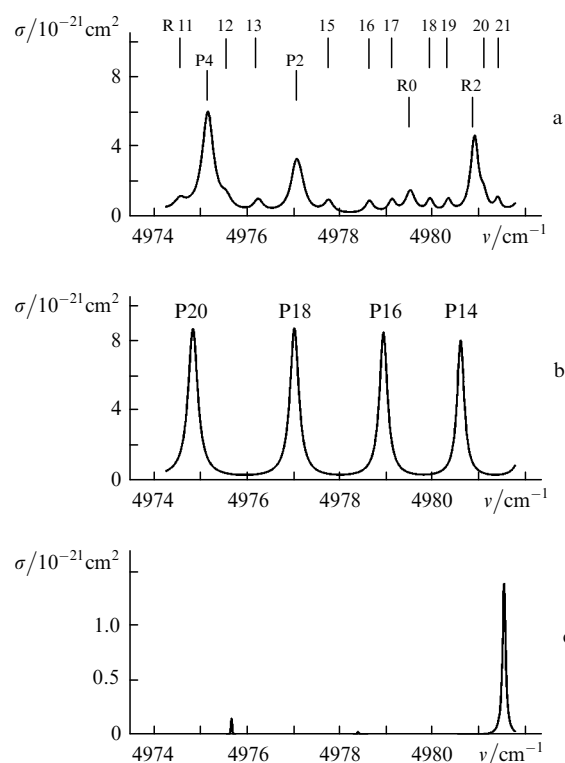


Figure 4. Absorption spectra of $^{12}\text{CO}_2$ (a), $^{13}\text{CO}_2$ (b), and H_2O (c) molecules synthesised by using the HITRAN database taking into account line broadening at atmospheric pressure.

ratio of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations. At the signal averaging time of ~ 6 min, we did not observe the rise in the Allan variance which is specific for low-frequency instabilities (drift of the parameters) of the setup. The dependence almost coincides with the straight line corresponding to an averaged normal noise. From this, we estimated the measurement accuracy, which is 0.04 % in averaging over a time lapse of 6 min.

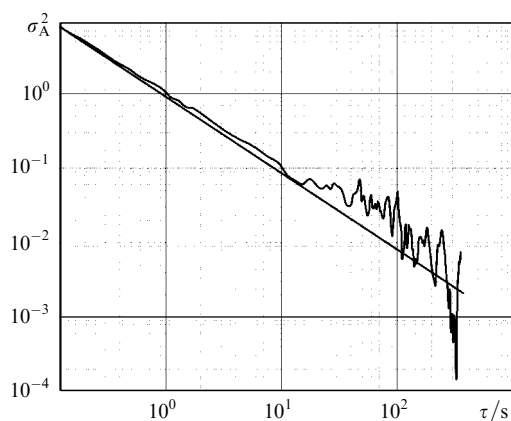


Figure 5. Allan variance σ_A^2 for the ratio of carbon isotope concentrations in human exhaled air. The straight line corresponds to extrapolation of the normal noise behaviour.

The suggested method allows one to take measurements with unresolved complicated spectra, because it does not necessitate solving an inverse problem on determining the contribution from separate spectral lines into the entire spectrum. In our case, the measurements were made in the MC at atmospheric pressure. The intensities of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ absorption lines in the chosen spectral range differed by a factor of approximately 90. Further enhancement of the measurement accuracy is possible. For example, by choosing a spectral range with comparable spectral line intensities of various isotopes one can increase the accuracy due to a better signal-to-noise ratio. This can be achieved by using transitions with substantially different rotational quantum numbers. On the other hand, the employment of such transitions results in a stronger influence of temperature variations on the measurement accuracy. In our case, the temperature measurement accuracy of 0.5 K leads to the error of 0.3 % for isotope concentration measurement. The sensitivity to the temperature variation is about three times lower than that in the case of comparable intensities [2]. In addition, our approach is capable of correcting temperature variations because the spectra are calculated in each measurement cycle. According to our estimates, the temperature fluctuations over the time lapse of ~ 6 min result in the measurement error of less than 0.01 %.

The spectrum calculations were performed for Voigt and Lorentz line profiles. The use of the Lorentz line profile leads to a systematic error of the value of absolute ratio of isotope concentrations. Nevertheless, the relative error in both the cases is the same. Thus, in the case when the relative variation in the concentration ratio for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ molecules is important, one can employ the Lorentz profile of spectral lines, which reduces the spectrum calculation time and suggests a higher repetition frequency of laser pulses.

4. Conclusions

Employment of the multichannel diode spectroscopy technique together with the method of multidimensional linear regression in processing absorption spectra of gas components provides high-accuracy measurements under conditions of overlapping spectral lines with strongly differing intensities. A high measurement accuracy is provided by the frequency binding to the whole array of absorption lines in the tuning range of the laser frequency and by suppressing the noise of the detected signal caused by the intensity fluctuations of laser radiation via using an additional channel for measuring the baseline. The precision of measuring the concentration ratio for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ molecules in human exhaled air by the absorption on weak lines in the range of $\sim 2 \mu\text{m}$ at atmospheric pressure was 0.04 % at the concentration of carbon dioxide varied from 2.5 % to 3.5 % in various experiments.

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