External-cavity diode laser spectrometer for measuring the concentration ratio $^{13}CO_2/^{12}CO_2$ by absorption in the range of 1.6 μm

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Abstract. **The method for determining the carbon isotopic ratio from CO$_2$ absorption spectra in the optical cavity containing atmospheric air with the natural contents of carbon dioxide ~0.03 % is described. The measurements are performed at atmospheric pressure in the conditions of overlapping absorption lines. The measurement accuracy is 0.3‰.**

1. Introduction

The diagnosis of objects by using isotopic tags is widely used in ecology, technique, medicine, etc. Important are the methods of analysis by isotopes of carbon bound to molecules of carbon dioxide in gas phase; in this case, the measured parameter is the isotopic ratio $\delta^{13}C = (\gamma/0.011237 - 1) \times 1000‰$, where $\gamma = [^{13}C^{16}O_2]/[^{12}C^{16}O_2]$ [1]. The lower the fraction of CO_2 in gas, the stronger the requirements to measurement sensitivity and accuracy. In real objects, contents of carbon dioxide in ambient atmosphere may differ by several orders of magnitude. For example, volcanic gases comprise approximately 20 % of carbon dioxide, human expired air contains 3 %, and the standard atmosphere contains from 0.03 % to 0.04 % of carbon dioxide.

The isotopic ratio $\delta^{13}C$ in these and many other examples carries important information. By presence of volcanic gases, the composition and dynamics of internal Earth spheres are revealed; isotopic tests of expired air in medicine are used for diagnosing about 20 diseases; the value of $\delta^{13}C$ in room air and in open atmosphere points to sources of gas contamination discerning, in particular, not only the contributions from natural and anthropogenic factors but also their geographical origin [1, 2]. Naturally, control of the isotopic ratio is important in isotope separation technologies, for example, in plasma technologies [3].

Traditionally this information is obtained by means of mass-spectrometry. In addition to a high-resolution isotopic mass-spectrometer itself, an analytical complex convention-ally includes a gas chromatograph and a system for gas sampling and preparation. The latter in most cases is only used for selecting carbon dioxide which is used for measuring the parameter $\delta^{13}C$.

Complexity, high cost and poor mobility of such complexes inspired origin of alternative methods based on laser spectroscopy. There are three main spectral bands in which the cross sections σ substantially differ: 4.3 μm ($\sigma \sim 10^{-19}$ cm^2), 2 μm ($\sigma \sim 10^{-22}$ cm^2) and 1.6 μm ($\sigma \sim 10^{-24}$ cm^2). Operation in the most sensitive to absorption range $\lambda \approx 4.3$ μm earlier required cryogenic equipment; however, presently such works are in progress due to creation of quantum-cascade lasers. The range $\lambda \approx 2$ μm is appropriate, although it requires unique diode lasers. The range $\lambda \approx 1.6$ μm is quite suitable because there are many commercially accessible lasers and detectors in this range.

In most works, gases with a high content of CO_2 were studied. A mobile laser spectrometer for measuring $\delta^{13}C$ in atmosphere with the accuracy $\Delta\delta^{13}C = 0.5‰$ near a volcanic crater was described in [4]. A cycle of investigations has been performed on the development of laser methods for isotopic analysis of human expired air which are in demand [2]. According to medical standards, the required accuracy of such measurements, as in the previous case, was $\Delta\delta^{13}C \leqslant 0.5‰$. In recent years the accuracy in some works was enhanced to $\Delta\delta^{13}C = 0.07‰$ in the range $\lambda \approx 2$ μm [5] and even to 0.06‰ [6]. Although the total concentration of CO_2 in expired air or in modelling mixtures [7] is several times lower than in volcanic gases it is still sufficiently high.

Laser methods were rarely employed for investigating isotopic ratios in ambient air. We may recall the measurements taken in the range $\lambda \approx 4.3$ μm [8–10] with quantum-cascade lasers and parametric generators.

The common feature of all mentioned and some other works on laser spectroscopy is that the gas sample is placed to an optical cell and the gas pressure is lowered to several or dozens Torr in order to separate, moderately broadened by pressure, absorption lines in a rotational structure of vibration bands referring to different isotopic modifications of the molecule. This complicates the experimental technique. An exception is paper [5] in which a high-precision method for isotopic analysis of the spectral lines broadened by pressure in real atmosphere was developed. Since measurements in [5] were performed for human expiration rich in carbonic dioxide, a sufficiently simple multipass cell provided needed absorption along the optical path.

The present work is aimed at combining the technique developed in [5] with an optical resonator that provides a longer optical path for measuring the carbon isotopic ratio $\delta^{13}C$ in ordinary atmosphere at low concentration of carbonic dioxide.

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2. Spectrometer

In developing the spectrometer we employed the experience on measuring $\delta^{13}C$ [5] in the spectral range near 2 μm. This range corresponded to the range of diode laser tuning 4977.4–4978.9 cm^{-1} and included the absorption lines of $^{12}CO_2$ and $^{13}CO_2$ isotopes, respectively:

$$\nu = 4978.022037 \text{ cm}^{-1}, \alpha_0 = 3.2 \times 10^{-4} \text{ cm}^{-1}$$

and

$$\nu = 4978.607720 \text{ cm}^{-1}, \alpha_0 = 2.3 \times 10^{-6} \text{ cm}^{-1},$$

where ν is the wavenumber (for the line centres without pressure shift); and α_0 is the absorption coefficient at a centre of the Voigt profile of line at atmospheric pressure. The needed absorption sensitivity was provided by using a multipass Herriott cell with the optical length of ~24 m. The following problems and limitations have been noticed:

1) absorption on the isotope lines differs by more than two orders of magnitude;

2) a weak water absorption line fits the range of mentioned transitions of CO_2, which requires taking it into account in the modelling;

3) calculations with data from [5] (the diameter of mirrors is 30 mm, the coupling hole diameter is 3 mm, the laser Gaussian beam diameter is 1.2 mm) show that deviation of the beam axis from the axis of the hole by more than 20 μm increases the losses of intensity of output radiation by a factor of greater than 2×10^4. Such random deviations are quite probable due to mechanical instabilities of the optical unit and are the main source of intensity fluctuations for radiation

passed through the cell in this scheme, which limit the measurement accuracy of $\delta^{13}C$.

In designing a new spectrometer we tried to minimise or exclude the influence of these factors.

Figure 1 shows a scheme of the experimental setup. Based on the analysis of molecule spectral database [11] we have chosen the spectral range near $\lambda = 1605$ nm in which the absorption lines of isotopes $^{12}CO_2$ and $^{13}CO_2$ are present, respectively:

$$2\nu_1 + 2\nu_2 + \nu_3 \text{ (R0)}, \nu = 6228.689985 \text{ cm}^{-1}, \alpha_0 = 4.5 \times 10^{-8} \text{cm}^{-1}$$

and

$$\nu_1 + 4\nu_2 + \nu_3 \text{ (P16)}, \nu = 6228.433041 \text{ cm}^{-1}, \alpha_0 = 6.2 \times 10^{-9} \text{cm}^{-1}.$$

This range has no lines of other molecules and the absorption coefficients of different isotopes differ by less than an order of magnitude. This range is difficult for measurements due to low values of absorption coefficients as compared to the range $\lambda \approx 2$ μm, and so the optical path should be made longer.

The employed diode laser had a fibre pigtail (FITEL), line width of less than 10 MHz, output power of 40 mW and was tuned by injection current in the frequency range 6227.9–6229.5 cm^{-1}. The injection current had a trapezoidal shape with the duration of 10 ms and pulse repetition rate of 100 Hz. The laser beam in the fibre tract was split to two parts. One part was directed to the analytical channel where the sample of air was placed into the optical resonator OR of length $l = 45$ cm formed by mirrors with the reflection coefficients of 0.9999 and radius of curvature of 1 m. The optical path in this resonator was estimated as $\sim l/(1 - r) \sim 5$ km. The light beam
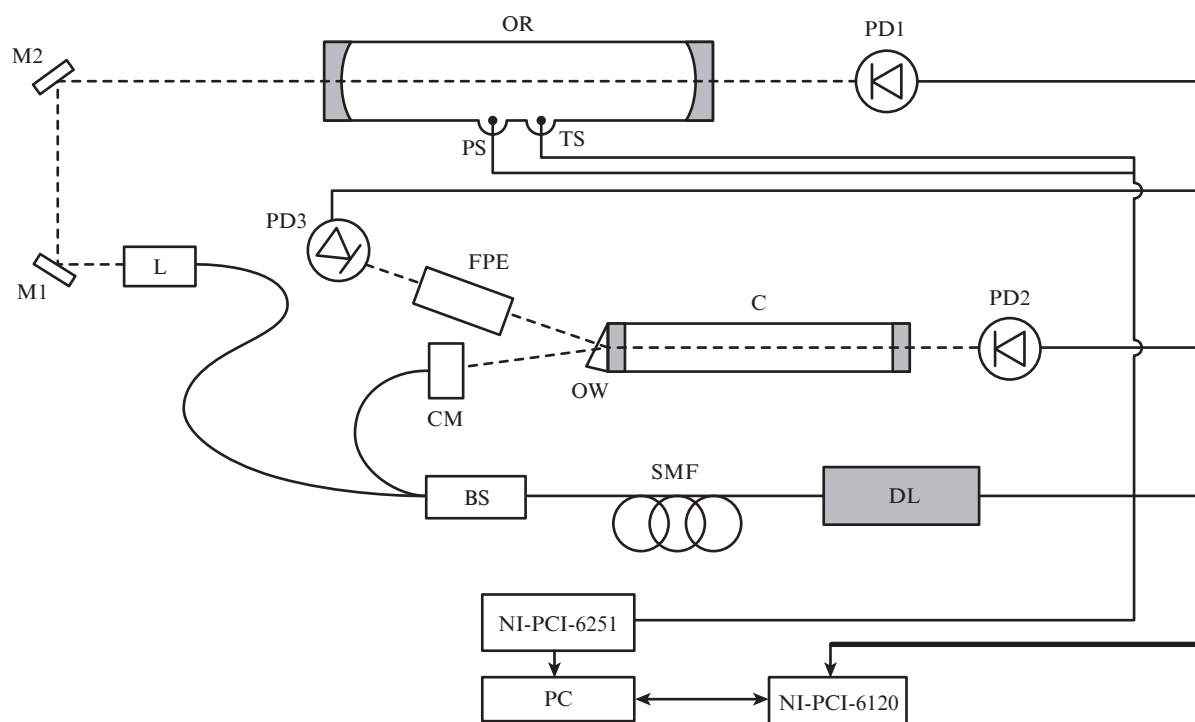

Figure 1. Scheme of the experimental setup:
(DL) diode laser; (SMF) single-mode fibre; (BS) beam splitter; (L) lens; (CM) collimator; (M1, M2) mirrors; (OR) optical resonator with air; (OW) optical wedge; (C) cell with CO_2; (FPE) Fabry–Perot etalon; (TS) and (PS) temperature and pressure sensors; (PD1, PD2, PD3) photodetectors; (NI-PCI-6120) and (NI-PCI-6251) multichannel input-output cards; (PC) computer.

was injected to the resonator along the axis by a matching lens L and mirrors M1 and M2. Employment of the fibre tract minimised possible perturbations of the light beam in an open space in front of the resonator.

The transmission τ of the Fabry–Perot resonator OR with an absorbing medium absent inside it is determined in the maximum [12, 13] by the expression $\tau = t^2/(1 - r)^2$, where t and r are the transmission and reflection coefficients of mirrors with respect to power. According to information from a mirror producer (LAYERTEC), $t \sim 10^{-5}$, i.e., $\tau \sim 10^{-2}$. This is noticeably less than in the Herriott cell (~0.7). Light attenuation by the resonator outside the absorption line is partially compensated for by a considerably higher laser power than in the case of analysing human expiration [5] and by more sensitive detection. Radiation passed through the resonator was detected by an InGaAs-photodetector PD1 (Hamamatsu G8370-01) with a specially developed trans-impedance amplifier that had the gain of $\sim 5 \times 10^7$ and relatively narrow bandwidth of ~50 kHz.

The other part of radiation after the fibre beam splitter BS was split once more by an optical wedge OW and directed to frequency calibration channels. One of the channels included the cell C with pure CO_2 at low pressure (~100 Torr). The position of the narrow absorption line of the main isotope was used as the absolute frequency reference [5]. Radiation reflected from the wedge OW passed to another channel, where a quartz Fabry–Perot cavity standard with the base of 10 cm was placed, and was used for obtaining the relative frequency scale in the tuning range of the laser radiation frequency. Radiation in both channels was detected by standard InGaAs-photodetectors (PDA10CS, ThorLabs) PD2 (the bandwidth is 775 kHz, the gain is 10^4) and PD3 (the bandwidth is 8.5 MHz, the gain is 10^3).

It was shown [5] that high-accuracy measurements of the isotopic ratio need taking into account automatically temperature and gas pressure variations in the analytical cell when light signals are processed. In our case it was provided by pressure and temperature sensors operating in the absolute scale with the inaccuracy of 10^{-2} mbar and 10^{-2} K, respectively.

Even more critical is maintaining the temperature of laser cooling, which was provided by a Peltier element with the inaccuracy of 10^{-4} K. In addition, the temperature was optically stabilised with the accuracy of 10^{-5} K. Such a level of stabilisation is kept for ~1 s, which corresponds to ~100 cycles of laser frequency tuning. The optical stabilisation of temperature is more thoroughly described in [5].

Analogue signals from the photodetectors and laser control unit were transmitted to a four-channel input–output NI-PCI-6120 card (800 kHz, 16 bit, National Instruments), and from the temperature and pressure sensors – to a multichannel NI-PCI-6251 card (600 kHz, 16 bit, National Instruments). Output digital signals from these cards were processed in a computer.

3. Measurement method and results

The approach suggested, similarly to [5], is based on the fact that the absorption spectra of CO_2 are well studied and can be reliably calculated with high accuracy. Presently, needed data can be found in several databases including HITRAN [11]. The approach suggests comparing the entire spectrum of measured intensities with the spectrum synthesised from spectroscopic data rather than comparing intensities of light passed through the absorbing medium in separate spectral sections. This can be technically realised, for example, by using a mathematical method known as multidimensional linear regression [5, 14]. In this case, as applied to the scheme of spectrometer described and formulated problem, the spectra can be juxtaposed by using the formula:

$$\frac{\Delta I_a(v)}{I_a(v)} = \sum_i k_i \alpha_i(v) + P^{(n)}(v). \tag{1}$$

Here, $I_a(v)$ is the intensity of light passed through the analytical channel without an absorbing medium (baseline); ΔI_a is the intensity variation due to the absorption in medium; k_i are the coefficients of linear regression; $\alpha_i(v)$ are the simulated spectra of $^{12}CO_2$ and $^{13}CO_2$ molecule absorption; and $P^{(n)}(v)$ is a polynomial of degree n introduced for taking into account the baseline. Regression analysis of measured spectrum showed that the employment of the correction polynomial $P^{(n)}(v)$ at $n = 1$ yields good accuracy. The Voigt profiles of lines in the spectrum were taken for simulation and the allowance was made for a pressure line shift.

Application of this method in diode laser spectroscopy on long traces and in multipass non-resonance cells are described in [5, 14] in more detail. In our case a peculiarity arises related with a mode structure in the cavity as an analytical device. The structure makes the spectrum $I_a(v)$ discrete, which hinders the employment of expression (1). The problem has been solved in the following way. The laser radiation was slightly modulated in amplitude (modulation of injection current with the depth of ~0.01) at the frequency (400 kHz) that was greater than the bandwidth of photodetector PD1 with an amplifier (50 kHz). In this case, the depth of frequency modulation approximately corresponded to the free spectral range of cavity (~300 MHz).

This approach does not affect the Q-factor of the cavity and the effective optical path length; however, the mode structure in the detected spectrum is suppressed. Nevertheless, the spectral resolution falls because the absorption spectrum is smoothed by the instrumental function with the width determined by the depth of frequency modulation. This may result in a systematic measurement error. To exclude it, the synthesised spectrum $\alpha_i(v)$ in the initial regression formula (1) should be substituted for the spectrum

$$\alpha_i^*(v) = \int_{v-\Delta v/2}^{v+\Delta v/2} \alpha_i(v') \Pi(v - v') dv', \tag{2}$$

where Δv is the width of instrumental function; and $\Pi(v)$ is the rectangular instrumentation function.

In Fig. 2 one can see the intensity of light passed through the resonator OR and detected by photodetector PD1 after averaging for 2 s over 200 cycles of laser frequency scanning. The total inclination of this dependence reflects the behaviour of the baseline, on the background of which one can see the absorption spectrum structure of the substance. By performing the regression procedure according to formula (1) one can find the model spectrum corresponding to the experiment at the pressure and temperature measured by the corresponding sensors PS and TS (762 Torr, 20.4 °C). This spectrum is shown in Fig. 2 [curve (*2*)].

The same spectrum after performing regression and subtraction of the baseline is presented in Fig. 3, it corresponds to
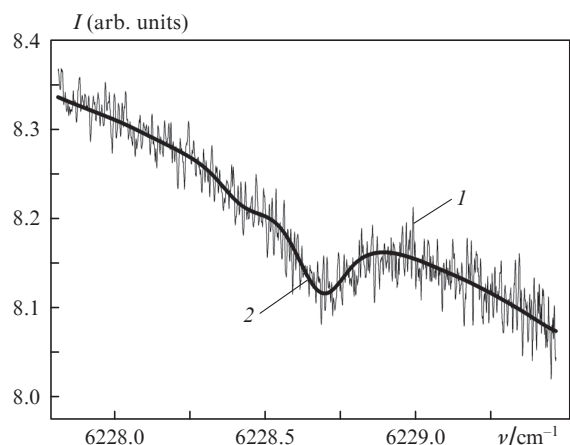
Figure 2. Experimental spectrum (*1*) recorded in the analytical channel and simulated spectrum (*2*).

$\delta^{13}C = -9.0‰$. The inset shows an enlarged fragment, in which the dashed curve refers to the spectrum after regression without an additional frequency modulation (2) in the simulated spectrum. One can see that in our conditions the modulation weakly affects the spectrum.
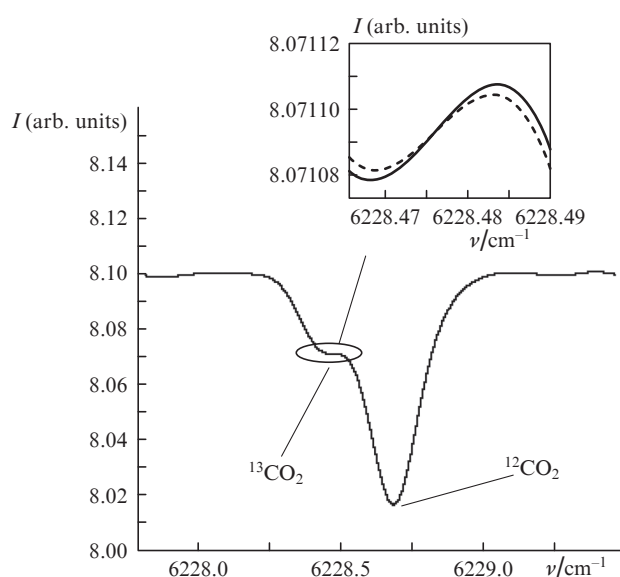

Figure 3. Absorption spectrum of CO_2 obtained by performing regression of the spectrum in Fig. 2 and subtracting the baseline. Dashed curve in the inset corresponds to the recovered spectrum without taking into account additional frequency modulation.

Mass-spectrometric investigations performed earlier showed that from 1950s to 2000s the carbon ratio δ^{13} has shifted from $-7‰$ to $-8.5‰$ [1] due to changed properties of natural, anthropogenic and technogeneous sources of carbon. This is confirmed by our measurements. Slightly higher absolute value of the ratio in our measurements may be related with presence of people in our laboratory, in which case CO_2 is released with a greater ratio $\delta^{13}CO_2$ (approximately $-27‰$ [2]).

The inaccuracy of our measurements related with random factors was verified by Allan variance. Figure 4 presents Allan variance for the isotopic ratio $\delta^{13}C$. One can see that the accu-

racy of determining $\delta^{13}C$ (square root of dispersion) is 0.3‰ after averaging for ~3000 s. The measurement presision was additionally tested in a series of subsequent experiments in which the root-mean-square deviation of the measured value was also 0.3‰. Deviations of Allan variance from the straight line describing normal noise in the region with the centre at ~100 s are specific features, which, in our opinion, can be related with the presence of regular fluctuations of parameters of the optical system at frequencies above the drift frequency. Thus, the isotopic ratio in a laboratory room is $-9.0‰ \pm 0.3‰$. Note that data [11] on the cross section of the absorption line of $^{13}CO_2$ used in our measurements are given with the inaccuracy of greater than 20%. This may affect the corresponding inaccuracy of measuring the absolute value of $\delta^{13}C$. Nevertheless, the obtained measurement presision of 0.3‰ remains unamended.
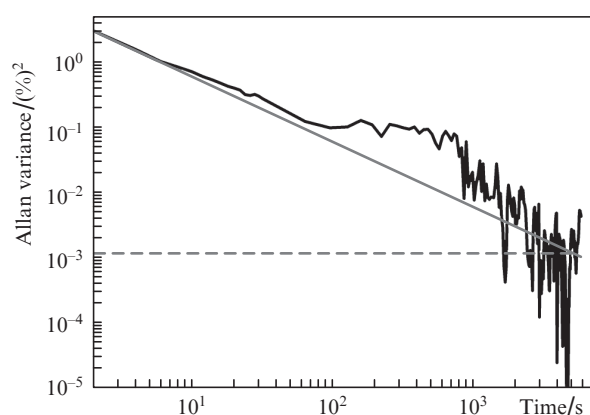

Figure 4. Allan variance for isotopic ratio $\delta^{13}C$.

4. Conclusions

The method for determining the carbon isotopic ratio in atmospheric air is suggested. It is based on the employment of the linear regression method in measuring the absorption of radiation of a tunable diode laser by CO_2 molecules in an external high-Q resonator filled with atmospheric air. The technique is suggested for regression comparison of absorption spectra when the passing radiation is detected only on eigenfrequencies of the resonator. For realising the method, a three-beam spectrometer was used, which provided the measurement presision of isotope ratio $\Delta\delta^{13}C = 0.3‰$. This result is comparable with results of previous laser measurements; however it was obtained in the conditions where the total contents of CO_2 in gas is by two-three orders of magnitude less and corresponds to its contents in the standard atmosphere of Earth.

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