

Systematic errors in diode-laser measuring the relative content of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$

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Abstract. Systematic errors appearing during measurements of the relative content of carbon dioxide gas isotopic isomers $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ with the help of mid-IR diode lasers tunable in the 4.35- μm region. The main sources of such errors are the luminescent component in the diode laser radiation, interference of analytic CO_2 absorption lines, as well as temperature and concentration variations of the gaseous medium being analysed. Based on simulations an analytic expression is obtained describing the systematic errors, which can be used to compare the parameters of analytic pairs of lines applied for isotopic analysis.

Keywords: tunable diode lasers, carbon isotope ratio $^{13}\text{C}/^{12}\text{C}$, high-resolution molecular spectroscopy.

1. Introduction

Laser analysis of the relative content of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in exhaled air is one of the promising approaches in non-invasive (without affecting the organism) medical diagnostics using preparations labelled by the stable carbon isotope ^{13}C [1–3]. Several approaches have been proposed during the last decade to solve the problem of isotopic analysis of CO_2 with the help of lasers [4–7]. An analyser based on mid-IR tunable diode lasers (TDL) (4.35 μm) and described in [8] can be used for high-precision measurements of the vibration–rotation transmission spectra of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, and for determining their relative concentration from a comparison of the absorption intensities in individual lines of these molecules.

Three pairs of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lines at 2293, 2297 and 2301 cm^{-1} [8] (Fig. 1) are optimal for isotopic analysis of CO_2 in the spectral region of 4.35 μm . In this spectral region, the absorption lines of these isotopic modifications of CO_2 have comparable intensities for quite different abundances of stable carbon isotopes in nature, corresponding to the isotope ratio of ~ 0.011 for the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations analysed in actual practice. Because of the interference of several absorption bands of CO_2 in this spectral range, the lines are closely spaced and are partially

overlapped. Under such conditions, it is difficult to measure absorption in the lines since the reconstruction of the laser pulse envelope and zero absorption levels in each line is a complicated task. The relative concentration of isotopic modifications can be measured in this case by using actually observed resonances of the transmission spectrum, which are not exactly the isolated absorption lines.

Absorption at the centre of the line of each isotopic isomer is calculated by using a number of simplifications, as shown in Fig. 2. The optical zero level Z_{opt} of the signal being detected is taken as the level of total absorption. This rules out the presence of a luminescent component or a weak side mode in the TDL radiation. In the absence of absorption, the envelope profile in each analytic line is replaced by a straight line connecting two peaks in the transmission spectrum that are closest to the resonance under consideration.

For the analytic line of each isotope, the spectral analysis according to this scheme leads to a certain optical density

$${}^i\chi_{\text{meas}} = -\ln \left[\frac{{}^i I({}^i\nu_0)}{{}^i I_0({}^i\nu_0)} \right] = {}^i\kappa_{\text{eff}}({}^i\nu_0) {}^i c l,$$

where ${}^i c$ is the concentration of the i th isotopic isomer in the gas mixture; ${}^i\kappa_{\text{eff}}({}^i\nu_0)$ is the effective absorption coefficient at the frequency corresponding to the centre of the line; and l is the optical path length. Obviously, the quantity ${}^i\kappa_{\text{eff}}({}^i\nu_0)$ calculated from this relation will be slightly different from the actual value that could be obtained in the case of an isolated line.

The ratio of the optical densities ${}^i\chi_{\text{meas}}$ for the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lines, which has to be determined as a result of the isotopic analysis, is

$$\begin{aligned} R_\chi &= \frac{{}^{13}\chi_{\text{meas}}}{{}^{12}\chi_{\text{meas}}} = \frac{{}^{13}\kappa_{\text{eff}}({}^{13}\nu_0) {}^{13}c}{{}^{12}\kappa_{\text{eff}}({}^{12}\nu_0) {}^{12}c} \\ &= \ln \left[\frac{{}^{13}I({}^{13}\nu_0)}{{}^{13}I_0({}^{13}\nu_0)} \right] / \ln \left[\frac{{}^{12}I({}^{12}\nu_0)}{{}^{12}I_0({}^{12}\nu_0)} \right]. \end{aligned} \quad (1)$$

In this case, the required ratio of concentrations of the isotopic isomers in the investigated medium can be written in the form

$$\begin{aligned} R &= \frac{{}^{13}c}{{}^{12}c} = \frac{{}^{12}\kappa_{\text{eff}}({}^{12}\nu_0)}{{}^{13}\kappa_{\text{eff}}({}^{13}\nu_0)} \ln \left[\frac{{}^{13}I({}^{13}\nu_0)}{{}^{13}I_0({}^{13}\nu_0)} \right] / \ln \left[\frac{{}^{12}I({}^{12}\nu_0)}{{}^{12}I_0({}^{12}\nu_0)} \right] \\ &= \frac{{}^{12}\kappa_{\text{eff}}({}^{12}\nu_0)}{{}^{13}\kappa_{\text{eff}}({}^{13}\nu_0)} R_\chi. \end{aligned}$$

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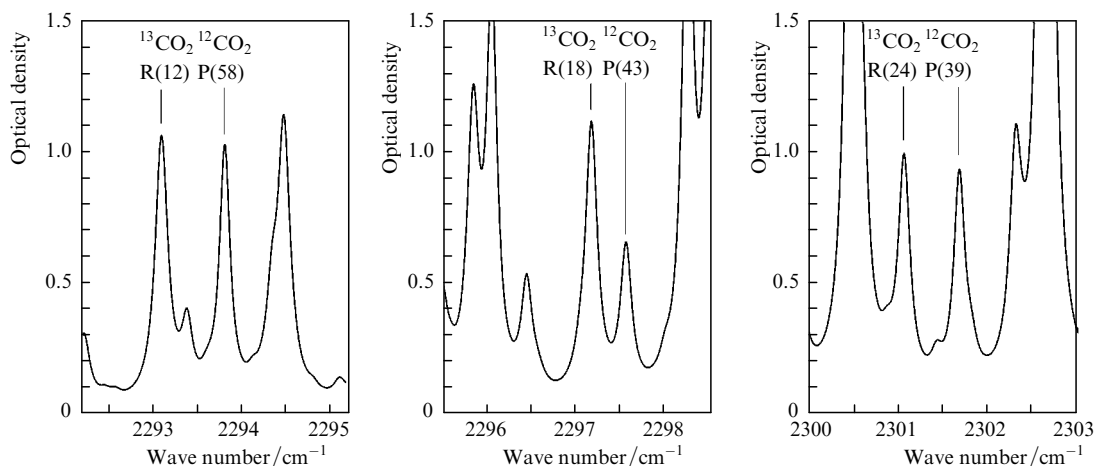


Figure 1. Absorption spectra for three pairs of lines of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ suitable for spectral isotopic analysis and recorded with the help of a TDL in the 4.35- μm spectral region at a total pressure ~ 750 Torr of the air mixture, a CO_2 partial pressure of 20 Torr, ratio of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ concentrations equal to 0.0113, and an optical path length of 10 cm.

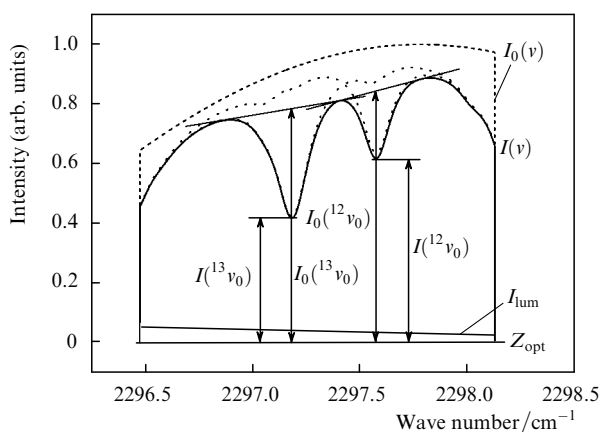


Figure 2. One of the analytic line pairs of CO_2 and the parameters used for calculating the carbon isotope ratio; $I_0(v)$ is the laser radiation envelope in the absence of absorption; $I(v)$ is the transmission spectrum being recorded; I_{lum} is the luminescence component; Z_{opt} is the optical zero level; the dotted curves are the envelopes in the absence of absorption in one of the analytic lines.

Since κ_{eff} differs from the actual absorption coefficient in the line, the value of R_χ calculated from the experimental data will also differ from the value R_{tab} obtained from the tabulated parameters of the absorption lines of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ (intensity and line-broadening coefficient, as well as the standard relative abundance of isotopic isomers).

The emergence of systematic errors in the isotopic analysis, arising during measurements of the parameter R_χ with the help of a TDL and its substitution for the required value of R deserves special attention. Below, the results of analysis of deviations of R_χ from R_{tab} caused by the variations in some factors are presented, and algorithms and methods are proposed for taking these deviations into account.

2. Sources of systematic errors in isotopic analysis

Under conditions of actual experiments using the diode laser spectroscopy, the systematic errors in determining the

isotopic ratio of carbon are caused by the errors of measurement of transmission spectrum of the gas mixture under consideration, and with the calculation of resonant absorption. The main sources of systematic errors arising during the recording of transmission spectra with the help of TDLs were considered earlier in [8].

In this work, we analyse the errors caused by variations in spectroscopic parameters upon variations in temperature of the gas mixture and by peculiarities of a TDL (the presence of a luminescent component in the multimode radiation and the specific shape of the laser pulse envelope). The effect of these factors was simulated with the help of computer calculations. This enabled us to compare the analytic parameters of various pairs of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lines as well as to determine the stability of results to a variation of the spectral recording conditions, estimate the systematic errors caused by various factors, determine the mutual relation between them under various experimental conditions, and select the optimal regimes for an analysis of the carbon isotope ratio.

In the course of simulation, we used the transmission spectra of CO_2 emulated for the conditions of exhaled air based on the tabulated parameters of CO_2 lines [9] taking into account the investigated factors as well as the spectral analysis algorithms and procedures that were used for analysing the spectra measured experimentally with the help of a TDL [8]. Such an approach was justified by the fact that an exact analytic description of systematic errors is hampered due to the complexity of the structure of the CO_2 spectra being analysed (many closely spaced lines and a strong effect of the wings of higher-intensity lines) as well as a large number of factors affecting the values of parameters of these spectra.

The most significant reasons behind systematic errors in the data obtained during the TDL measurement of the carbon isotope ratio with the help of a TDL are:

- (i) temperature sensitivity of the ratio of analytic line intensities;
- (ii) presence of a luminescent component in the TDL spectrum, leading to an error in determining the zero transmission level;
- (iii) effect of the algorithm used for analysing the complex profile of the absorption spectrum formed by

the wings of closely spaced high-intensity absorption lines; and

(iv) dependence of result on the absolute value of absorption in analytic lines due to the presence of the above three factors.

This set of parameters was included in the analysis in the form of parameters being varied during simulation.

3. Simulation technique

In order to calculate the spectra for various combinations of variable parameters, laser transmission spectra of CO_2 were emulated at the first stage of simulation for various experimental conditions under which the spectra were recorded with the help of a TDL. This stage consists of a number of consecutive steps.

First of all, the parameters of lines involved in simulation of the investigated spectral regions (near 2293, 2297 and 2301 cm^{-1}) are calculated at various temperatures under the conditions of standard relative concentration of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ equal to 0.0113 [10]. Calculations were performed by using the HITRAN96 database [9] and temperature dependences of the intensities and linewidths from this database. It included absorption lines of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ separated by $\pm 10 \text{ cm}^{-1}$ from the pairs of lines used for isotope analysis and having an intensity of at least $1 \times 10^{-23} \text{ cm mol}^{-1}$. In the course of calculations, the temperature was varied in the range 287–301 K with a step of 2 K.

After this, the absorption spectra at each temperature were emulated for the pair of CO_2 lines under conditions corresponding to the atmospheric pressure. In this case, the frequency increment used for calculating the spectra (10^{-3} cm^{-1}), the separation of the lines involved in calculations ($\pm 10 \text{ cm}^{-1}$), the length of the spectral segments being computed (4 cm^{-1}) and the line shape (Lorentzian) were specified.

The calculated absorption spectra were then used for emulating several series of transmission spectra, equivalent to those recorded experimentally with the help of a TDL. During calculations at each temperature, the relative concentration of CO_2 in air was varied from 0.1 % to 4 % with a step of 1 %, while the luminescent component in the laser

spectrum was varied from 0 % to 9 % with a step of 3 %. The optical path length was set at 10 cm, and the total pressure was set at 760 Torr. As a result, a series of transmission spectra was obtained for each analytic pair of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ lines with different variable parameters used in the investigations (a total of 160 spectra were obtained for each pair of lines).

At the next stage, the emulated transmission spectra were subjected to the procedure and algorithm described in [8] for calculating the parameter R_λ^m for $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ lines, which were used for processing the spectra registered with the help of a TDL.

Figure 3 shows the results of calculation of $R_\lambda^m(T, p_{\text{CO}_2}, I_{\text{lum}}) = {}^{13}\chi_m / {}^{12}\chi_m$ for three pairs of lines shown in Fig. 1. The dependences of $R_\lambda^m(T, p_{\text{CO}_2}, I_{\text{lum}})$ on absorption in $^{13}\text{CO}_2$ lines, i.e., on ${}^{13}\chi_m$, are shown for various temperatures and luminescence components (groups of four points each) in the TDL radiation. One can see that the sensitivity of the obtained values to the variation of absorption in the lines and hence to the CO_2 concentration and the luminescence component depends on temperature. Under certain conditions, the effect reverses its sign. This is primarily due to the temperature dependence of the ratio of line intensities for different isotopic isomers constituting the pair of lines. The systematic error associated with the above factors is the higher, the larger the difference between absorptions in the lines used.

At temperatures corresponding to the equalisation of line intensities in the pair, the highest stability of the data to the variation of absorption or the luminescence component is observed. One can see from Fig. 3 that this happens at a temperature of $\sim 293 \text{ K}$ ($\sim 20^\circ \text{C}$) for the pair of lines at 2293 cm^{-1} , and at a temperature of $\sim 302 \text{ K}$ ($\sim 29^\circ \text{C}$) for the pair at 2301 cm^{-1} . No data are available for the stability range in the working temperature range of 15–35 $^\circ \text{C}$ for the 2297 cm^{-1} pair, the intensities of whose lines differ by a factor of 2 at room temperature.

4. Derivation of functional dependences

The next stage of simulation involves the derivation of functional dependences describing the observed spread of

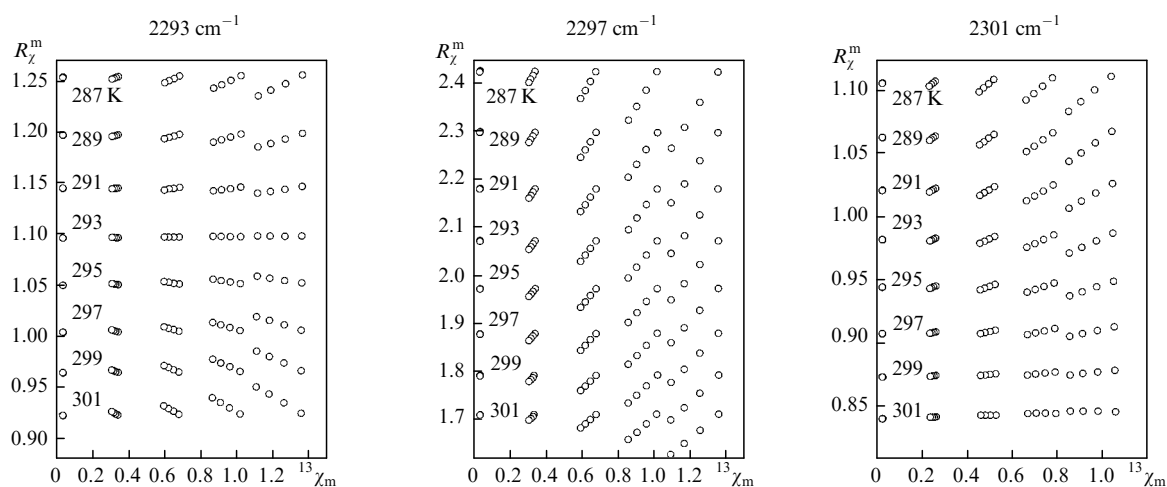


Figure 3. Dependence of the ratio of theoretical absorption coefficients in analytic lines of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ on absorption in the $^{13}\text{CO}_2$ line at various temperatures for different values of the luminescence component (groups of four points each) in TDL radiation for the three doublets used in the investigations.

the data. In other words, it is required to determine the form of the function

$$R^m = R_\lambda^m(T, A, L)$$

and find the values of the constants appearing in it. Here, T is the temperature; $A = {}^{13}\chi_m$ is the ${}^{13}\text{CO}_2$ line amplitude being measured; and L is the relative fraction of the luminescent component in the TDL signal.

An analysis of the data shows that one can first try to find out how the result is affected by the variation of temperature dependence of the intensity ratio of the absorption lines used in the simulation. For this purpose, it is convenient to present the function R^m in the form

$$R^m = R_0^m(T) \left[1 + \frac{\varepsilon(T, A, L)}{1000} \right],$$

where $\varepsilon(T, A, L)$ is the correction to the main value of the absorption ratio for various isotopes, which depends on the varying factors T , A , and L ; and $R_0^m(T)$ is the temperature dependence of the ratio of the isotopic isomer lines in the absence of other perturbing factors.

Figure 4 shows the dependence of $\varepsilon(T, A, L)$ on absorption in the ${}^{13}\text{CO}_2$ line for various doublets. As in Fig. 3, the parameters being varied in this case are the temperature and the luminescence component. The values of $R_0^m(T)$ for each temperature used in simulation is determined by extrapolating the theoretical results for $L = 0$ to the region of small absorptions, where $A \approx 0$. It was found that in the investigated temperature range, the dependence $R_0^m(T)$ can be described quite accurately with the help of a quadratic relation in temperature of the type

$$R_0^m(T) \approx R_0 + R_1 T + R_2 T^2, \quad (2)$$

where the coefficients R_0 , R_1 and R_2 are determined for each doublet with the help of approximants that describe

Table 1. Expansion coefficients in expression (3).

| Parameters | Line pairs | | |
|------------|-----------------------|-----------------------|-----------------------|
| | 2293 cm^{-1} | 2297 cm^{-1} | 2301 cm^{-1} |
| R_0 | 35.98 | 98.83 | 25.17 |
| R_1 | -0.2140 | -0.6078 | -0.1457 |
| R_2 | 0.0003241 | 0.0009472 | 0.0002157 |
| B_0 | -14.40 | -49.61 | 393.4 |
| B_1 | 0.05394 | 0.2639 | -2.780 |
| B_2 | 0 | -0.000322 | 0.00496 |
| M_0^0 | -34.06 | -22.32 | 0.3400 |
| M_1^0 | 0.1166 | 0.06749 | -0.01618 |
| M_2^0 | 0 | 0 | 0.0000502 |
| M_0^1 | -19.06 | -8.376 | -1.48 |
| M_1^1 | 0.06513 | 0.02418 | 0.0026 |
| M_2^1 | 0 | 0 | 0 |
| M_0^2 | -23.31353 | -4.29897 | 389.08 |
| M_1^2 | 0.07962 | 0.0107 | -2.907 |
| M_2^2 | 0 | 0 | 0.00537 |
| K_0 | 1 | 1 | 1 |
| K_1 | 0.001 | 0.00045 | 0.00084 |
| K_2 | 0.006 | 0.0105 | 0.009 |

Note: The number of points processed in each case $N = 160$.

the computational data most correctly. Table 1 contains the obtained values of the coefficients R_0 , R_1 and R_2 .

It follows from Fig. 4 that the dispersion of data upon a variation of temperature, absorption intensity and luminescence component have a quite regular and orderly form that is typical of each of the investigated doublets. Note that upon a variation of these parameters in the above-mentioned intervals, the maximum spread for the 2293 cm^{-1} doublet is $\sim 45\%$. The corresponding values for the doublets 2297 cm^{-1} and 2301 cm^{-1} are $\sim 68\%$ and $\sim 28\%$ respectively, i.e., the last doublet is the least sensitive to temperature variations.

A detailed analysis of the function $\varepsilon(T, A, L)$ shows that it can be presented as the product of the absorption coefficient of ${}^{13}\text{CO}_2$ being measured and the sum of two

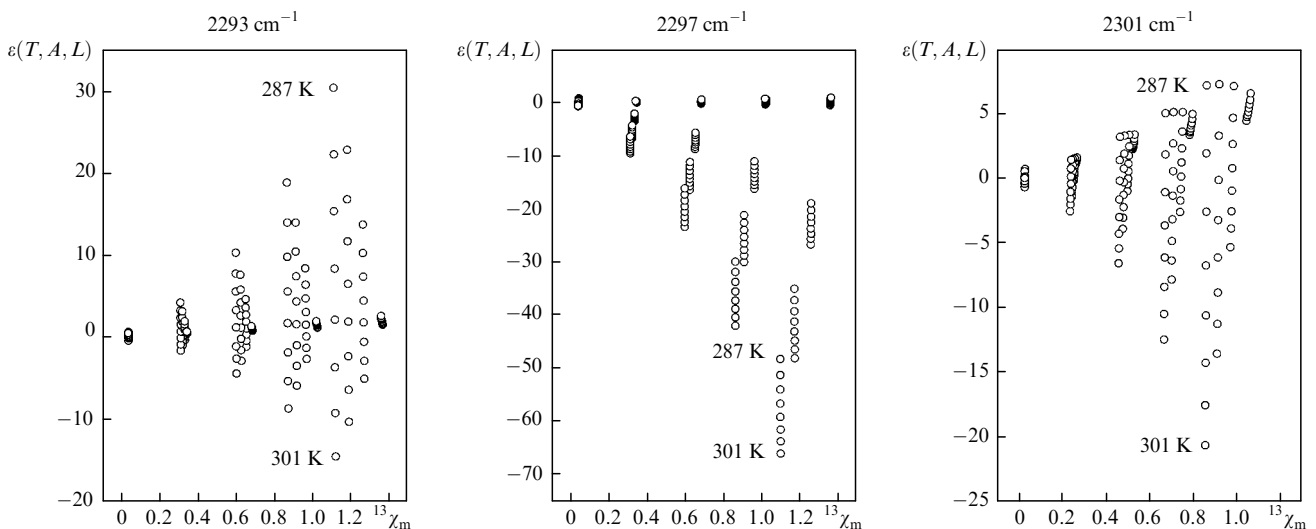


Figure 4. Variation of the values of $\varepsilon(T, A, L)$ calculated by taking into account the temperature factor $R_0^m(T)$ upon a variation of absorption in the ${}^{13}\text{CO}_2$ line and the luminescence component of TDL radiation for the three doublets used in the investigations. Here and in the remaining figures, the temperature is varied from 287 to 301 K in each series of eight points corresponding to the given luminescence level.

functions, one of which depends only on temperature, i.e.,

$$\varepsilon(T, A, L) = A[\beta(T) + \xi(T, A, L)].$$

In this case, the function $\beta(T)$ describes the calculated data obtained for the case $L = 0$, while the function itself can be presented as a quadratic expansion in powers of temperature:

$$\beta(T) = B_0 + B_1T + B_2T^2.$$

The values of the expansion coefficients B_0 , B_1 and B_2 are determined for each doublet from an analysis of the computational data (see Table 1).

In this case, the function $\xi(T, A, L)$, which is a small residual correction to the effect of the luminescence component being considered, is characterised by the fact that it can be presented as the product of the luminescence component L itself, the polynomial $\kappa(L, A)$ of expansion in L and A , and the polynomial $\mu(T, A)$ of expansion in powers of T and A , i.e.,

$$\xi(T, A, L) = L\kappa(L, A)\mu(T, A),$$

$$\mu(T, A) = (M_0^0 + M_1^0T + M_2^0T^2)$$

$$+ (M_0^1 + M_1^1T + M_2^1T^2)A + (M_0^2 + M_1^2T + M_2^2T^2)A^2,$$

$$\kappa(L, A) = K_0 + (K_1 + K_2A^2)L.$$

Figure 5 shows the spread of the computational data obtained after taking into account the effect of the cofactor $L\kappa(L, A)$, i.e., the parameter $\mu(T, A) = \xi(T, A, L)/L\kappa(L, A)$.

The figure shows approximation curves drawn through the calculated values obtained for different parameters being varied (temperature and luminescence component of the TDL). These curves can be used to find the coefficients of expansion of the polynomial $\mu(T, A)$ in powers of temperature and absorption in the line $^{13}\text{CO}_2$ that match best with the calculated data (see Table 1).

Thus, the final expression describing the main dependences of the isotope ratio R^m being evaluated on temperature, absorption in the line $^{13}\text{CO}_2$ and the fraction of the luminescence component of the signal can be presented in the form

$$R_\chi^m(T, A, L) = R_0^m(T) \left\{ 1 + \frac{1}{1000} A[\beta(T) + L\kappa(L, A)\mu(T, A)] \right\}. \quad (3)$$

The difference between the value of $R_\chi^m(T, A, L)$ obtained from a processing of the data on emulated spectra and the value of $R_\chi^{\text{calc}}(T, A, L)$ obtained from (3) with the help of the obtained coefficients, i.e.,

$$\delta R(T, A, L) = R_\chi^m(T, A, L) - R_\chi^{\text{calc}}(T, A, L)$$

characterises the quality of the computational data described with the help of formula (3).

Figure 6 shows the spread in the values of $\delta R(T, A, L)$ obtained for the doublets used by us as a function of absorption in the line $^{13}\text{CO}_2$ determined with the help of the technique described above. The expansion parameters obtained in the course of simulation and fitting of the data for $R_\chi^m(T, A, L)$ are shown in Table 1 for each doublet. Note that for the pair of 2293 cm^{-1} lines, the mean deviation is $\delta R = -0.00047\%$, and the standard deviation (Sd) is 0.0756% , while the root-mean-square deviation (Se) is equal to 0.0077% . The corresponding values for the pairs of 2297 cm^{-1} and 2301 cm^{-1} lines are $\delta R = -0.000102\%$

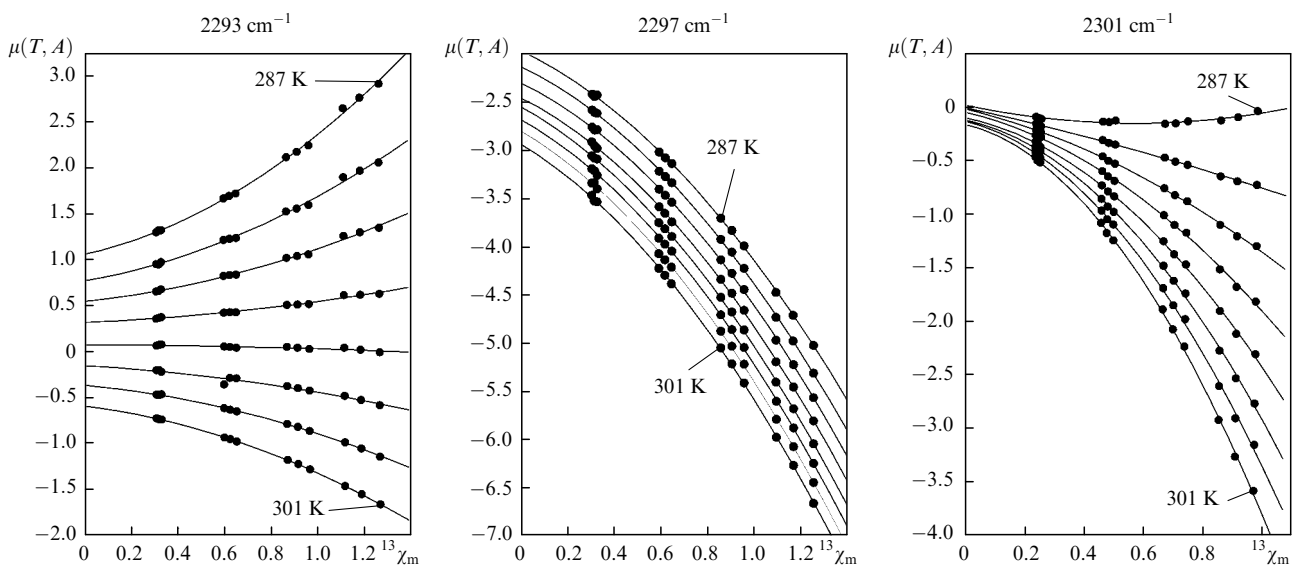


Figure 5. Spread of the theoretical points after normalisation to the polynomial $L\kappa(L, A)$ and the result of fitting of approximation curves for finding the parameters of the polynomial $\mu(T, A)$.

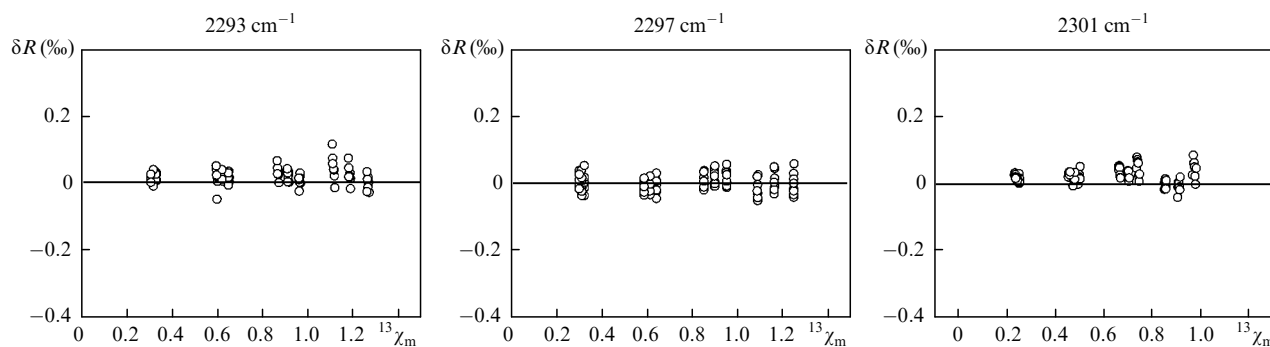


Figure 6. Spread of the resulting remainder after fitting of the data calculated by (3).

and 0.02334 ‰, $S_d = 0.026$ ‰ and 0.02157 ‰, $S_e = 0.00267$ ‰ and 0.0022 ‰, respectively. It is also worthwhile to note that the mean-square error in fitting of the data obtained by using the above parameters is less than 0.1 ‰. Thus, the precision with which systematic errors are evaluated by controlling the variable parameters (temperature, partial pressure of CO_2 , and luminescence component) and by incorporating the corrections in the obtained values in accordance with formula (3) can be much higher than the precision (~ 0.5 ‰) with which the carbon isotope ratio must be measured for diagnostic applications.

5. Discussion of results of simulation

The results of simulation can be used for comparing the analytic properties of the pairs of lines under consideration with a view to minimise and/or consider the possible systematic errors in data. Such results were used to calculate the temperature coefficient $R(T)$ and amplitude coefficient $\beta(T)$ at room temperature (20 °C) in the absence of a luminescence component in the laser signal, as well as the temperature at which the obtained data are least sensitive to luminescence. These values are presented in Table 2.

Table 2. Comparative parameters of the line pairs of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$.

| Parameter | Line pairs | | |
|---|-----------------------|-----------------------|-----------------------|
| | 2293 cm^{-1} | 2297 cm^{-1} | 2301 cm^{-1} |
| Temperature coefficient for $T = 293 \text{ K}$, $L = 0$ / ‰ K^{-1} | -24 | -26 | -19 |
| Amplitude factor for $T = 293 \text{ K}$, $L = 0$ (‰) | 1.40 | 0.069 | 4.67 |
| Temperature of lowest sensitivity to the luminescence component at $\mu = 0$, $A = 1/\text{K}$ | 293.9 | 351.5 | 301.8 |

An analysis of the data presented in Table 2 shows that in order to minimise the temperature dependence of the results of carbon isotope ratio analysis, the 2301 cm^{-1} pair is a bit more preferable since the 2293 cm^{-1} and 2297 cm^{-1} line pairs have similar properties. The dependence of the result on the absorption line amplitude for zero luminescence component at $T = 293 \text{ K}$ is the weakest for the 2297 cm^{-1} pair of lines. When this doublet is used, the variation in the absorption coefficient of lines by unity causes a deviation of the obtained values of the isotopic ratio by just ~ 0.07 ‰. For the pair of 2293 cm^{-1} lines, a

variation in the result by ~ 0.5 ‰ will be observed only for a 30% difference in the absorption coefficients in the line. Hence in this case also the results are quite stable to the filling errors for the analytic cell. A much stronger dependence is observed for the 2301 cm^{-1} line pair, and the line amplitude must be kept constant to within 10 % if this pair of lines is used. This may be due to the effect of the closely spaced CO_2 absorption lines of much higher intensity.

It follows from formula (3) that the calculated value of R_χ will not depend on the magnitude of the luminescence component if either of the two polynomials $\kappa(L, A)$ and $\mu(T, A)$ is put equal to zero. Since $\kappa > 1$, we can equate $\mu(T, A)$ to zero and thus determine the temperature at which the obtained data on isotopic analysis will be stable to the effect of luminescence for a certain value of absorption (for example, ~ 1). It can be seen from Table 2 that this is observed at room temperature for line pairs 2293 and 2301 cm^{-1} , and hence this peculiarity can be used in measurements when required. However, the highest sensitivity to luminescence is observed at room temperature for the pair of 2297 cm^{-1} lines. Hence, on the whole, the properties of the pair of 2293 cm^{-1} lines make it most suitable for practical applications.

By monitoring the parameters T , A , and L with the required degree of precision, we can use simulation to estimate the systematic errors in the experimental data for determining the carbon isotope ratio on account of the variation in the measuring conditions, and then introduce the necessary corrections. For example, the correction factor used for investigating samples with different CO_2 concentrations can be determined for a fixed luminescence component and at a constant temperature. Conversely, the effect of variation in the ambient temperature can be taken into account for a constant L and for nearly equal absorption amplitudes in the lines. The introduction of such corrections makes it possible to reduce the obtained experimental data to the standard experimental conditions.

6. Conclusions

We have analysed the systematic errors that can arise during measurement of the relative concentration of the isotopic isomers $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ with the help of mid-IR tunable diode lasers in the 4.35- μm spectral region. As the possible main sources of such errors, we considered the luminescence component in the diode laser radiation, interference of analytic absorption lines of CO_2 , as well as temperature and concentration variation in the gaseous medium being analysed. As a result of simulation, a relation

was obtained to describe analytically the emerging systematic errors and to compare the parameters of the analytic pairs of lines used in the isotopic analysis. This relation can be used to make corrections to the obtained experimental results and minimise the systematic error to less than 0.1%, which is important for practical applications of this technique for medical diagnostics.

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References

1. Kuznetsov A.I., Logachev A.P., Stepanov E.V. *Izv. Akad. Nauk SSSR*, (10), 1909 (1990).
2. Ivashkin V.T., Nikitina E.I., Stepanov E.V., Milyaev V.A., Zyryanov P.V., in *Helicobacter Pylori: Revolyutsiya v gastroenterologii* (Revolution in Gastro-Enterology) (Moscow: Slovo, 1999).
3. Stepanov E.V., Milyaev V.A., Selivanov Yu.G. *Usp. Fiz. Nauk*, **170**, 458 (2000).
4. Becker J.F., Sauke T.B., Loewenstein M. *Appl. Opt.*, **31** (12), 1921 (1992).
5. Cooper D.E., Martinelli R.U., Carlisle C.B., Riris H., Bour D.B., Menna R.J. *Appl. Opt.*, **32** (33), 6727 (1993).
6. Higashi Y., Ohohara H., Sasaki Y. *Igaku*, **4**, 8 (1994).
7. Murnick D.E., Peer B.J. *Science*, **263**, 945 (1994).
8. Stepanov E.V. *Kvantovaya Elektron.*, **32**, 981 (2002) [*Quantum Electron.*, **32**, 981 (2002)].
9. Rothman L.S., Rinsland C.P., Goldman A., Massie S.T., Edwards D.P., Flaud J.-M., Perrin A., Camy-Peyret C., Dana V., Mandin J.-Y., Schroeder J., McCann A., Gamache R.R., Watson R.B., Yoshino K., Chance K.V., Jucks K.W., Brown L.B., Nemtchinov V., Varanasi P. *J. Quant. Spectr. Rad. Transfer*, **60**, 665 (1998).
10. Grigor'ev I.S., Meilikhov E.Z. (Eds) *Fizicheskie velichiny: Spravochnik* (Handbook of Physical Quantities) (Moscow: Energoatomizdat, 1991).