

Frequency modulation upon nonstationary heating of the p–n junction in high-sensitive diode laser spectroscopy

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Abstract. A special type of modulation of the injection current of a diode laser is proposed at which the frequency modulation of radiation is not accompanied by the residual amplitude modulation. This method considerably reduces the influence of the diode laser radiation instability on the recorded absorption spectra. This allows a prolonged monitoring of small amounts of impurities in gas analysis by retaining a high sensitivity. Prolonged measurements of absorption spectra are performed at a relative absorption of 8×10^{-7} . By using a 50-cm multipass cell with the optical length of 90 m, the absorption coefficient of $1.2 \times 10^{-10} \text{ cm}^{-1}$ was detected. As an example, the day evolution of the background concentrations of NO_2 molecules was measured in the atmosphere.

Keywords: diode laser spectroscopy, frequency modulation, laser diode.

1. Introduction

One of the promising directions in gas analysis is based on the use of tunable diode lasers (DLs) [1]. The measurement sensitivity is determined by the minimal detectable absorption. When weak absorptions are measured, the intensity of the emission spectrum of a laser in the absence of absorption (base line) can exceed the intensity of absorption lines by many orders of magnitude. The base line of DLs can have local frequency features, which are unstable in time. These features are poorly distinguishable from real absorption lines and adversely affect the accuracy and sensitivity of measurements. The influence of the base-line features on the detected absorption spectrum can be minimised by modulating the radiation frequency of DLs.

Various methods for modulating the DL frequency and related detection methods are considered in detail in review [2]. The DL radiation frequency is usually modulated by modulating the amplitude of the injection current of the laser with the help of a generator of sinusoidal or rectangular signals. The modulating signal or its second

harmonic is used as the reference signal for synchronous detection of photodetector signals. At the output of a synchronous detector, the first or second derivative of the absorption spectrum is detected, respectively.

It is obvious that upon modulation of the injection current, both the DL radiation frequency and intensity are modulated. The residual amplitude modulation of radiation (after signal processing) not always can be separated from the amplitude modulation related to the interaction of frequency-modulated radiation with an absorbing medium, which complicates the recording of weak absorption spectra and impairs the sensitivity.

When the first harmonic is detected, the residual amplitude modulation is large, and this method is rarely used. The detection of the second harmonic provides theoretically a complete elimination of the residual amplitude modulation, and this method is often called the zero-base line method. But this is the case only for the linear light–current characteristic of a DL, when the DL output power linearly depends on the injection current.

In this paper, we propose a new method for the frequency modulation of the DL radiation, which almost completely eliminates the residual amplitude modulation and allows one to record directly the first derivative of the absorption coefficient on a medium under study. The method is based on the use of multifunctional input–output signal controllers specifying an arbitrary shape of the injection current of the laser, which can be performed synchronously with recording the optical signal. This allows one to discard additional generators and lock-in detectors and to process optical signals by using programming.

2. Experimental

Figure 1 shows the scheme of the experimental setup. A 5-mW, 635-nm (15750 cm^{-1}) Toshiba DL with a Fabry–Perot resonator was used. The laser equipped with a thermal resistor was mounted on a Peltier thermoelectric element inside a hermetically sealed housing. A spectrometer had three optical channels: the analytic channel (with the PD1 photodetector), reference channel (with PD2), and base-line recording channel (with PD3). Hamamatsu S1336 silicon photodiodes were used as photodetectors. A cell of length 18 cm with an absorbing gas was placed in the reference channel. In our case, the cell was filled with NO_2 at a concentration of about 1% (9600 ppm) diluted with nitrogen to the atmospheric pressure. This provided the relative absorption in nitrogen dioxide in the reference channel at the level of 3%–5%. Cells with nitrogen at the

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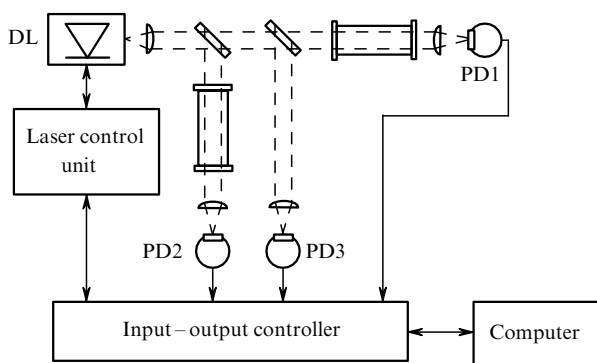


Figure 1. Scheme of the experimental setup.

atmospheric pressure containing NO_2 at different low concentration were placed in the analytic channel.

The DL was controlled and absorption spectra were recorded by using a multifunctional NI-PCI6120 input-output controller programmed with a LabView 7.1 system. The controller included four analogue-to-digital (ADC) and two digital-to-analogue (DAC) 16-bit converters with the sampling frequency up to 1 MHz. One ACD and one DAC channel were used to stabilise the DL temperature, three ACD channels were used to record photodetector signals in three optical channels and one DAC channel was employed to control the injection DL injection current.

The DL injection current pulses had repetition rates between 30 and 200 Hz and the amplitude varying from 30 to 60 mA. Figure 2 shows the shape of one current period. The injection current period consists of three regions: the zero-current region, which is used to record 'the optical zero' (a), the region of stationary lasing (b), and the region of scan and modulation of the DL frequency (c).

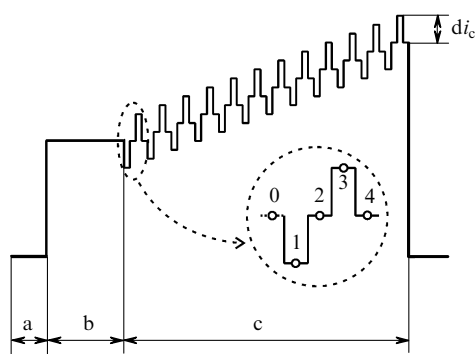


Figure 2. Schematic shape of one period of the DL injection current (the real number of modulation periods in the region c is from 200 to 1000). The inset shows the shape of one modulation period of the injection current.

The inset in Fig. 2 shows the shape of one modulation period of the DL injection current of duration 10–40 μs . The modulation occurs due to periodic decrease (point 1) and increase (point 3) of the injection current by the value d_{i_c} . The values of the current at points 2 and 4 are equal, and therefore the laser radiation intensities at these points in the absence of an absorbing medium are also virtually the same. At the same time, the DL radiation frequencies at points 2 and 4 are different. This is explained by the fact that

the temperature of the active region of the laser at point 1 decreases due to the decrease in the injection current, and the temperature at point 2 is lower than that at point 0 because it has no time to return to its stationary value. On the contrary, the temperature at point 3 increases, and it is higher at point 4 than at point 0. Some difference between the DL radiation intensities at points 2 and 4 caused by the temperature dependence of the threshold current of the laser during the recording of spectra is the effect of the higher-order smallness.

Signals from all three optical channels are divided after recording into four data arrays $I_n(i)$ ($n = 1-4$, i is the numbering of the array point). For example, $I_3(i)$ is the array of DL radiation intensities recorded in one of the channels at instants corresponding to points 3 in the inset in Fig. 2. Figure 3 shows these four intensity arrays recorded in the third base-line channel. No absorption in the atmosphere is observed in this case due to a short optical path (~ 20 cm). One can see that the radiation intensities in arrays corresponding to points 2 and 4 in the modulation period coincide.

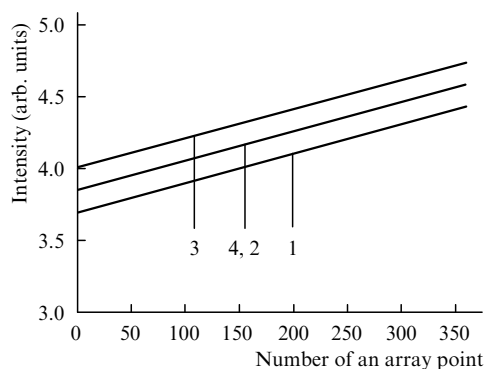


Figure 3. Radiation intensity recorded in the base-line channel. The numbers denote the arrays of the corresponding points of the modulation period (see Fig. 2).

In the presence of an absorbing medium, similar points of the four arrays have different frequencies. The arrows in Fig. 4 show the positions of the maximum of one of the absorption lines of NO_2 in these arrays in the reference channel. The analysis of the difference of frequencies of

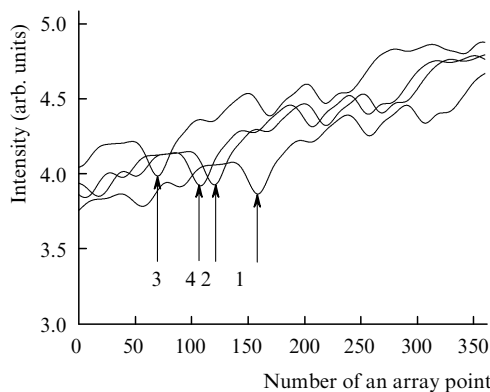


Figure 4. Intensity recorded in the reference channel with an NO_2 cell. The numbers denote the arrays of the corresponding points of the modulation period (see Fig. 2).

arrays 1 and 3 corresponds to the traditional modulation method and of arrays 2 and 4 – to the proposed modulation method with the nonstationary heating and cooling of the active region of the laser. To obtain the required modulation depth of the radiation frequency of the order of the absorption linewidth, the modulation depth of the DL injection current in our method should be several times greater than that in the traditional modulation method.

3. Noise parameters of the absorption spectrum

Let us compare the noise parameters and limiting sensitivities of the proposed and traditional frequency modulation methods. The injection current modulation shown in Fig. 2 allows one to find the difference quantities in the transmission spectrum of a medium under study by three different methods (depending on the used points of the modulation period). These difference quantities are proportional to the derivatives of the absorption spectrum with respect to the modulation period. Because in the modulation spectroscopy they are called the derivatives of the absorption spectrum, we also will use this terminology, according to which $I_{d1}(i) = I_3(i) - I_1(i)$ is the first derivative of the absorption spectrum calculated by points 1 and 3; $I_{d2}(i) = I_3(i) + I_1(i) - 2I_2(i)$ is the second derivative of the absorption spectrum calculated by points 1, 2, and 3; and $I_{d1T}(i) = I_4(i) - I_2(i)$ is the first derivative of the absorption spectrum related to the nonstationary heating and cooling of the laser at points 2 and 4.

Because the laser radiation intensity can change considerably during the frequency scan, the calculated derivatives should be normalised to the base line, i.e. the incident radiation intensity. If weak absorption is measured, the derivatives can be normalised to the intensity in the given optical channel averaged for the modulation period of the injection current, i.e. to the value $I_N(i) = [I_2(i) + I_4(i)]/2$. As a result, we obtain the arrays of normalised derivatives whose values are independent on the incident radiation intensity:

$$A_{d1}(i) = \frac{I_{d1}(i)}{I_N(i)}, \quad A_{d2}(i) = \frac{I_{d2}(i)}{I_N(i)}, \quad A_{d1T}(i) = \frac{I_{d1T}(i)}{I_N(i)}.$$

The normalised derivatives of the absorption spectrum in the reference channel are shown in Fig. 5. The modulation depth of the DL injection current was 0.3 mA when A_{d1} and A_{d2} were recorded and 1.5 mA for recording A_{d1T} .

The noise parameters of different derivatives of the absorption spectrum were estimated by the Allan variance plots [3]. The Allan variance method, which is widely used to analyse the noise type in spectral measurements, allows one to determine the optimal time and the number of accumulations of a quantity being measured to obtain the maximum signal-to-noise ratio. The Allan plots are constructed in a double logarithmic scale as the dependence of the Allan variance on the number of accumulations of a quantity being measured. If the measured quantity includes only the normal random noise, the Allan plot has a constant slope equal to -1 because the dispersion of the normal noise is inversely proportional to the number of measurements. If the system has noises of other types (drift, $1/f$ and $1/f^2$ noises), the Allan plot achieves its minimum at a certain number of accumulations, and the further accumulation of the quantity being measured reduces the signal-to-noise ratio. The application of the Allan variance to analyse

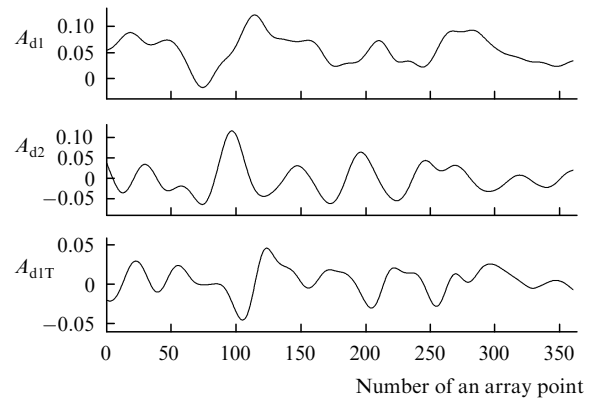


Figure 5. Normalised derivatives of the absorption spectrum.

the noise and limiting sensitivity in diode laser spectroscopy is described in detail in [4].

The Allan variance was measured by using a 5-cm cell containing 28 ppm NO_2 diluted with nitrogen to the atmospheric pressure, which was placed in the analytic channel of the spectrometer. The relative absorption in NO_2 under these conditions was about 4×10^{-5} . Measurements were performed for three different types of derivatives at one fixed point of the absorption spectrum. The time between measurements was 30 ms. The Allan variance plots for A_{d1} , A_{d2} , and A_{d1T} are presented in Fig. 6.

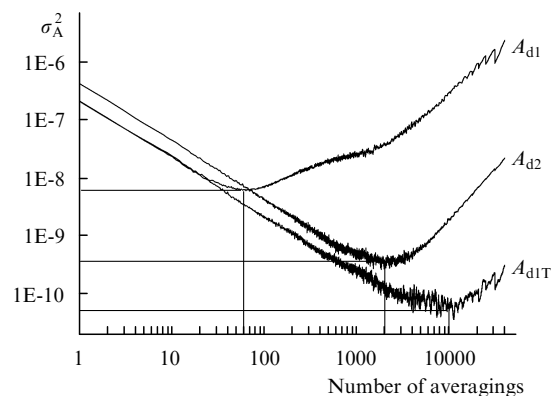


Figure 6. Allan variance plots for A_{d1} , A_{d2} , and A_{d1T} .

One can see that the first derivative A_{d1} of the absorption spectrum calculated by points 1 and 3 has a strong drift, and for the number of averagings above 60 (corresponding to the accumulation time of 2 s), the signal-to-noise ratio can only decrease. The second derivative A_{d2} calculated by points 1, 2, and 3 has the optimal number of averagings of about 2000 (accumulation time is 60 s). The derivative A_{d1T} with the optimal number of averagings of 10000 (accumulation time is 300 s) has the best noise parameters.

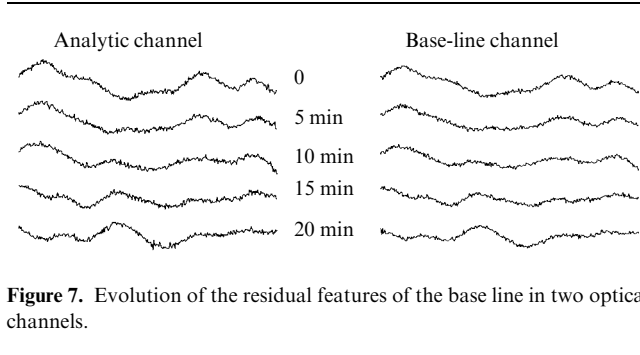
Table 1 presents the noise parameters of three different derivatives of the absorption spectrum obtained by using the Allan variance plots. The first derivative A_{d1T} related to the nonstationary heating and cooling of the laser at points 2 and 4 admits a prolonged accumulation of a signal with a large number of averagings and allows one to obtain the signal-to-noise ratio at each point of the spectrum that is three times larger than that obtained by using the second derivative A_{d2} .

Table 1. Noise parameters of different derivatives of the absorption spectrum.

Derivatives of the absorption spectrum	Optimal number of averagings	Accumulation time/s	Minimal dispersion σ_A^2	Maximum signal-to-noise ratio $(\sigma_A^2)^{-1/2}$
A_{d1}	60	2	6.4×10^{-9}	1.3×10^4
A_{d2}	2000	60	3.7×10^{-10}	5.3×10^4
A_{d1T}	10000	300	4.2×10^{-11}	1.5×10^5

The recording of the first derivative A_{d1T} related to the nonstationary heating and cooling of the laser provides the best suppression of the residual amplitude modulation of the DL radiation. However, we have failed to achieve a complete suppression, and the residual amplitude modulation is manifested in the residual features of the base line of the DL, namely, in the fact that even in the absence of an absorbing medium, the recorded emission spectrum of the laser has a structure masking the absorption spectrum. The compensation of the residual features of the base line can substantially enhance the sensitivity of the spectrometer, but the problem is complicated because these features can be unstable in time. The features of the base line in different optical channels can have different shape due to, for example, the spatial inhomogeneity of the DL radiation and different types of radiation interference in different optical paths.

Figure 7 shows the evolution of the residual features of the base line recorded in two optical channels of the spectrometer for 20 min. One can see that the shape of the base line in both channels considerably changes during 15–20 min. Therefore, the residual features cannot be compensated by recording them preliminary and then subtracting from the recorded spectra. At the same time, the shapes of features in different optical channels at each instant almost completely coincide, although their amplitudes can differ. This fact allows one to take into account the residual features in the analytic channel with the help of a linear regression, by using their shape from the base-line channel.

**Figure 7.** Evolution of the residual features of the base line in two optical channels.

4. Processing of absorption spectra for measuring low concentrations of particles

The limiting sensitivity of a diode laser spectrometer is determined not only by the operation regime of the laser and the method of recording absorption spectra, but also by the spectrum-processing method and the algorithm for calculating the concentration of an absorbing material. In this paper, we used signals from three optical channels (analytic, reference, and base line) and employed the method of multidimensional linear regression.

When the modulation of the DL radiation frequency is used and the derivatives of the absorption spectrum are recorded, the influence of the features of the base line on the recorded spectrum is strongly, although not completely, suppressed, and therefore the normalised derivative recorded in each of the optical channels can be written in the form

$$A(i) = kS(i) + ai^3 + bi^2 + ci + d + G(i),$$

where k is a coefficient proportional to the concentration of absorbing molecules and the optical path; $S(i)$ is the corresponding derivative of the absorption spectrum of the matter under study; $ai^3 + bi^2 + ci + d$ is the third-degree polynomial taking into account the residual influence of the base line caused by the amplitude modulation of the DL; and $G(i)$ takes into account other features of the shape of the laser base line, which cannot be taken into account by the third-degree polynomial.

Note that the absorption spectrum of the matter under study is absent in the base-line channel, while in the reference channel this spectrum is quite intense compared to the residual base line. Taking also into account that, according to our experimental data (Fig. 7), the shapes of residual features $G(i)$ are identical at each instant in the analytic and base-line channels, the signals in three optical channels can be written in the form

$$A_{An}(i) = k_{An}S(i) + a_{An}i^3 + b_{An}i^2c_{An}i + d_{An} + m_{An}G(i),$$

$$A_{Ref}(i) = k_{Ref}S(i),$$

$$A_{BL}(i) = a_{BL}i^3 + b_{BL}i^2 + c_{BL}i + d_{BL} + m_{BL}G(i),$$

where the indices An, Ref, and BL refer to the analytic, reference, and base-line channels, respectively.

The concentration N_{An} of matter in the analytic channel of optical length L_{An} is related to the concentration N_{Ref} in the reference channel of length L_{Ref} in the case of low absorption by the relation

$$N_{An} = N_{Ref} \frac{L_{Ref}}{L_{An}} \frac{k_{An}}{k_{Ref}}.$$

Thus, knowing the concentration N_{Ref} of matter in the reference channel, it is necessary to find the ratio k_{An}/k_{Ref} . To do this, one should solve the linear regression problem and find the signal $A_{An}(i)$ in the analytic channel as a combination of the reference signal $A_{Ref}(i)$, the third-degree polynomial $P^{(3)}(i) = ai^3 + bi^2 + ci + d$, and the signal $A_{BL}(i)$ in the base-line channel:

$$A_{An}(i) = \gamma_{reg} A_{Ref}(i) P^{(3)}(i) + C A_{BL}(i),$$

where $\gamma_{reg} = k_{An}/k_{Ref}$ is the required coefficient of regression and C is the coefficient characterising the ratio of

residual features $G(i)$ of the same shape in the analytic and base-line channels.

We solved this problem in the LabView medium by using the modified virtual General LS Linear Fit tool incorporated into the standard configuration of the program.

5. Determination of the limiting sensitivity of measuring the NO₂ concentration

To determine the limiting sensitivity of the spectrometer, we measured the NO₂ impurity concentrations in a 5-cm cell at the concentration 28 ppm in nitrogen at the atmospheric pressure. We detected the second derivative A_{d2} of the absorption spectrum and the first derivative A_{d1T} related to the nonstationary heating and cooling of the laser. The modulation depth of the DL injection current was 0.3 and 1.5 mA, respectively. Signals were processed by the method of linear regression of the signal in the analytic channel by signals in the reference and base-line channels and by the coefficients of a third-degree polynomial. The NO₂ concentration was calculated from the coefficient of regression γ_{reg} . The Allan variance was determined for the product of the concentration by the optical path NL (in ppm m). Figure 8 presents the corresponding Allan variance plots.

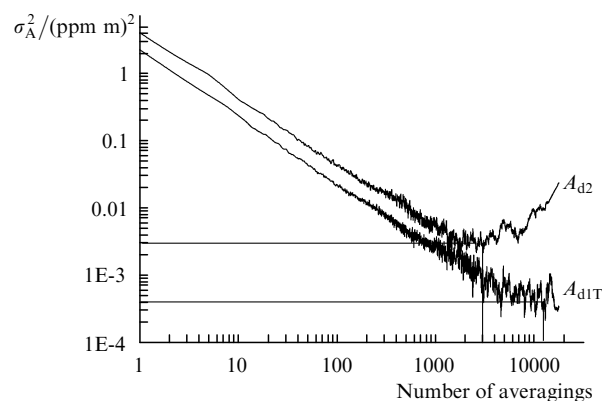


Figure 8. Allan variance plots for the NO₂ concentration upon recording the second derivative A_{d2} by points 1, 2, and 3 and the first derivative A_{d1T} by points 2 and 4.

Upon recording the first derivative A_{d1T} related to the nonstationary heating and cooling, the minimal dispersion is 3.9×10^{-4} (ppm m)², whereas the second derivative A_{d2} gives the dispersion that is almost an order of magnitude higher [3.1×10^{-3} (ppm m)²]. Because the limiting sensitivity (standard deviation) is equal to the square root of the minimal Allan variance, the recording of A_{d1T} and A_{d2} provides the limiting sensitivity equal to 20 and 56 ppb m, respectively, which corresponds to the relative absorption in NO₂ equal to 6×10^{-7} and 1.6×10^{-6} , respectively.

The limiting relative-absorption sensitivity of 6×10^{-7} is comparable with the best results achieved at present [1]; however, the methods used by other authors can provide this sensitivity only for measurements times no more than a few minutes. At longer measurement times, the sensitivity decreases due to, as a rule, the uncontrollable drift of the laser base line features. For this reason, prolonged measurements requiring a high sensitivity are performed by periodically calibrating a spectrometer every several minutes

[5]. Such a calibration is carried out by evacuating the analytic cell and filling it with a gas, which does not absorb in the working spectral range (the so-called zero gas).

The method for recording and processing absorption spectra used in our experiments allows us to take into account the drift of the laser base line features and perform prolonged high-sensitivity measurements without periodic calibration of the system. Figure 9 presents the measurements of NO₂ at the concentration 28 ppm in a 5-cm cell. The measurements were performed for 5 h with the 1-min interval between separate measurements. Upon recording the first derivative A_{d1T} by points 2 and 4, the measured concentration was 27.7 ± 0.6 ppm, which corresponds to the standard deviation of the relative absorption coefficient of about 8×10^{-7} . Upon recording the second derivative A_{d2} by points 1, 2, and 3, the short-term measurement accuracy was somewhat worse (± 0.9 ppm); however, during prolonged measurements a considerable drift was observed, and the measurement accuracy achieved ± 5 ppm.

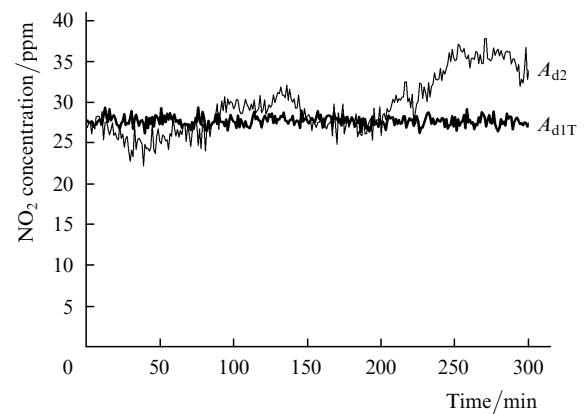


Figure 9. Long-term measurements of the NO₂ concentration in a cell by recording the first derivative A_{d1T} by points 2 and 4 and the second derivative A_{d2} by points 1, 2, and 3.

6. Measurements of the background NO₂ concentration in the atmosphere

The use of the frequency modulation producing the nonstationary heating and cooling of the active region of a laser provides the measurement of the NO₂ concentration with the sensitivity as high as 20 ppb m over the optical path of 5 cm. A direct extrapolation of these values shows that, by using a multipass optical system of length 100 m, we can achieve the sensitivity of 0.2 ppb. However, the multipass system can introduce the additional noise and drift to the recorded signal, and therefore the parameters of a spectrometer with such a system require a direct experimental verification.

We placed a 50-cm multipass Herriot cell [6] with the optical path of about 90 m in the analytic channel of the spectrometer. The cell was used without the external housing, which allowed us to measure the content of NO₂ in the atmosphere. The background content of NO₂ in the atmosphere was, according to different measurements, from a few units to a few tens of ppb; it is pointed out that this content can considerably vary depending on the measurement site and time.

Figure 10 presents the background concentration of NO_2 measured under laboratory conditions for 7 h. The NO_2 concentration changed during the experiment from 3 to 12 ppb. Previous measurements of NO_2 in a 5-cm cell (Fig. 9) suggest that the measured values correspond to the real variation in the content of NO_2 in the atmosphere and are not related to any instrumental drifts. The limiting sensitivity of the spectrometer in this experiment was estimated as 0.5 ppb from the standard deviation of the NO_2 concentration measured for a short time (of the order of 10 min), which is approximately 2.5 times worse than the value obtained by a direct extrapolation of measurements performed in a short cell. This sensitivity corresponds to the measurement error of the absorption coefficient equal to $1.2 \times 10^{-10} \text{ cm}^{-1}$.

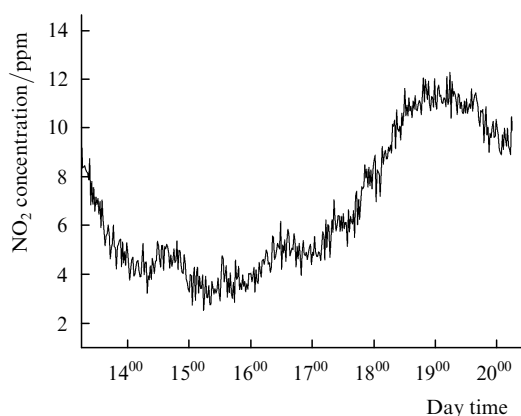


Figure 10. Background NO_2 concentration in the atmosphere.

The concentration of NO_2 in the atmosphere was recently measured by using a DL in [7]. Measurements were performed, as in our paper, at a wavelength of 635 nm. In the case of a standard frequency modulation, an optical path of 160 m, and averaging over 256 recorded spectra, the sensitivity was 8 ppb. The sensitivity obtained in our paper is considerably higher, demonstrating the advantage of our method of high-sensitive spectroscopy.

7. Conclusions

The method of frequency modulation with the nonstationary cooling and heating of the active region of a diode laser proposed in our paper provides almost a complete suppression of the residual amplitude modulation of radiation. The limiting sensitivity of the method in measurements of the relative absorption by NO_2 at low concentrations is about 8×10^{-7} . A substantial advantage of the method is its good long-term stability. This makes it possible, on the one hand, to accumulate a signal for a long time to improve the signal-to-noise ratio and, on the other, to monitor low concentrations of gases for a long time with the impairment of the sensitivity and without periodic calibrations of the spectrometer. The background concentrations of NO_2 were measured in the atmosphere for 7 h at a level of 3–12 ppb with an accuracy of 0.5 ppb.

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