

# Measurement of formaldehyde H<sub>2</sub>CO concentration in air using diode vertical-cavity lasers

V.Ya. Zaslavskii, A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, S.M. Chernin

**Abstract.** A two-channel gas-analysing spectrometer is developed using a vertical-cavity surface-emitting laser (VCSEL) ( $\lambda = 1.79 \mu\text{m}$ ) and a multi-pass cell (total optical length 39 m) for studying the absorption spectra and measuring the background concentration of formaldehyde. High-resolution absorption spectra of formaldehyde are obtained within the VCSEL frequency tuning range ( $\lambda \sim 1.79 \mu\text{m}$ ). Changing the background concentration of H<sub>2</sub>CO, the sensitivity limit of the gas analyser is estimated.

**Keywords:** diode laser, temperature stabilisation, modulation, interference noise suppression, correlation processing.

## 1. Introduction

Measuring the formaldehyde (H<sub>2</sub>CO) concentration is of primary importance due to the wide use of formaldehyde in chemical industry, production of building materials, medicine, and other fields. Having penetrated into the organism, formaldehyde causes a general toxic effect, at the same time having the irritating, allergenic and carcinogenic properties. According to the World Health Organization data, formaldehyde is recognised as carcinogenic [1]. Formaldehyde is involved in global environmental processes. In the course of photochemical processes in the atmosphere, including its upper layers, it is produced in the reaction of hydroxyl radical OH with methane CH<sub>4</sub>, and then dissociates under the action of light, producing free radicals.

The maximal acceptable average daily concentration of formaldehyde in the atmosphere is 0.5 ppm, the background concentration being not greater than 8 ppb. The measurements of background formaldehyde concentration, using the methods of diode laser spectroscopy (DLS), seem to be promising, because they provide high sensitivity of measurements, and the devices based on near-IR diode lasers (DL) combine high operation speed with compact size and mobility. Diode laser molecular detection is based on the presence of absorption spectral lines of the molecule in the oscillation band of the DL. The data on the fine vibration-rotational structure of the formaldehyde absorption spectra in the near-IR region (1–2  $\mu\text{m}$ ) are scanty, and in the

spectral database HITRAH-2008 the formaldehyde spectra are presented only in the mid-IR region (3–12  $\mu\text{m}$ ) [2, 3]. Hence, the studies of the formaldehyde absorption spectra in the near-IR range ( $\lambda \sim 1.8 \mu\text{m}$ ) using DLS is of both the scientific and the practical interest. Measuring the H<sub>2</sub>CO concentration in the mid-IR spectral range requires cryogenics and special IR optics. This makes the gas analysers substantially more complex and expensive, and the practical use of such devices is limited by their large size, high energy consumption [4, 5] and cost. That is why we studied the possibility to create a compact gas analyser for measuring the background formaldehyde concentration in the near-IR region. For this purpose we used a diode vertical-cavity surface-emitting laser (VCSEL), oscillating at  $\lambda = 1.79 \mu\text{m}$

## 2. Experimental setup

Figure 1 shows a schematic diagram and a photograph of the two-channel diode laser spectrometer for studying the absorption spectra and measuring the concentration of H<sub>2</sub>CO in the near-IR region. By means of a beamsplitter the DL radiation is directed into the analytic channel and into the reference one.

In the analytic channel, depending on a particular problem, we used either an ordinary optical cell 2 m long, or a multi-pass evacuated cell with the base length of 25 cm and the total optical length of 39 m. In the reference channel a Fabry–Perot interferometer was placed with the region of free dispersion of  $0.04983 \text{ cm}^{-1}$ , aimed at linearisation of the frequency scale. In this channel the mounting of a reference low-pressure methane cell was also provided for temperature stabilisation of the DL crystal with respect to the absorption line of the reference gas, and for absolute referencing of the spectral frequency scale. As a source of formaldehyde we used its 40% aqueous solution (formalin). The DL spectrometer was controlled by an electronic unit, interfaced with a 16-bit input-output board NI PCI-6052E. The sampling rate of the board was 333 kHz. The code for controlling the DL spectrometer and processing the signals is written in LabView 9.0 graphical programming environment using NI DAQ 8.2 drivers.

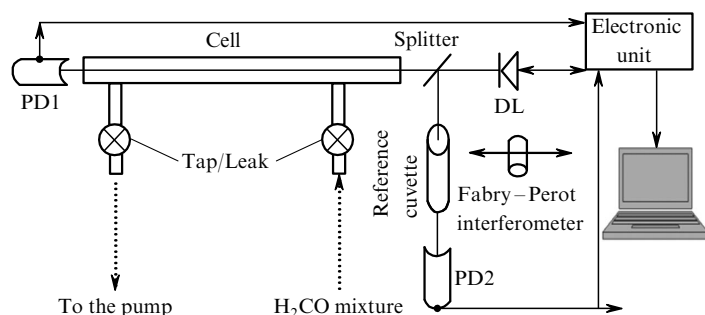
*The diode laser.* A VL-1790-1-SP-C-C5 diode VCSEL (Vertilas, Germany) [6] was used as a radiation source. In contrast to traditional DLs, in which the crystal faces, playing the role of cavity mirrors, are perpendicular to the plane of p–n junction, in this type of lasers the axis of the cavity with specially created dielectric epitaxial mirrors is oriented vertically. With the effective length of the active region 1–5  $\mu\text{m}$  the frequency tuning range of the DL may

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**Figure 1.** Schematic diagram and photograph of the two-channel DL spectrometer. PD1 and PD2 are photodetectors with preamplifiers in the analytic and the reference channel, the tap and the leak are elements of the vacuum system for gas mixture puffing/evacuation.

exceed  $20 \text{ cm}^{-1}$ . The basic characteristics of the laser at the diode temperature  $25^\circ\text{C}$  are presented below.

Radiation power/mW	0.6
Wavelength/nm	1790
Threshold current/mA	0.9
Maximal current/mA	15
Maximal tuning range/nm	3
Oscillation line width/MHz	30
Current tuning coefficient	
$\frac{\Delta\lambda}{\Delta I}/\text{nm mA}^{-1}$	0.7
Temperature tuning coefficient	
$\frac{\Delta\lambda}{\Delta T}/\text{nm }^\circ\text{C}^{-1}$	0.11
Beam angular divergence/deg	20

The DL was pumped by trapezoidal current pulses having the duration  $\tau \sim 1 - 3 \text{ ms}$  and the repetition rate  $200 \text{ Hz}$ . The maximal pump current did not exceed  $4 \text{ mA}$ . The frequency tuning of the DL radiation was provided via the variation of the refraction index in the active region of the laser crystal at the moment of pump current pulse passage. For the mentioned DL pump current parameters the frequency tuning range  $\delta\nu$  reached  $\sim 6 \text{ cm}^{-1}$ . The temperature stabilisation of DL frequency scanning cycles was implemented by means of a Peltier thermoelement and a thermal sensor, embedded in the DL unit. The PI control law and the additional regime of thermal stabilisation with respect to an absorption line of a reference gas were used. These measures ensured the temperature stabilisation of the DL crystal at the level of  $2 \times 10^{-5} \text{ }^\circ\text{C}$ .

**Photodetectors.** InGaAs photodiodes G8371 (Hamamatsu, Japan) [7] (the diameter of active area  $1 \text{ mm}$ ) with a Peltier thermoelement and a thermistor embedded were used as photodetectors. The detection ability of the diodes was  $D^* \sim 2 \times 10^{12} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ , the spectral response in the laser oscillation region was  $S = 1.07 \text{ A W}^{-1}$ . The signals from the photodetectors were input to preamplifiers having the band width  $67 \text{ kHz}$  and the conversion ratio  $20 \text{ V mA}^{-1}$ .

### 3. $\text{H}_2\text{CO}$ absorption spectra within the frequency tuning range of the DL

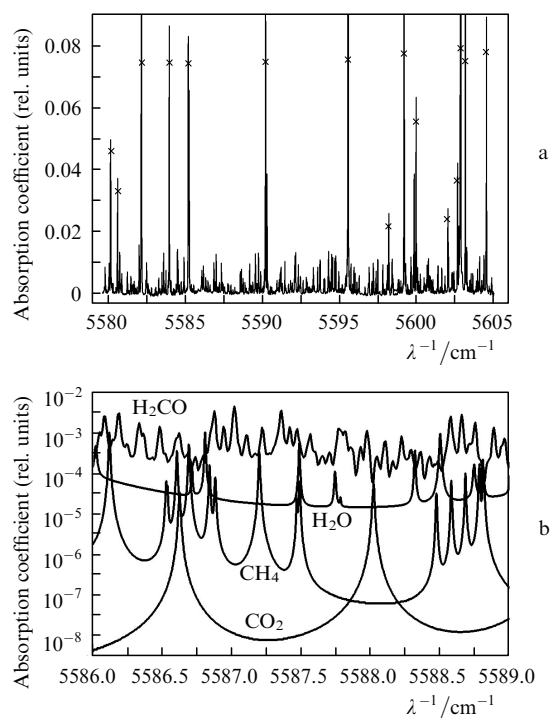
The DL oscillation frequency region covers vibration-rotational lines of  $\text{H}_2\text{CO}$ , belonging to overtone and combination molecular vibrational bands. The most intense

in this range is the band  $2\nu_5$  [2]. The P-branch lines of this band fall into the tuning region of the DL.

To record the formaldehyde spectra the  $200\text{-cm}$ -long cell was used. The pressure in the cell was measured by means of an Elemer pressure sensor (the measurement range  $0 - 100 \text{ kPa}$ , the error  $0.2\%$ ). The temperature was monitored with a thermal sensor. To avoid interference, the wedge-shaped windows were used with the wedge angle  $10'$ . Before recording the spectrum the cell and the formalin container were evacuated and degassed. Then, using the leak, the water and formaldehyde vapours were let into the cell. The total pressure of the gas mixture in the cell at the temperature  $23^\circ\text{C}$  was kept to be  $10 - 16 \text{ Torr}$ , which provided recording narrow, not broadened absorption lines of  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ .

To linearise the frequency scale of the spectra, a Fabry-Perot interferometer was placed into the reference channel. The transformation of the temporal scale of the spectrum into its frequency counterpart was performed by cubic spline processing of the transmission maxima of the Fabry-Perot etalon, provided that the free dispersion of the latter is known ( $0.04973 \text{ cm}^{-1}$ ). For absolute referencing of the scale the well-known water absorption lines were used. The frequencies of these lines were taken from the HITRAN-2008 spectral database.

At continuous scanning of the oscillation frequency by varying the DL crystal temperature in the range  $4 - 50^\circ\text{C}$  and fixed values of the pump currents a survey high-resolution absorption spectrum of formaldehyde vapour was recorded. Figure 2a represents the absorption spectrum with strong water vapour lines used as frequency reference. It is seen that in the frequency tuning region of the DL the  $\text{H}_2\text{CO}$  absorption spectra have complex vibration-rotational structure, the absorption coefficient being not greater than  $0.02$ . The relative error of the frequency measurement was less than  $0.0004 \text{ cm}^{-1}$  and was determined by the instability of the DL temperature and by the accuracy of locating the maxima of the absorption peaks in the Fabry-Perot frequency standard. The absolute error of the frequency scale was determined by the accuracy of locating the  $\text{H}_2\text{O}$  line centres, given in the HITRAN-2008 database. To measure the background concentrations of formaldehyde the spectral region  $5586 - 5589 \text{ cm}^{-1}$  was chosen (see Fig. 2b), in which the influence of interfering lines of atmospheric gases  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  was minimal. The model spectra of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  molecules in the air were calculated under the following conditions: the optical path was  $39 \text{ m}$ , the total pressure was  $25 \text{ Torr}$ , and



**Figure 2.** Survey high-resolution spectrum of the formaldehyde vapour, recorded using the VSCSEL (a), and the model spectra of the H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> molecules in air together with the typical spectrum of formaldehyde (b). The lines of water vapour are marked with crosses.

the content of water, carbon dioxide and methane was 1 %, 0.03 % and 1.5 ppm, respectively. The spectral parameters of the lines were taken from the HITRAH-2008 database. The spectra were calculated using the Line by Line procedure and the Voigt contour [8].

#### 4. Modulation regime of DL oscillation for recording weak absorption

For DLS recording of weak absorption lines (absorption coefficient less than  $\sim 10^{-4}$ ) use is made of an algorithm that, besides the traditional technique of signal acquisition followed by filtration, involves the specification of the particular shape of the pump current pulse that minimises the flicker noise component in the reception path and the temporal drift of the base line.

A two-pulse regime of the laser pumping was used. One pulse provided the frequency referencing to the closest doublet line of water for the thermal stabilisation of the laser. The other pulse was used to record the formaldehyde absorption spectra. The amplitudes and the front slopes of the pump current pulses were controlled independently, which allowed precise change of the pump current value and frequency tuning in each pulse. The repetition rate of the pulses was 200 Hz, their duration varying in the range 1–5 ms.

Each pulse of the DL pump current was amplitude-modulated with the frequency, equal to the sampling rate of the NI PCI-6052E board. The preamplifier transmission frequency was 60 kHz. The modulation depth was chosen to provide the oscillation frequency shift by a half-width of the formaldehyde absorption lines and to obtain the maximal contrast of absorption. Further mathematical processing of

the amplitude-modulated signals included the following steps:

(i) Taking the logarithm of the frequency-shifted signal components in correspondence with the Bouguer–Lambert–Beer law and obtaining the effective first derivatives with respect to time.

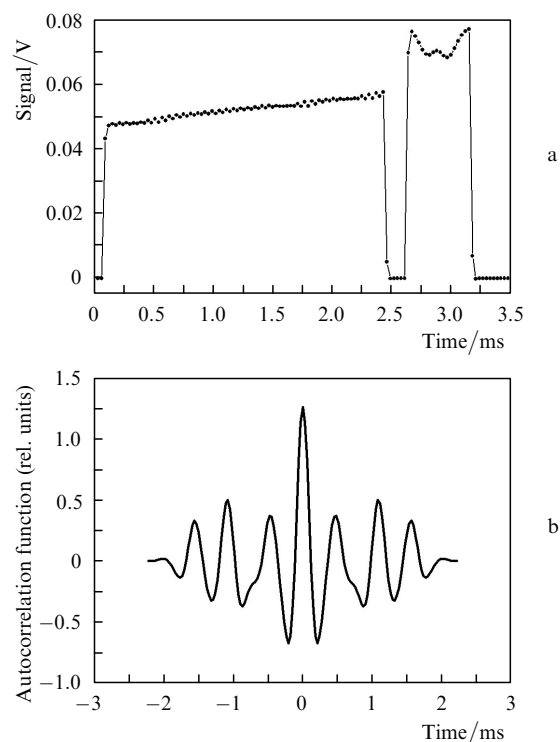
(ii) Autocorrelation convolution of the derivatives of the reference signal and cross-correlation convolution of the reference and analytic signals. This procedure provides additional filtration of the desired signal, distorted by the noise.

(iii) Linear fitting of the cross-correlation function to the autocorrelation one and determining the coefficient of coincidence for the functions. The concentration  $C$  of the studied gas is proportional to the coefficient of coincidence  $\alpha$  and is determined by the formula

$$C = \frac{\alpha p_r l_r}{p_a l_a} 10^6, \quad (1)$$

where the concentration  $C$  is expressed in ppm;  $p_r$ ,  $p_a$  are the gas pressure values in the reference and analytic cell,  $l_r$ ,  $l_a$  are their optical lengths.

Figure 3 shows an example of the shape of the DL pump current pulse and the autocorrelation function of the reference signal.



**Figure 3.** The shape of the DL pump current pulse (a) and the autocorrelation function of the reference signal.

#### 5. Study of noise characteristics of the DL spectrometer

In the study of the optoelectronic tract of the analytic channel the most attention was paid to finding the noise sources, caused by the interference of laser radiation at the

reflecting and scattering surfaces of mirrors and the windows of the multi-pass matrix cell. Due to the specificity of image formation at the mirrors and objective lenses of the multi-pass cell (Fig. 4), as well as to non-perfect mirror surfaces, the residual interference (fringing) is always present [9] and produces noises that limit the sensitivity of the device. By means of specially developed programs the interference noise sources were determined.

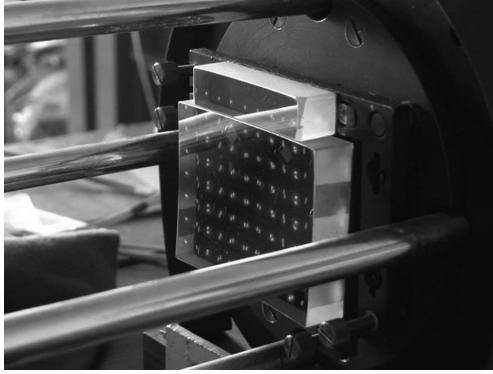


Figure 4. Mirror unit of the multi-pass cell.

Figure 5a illustrates the dependence of the Fourier transform amplitude of the signal upon the distance  $L$  between the laser and the sources of secondary radiation that interferes with the primary radiation of DL in the evacuated multi-pass cell. A wide peak at  $L = 50$  cm is clearly seen; one can see also the interference peaks at  $L = 1 - 3$  cm,  $10 - 13$  cm and  $30$  cm.

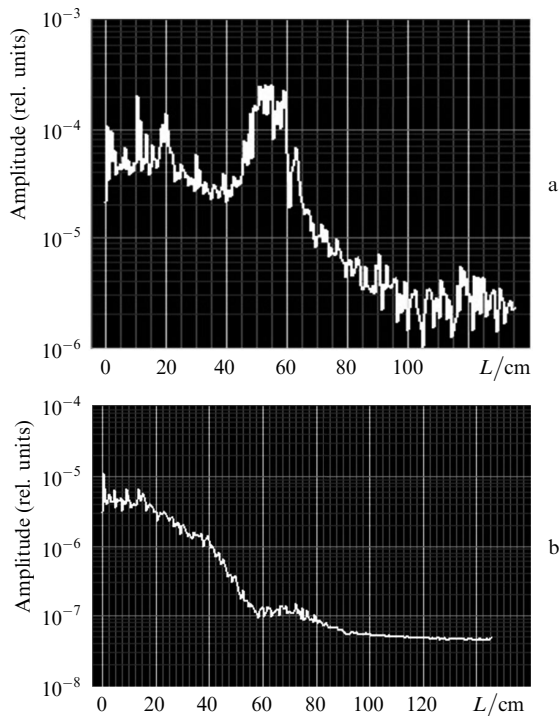


Figure 5. The amplitude of the signal Fourier transform versus the distance between the laser and the sources of secondary radiation in the evacuated multi-pass cell (a) and the result of the interference suppression with a white noise (b).

To suppress the interference, an additional wide-band ( $2 - 30$  MHz) source (voltage generator) was created and connected directly to the power socket of the laser. Its operation resulted in the additional white-noise modulation of the DL pumping current with a small amplitude ( $I_{\text{noise}} \sim 0.02$  mA), which led to the increased effective line width of the DL oscillation and, therefore, to lower spatial coherence and interference noise. In Fig. 5b one can see the result of the white noise source application, namely, a substantial suppression of the interference noise.

## 6. Determination of the minimal detectable absorption

To determine the minimal detectable absorption of formaldehyde with the DL spectrometer we used a procedure for calculating the Allan deviation [10]. This procedure allows one to study the noises of the optoelectronic path of the spectrometer in the time domain and thus to determine the spectrometer sensitivity limit. According to this procedure, the array of concentration values  $C(n)$ , measured during the time  $t$  ( $n = 1, \dots, N$  is the number of elements in the array,  $t = N\tau$ ,  $\tau$  is the time of each measurement) is sampled into subsets of lower dimension  $N/K$  ( $K = 1, \dots, N/2$ ). Then the Allan deviation  $\sigma_A(K)$  is given by the following expression:

$$\sigma_A(K) = \left\{ \frac{1}{N} \sum_{n=1}^N [C_K(n) - \overline{C_K(n)}]^2 \right\}^{1/2}, \quad (2)$$

where

$$C_K(n) = \frac{1}{\sqrt{2K}} \left[ \sum_{i=K(n+1)}^{K(n+2)} C(i) - \sum_{i=Kn}^{K(n+1)} C(i) \right].$$

The procedure for calculating the Allan deviation, based on Eqn (2), was incorporated into the master program, controlling the DL spectrometer. To obtain the array  $C(n)$  during the time  $t$  equal to several tens of minutes, the measurements of formaldehyde concentration were carried out in the empty multi-pass cell. By means of these measurements the minimal detectable absorption of  $\text{H}_2\text{CO}$  was determined. Then, using Eqn (2), the quantity  $\sigma_A(K)$  was calculated. In Fig. 6 the results of the measurement of the Allan deviation versus the time of averaging are presented. It is seen that the minimal detectable absorption in the cell approaches  $2 \times 10^{-7}$  at the averaging time 3 s.

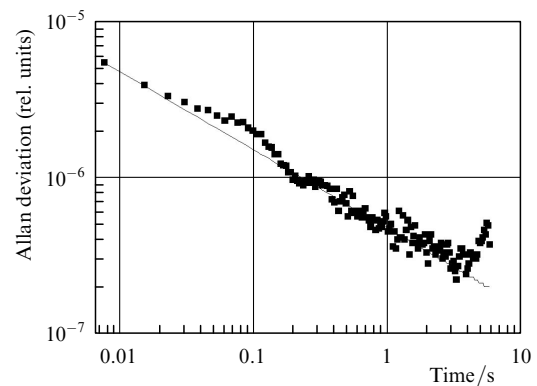
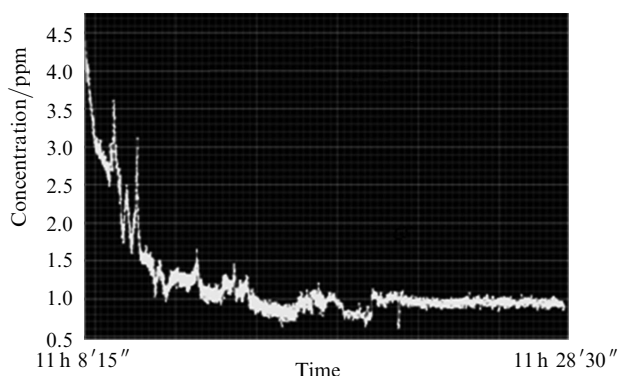


Figure 6. The Allan deviation versus the time of averaging.

## 7. The results of H<sub>2</sub>CO concentration measurements

The measurements were carried out at different concentrations of the aqueous solutions of H<sub>2</sub>CO in the regime of air flow through the multi-pass cell at the pressure of  $25 \pm 0.1$  Torr (Fig. 7). Each spike in Fig. 7 is a result of injection of a background dose of formaldehyde into the cell. The relative error of the measurement of H<sub>2</sub>CO concentration was 17 ppb for the averaging time of 300 ms. The absolute error of the measurements was determined by the error of determination of the absorption cross-sections for the selected lines of formaldehyde, its value being equal to 15 % [2].



**Figure 7.** The results of the real-time measurement of formaldehyde concentration.

## 8. Conclusions

Based on a VCSEL diode and a multi-pass cell, a two-channel spectrometer is developed for studying the absorption spectra and measuring the concentration of H<sub>2</sub>CO in the near-IR region.

A survey absorption spectrum of formaldehyde is measured in the temperature range 4–50 °C (5579–5605 cm<sup>-1</sup>) and the analytic region of H<sub>2</sub>CO detection is chosen, where the influence of ‘interfering’ absorption lines of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> is minimal.

A software package is developed in the LabView environment, aimed at the control of the gas analyser, acquisition and processing of measurement data. Various sources of noise in the optoelectronic path of the gas analyser are investigated, optimal ways and regimes for noise suppression are chosen.

The measurements of the formaldehyde concentration in air are carried out. The relative error of the H<sub>2</sub>CO concentration measurement was 17 ppb for the time of a single measurement equal to 300 ms.

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