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Tunable quantum cascade laser for methane concentration measurement

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We report spectral studies of methane using a quantum cascade laser (QCL) with an external resonator in the Littrow configuration operating in 7550−7750 nm range. We demonstrate this setup to allow detection of methane concentrations as low as 165 ppm, which is over 250-fold below the lower explosive limit of methane concentration in the atmosphere. We also discuss the potential for increasing the sensitivity of methane detection scheme.

Keywords: quantum cascade laser, methane, gas analysis, infrared spectroscopy.

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Methane (CH_4) is one of the most important greenhouse gases that accelerates global warming significantly. Its thermal effect per unit mass exceeds that of carbon dioxide (CO_2) [1]. Although the concentration of methane in the atmosphere is lower than that of carbon dioxide, its short-term impact on climate is significantly more profound [2]. Methane is produced in the process of decomposition of organic matter in an oxygen-free environment (e. g., in swamps or peat bogs) [3]. The contributions of natural sources are combined with those of anthropogenic ones: oil and gas production, agriculture, waste disposal.

Methane concentration monitoring is important not only in the context of the fight against global warming, but also for ensuring the safety of industry and human activities. Natural gas leaks may cause explosions and poisoning in apartment buildings, mines, and factory facilities [4]. Therefore, timely detection of methane is an important factor of reduction of accident risks and economic losses.

Studies of methane absorption spectra in the infrared (IR) range, where this gas has characteristic vibrational-rotational absorption lines, are of particular importance. This provides an opportunity to detect even low concentrations of CH_4 [5]. However, measurements are complicated by overlapping with spectra of other low-molecular gases.

Two regions of intense absorption (around 3000 and 1300 cm^{-1}, which corresponds to 3000 and 7650 nm, respectively) with comparable intensity maxima are distinguished in the methane spectrum (Fig. 1, curve *2*). Both regions are associated with rotational vibrations and have a similar spectral profile: a high density of lines in the center and equidistant lines with decreasing intensity at the edges.

Coherent radiation sources, such as quantum cascade lasers (QCLs), are used for precise analysis of methane absorption spectra. Lasers of this type were proposed by Kazarinov and Suris in 1971 [6] and fabricated by Capasso et al. in 1994 [7]. The alternatives here are diode lasers [8], interband cascade lasers (ICLs) [9], and optical parametric oscillators (OPOs) [10]. However, diode lasers and ICLs cannot probe the 1300 cm^{-1} region. QCLs have an advantage over OPOs in their small size and significantly higher efficiency [11].

In the present study, we report the results of experiments on QCL detection of methane within the 7550−7750 nm (1290−1325 cm^{-1}) range, where, according to the HITRAN database, transparency windows for other low-molecular gases are found. A tunable QCL with an external resonator in the Littrow configuration [12] was used for detection. QCLs emitting in the $\sim$ 7500−8000 nm spectral region were fabricated for experiments. QCL heterostructures were synthesized by two-stage epitaxial growth on indium phosphide substrates [11,13]. The grown heterostructures were subjected to post-growth processing to fabricate QCL chips, which were mounted with the epitaxial layer facing down on primary copper heat sinks. The post-growth process was detailed in [14].

It is known that the absorption spectrum in the mid-IR range is sensitive to changes in atmospheric composition, temperature, pressure, and humidity. Therefore, the absorption spectra of methane were measured in the atmosphere of a laboratory room using a Bruker Vertex 70v Fourier spectrometer with a resolution of 0.2 cm^{-1} (Fig. 1, curve *1*).

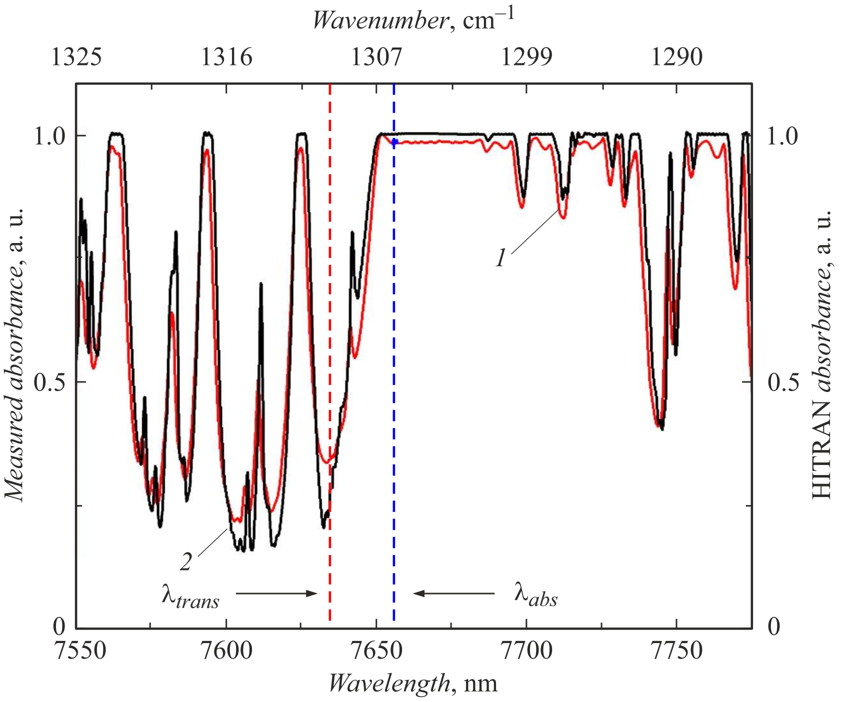

Figure 1. Absorption spectrum of methane in the laboratory atmosphere measured using a Bruker Vertex 70v Fourier spectrometer (curve *1*) and absorption spectrum of methane from the HITRAN database (curve *2*) near $\sim 1300\,\mathrm{cm}^{-1}$.

Single-frequency differential absorption spectroscopy is the most sensitive and versatile method for optical determination of gases in the atmosphere [15]. The method relies on sequential or simultaneous detection of two wavelengths: λ_{abs} (with maximum absorption) and λ_{trans} (in the transparency region). The specific value of λ_{abs} for experiments is set at the center of the absorption spectrum with a high line density, and λ_{trans} is positioned in the transparency window. Studies were carried out within the 7550–7750 nm ($1290-1325\,\mathrm{cm}^{-1}$) spectral range, which covers both the transparency window (~ 7639 nm, $\sim 1309\,\mathrm{cm}^{-1}$) and intense methane absorption lines (~ 7656 nm, $\sim 1306\,\mathrm{cm}^{-1}$). The use of a single source tunable over a wide spectral range simplifies the design, but the performance is limited by the switching speed. An alternative approach is to use a QCL with distributed feedback [16] or a compound resonator [17]. However, such lasers have a narrow tuning spectrum, which is often insufficient for reliable switching between the transparency and absorption regions, necessitating the use of two lasers for detection of λ_{trans} and λ_{abs}.

The QCL tuning spectra were recorded with a Bruker Vertex 70v Fourier spectrometer. The output mirror of the tunable QCL was positioned at the focus of the collecting mirror of the spectrometer. The spectra of QCL tuning with a step of ~ 5.5 nm recorded through a cuvette filled with atmospheric air or methane (the concentration of CH_4 was 100 %) are shown in Figs. 2, *a* and *b*, respectively. The presented results illustrate a solid overlap of the tuning spectrum with intense methane absorption lines near $1300\,\mathrm{cm}^{-1}$. The comparison of transmission spectra obtained using the tunable QCL (curve *1*) and the internal source of Bruker Vertex 70v (globar, curve *2* in Fig. 2, *c*) reveals their close agreement (if one takes into account the difference in spectral resolution).

Studies of methane concentrations simulating real-world conditions were carried out. The experimental setup was an optical line featuring the QCL, a collimating aspherical lens ~ 5 mm in diameter with an antireflection coating (with a transmittance of 99 %), a system of mirrors with an overall reflectance of 0.8, a gas cuvette 10 cm in length with KBr windows 6 mm in thickness (with an overall reflection loss of 16 %), and a Thorlabs P100D power meter with an S401C thermoelectric measuring head (spectral sensitivity, 0.2–20 μm 99 %; minimum detectable power, 10 μW; maximum detectable power, 1 W with an accuracy of 1 μW). The total length of the line was close to 5.8 m; the total turn angle, which was introduced to simulate a route around the perimeter of the room, was 270°. The diagram of the experimental setup is shown in Fig. 3.

The experiments consisted in measuring the optical power at λ_{abs} and λ_{trans} with the gas cuvette filled with methane of varying concentrations introduced into the optical line. The average concentration of methane along the entire optical line was calculated as

$$C = \frac{cl}{L},$$

where c is the concentration of methane in the gas cuvette, l is the gas cuvette length, and L is the total length of the optical line. Methane concentrations of 10 and 1 % in

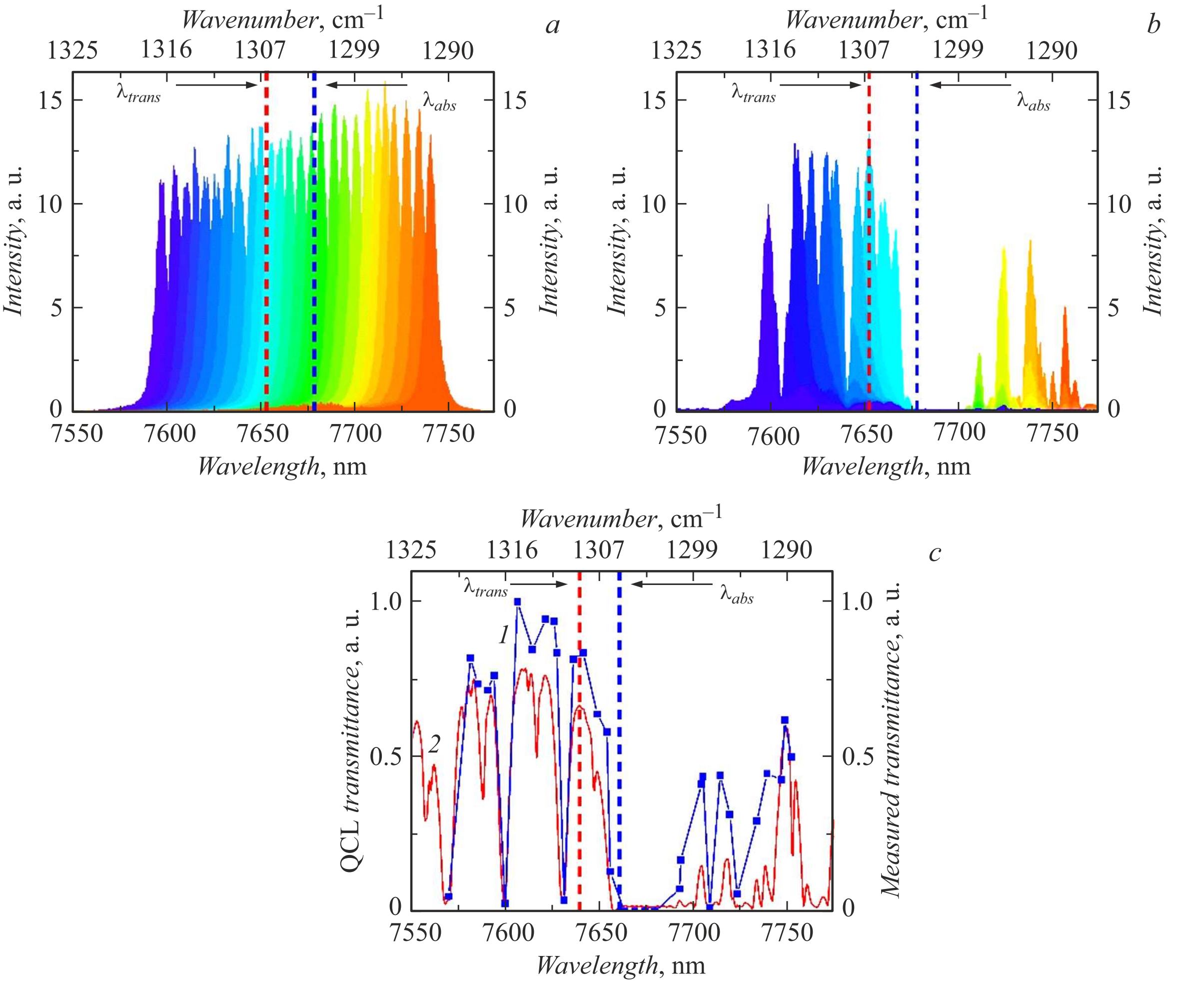

Figure 2. QCL tuning spectrum recorded by the Bruker Vertex 70v Fourier spectrometer: *a* — through a cuvette with air; *b* — through a cuvette with methane. *c* — Transmission spectra of methane measured by the tunable QCL (curve *1*) and with the use of the internal source of Bruker Vertex 70v (globar, curve *2*).

the cuvette were set by pumping out 100 % methane to a pressure of 100 and 10 mbar, respectively; letting in air to atmospheric pressure; and closing the valve. Thus, the overall concentration of methane in the optical line with a length of 5.8 m was 16 580 ppm (1.658 %), 1658 ppm (0.165 %), and 165 ppm (0.0165 %) at a methane concentration in the cuvette of 100, 10, and 1 %, respectively.

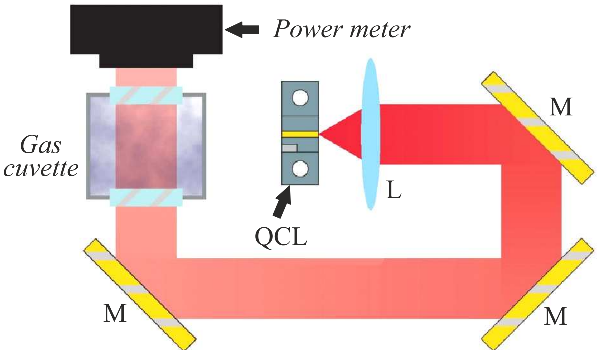

Figure 3. Schematic diagram of the experimental setup for measuring the methane concentration in an optical line. M — mirror; L — lens.

Owing to the presence of other gases with absorption lines in the mid-IR range, the choice of wavelengths for methane detection is important. Lines around 7658 nm (absorption) and 7639 nm (transmission), where water, ethanol, methanol, acetone, CO_2, and CO have no absorption, were used in the study. However, the Fourier spectrometer revealed background absorption (Fig. 1, curve *1*).

To improve accuracy, the methane concentration was determined with account for the overlap with other gases and the background. The system was calibrated by measuring the background radiation power without scanning radiation at each point separately; in addition, the scanning radiation power was measured without the gas cuvette at each point separately, and further power readings were normalized to readings obtained without methane in the cuvette. This procedure renders it unnecessary to introduce the transmittance of optical elements of the system, since it takes into account the signal–noise ratio at the end of the optical path and is performed at each point separately. The results are presented in Fig. 4: points *1* — absorption at 7657.5 nm (1305.9 cm^{-1}); points *2* — transmission at 7639 nm (1309 cm^{-1}).

The minimum recorded concentration of methane in the optical line $\sim$ 5.8 m in length was 165 ppm with a roughly 10 % difference in power at the absorption and transmission wavelengths (20 μW, which is 20 times higher than the sensitivity of the power meter used and 2 times higher than the background level). The sensitivity may be increased through the use of more sensitive photodetectors or a longer optical path. Studies into the detection of various substances with QCLs have already been conducted earlier. For example, a QCL with distributed feedback was used in [5] to detect acetone at the level of 1.44 ppm, and the sensitivity to ethanol and acetone achieved in [18] with the use of a tunable laser was at the level of 22 and 60 ppm, respectively. It should be noted that the measuring setups in these studies had an order of magnitude greater distance of radiation propagation within the cuvette (more than 50 m), which ensures a proportionally greater measurement accuracy at low concentrations. An enhancement of sensitivity to a similar (or better) level may be achieved by eliminating background illumination and suppressing the intrinsic noise of the system through modulation of the signal and its lock-in detection. At a megahertz modulation frequency, it is reasonable to expect a 2–3 orders of magnitude reduction in noise and a corresponding increase in sensitivity (i.e., up to $\sim$ 1 ppm). However, we did not take into account the background concentration of methane on the optical line outside the cuvette. In our view, this omission and background illumination may be one of the key factors limiting the demonstrated sensitivity of the system, since a single re-injection of methane into the cuvette produces a background concentration on the order of 0.01 % (100 ppm) in a room with a volume of approximately 100 m^3.

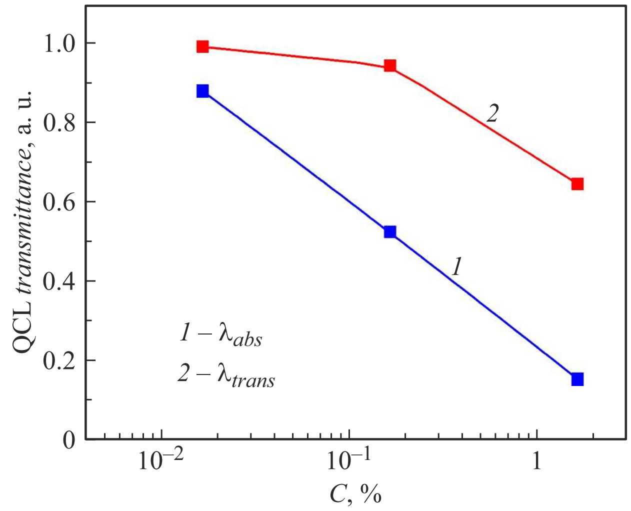

Figure 4. Transmission of single-frequency QCL radiation through methane of different concentrations at the 7658 nm absorption line (curve *1*) and the 7639 nm transmission line (curve *2*).

Leaking methane is lighter than air and rises up, creating concentration gradients that complicate measurements. Since the system scans just a 5.8-m-long optical line, a non-uniform gas distribution within the room and concentration gradients may lead to measurement errors. To improve accuracy, one needs to take into account the room dimensions and place sensors at potential sites of gas leakage or accumulation (e. g., near ventilation shafts or gas transit equipment).

Thus, the results of studies into methane detection with a tunable QCL were presented. A simple mid-IR detection scheme with the QCL used for differential absorption spectroscopy was proposed and implemented. The sensitivity achieved in experiments with a 5.8-m-long optical line of a complex geometry was close to 165 ppm, which is more than 250 times lower than the minimum explosive concentration of methane in the atmosphere (from 44 000 to 150 000 ppm) [4,19]. This makes the method potentially suitable for practical implementation. The sensitivity may be raised further by increasing the length of the optical path, switching to more sensitive photodetectors, and performing signal accumulation.

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Conflict of interest

The authors declare that they have no conflict of interest.

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