DOI 10.1007/s10812-022-01419-0
Journal of Applied Spectroscopy, Vol. 89, No. 4, September, 2022 (Russian Original Vol. 89, No. 4, July–August, 2022)

MID-IR RANGE QUANTUM-CASCADE LASERS IN COMPACT OPTOACOUSTIC GAS ANALYZERS

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UDC 621.375.826;534

The generation regimes of quantum-cascade lasers for optoacoustic sensors of methane and ammonia are examined, and the tuning and output characteristics of these lasers depending on current and temperature are presented. The results of experiments on the concentration sensitivity of working samples of the test instruments developed on the basis of these lasers are presented. It is shown that the linear dynamic range of measurement of methane concentration by the optoacoustic gas analyzer covers approximately four decades: from ~0.3 to ~2000–3000 ppm CH_4.

Keywords*: quantum-cascade laser, optoacoustic sensors, methane, ammonia.*

Introduction. The combustion of fossil fuels for energy production has increased enormously since the beginning of the industrial revolution. Large quantities of gaseous air pollutants have been emitted into the atmosphere, and this has affected the natural cycles of physical and chemical regulation that had for a long time remained unaffected. The long-term increase of global atmospheric pollution has been documented by studies of polar snow and ice samples, which contain small air bubbles and provide unique historical data on the past composition of the earth's atmosphere. An increase in the concentrations of CH_4 and CO_2 (the main "greenhouse" gases) was confirmed on the basis of these studies with the largest concentration gradients recorded in the second half of the 20th century.

One of the most promising methods of spectroscopy is laser optoacoustic (OA) spectroscopy (LOAS) [1–5], which has advantages such as simple tuning, easy calibration, high sensitivity, and a wide dynamic range. Unlike chromatography it is possible by the LOAS method to achieve practical monitoring of the composition of the atmosphere in real time.

To carry out the LOAS method it is necessary to ensure that the wavelength of the laser emission coincides with wavelength of the absorption of the investigated marker gas [3]. At present various tuneable sources of radiation in the near-IR region are used for operational gas analysis by the LOAS method: CO and CO_2 lasers, parametric light generators (PLG), quantum-cascade lasers (QCL), etc. [5]. The small size, simplicity, and reliability of the OA detectors (OAD) make it possible to use them with suitable laser sources. Recent advances in the development of semiconductor lasers have therefore had a large effect on increasing the production of compact OA gas analyzers.

The application, performance verification, and testing of an optical gas leak detector set up with mid-IR quartz-enhanced OA spectroscopy (QEPAS) were reported in [6]. The QEPAS detector was used in the vacuum test station for mechatronic components. The radiation source was a QCL with λ =10.56 μm, which coincides with the strong absorption band of sulfur hexafluoride (SF_6). The SF_6 gas was used as leak indicator. The lowest detectable concentration of the QEPAS 2.7 detector is 2.7 ppb with an integration time of 1 s, which corresponds to leak sensitivity in the region of 10^{-9} mbar.L/s, comparable with modern leak detectors.

In [7] an OA module was developed for the detection of methane by combining a new interband cascade light-emitting device (ICLED) at λ = 3.2 μm with a compact differential OA cell. The ICLED with a 22-cascade interband active core generated collimated radiation with a power of ~700 μW. In order to increase the length of the absorption region in the gas an aluminum-coated concave reflector was placed next to the OA cell. The use of the ICLED and reflector with the

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OA cell led to the creation of a reliable and portable detector without any moving parts. The characteristics of the detector were assessed by means of the working pressure, sensitivity, and linearity. A detection limit of 3.6 ppmv was achieved with an integration time of 1 s.

The authors of [8] reported an ultrahigh-sensitivity and reliable CH_4 detector based on an interpole cascade laser (ICL) at $\lambda = 3.3$ μm and a differential OA cell. The wavelength of the ICL radiation corresponds to the main absorption band of CH_4 at 2988.705 cm^{-1} with intensity of $1.08.10^{-19}$ cm/molecule. The two-pass and differential design of the OA cell effectively increases the amplitude of the signal and reduces its background noise. The degree of modulation of the wavelength, the working pressure, and the stimulation of the relaxation *V–T* were optimized for the highest detection limit of the sensor. With an integration time of 90 s the detection limit was 0.6 ppb. Additional water or air cooling of the laser is not required, and this makes it possible to produce a compact and reliable CH_4 detector.

The application, calibration, and outdoor testing of a 19-inch QEPAS detector designed to monitor carbon monoxide in ambient air in real time were described in [9]. Since CO acts as a slow energy relaxer when excited in the mid-IR spectral region its QEPAS signal is affected by the presence of relaxation promoters such as water vapor or quenchers like molecular oxygen. All the CO relaxation processes with typical collision partners in the ambient air matrix were analyzed in detail, this information was used to assess the effects due to oxygen and humidity, and the real concentration of CO was obtained. The sensor was tested in the open air in a busy urban area for several hours giving results comparable with the daily averages reported by the local air inspection agency with CO concentration spikes that correlated with the passage of heavy-duty transport.

The detection of mixtures of N_2O and CH_4 in dry nitrogen with a QEPAS detector using an array of 32 QCLs with distributed feedback in the range 1190–1340 cm^{-1} as excitation source was reported in [10]. Methane detection gave up to a minimum detection limit of 200 ppb with block integration time of 10 s. The sensor exhibited a linear response in the region of 200–1000 ppm. Three mixtures of N_2O and CH_4 in nitrogen at atmospheric pressure were analyzed. The ability of the developed QEPAS sensor to determine the concentrations of N_2O and CH_4 selectively despite the significant overlap of the corresponding absorption spectra in the studied spectral range was demonstrated.

A sensitive OA sensor system for detecting sulfur dioxide (SO_2) at the level of parts per billion based on a continuous high-power QCL at room temperature with a resonator geometry and an external diffraction grating was investigated in [11]. For the highest intensity of the SO_2 absorption line the QCL excitation wavelength was set at 7.41 μm. A custom differential OA cell with two identical resonators for gas flow rates of up to 1200 cm^3/min was designed. A qualitative theoretical model was used in order to understand the dynamic processes of adsorption and desorption of SO_2 in the cell walls. The detection limit was $1\sigma = 2.45$ ppb. In [12], the experimental absorption spectra of more than 20 different substances were presented, and the possibilities of a laser gas analyzer in which a QCL was used as radiation source were investigated.

In the present work, the operating modes for the generation of QD7500CM1 and QD10500CM1 QCLs for methane and ammonia OA sensors are examined, and the tuning and output characteristics of the lasers are presented as a function of current and temperature. The results of experiments on the concentration sensitivity of the instruments developed on the basis of these lasers are presented. The threshold sensitivity of the OA gas analyzer of the sensor amounted to $1\sigma \sim 49$ ppb CH_4.

Experimental. The experimental absorption spectrum of methane in the region of 2.5–4.5 μm was recorded with the OA gas analyzer based on the combined PLG (Fig. 1b) [8, 10]. The N_2 + 1000 ppm CH_4 gas mixture was used. The spectral resolution of the gas analyzer was ~5 cm^{-1}. As seen, the form of the experimental absorption spectrum of methane in the band centered at ~3.3 μm coincides on the whole with the form of the absorption spectrum of CH_4 from the NIST database [13] (Fig. 1a). The absorption spectrum of the water vapor that is present in small amounts in the composition of the gas mixture with methane impurity is observed in the region of 2.7–2.8 μm (Fig. 1b). The absorption of water vapor in the ambient atmosphere can be one of the factors that interfere with detection of the background concentration of CH_4.

The QD7500CM1 quantum-cascade laser (Thorlabs, Inc.) is a compact discrete-mode semiconductor laser in the mid-IR range (7.5–7.7 μm) and is a distributed feedback DFB laser that provides single-mode generation. The QD7500CM1 QCL is enclosed in a temperature-stabilized holder developed at the Novosibirsk State University (NSU). The laser current and the temperature are controlled by a controller developed at the NSU. An IMO-2N power meter, an Angstrom IR-III wavelength meter (λ-meter), and a Pyrocam IV camera were used to measure the QCL radiation parameters. The wavelength of the QCL radiation depends on the temperature and current. The average generating power of the laser in continuous mode ($T = 25^oC$, current 200 mA) is ~40 mW, the tuning range is ~1.5 cm^{-1}, and the width of the emission spectrum is in tens of MHz. The radiation intensity distribution in the cross section of the beam is close to single-mode, and the radiation polarization

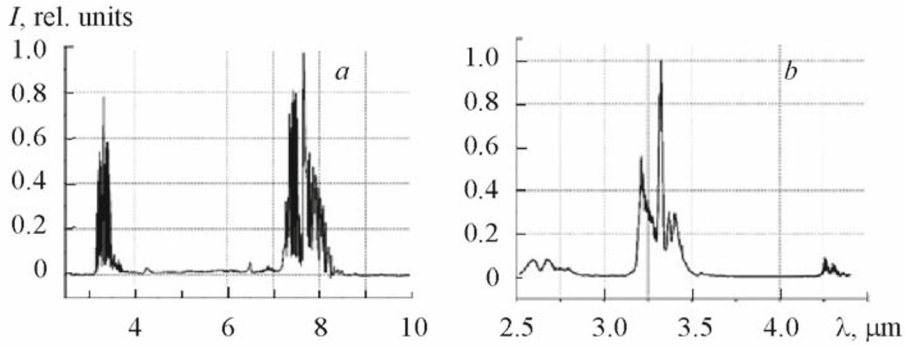

Fig. 1. The absorption spectrum of methane in the region of 2.5–10 μm from the NIST spectral database [13] (a) and the experimental absorption spectrum of methane (N_2 + 1000 ppm CH_4 gas mixture) in the region of 2.5–4.5 μm recorded with the OA gas analyzer [12] on the basis of the combined PLG with smooth wavelength tuning range of 2.5–10.8 μm (b).

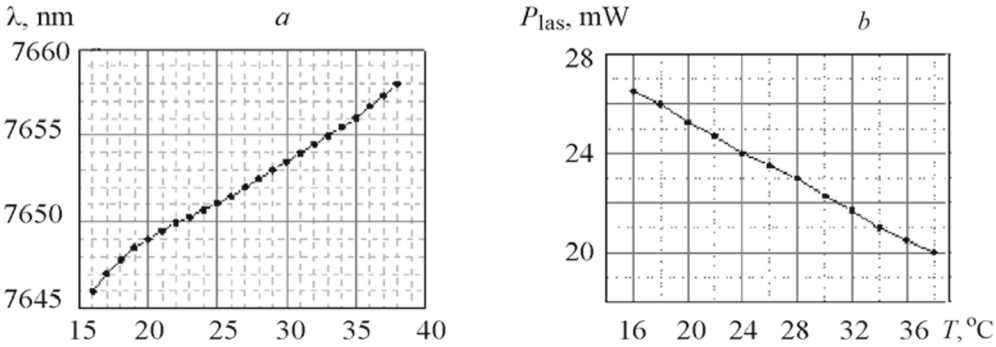

Fig. 2. Dependence of the wavelength (a) and average power (b) of the QCL emission on the working temperature of the laser in the pulse-periodic mode (1800 Hz, meander, current 180/60 mA).

is linear. As in most works on OA spectroscopy [1–5], we used the laser radiation obturation method to modulate the radiation. The procedure was realized in the following way: the laser current was scanned in a specific range, the lower point of the range was always below the laser generation threshold, and the upper point was defined as the value corresponding to 80% of the operating current. In this case, the average value of the current (at the given temperature) corresponds to the previously selected working point, where the laser generation line coincides with the absorption maximum of the gas that is being detected. The scanning frequency of the laser was equal to half of the OAD resonance frequency. The position of the current interval was controlled according to the maximum power of the OAD signal.

In the pulse-periodic mode (1800 Hz, meander, current 180/60 mA) the emission wavelength of the QD7500CM1 being investigated increases smoothly with increase in the radiator temperature (Fig. 2a), and the average radiation power (~20–27 mW) decreases (Fig. 2b). The threshold current of the QCL is ~70 mA. Here, in comparison with the continuous operating regime the instability of the QCL emission wavelength increases appreciably due to change of the laser current during the pulses. Thus, close to the working point (T = 28°C, λ ~ 7652 nm) the average power of the QCL emission in the pulse-periodic regime is 23–24 mW, and the integral width of the emission spectrum in the pulse is not more than ~0.2–0.3 cm^{-1}. The integral width of the emission spectrum in the pulse was estimated against the standard function of the Angstrom WS6-III λ-meter. The broadening of the emission spectrum of the QCL clearly arises from the so-called "chirp" effect with change of the current during the pulses. The optical scheme of the gas analyzer based on QCL is identical with the scheme in [14, 15], but QCL and the current and temperature controller developed at the NSU were used instead of the PLG.

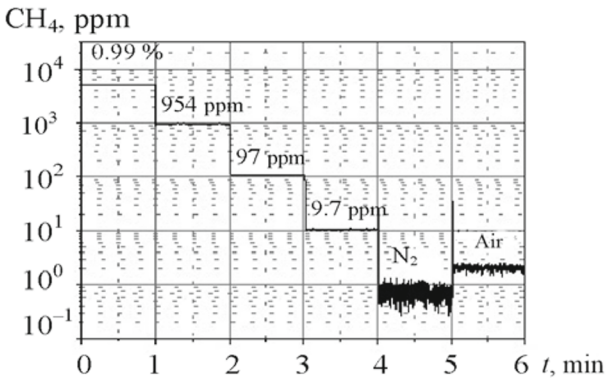

Fig. 3. Experimental records of the normalized responses of the resonance differential OAD (*PAD*/*Pyro*) filled with the test gas mixture N_2 + 0.99% CH_4, N_2 + 954 ppm CH_4, N_2 + 954 ppm CH_4, N_2, nitrogen, and air at atmospheric pressure and room temperature.

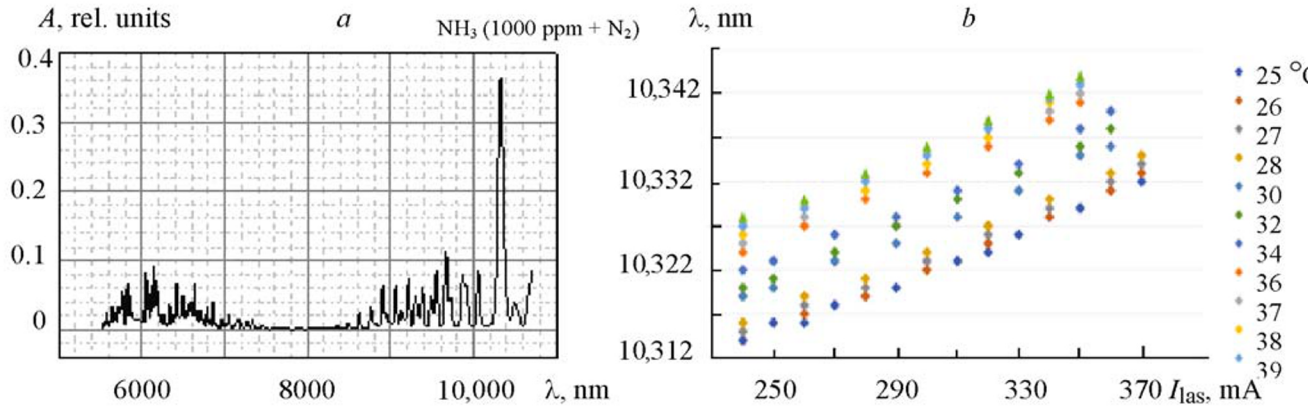

Fig. 4. Experimental absorption spectra of water vapor (5.5–7.6 μm) and ammonia (8.2–10.7 μm) (a) and dependence of the wavelength of QD10500CM1 laser on the working current and temperature (b).

Experimental records of the responses of the resonance differential OAD (*PAD/Pyro*) filled with the test gas mixture N_2 + 0.99% CH_4, N_2 + 954 ppm CH_4, N_2 + 954 ppm CH_4, N_2 + 97 ppm CH_4, nitrogen, and air at atmospheric pressure and room temperature are presented in Fig. 3. The linear dynamic range for measurement of the methane concentration by means of the OA gas analyzer amounted to approximately four decades: from ~0.3 to ~2000–3000 ppm of CH_4. The working temperature of the QCL is $T_0 = 23.3^oC$.

Quantum-Cascade Laser QD10500CM1 for an Ammonia Detector. Figure 4a shows the experimental absorption spectra of water vapor (5.5–7.6 μm) and ammonia (8–10.7 μm) recorded with the OA gas analyzer based on the combined PLG [14]. The N_2 + 1000 ppm NH_3 gas mixture was used. The spectral resolution of the OA gas analyzer was ~5 cm^{-1}. The absorption spectrum of water vapor present in small amounts in the employed gas mixture with ammonia impurity is observed in the region of 5.5–7.6 μm. The presence of water vapor in ambient air is not an interfering factor in the detection of the concentration of ammonia in air.

Figure 4b shows the dependence of the wavelength of the QD10500CM1 laser on the working current and temperature. In the pulse-periodic regime (1800 Hz, meander, current 370/230 mA) the emission wavelength increases smoothly with increase of the temperature of the emitter while the average power of the emission falls (~13–10 mW). The threshold current of the QLC is ~240 mA. Close to the working point ($T = 39.8^oC$, λ ~ 10,341 nm) the average power of the QLC emission in the pulse-periodic regime is 10–11 mW. The integral width of the emission spectrum in the pulse ≤0.1–0.3 cm^{-1} was estimated in the standard option of the Angstrom WS6-III λ-meter.

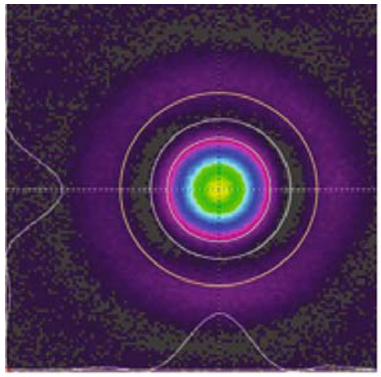

Fig. 5. Profile of output laser emission beam at temperature 25°C and current strength 350 mA.

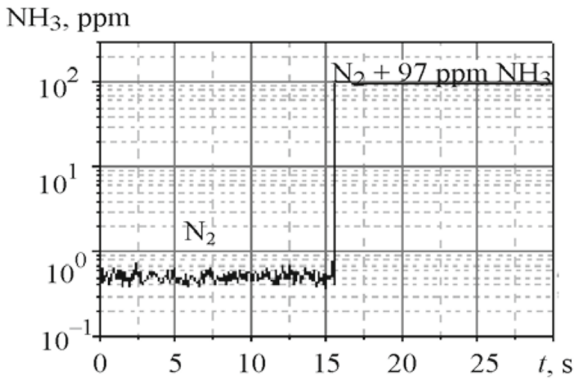

Fig. 6. Experimental records (15 s each) of the normalized responses of the resonance differential OAD filled with nitrogen or with the gas mixture being tested N_2 + 97 ppm NH_3; T_{QCL} = 33.5°C, f = 1780 Hz, P_{QCL} = 9.15 mW.

Figure 5 shows the beam profile of the QD10500CM1 laser with an aspherical C028TME-F lens with focal length 5.95 mm at a distance of 75 mm from the source, current 350 mA, and temperature 25°C.

The optical scheme of the gas analyzer based on QCL is identical to the scheme presented in [14–16], but the QCL was used instead of the PLG. The current and temperature of the QCL were controlled by means of a serial controller (Laser Diode/Temperature Controller; ITC4002QCL model, Thorlabs, Inc.). Figure 6 shows the experimental records (15 s each) of the normalized responses of the resonance differential OAD (*PAD*/*Pyro*) filled with nitrogen or with the test gas mixture N_2 + 97 ppm NH_3 at atmospheric pressure and room temperature. The working temperature of the QCL is T_0 = 33.5°C. Both fragments of the record were calibrated against the authentic concentration of ammonia in the composition of the gas mixture being tested (97 ppm).

Conclusions. Examples of an optoacoustic gas analyzer based on a quantum-cascade laser (7.65 μm) with an average power of ~27–30 mW in the pulse-periodic regime were investigated. It was shown that the background concentration of methane in air (~2–3 ppm CH_4) can be measured with an optoacoustic laser gas analyzer using a quantum-cascade laser in the region of 7.65 μm. The threshold sensitivity of this optoacoustic gas analyzer is 1σ ~ 49 ppb CH_4. When the QD7500CM1 quantum-cascade laser was used as laser source for an optoacoustic methane sensor the linear dynamic range of the methane concentration measurements using the optoacoustic gas analyzer covered approximately four decades: from ~0.3 to ~2000–3000 ppm CH_4.

Investigations of an optoacoustic gas analyzer for ammonia based on the QD10500CM1 quantum-cascade laser were carried out. The threshold sensitivity of the optoacoustic gas analyzer is 1σ ~ 74 ppb NH_3 with the QD10500CM1 laser in the region of 10.341 μm. Work is currently underway to reduce the noise level of the microphones (microphone

optimization and selection of the quietest samples), which should lead to a significant increase in the sensitivity of the optoacoustic systems.

Acknowledgments. The work on the design, manufacture, and testing of experimental samples of methane and ammonia sensors was supported by the Russian Science Foundation (Grant no. 17-72-30006-P). The spectra of methane were recorded with the combined parametric light generator according to state assignment FSUS-2020-0036. The experimental data for the absorption of ammonia vapor over a wide range of wavelengths were obtained with financial support from the Russian Foundation for Basic Research (Project No. 19-32-60055).

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