

## APPLICATIONS OF MID-IR LASERS

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The new stage is creation of the multicomponent laser gas-analyzer for early diagnostics and measure of pollutants in atmosphere with the high sensitivity on the level  $-10^{-8} + 10^{-9}$ . Thus in this work was established that mid-IR lasers are very promising for creation of: a) Devices for early diagnostics and control of therapy; b) Devices for the atmosphere monitoring of  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and other components content in the air on of the level of  $10^{-7}$ - $10^{-9}$  of main components; c) New type spectrometers with  $10^{-4}\text{cm}^{-1}$  resolution; d) Technological control devices for chemistry, metallurgy, electronics.

Three types of compound semiconductor materials are used to make mid-IR lasers: IV-VI materials (lead salts), III-V materials containing antimony, III-V quantum cascade (QC) structures. Mid-IR lasers made from IV-VI compound semiconductors are in the best position to reach pulse and CW operational temperature above 200-220 K, when thermoelectric cooling modules operate. However today the operating temperature for the most of laser devices in practical experiments is 77 K (liquid nitrogen temperature).

Mid-IR lasers were fabricated on the basis of IV-VI multicomponent semiconductor materials, which allow to reduce the generation threshold, and increase radiation power [1]. The lasers are easily tunable under external influence – temperature, magnetic field, pressure and operate in the spectral range 5-25  $\mu\text{m}$  which involves “atmospheric windows” and oscillatory-rotatory absorption bands of the most molecular gases. Therefore they are mainly used in the following fields:

1. High – resolution molecular spectroscopy.
2. Analysis of gas mixture samples at a low pressure.
3. Measurements in the open atmosphere.

In table 1. basic parameters of pulsed lasers are presented.

Table 1

Parameters measured	Parameter variation range
1. Operating temperature range T, K	77-180
2. Total range of radiation frequency tuning with current and temperature, $\text{cm}^{-1}$	200-300
3. Range of a single mode tuning $\text{cm}^{-1}$	0.5-4
4. Power in all modes, mW	1-5
5. Power in a single mode, mW	0.1-1.5
6. Rate of radiation frequency tuning of a single mode, $\text{cm}^{-1}/\text{s}$	$10^2$ - $10^6$
7. Generation linewidth, $\text{cm}^{-1}$	$\leq 10^{-4}$

Requirements imposed upon semiconductor lasers depend essentially on the problem being decided. The most stringent of them are determined by molecular spectroscopy problems and in particular, by spectroscopy of collisional broadening and shift with the spectral resolution  $\delta\nu \leq 10^{-3}\text{cm}^{-1}$  and  $S/N$  ratio  $\approx 10^3$  which is important for the required precision level of measurements.

For the spectral absorption gas analysis performed at a reduced pressure (e. g. sampling into a multipass optical cell) the spectral resolution  $\approx 10^{-3}$ - $10^{-2}\text{cm}^{-1}$  should be provided, which is necessary for a spectral contrast increase and selective isolation of separate slightly broadened lines at the expense of a buffer gas pressure – air, as a rule. At the output of the recording system the  $S/N$  ratio should be  $\geq 10^3$ . In this case detection of molecular impurities with minimal relative

concentration  $C_{min} = \frac{1}{\sigma l N_0} \cdot \frac{\Delta P}{P} = 10^{-7}$  is possible

(Here the absorption cross-section  $\sigma = 10^{-17}\text{cm}^2$ , the absorbing layer thickness  $l = 100\text{m}$ , the total molecular number per unit

volume  $N_0 = 10^{17}\text{cm}^{-3}$ ,  $\frac{\Delta P}{P} = \frac{N}{S}$ ). The important

feature of this problem is the need for such high parameters at field measurements, i. e. at laser operating temperatures not less than 80-100 K (liquid nitrogen temperature).

During measurements in the open atmosphere, at so-called route measurements, the resolution may be below  $\approx 10^{-2}\text{cm}^{-1}$ . However, high output power of semiconductor lasers is also required in order that after passing the route up to 500 m long the  $S/N$  ratio at the output of the recording system (without accumulation) should be not less than  $10^3$ .

Let us define laser's power satisfying the above mentioned requirements. Laser power can be estimated as  $P = P_n S/N$ , here  $P_n = NEP \sqrt{\Delta B}$  - noise power,  $NEP \approx 10^{-10}\text{W Hz}^{-1/2}$  - power equivalent to noise for Ge or Si and CdHgTe photodetectors. Then at  $\Delta B = 1\text{MHz}$  mode radiation power  $P_n \approx 100\mu\text{W}$  is required to obtain  $S/N \approx 10^3$ .

Together with the Institute of General Physics and Institute of Spectroscopy Russian Academy of Sciences out investigations were realized in high-resolution spectroscopy, applied spectroscopy and gas analysis; using heterolasers with PbSnSeTe isoperiodic layers and homolasers with controlled carrier concentration.

**High – resolution spectroscopy.** Absorption spectra of a whole numbers of molecular gases:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{O}_3$ ,  $\text{SF}_6$ ,  $\text{GeH}_4$ ,  $\text{CF}_4$ ,  $\text{CO}_2$  and etc. have been recorded with high – resolution and investigated. In particular, by application of lasers with controlled carrier concentration profile  $n^+ - n^-$

PbSe, extended and completely resulted areas of SO<sub>2</sub> absorption spectra in the ν<sub>1</sub> and ν<sub>3</sub> fundamental band region have been investigated [2]. Frequencies and intensities of 497 absorption lines have been determined. The accuracy of line frequencies measured experimentally is 3·10<sup>-4</sup> cm<sup>-1</sup>, which is significantly above the error ≈ 10<sup>-3</sup> cm<sup>-1</sup> of theoretical description based on the available theoretical models. In this case the generation pulse was up to 700 μs, which allowed to use comparatively low tuning rates and to obtain the

mentioned accuracy of spectral parameter measurement.

CF<sub>4</sub> molecule spectrum was also recorded at a temperature T=77 K [3], which allowed to decrease the Doppler linewidth and observe in more detail the thin multiplet structure in the region of "overtone". The perfectly resulted spectrum obtained experimentally in this work is necessary for a quantitative evolution describing ν<sub>3</sub> CF<sub>4</sub> band R branches for high values J ≥ 20.

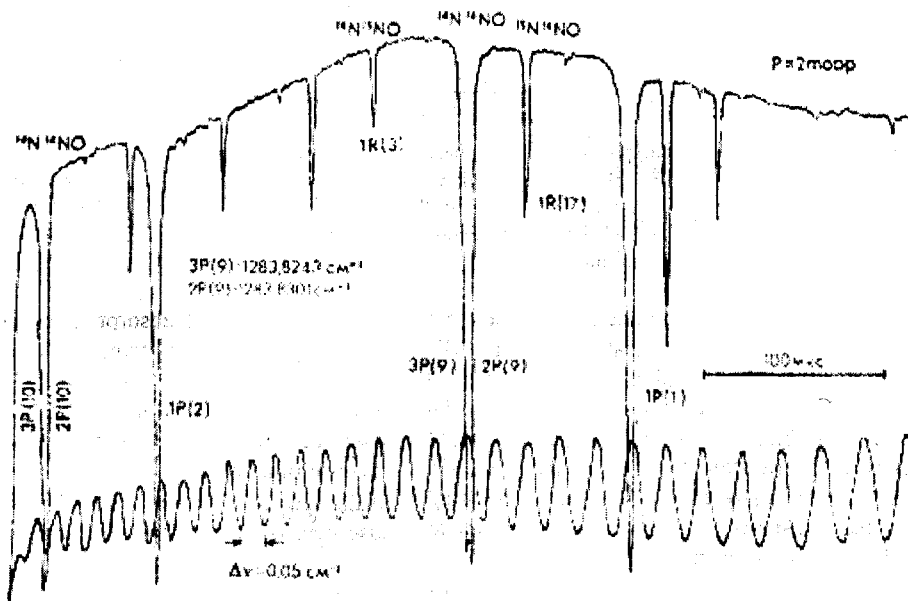


Fig. 1. N<sub>2</sub>O molecular spectrum in the range 1282.9-1284.4 cm<sup>-1</sup>

In fig. 1 N<sub>2</sub>O molecular spectrum portion within 1282,9 – 1284,4 cm<sup>-1</sup> is shown [1]. The spectrum is recorded at a single diode laser frequency scan. On the spectrum the lines of three isotopic modifications of N<sub>2</sub>O <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O (1283, 669 cm<sup>-1</sup>), <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O (1283, 824cm<sup>-1</sup>), <sup>14</sup>N <sup>15</sup>N <sup>16</sup>O (1283, 919 cm<sup>-1</sup>) are clearly seen. In P(9) band 5·10<sup>-3</sup> cm<sup>-1</sup> resolution is obtained. Below a Fabry – Perot etalon spectrum with 0,05 cm<sup>-1</sup> free dispersion region is given.

**Applied spectroscopy.** In [4] a new method of TEA CO<sub>2</sub>

– laser generation linewidth determination is proposed and used. Knowledge of TEA CO<sub>2</sub> – laser generation linewidth is important for evolution of molecule oscillatory excitation under non – collisional conditions from separate rotatory levels. The method of "burning out" of the downfall in the SF<sub>6</sub> absorption spectrum in a pulse supersonic stream (fig. 2) and further measurement of the downfall with heterolaser enabled one to establish a CO<sub>2</sub> laser generation spectrum width 0,013±0,002 cm<sup>-1</sup>.

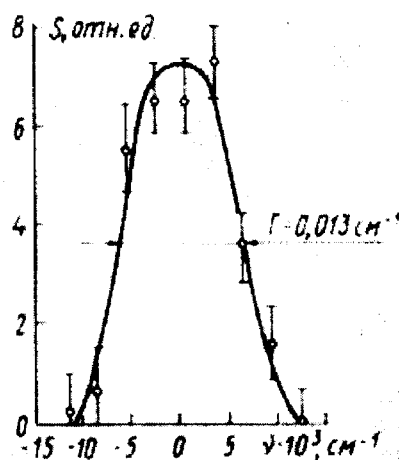
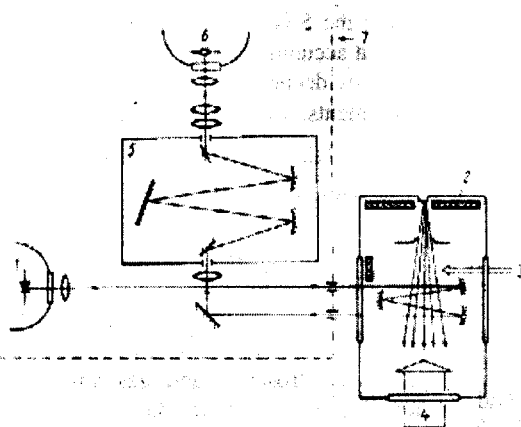


Fig. 2. Experimental plant scheme: a) 1- Di, 2- vacuum chamber with a nozzle, 4 – CO<sub>2</sub> laser measurement, 5- diffusion monochromator, 6- photoresistor, 7 – screen  
b) induced clarification S in the SF<sub>6</sub> molecule absorption spectrum

**Gas analysis possible.** On the basis of developed  $\text{NH}_3$  microconcentration analysis operating within  $\approx 10\mu\text{m}$  wave length range, where ammonia has the most intensive absorption lines up to  $10^{-2} \text{ cm}^{-2} \cdot \text{atm}^{-1}$  [5]. Application of Ag Cl - Ag Br fiber optics, multipass cells and heterolasers for the  $10\mu\text{m}$  range allows to achieve a minimally detectable ammonia concentration in the mixture -  $10^{-7}$  and the sensitivity can be brought to  $10^{-9}$  with a signal accumulation time increase. This sensitivity is sufficient for a measurement of  $\text{NH}_3$  background content in the atmosphere (which is  $10^{-8}$ ).

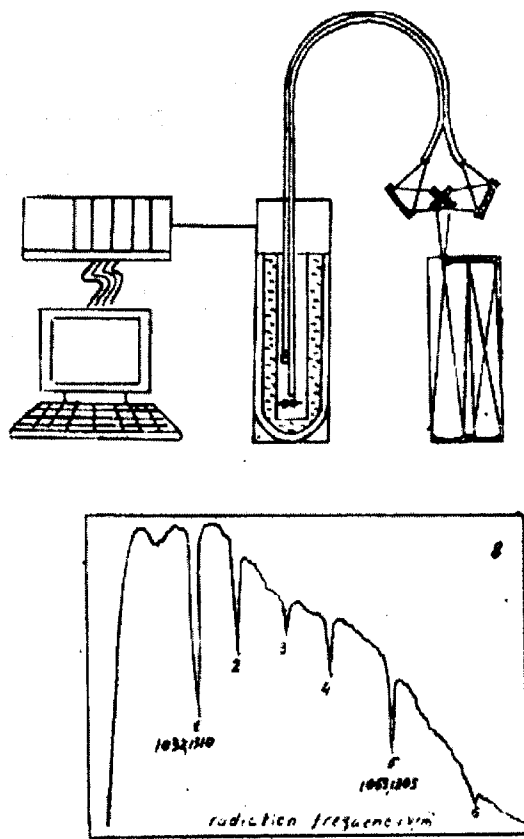


Fig.3. a) Fiber-optics gas analyzer scheme  
b)  $\text{NH}_3$  transmission spectrum in the range 1030-1055 $\text{cm}^{-1}$

Compact fiber optical devices also enable one to carry out classical spectral investigations. As an example a number of  $\nu_2$  fundamental ammonia absorption band lines were recorded whose parameters are given in table 2.

Table 2

N	Line colentification	Line frequency $\text{cm}^{-1}$	Line intensity $\text{cm}^{-2} \cdot \text{atm}^{-1}$
1	aR (4.3)	1032, 1310	5,2
2	aR (4.2)	1033, 1358	3,1
3	aR (5.5)	1049, 3464	1,2
4	aR (5.4)	1051, 5120	1,9
5	aR (5.3)	1053, 1305	4,6
6	aR (5.2)	1054, 2527	2,5

The application of fiber optics elements (fig. 3) simplifies essentially the optical scheme and device tuning.

In [6] lasers were used for  $\text{SO}_2$  detection in the spectral ranges 1280 and 1065  $\text{cm}^{-1}$ .

$\text{SO}_2$  spectrum portion evolution with a change in the buffer gas (nitrogen) pressure has been investigated.  $\text{SO}_2$  line collisional broadening coefficients are determined and the dependence of spectrum contrast on partial pressures in the mixture is studied, which is necessary for the choice of optimal conditions for  $\text{SO}_2$  recording in the atmosphere.

Multifunctional spectrometer on the basis of tunable mid-IR lasers was developed and created: with high resolution on the  $10^{-4} \text{ cm}^{-1}$  level, multicomponent gas analysis with  $10^{-7}$  -  $10^{-8}$  sensitivity, bench for investigation of new types of photoreceivers and lasers [7].

The new stage is creation multicomponent laser gas-analyzator for early diagnostics and measure pollutants in atmosphere with high sensitivity on the level  $-10^{-8} \div 10^{-9}$  [8-9]. Thus in this work was established that mid-IR lasers are very promising for creation of:

1. Devices for early diagnostics and control of therapy.
2. Devices for atmosphere monitoring  $\text{SO}_2$ , CO,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and other components content in the air on the level of  $10^{-7}$ - $10^{-9}$  of main components.
3. New type spectrometers with  $10^{-4} \text{ cm}^{-1}$  resolution.
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## **ORTA DİAPAZONLU İQ-LAZERLƏRİN TƏTBİQLƏRİ**

$A^{IV}B^{VI}$  birləşmələrinin çoxkomponentli bərk məhlulları əsasında orta diapazonlu IQ lazerlər sürmə tərkibli  $A^{III}B^V$  birləşmələri əsasında olan kaskad tipli lazerlərə nisbətən 200-220 K temperaturlarda impuls və kəsilməz rejimlərdə işləmək üçün daha perspektivlidir.

Bu lazerlərin yüksək ayırdetməli lazer spektroskopiyasında, tətbiqi spektroskopiyada və qaz analizində işlənmə nümunələri göstərilmişdir.

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## **ПРИМЕНЕНИЯ ИК-ЛАЗЕРОВ СРЕДНЕГО ДИАПАЗОНА**

Для среднего ИК диапазона лазеры на основе многокомпонентных твердых растворов соединений  $A^{IV}B^{VI}$  перспективнее каскадных лазеров и содержащих сурьму на основе соединений  $A^{III}B^V$  для работы в импульсном и непрерывном режимах при температурах 200 – 220 К лазеры в среднем ИК диапазоне.

Рассмотрены применения этих лазеров в спектроскопии высокого разрешения, прикладной спектроскопии и газоанализе.