Parameters of an electric-discharge generator of iodine atoms for a chemical oxygen – iodine laser

V.N. Azyazov, M.V. Vorob'ev, A.I. Voronov, N.V. Kupryaev, P.A. Mikheyev, N.I. Ufimtsev

Abstract. **Laser-induced fluorescence is used for measuring the concentration of iodine molecules at the output of an electric-discharge generator of atomic iodine. Methyl iodide CH_3I is used as the donor of atomic iodine. The fraction of iodine extracted from CH_3I in the generator is $\sim 50\%$. The optimal operation regimes are found in which $80\% - 90\%$ of iodine contained in the output flow of the generator was in the atomic state. This fraction decreased during the iodine transport due to recombination and was $20\% - 30\%$ at the place where iodine was injected into the oxygen flow. The fraction of the discharge power spent for dissociation was $\sim 3\%$.**

1. Introduction

The active medium of a chemical oxygen – iodine laser (COIL) is usually obtained by mixing molecular iodine vapour with a flow of oxygen in the excited singlet state $O_2(^1\Delta)$ in which iodine molecules rapidly dissociate to atoms. The COIL operates at the spin – orbit $I(^2P_{1/2}) \to I(^2P_{3/2})$ transition in atomic iodine. Inversion at the laser transition is achieved due to the resonance EE-exchange in the process

$$O_2(^1\Delta) + I(^2P_{3/2}) \leftrightarrow O_2(^3\Sigma) + I(^2P_{1/2}).$$
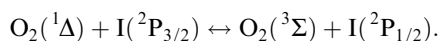
The method of preparation of the active medium of a COIL by mixing molecular iodine vapour with the oxygen flow has both advantages, for example, the absence of an additional unit in the scheme for generating iodine atoms, and disadvantages. First, the sublimation of the I_2 vapour in the COIL is performed by using a molecular-iodine vapour generator. The temperature of the heated iodine flow in

V.N. Azyazov, M.V. Vorob'ev, A.I. Voronov, N.V. Kupryaev, P.A. Mikheyev, N.I. Ufimtsev Samara Branch, P.N. Lebedev Physics Institute, Russian Academy of Sciences, ul. Novo-Sadovaya 221, 443011 Samara, Russia; e-mail: azyazov@fian.smr.ru, mikheyev@fian.smr.ru

high-power COILs achieves 420 K [1]. To avoid the condensation of iodine on the walls, the transportation channel and the mixing unit are heated. This leads to the heating of the active medium, which reduces the laser efficiency. Second, about 10 % of singlet oxygen $O_2(^1\Delta)$ is spent for the dissociation of I_2. The energy spent for this can be transformed to laser radiation by using iodine atoms instead of molecules. According to the optimistic estimate [2], this can enhance the chemical efficiency of a COIL up to 40 %. Third, I_2 molecules efficiently quench $I(^2P_{1/2})$, which reduces the energy loss, decreases the length of the active zone along the flow and restricts the optimal concentration of iodine atoms and, therefore, restricts the small-signal gain. In the absence of I_2 in the active medium, the gain and the active-zone length along the flow can be increased. Thus, the injection of preliminarily prepared iodine atoms into the singlet oxygen flow instead of iodine molecules can be used to increase the COIL efficiency.

A promising method for obtaining the required amounts of atomic iodine is the dissociation of iodine-containing molecules in electric-discharge plasmas. The first experiments with self-sustaining discharges were performed [3, 4] by using I_2 as the donor of iodine atoms, He and Ar as gas carriers for iodine vapour, and microwave and radiofrequency discharges as plasma sources. It was found [3] that only $20\% - 40\%$ of I_2 molecules dissociated, but nevertheless the increase in the output power was observed in both cases. Recently [5], a dc discharge was used for the external production of iodine atoms in a supersonic COIL. The degree of preliminary dissociation of I_2 in this work was low (only 2 %). However, even such a small amount of preliminarily produced atomic iodine resulted in the increase in the output power by 80% due to increase in the dissociation rate of iodine molecules along with a relatively low consumption of atomic iodine. When the iodine consumption was increased only by 30 %, the output characteristics of the laser in the presence and absence of the discharge were almost identical. The improvement of the output parameters of COILs observed in regimes with the preliminary dissociation of iodine is explained in [3 – 5] by favourable conditions for the dissociation of I_2 in the active medium due to the presence of I atoms required to initiate the chain dissociation reaction. A low dissociation degree of iodine molecules in the discharge plasma is explained by a relatively low cross section for dissociation of I_2 by electrons.

It was shown in [6 – 9] that methyl iodide CH_3I is a suitable donor of iodine atoms. A pulsed COIL with the volume production of iodine atoms in a pulsed electric

discharge was investigated in [6, 7]. Laser pulses of duration ~ 10 μs were obtained when the concentration of atomic iodine achieved 1.8×10^{15} cm^{-3}. No influence of the products of reactions initiated by the electric discharge on the output parameters of the laser was observed during the pulse. The operation regimes of a continuous electric-discharge generator of atomic iodine in a vortex gas flow were studied in [8, 9]. The concentration of iodine atoms up to 10^{16} cm^{-3} was achieved for the pressure of the argon carrier gas up to 30 Torr [9] and the gas temperature at the generator output about 500 K [8].

The gas pressure in the iodine flow in conventional COILs is $p \geqslant 20$ Torr and the gas temperature is maintained at $320 - 330$ K to avoid the condensation of iodine vapour on the walls of the transportation channel and gas mixing unit [1, 10–14]. A high temperature in the iodine flow is undesirable because the conversion efficiency of energy stored in singlet oxygen to laser radiation decreases with increasing the active medium temperature. Thus, the parameters of the flow at the output of the atomic iodine generator should be as follows: the total gas pressure $p > 20$ Torr, the concentration of iodine atoms $N_I \geqslant 10^{16}$ cm^{-3}, and the gas temperature $T \leqslant 350$ K. The higher the gas pressure in the iodine flow, the more efficient systems for gas mixing can be used. However, an increase in pressure is restricted by two factors. First, as pressure is increased, the discharge becomes unstable and, second, the rate of homogeneous recombination of iodine atoms increases both in the discharge zone and in the transportation channel between the atomic iodine generator and the injector of the iodine flow into the active medium of the laser. The concentration ratio of atomic and molecular iodine at the output of the discharge device depends on its parameters and is unknown beforehand. In addition, during the transport of iodine to the region of its mixing with singlet oxygen the iodine atoms have time to recombine partially. The recombination rate strongly depends on the carrier gas temperature, which changes during the transport of atoms from the discharge to the active medium. Thus, to obtain reliable data on the concentration of I$_2$ in the carrier-gas flow, experimental measurements are needed. The aim of this paper is the experimental measurement of concentrations of I$_2$ in the products of an electric-discharge generator of iodine atoms.

2. Experiment

We used in experiments an electric-discharge generator of iodine atoms based on a dc glow discharge with coaxial electrodes [9] producing iodine atoms at concentrations up to 10^{16} cm^{-3} at the Ar carrier gas pressure up to 30 Torr. The donor of atomic iodine was methyl iodide CH$_3$I which efficiently dissociates in the discharge. Examples of its application in similar experimental setups are presented in [15, 16].

To measure the concentration of I$_2$ behind the discharge zone and along the carrier-gas flow, we developed the method for measuring the concentration of molecular iodine based on the laser-induced fluorescence (LIF) of I$_2$ vapour, which was excited by the second harmonic of a cw Nd laser at 532 nm. This method can be used to measure the concentrations of I$_2$ in the range from $\sim 10^{13}$ cm^{-3}, which are typical for the active medium of COILs; the size of the region being measured in these experiments was only several millimetres.

Fluorescence was excited by a diode-pumped, frequency-doubled cw WL-LAG532-5 Nd : YAG laser. The laser linewidth was smaller than the distance between rotational transition lines in I$_2$ molecules, and therefore to obtain LIF, it was necessary to provide the laser tuning. We found that this could be achieved by slightly varying the laser housing temperature.

The temperature was varied by using a device consisting of a Peltier cooler, an ohmic heater, a thermal sensor, and an electronic temperature controller. Our experiments showed that the concentrations of I$_2$ could be measured most reliably when temperature changed approximately by 1 °C for the time ~ 30 s (rather than upon precise temperature stabilisation). In this case, the maximum LIF signal was observed when the laser frequency coincided with the frequency of one of the rotational transitions in the I$_2$ molecule. Figure 1 shows the typical LIF spectrum recorded in the spectral range from 600 to 800 nm by using an AvaSpec 3648 spectrometer with a resolution of 0.4 nm.
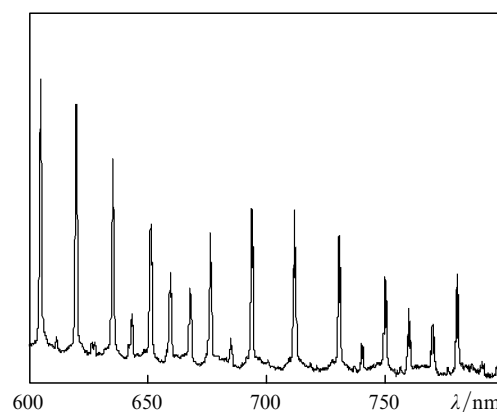

Figure 1. LIF spectrum of I$_2$ molecules recorded with a resolution of 0.4 nm.

The concentration of I$_2$ was measured in a continuous-flow chamber located behind rake-type or jet injectors. Figure 2 shows the scheme of the experimental setup. The parameters of a continuous-flow chamber are described in detail in [17, 18]. Iodine was produced with the help of an electric-discharge generator with coaxial electrodes [9, 17]. The pressure of the Ar carrier gas in the atomic iodine generator and in the transportation channel was 20 Torr, the
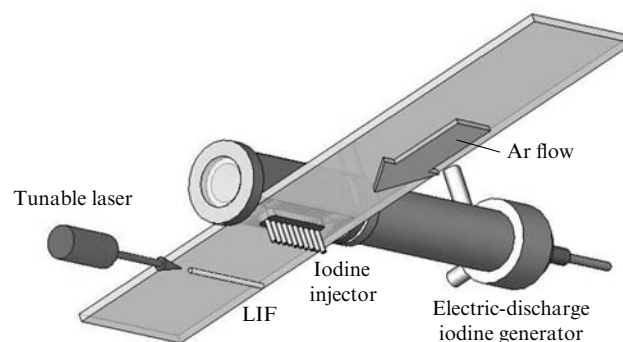

Figure 2. Scheme for measuring the I$_2$ concentration in a continuous-flow chamber behind an iodine injector.

gas flow rate in the generator was 2.5 mmol s^{-1}, and the discharge current was 1.2 A. The discharge voltage was varied from 290 to 350 V and depended on the CH$_3$I flow rate in the electric-discharge generator almost linearly.

Calibration was performed by using the known concentrations of I$_2$ measured from the absorption of radiation at 495 nm in a cell of length 50 cm. The temperature of the cell and water flowing around electrodes was maintained equal to 320 K. It should be taken into a account that the measurement error of the concentration of I$_2$ can depend on the difference in gas temperatures in the presence and absence of the discharge. The LIF signal intensity decreases with increasing temperature due to a decrease in the population of the zero vibrational level of I$_2$ molecules, the Doppler broadening of the absorption line and a decrease in the gas density. The gas heating ΔT in the discharge zone due to intense heat exchange with the walls was insignificant and did not exceed ~ 30 K. The numerical simulation performed by using the Comsol software packet showed that for the transportation time of 6 ms the average temperature of the flow due to its heat exchange with the walls of the channel exceeds the wall temperature only by $\Delta T \approx 5$ K, and therefore the measurement error of the concentration of I$_2$ by the LIF method does not exceed 10%.

To exclude the influence of scattered radiation from the exciting laser, the LIF signal was detected through an MDR-6 monochromator at 580 nm with the transmission band of 10 nm. The fluorescence emission of iodine molecules at the I$_2$(B–X) transition was delivered at the monochromator input through an optical fibre. The light flux at the monochromator exit was detected with a FEU-69b photomultiplier. The output electric signal of the photomultiplier was amplified in a U-7-1 precision amplifier with the passband 0–1000 Hz. Laser radiation was modulated with a mechanical chopper at a frequency of ~ 100 Hz. The data were accumulated with a National Instruments ADC board. The data were digitally processed in a personal computer. It was found experimentally that CH$_3$I molecules at concentrations typical for our experiments did not affect LIF signals.

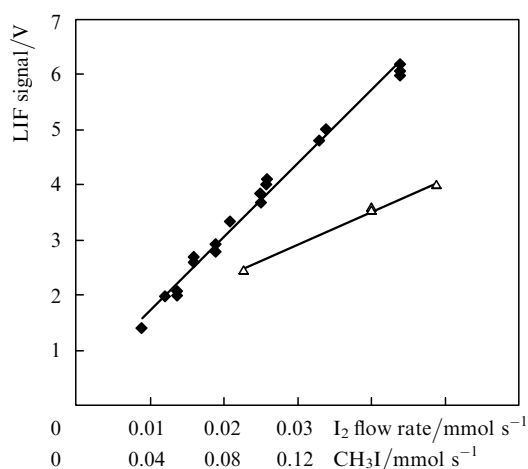Figure 3 shows the dependences of the LIF signal amplitude on the flow rates of I$_2$ (in the presence of the discharge) and CH$_3$I in the discharge generator for a jet injector. In this measurement cycle, Ar was delivered at the low rate 2.5 mmol s^{-1} into the continuous-flow chamber instead of singlet oxygen. The dissociation degree η of methyl iodide in the discharge, estimated from the results of previous experiments [17], was $\sim 50\%$. If all the iodine atoms recombined, the dependence on CH$_3$I would coincide with that on I$_2$ in Fig. 3. Our measurements showed that under conditions typical for the active oxygen–iodine medium, depending on the CH$_3$I flow rate, the content [I]/([I] + 2[I$_2$]) of iodine atoms in the iodine flow after the rake-type injector was 20% – 40% and after the jet injector –30% – 50%.

Iodine atoms recombined in the discharge chamber, transportation channel, and the iodine injector. Contributions from all these regions to recombination were determined by measuring the concentrations of I$_2$ along the gas flow at a pressure of 20 Torr, which was equal to that in the discharge camber. In these experiments, a steel cylindrical tube with the inner diameter of 1.5 cm, heated with ohmic heaters, was located directly behind the discharge part of the atomic iodine generator.

An aperture with some openings providing the required flow rate of the carrier gas was mounted in different places along the gas flow. At a distance of 5 cm behind the aperture, a Plexiglas insert was located in which LIF was excited and observed. Pressure behind the aperture at the observation point was 2–3 Torr, and the possible recombination of iodine atoms in the low-pressure region was neglected.

Figure 4 shows the results of measurements for three positions of the aperture. For the minimal initial flow rate of CH$_3$I ($G_{CH_3I} = 0.04$ mmol s^{-1}), the flow rate of I$_2$ is the same for all three gas transportation times $\tau_{tr} = 3.1$, 9.1, and 13.4 ms. This means that almost all iodine atoms produced in the discharge zone have recombined. The gas residence time in the discharge zone was 6 ms. One can see that the dependence of the flow rate of I$_2$ on the flow rate of CH$_3$I has a maximum in all cases, which is displaced to the greater flow rates of CH$_3$I with increasing the gas transportation time. It seems that this effect is related to the increase in the carrier gas temperature and a change in the plasma
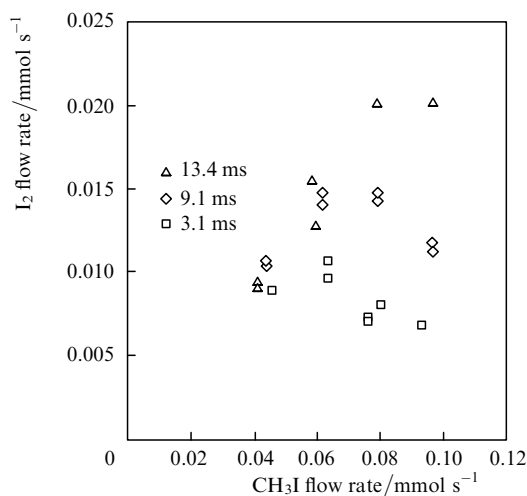

Figure 3. Dependences of the LIF signal amplitude for I$_2$ molecules on the I$_2$ ($\blacklozenge$) and CH$_3$I ($\triangle$) flow rates in the discharge generator for the jet injector at a pressure of 20 Torr and discharge current 1.2 A; the CH$_3$I dissociation degree is $\sim 50\%$.

Figure 4. Dependences of the I$_2$ flow rate on the CH$_3$I flow rate for different positions of the aperture corresponding to different iodine transportation times.
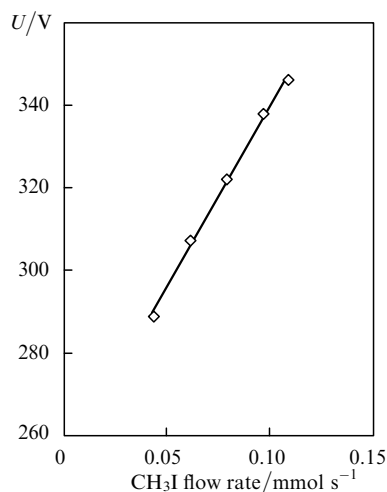
Figure 5. Dependence of the discharge voltage U on the CH_3I flow rate at the constant discharge current 1.2 A.

Figure 6. Theoretical (curves) and experimental (squares) I_2 concentrations for $G_{CH_3I} = 0.088$ mmol s^{-1}.

parameters with increasing the flow rate of CH_3I. Indeed, as shown in Fig. 5, the voltage U at the constant discharge current $I = 1.2$ A increases linearly with increasing the flow rate of CH_3I, and the voltage U_0 in the absence of CH_3I is ~ 250 V.

The fraction $\eta G_{CH_3I} q_b/(UI)$ of the discharge power spent for the dissociation of CH_3I molecules remains almost constant under our experimental conditions and is equal to $\sim 3\%$ (q_b is the C–I bonding energy equal to 234 kJ mol^{-1}). As the discharge voltage is increased, plasma parameters change so that the fraction of iodine atoms in gas increases.

The results of measurements were compared with one-dimensional numerical simulation of the recombination of iodine atoms in the transportation channel in reactions

$$I + I + M \rightarrow I_2 + M, \qquad (1)$$

$$I + I + wall \rightarrow I_2 + wall, \qquad (2)$$

where M = Ar, CH_3I and I_2 at temperature 350 K and argon pressure 20 Torr. We used in calculations the temperature dependences of the rate constants of thee-body processes (1) measured in cm^6 s^{-1}, which were taken from [19, 20, 21], respectively

$$K_{Ar}(T) = \frac{10^{9.439 - 2.418L + 1.911L^2}}{6.02^2} \times 10^{-40}, \ L = (T/300),$$

$$K_{CH_3I} = \frac{10^{15.36} e^{1283/T}}{(6.02 \times 10^{23})^2},$$

$$K_{I_2}(T) = \frac{10^{10.65} T^{1.5} e^{2677/T}}{(6.02 \times 10^{23})^2}.$$

The recombination probability of iodine atoms on the wall [reaction (2)] was set equal to 0.001 [22, 23].

The mass transfer of iodine atoms to the walls and their recombination were described as in [22]. Under our experimental conditions, the contribution of heterogeneous recombination (2) during the transportation proved to be small. The experimental points in Fig. 6 were obtained for $G_{CH_3I} = 0.08$ mmol s^{-1}. The best agreement between the
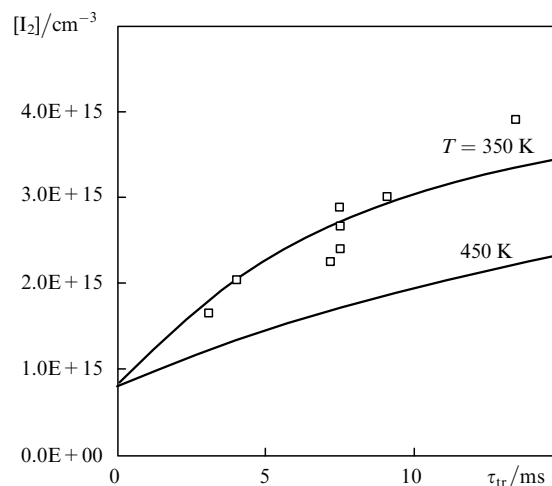
calculated and experimental concentrations of I_2 was achieved at $T = 350$ K and the initial concentrations of components $[CH_3I] = 1.4 \times 10^{16}$ cm^{-3}, $[I] = 7.8 \times 10^{15}$ cm^{-3}, $[I_2] = 8 \times 10^{14}$ см$^{-3}$.

The calculated curves in Fig. 6 illustrate the influence of the gas temperature on the recombination rate of iodine in the transportation volume. One can see that within 10 ms after the discharge, the fraction of iodine atoms at 350 K decreases from $\sim 90\%$ down to 35%, while at 450 K it decreases only down to 60%.

3. Conclusions

The atomic iodine generator based on a glow discharge with coaxial electrodes using CH_3I as the donor of iodine atoms can produce iodine atoms at concentrations up to $\sim 10^{16}$ cm^{-3} at Ar pressures in the discharge zone up to 20 Torr. The dissociation degree of CH_3I is $\sim 50\%$. The LIF measurements of the I_2 concentration have shown that the fraction of atomic iodine in iodine vapour at the output of the electric-discharge generator depends on the flow rate of methyl iodide, increasing with the flow rate.

The fraction of iodine atoms in the iodine flow at the generator output in optimal regimes was 80% – 90%. This was achieved for $G_{CH_3I} \approx 0.1 - 0.2$ mmol s^{-1} and the temperature of water flowing around the electrodes equal to 330 K. Nevertheless, due to the design of the setup, the iodine flow in the injector into singlet oxygen, depending on the injector type and the CH_3I flow rate, contained only 20% – 50% of atomic iodine and 50% – 80% of molecular iodine. Iodine atoms had time to recombine to a great extent both during the transportation time (~ 6 ms) and during the residence time in the rake-type injector. Therefore, the electric-discharge generator and the transportation system should be designed so that the iodine flow would be injected into the singlet oxygen flow immediately after the discharge.

At the constant discharge current, the discharge voltage increases linearly with the CH_3I flow rate, so that the fraction of energy spent for the dissociation of CH_3I molecules remains constant. The achieved total efficiency of the discharge energy input to the iodide dissociation did not exceed 3%. The studies of electric-discharge generators of iodine atoms are at the initial stage at present, and it is

hoped that their energy efficiency will be increased in the future.

The use of the atomic iodine generator in COILs makes it possible to increase the inversion lifetime in the active medium [17], which is important when efficient resonator schemes requiring the extended active medium along the gas flow are used in COILs. At present this is achieved by increasing the the gas velocity in the resonator. For this reason, light but expensive helium is used as a diluent in supersonic COILs [24]. However, in COIL schemes using atomic iodine generators and low-cost gases (nitrogen [10, 11, 13, 14] or carbon dioxide [12]) as diluents, the acceptable extension of the active medium along the gas flow also can be obtained.

References

1. Adamenkov A.A., Bakshin V.V., Bogachev A.V., et al. *Kvantovaya Elektron.*, **37**, 601 (2007) [*Quantum Elektron.*, **37**, 601 (2007)].
2. Carroll D.L., Solomon W.C., King D., et al. *Proc. of the International Conference on Lasers'99* (McLean, VA: STS Press, 2000) p. 69.
3. Endo M., Sugimoto D., Okamoto H., et al. *Jpn. J. Appl. Phys.*, **39**, 468 (2000).
4. Wakazono T., Hashimoto K., Takemoto T. *Proc. SPIE Int. Soc. Opt. Eng.*, **3574**, 290 (1998).
5. Katz A., Dahan Z., Rybalkin V., Waichman K., Barmashenko B., Rosenwaks S. *Appl. Phys. Lett.*, **90**, 161122 (2007).
6. Vagin N.P., Pazyuk V.S., Yuryshev N.N. *Kvantovaya Elektron.*, **22**, 776 (1995) [*Quantum Elektron.*, **25**, 746 (1995)].
7. Vagin N.P., Yuryshev N.N. *Kvantovaya Elektron.*, **31**, 127 (2001) [*Quantum Elektron.*, **31**, 127 (2001)].
8. Mikheyev P.A., Shepelenko A.A., Voronov A.I., Kupryaev N.V. *Kvantovaya Elektron.*, **32**, 1 (2002) [*Quantum Elektron.*, **32**, 1 (2002)].
9. Mikheyev P.A., Shepelenko A.A., Voronov A., et al. *J. Phys. D: Appl. Phys.*, **37**, 3202 (2004).
10. Zagidullin M.V., Nikolaev V.D., Svistun M.I., Khvatov N.A. *Kvantovaya Elektron.*, **35**, 907 (2005) [*Quantum Elektron.*, **35**, 907 (2005)].
11. Rybalkin V., Katz A., Barmashenko B.D., Rosenwaks S. *Appl. Phys. Lett.*, **85**, 5851 (2004).
12. Antonov I.O., Azyazov V.N., Mezhenin A.V., Popkov G.N., Ufimtsev N.I. *Appl. Phys. Lett.*, **89**, 051115 (2006).
13. Yang T.T., Bhowmik A., Burde D., et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **4760**, 537 (2002).
14. Azyazov V.N., Antonov I.O., Pichugin S.Yu., Safonov V.S., Svistun M.I., Ufimtsev N.I. *Kvantovaya Elektron.*, **33**, 811 (2003) [*Quantum Elektron.*, **33**, 811 (2003)].
15. Balan N.F., Gizatullin R.M., Dubrovskii A.V., et al. *Kvantovaya Elektron.*, **16**, 1587 (1989) [*Sov. J. Quantum Elektron.*, **19**, 1021 (1989)].
16. Vagin N.P., Zolotarev V.A., Kryukov P.G. et al. *Kvantovaya Elektron.*, **18**, 33 (1991) [*Sov. J. Quantum Elektron.*, **21**, 28 (1991)].
17. Mikheyev P.A., Azyazov V.N., Mezhenin A.V., et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **6346**, 63460J (2007).
18. Azyazov V.N., Heaven M.C. *AIAA J.*, **44**, 1593 (2006).
19. Ip J.K.K., Burns G.J. *Chem. Phys.*, **56**, 3155 (1972).
20. Engelman R. Jr, Davidson N.R. *J. Am. Chem. Soc.*, **82**, 4770 (1960).
21. Bunker D.L., Davidson N. *J. Am. Chem. Soc.*, **80**, 5090 (1958).
22. Hays G.N., Fisk G.A. *IEEE J. Quantum Electron.*, **17**, 1823 (1981).
23. Azyazov V.N. *Kvantovaya Elektron.*, **21**, 25 (1994) [*Quantum Elektron.*, **24**, 23 (1994)].
24. McDermott W.E., Stephens J.C., Vetrovec J., Dickerson R.A. *AIAA Paper № 97-2385* (1997).