

Kinetics of an oxygen–iodine active medium with iodine atoms optically pumped on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition

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Abstract. The kinetics of the processes occurring in an $O_2-I_2-He-H_2O$ gas flow in which photodissociation of molecular iodine at a wavelength close to 500 nm and excitation of atomic iodine on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition by narrow-band radiation near 1315 nm are implemented successively has been analysed. It is shown that implementation of these processes allows one to form an oxygen–iodine medium with a high degree of dissociation of molecular iodine and a relative content of singlet oxygen $O_2(a^1\Delta)$ exceeding 10%. Having formed a supersonic gas flow with a temperature ~ 100 K from this medium, one can reach a small-signal gain of about 10^{-2} cm^{-1} on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition in iodine atoms. The specific power per unit flow cross section in the oxygen–iodine laser with this active medium may reach $\sim 100 \text{ W cm}^{-2}$.

Keywords: optical pumping, singlet oxygen, iodine atom, oxygen–iodine laser, diode laser.

1. Introduction

Currently, interest is being shown in the development of high-power gas lasers with laser-diode pumping, where atoms of alkali metals [1–5] or rare gases [6, 7] are proposed to be active particles. An optically pumped oxygen–iodine laser is also considered, in which an oxygen molecule is excited to the $a^1\Delta$ state as a result of energy transfer from a photosensitizer, e.g., a fullerene molecule [8]. Inversion on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition in a iodine atom in an oxygen–iodine laser is formed as a result of resonant energy exchange with a singlet oxygen molecule $O_2(a^1\Delta)$:



Hereinafter, I^* , I , $O_2(X)$, $O_2(a)$ and $O_2(b)$ are, respectively, iodine atoms in the ${}^2P_{1/2}$, ${}^2P_{3/2}$ states and oxygen molecules in the $X^3\Sigma$, $a^1\Delta$ and $b^1\Sigma$ states. The key characteristic of the active medium of an oxygen–iodine laser is the quantity Y : the ratio of the concentration of oxygen molecules in the $a^1\Delta$ state to the total concentration of oxygen in the $a^1\Delta$ and $X^3\Sigma$ states.

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Received 9 July 2014; revision received 31 October 2014
Kvantovaya Elektronika 45 (8) 720–724 (2015)
Translated by Yu.P. Sin'kov

The inverse population on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition of iodine atom occurs at $Y > Y_{th}(T) = (2K_e + 1)^{-1}$, where $K_e(T) = 0.75\exp(401/T)$ is the equilibrium rate constant for reaction (1) at a temperature T . For example, the threshold values Y_{th} at $T = 300$ and 100 K are 0.15 and 0.012, respectively. The Y value for an oxygen–iodine laser with a chemical singlet oxygen generator generally exceeds 0.4, and an inverse population is formed at room temperature [9]. In an electric-discharge oxygen–iodine laser, $Y \leq 0.15$. Therefore, gas-dynamic cooling of the active medium is applied to obtain inverse population [10].

In this study, we consider the possibility of developing an optically pumped oxygen–iodine laser (OPOIL), in which the energy transfer from excited iodine atoms to oxygen molecules provides energy pumping of the O_2-I medium. To form an OPOIL active medium, a gas flow containing iodine atoms and oxygen molecules in the ground states is irradiated at the frequency of the ${}^2P_{1/2}-{}^2P_{3/2}$ transition in the iodine atom. The radiation may be incoherent and multidirectional, e.g., emitted by a diode laser array. The excited iodine atoms transfer energy to oxygen molecules, exciting them to the $a^1\Delta$ state. With an increase in radiation intensity, $Y \rightarrow Y_{th}(T_1)$, where T_1 is the flow temperature. Then the flow is subjected to sharp gas-dynamic cooling to a temperature $T_2 < T_1$, retaining the obtained relative content of $O_2(a)$ molecules. Due to the cooling, the inequality $Y > Y_{th}(T_2)$ can be satisfied.

In this case, inversion is formed on the ${}^2P_{1/2}-{}^2P_{3/2}$ transition in the iodine atom, and lasing becomes possible. To implement this scheme of an oxygen–iodine laser, one must, first, provide a sufficiently high concentration of iodine atoms using optical radiation. Second, in this method of optical pumping, the production rate of $O_2(a)$ molecules should exceed their de-excitation rate. The purpose of this study was to show that the kinetics of oxygen–iodine medium is not a hindrance for developing an OPOIL in principle.

2. Initial equations modelling the kinetics of an optically pumped oxygen–iodine medium

Figure 1 presents a block diagram of an OPOIL. An $O_2-I_2-He-H_2O$ gas flow (without iodine atoms) arrives at section (1), where it is illuminated by radiation of type A at a wavelength $\lambda_A \approx 500$ nm. This radiation causes photodissociation of iodine molecules. Then the mixture arrives at section (2), where it is illuminated by radiation of type B at a wavelength $\lambda_B \approx 1315$ nm. This radiation excites iodine atoms to the ${}^2P_{1/2}$ state.

The formation of excited iodine atoms initiates energy-exchange and relaxation processes, which are listed in Table 1. The rate constants are given for a temperature of 300 K, for

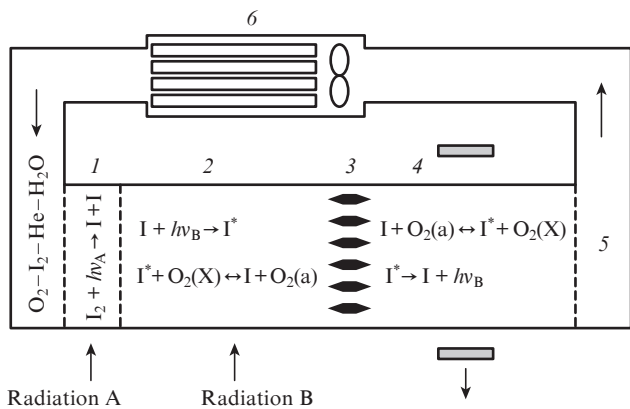


Figure 1. Block diagram of OPOIL: (1) section for photodissociation of iodine molecules; (2) section for optical pumping of oxygen molecules; (3) nozzle array; (4) cavity active region; (5) diffuser; (6) compressor and heat exchanger.

which they have been reliably determined. The processes leading to dissociation of iodine molecules in chemical reactions in section (2) are especially important for forming an active OPOIL medium. Iodine dissociation in the presence of $O_2(a)$, $O_2(b)$ and I^* is known to occur via a complex multichannel mechanism [11]. This dissociation can be described in a simplified form within the Heidner phenomenological model [15] with two dissociation channels. In one of them, an iodine molecule dissociates upon a collision with an $O_2(b)$ molecule (reaction 2). $O_2(b)$ molecules are mainly formed in reaction 6a. At a high degree of iodine molecule photodissociation ($\sim 10\%$), the production rate of $O_2(b)$ molecules in the pulling reaction $O_2(a) + O_2(a) \rightarrow O_2(b) + O_2(X)$ with a constant rate $\sim 4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [17] is much lower than in reaction 6a.

Table 1. Rate constants of the processes occurring in an oxygen–iodine medium at a temperature of 300 K.

Reaction number	Reaction	Reaction rate constants/ $\text{cm}^3 \text{ s}^{-1}$
1	$O_2(a) + I \rightarrow O_2(X) + I^*$	$k_{1f} = 7.6 \times 10^{-11}$ [12]
	$O_2(X) + I^* \rightarrow O_2(a) + I$	$k_{1b} = k_{1f}/K_e$, $K_e = 2.85$
2	$I_2 + O_2(b) \rightarrow 2I + O_2(X)$	$k_2 = 10^{-10}$ [13]
3	$I^* + I_2 \rightarrow I + I_2^*$	$k_3 = 3.6 \times 10^{-11}$ [14]
4	$I_2^* + O_2(a) \rightarrow 2I + O_2(X)$	$k_4 = 3 \times 10^{-11}$ [15]
5a	$O_2(a) + I \rightarrow O_2(X) + I$	k_{5a}
5b	$O_2(X) + I^* \rightarrow O_2(X) + I$	k_{5b} , $K_5 = k_{5a} + K_e k_{5b} = 10^{-15}$ [16]
6a	$O_2(a) + I^* \rightarrow O_2(b) + I$	$k_{6a} = 2.1 \times 10^{-13}$ [17]
6b	$O_2(a) + I^* \rightarrow O_2(X) + I^*$	k_{6b}
6c	$O_2(a) + I^* \rightarrow O_2(a) + I$	k_{6c}
6d	$O_2(a) + I^* \rightarrow O_2(X) + I$	k_{6d} , $K_6 = k_{6a} + k_{6b} + k_{6c} + 2k_{6d} = 6 \times 10^{-13}$ [18]
7	$O_2(b) + H_2O \rightarrow O_2(a) + H_2O$	$k_7 = 6.7 \times 10^{-12}$ [19]
8	$I_2^* + M \rightarrow I_2 + M$	$k_8^M = 3 \times 10^{-10}$ ($M = H_2O$), 3×10^{-12} ($M = O_2$), 10^{-14} ($M = He$) [*] ,
9	$I^* + H_2O \rightarrow I + H_2O$	$k_9 = 2 \times 10^{-12}$ [14]
10	$I + I(I^*) + M \rightarrow I_2 + M$	$k_{10}^M = 3.8 \times 10^{-30}$ ($M = I_2$) [20], 3.8×10^{-33} ($M = He$) [21], 1.2×10^{-32} ($M = O_2$) [21],

^{*}) assumed equal to k_8^{Ar} [15]; k_{10}^M is measured in $\text{cm}^6 \text{ s}^{-1}$.

Therefore, the influence of the pulling reaction on the production rate of $O_2(b)$ molecules can be neglected.

In the second channel, iodine dissociation occurs in two stages. In the first, a vibrationally excited iodine molecule I_2 is formed in reaction 3 ($v = 20-40$), which is denoted as I_2^* in Table 1. In the second stage, this molecule dissociates in reaction 4. The contribution of this channel to the dissociation rate of I_2 increases with increasing concentrations of $O_2(a)$ molecules and I^* atoms in the mixture. Quenching of electronically excited particles occurs in reactions 5, 6b–6d, 7 and 9, and recombination of iodine atoms occurs in reactions 10. The V–T cascade relaxation of iodine molecules from the vibrational levels with $v = 20-40$ to the levels with $v < 20$ is described by reaction 8. A small impurity of water provides transition of oxygen molecules from the $b^1\Sigma$ state to the $a^1\Delta$ state in reaction 7.

Let us assume the zones where the gas flow is illuminated by radiations of different types to be spatially separated: only photodissociation of iodine molecules occurs in section (1) and only optical pumping of iodine atoms is implemented in section (2). Sections (1) and (2) are considered to be located in a heat exchanger, which provides a constant gas flow temperature: $T_1 = 300 \text{ K}$. During the gas flow propagation in section (2), the relative concentration of $O_2(a)$ molecules increases. Having passed through nozzle array (3), the flow acquires a supersonic velocity and penetrates cavity (4). During gas-dynamic expansion, the gas temperature decreases, and inverse population arises on the $^2P_{1/2} - ^2P_{3/2}$ transition in iodine atoms. The energy accumulated in the gas mixture is converted into laser radiation in cavity (4). The developed laser medium is pumped out into atmosphere or repeatedly used in a closed cycle, as shown in Fig. 1.

The dependence of the total concentration of iodine atoms n_1 on the coordinate z along the flow direction in section (1) is found by solving the equation

$$V_1 \frac{dn_1}{dz} = 2\Gamma_A n_{I_2} - 2K_{10} n_1^2 \quad (2)$$

with the initial condition $n_1(z=0) = 0$. Here, $K_{10} = k_{10}^{O_2} N_{O_2} + k_{10}^{He} N_{He} + k_{10}^{I_2} n_{I_2}$; N_{O_2} , N_{He} and N_{I_2} are, respectively, the initial concentrations of O_2 , He and I_2 ; $n_{I_2} = N_{I_2} - 0.5n_1$ is the concentration of iodine molecules; V_1 is the flow velocity in sections (1) and (2); and Γ_A is the photodissociation rate iodine molecules under radiation of type A. The specific energy E_A , absorbed in a unit flow volume, can be determined from the equation

$$V_1 \frac{dE_A}{dz} = \varepsilon_A \Gamma_A n_{I_2}, \quad (3)$$

where $\varepsilon_A \approx 4 \times 10^{-19} \text{ J}$ is the energy of a photon with a wavelength $\lambda \approx 500 \text{ nm}$.

In section (2), the changes in the component concentrations along the flow direction are described by the rate equations:

$$V_1 \frac{dn_1}{dz} = 2k_2 n_b n_{I_2} + 2k_4 n_{I_2}^* n_a - 2K_{10} n_1^2, \quad (4)$$

$$V_1 \frac{dn_{I^*}}{dz} = -\Gamma_B g + k_{1f} n_a n_1 - \Gamma_{I^*} n_{I^*}, \quad (5)$$

$$V_1 \frac{dn_a}{dz} = -\Gamma_a n_a + k_{1b} n_X n_{I^*} + k_7 n_b N_{H_2O}, \quad (6)$$

$$V_1 \frac{dn_b}{dz} = k_{6a} n_a n_1^* - \Gamma_b n_b, \quad (7)$$

$$V_1 \frac{dn_{1_2}^*}{dz} = k_3 n_{1_2} n_1^* - \Gamma_{1_2}^* n_{1_2}^*, \quad (8)$$

where

$$\Gamma_{1_2}^* = (k_{1b} + k_{5b}) n_X + (k_{1f} + k_{6a} + k_{6c} + k_{6d}) n_a + k_3 n_{1_2} + k_9 N_{H_2O};$$

$$\Gamma_b = k_7 N_{H_2O} + k_2 n_{1_2};$$

$$\Gamma_{1_2}^* = k_4 n_a + k_8^{O_2} N_{O_2} + k_8^{He} N_{He} + k_8^{H_2O} N_{H_2O}; \text{ and}$$

$$\Gamma_a = (k_{1f} + k_{5a}) n_1 + (k_{6a} + k_{6b} + k_{6d} - k_{1f} - k_{5a}) n_1^* + k_4 n_{1_2}^*.$$

In these equations, n_X , n_a and n_b are the current concentrations of oxygen in the $X^3\Sigma$, $a^1\Delta$ and $b^1\Sigma$; n_1^* is the concentration of iodine atoms in the $2P_{1/2}$ state; $n_{1_2}^*$ is the total concentration of iodine molecules in the vibrational excited states with $v = 20-40$; and $g = 1.5n_1^* - 0.5n_1$ is the inversion density on the $2P_{1/2} - 2P_{3/2}$ transition in a iodine atom. The other designations in Eqns (2)–(8) are given in Tables 1 and 2.

3. Calculation results

Numerical calculations were performed for a wide range of gas mixture compositions, flow characteristics and optical pumping parameters. Table 2 contains close-to-optimal values of the parameters of the oxygen–iodine flow and optical pumping, for which the formation of the OPOIL active medium will be considered. The temperature of the medium was chosen to be 300 K, because reliable values of rate constants are known for this temperature; correspondingly, the calculation results are expected to be reliable.

Table 2. Parameters of an oxygen–iodine medium of the $O_2:I_2:He:H_2O = 100:2:500:1$ composition and optical pumping.

Parameters	Parameter values
Flow temperature (T_1)	300 K
Pressure (p_1)	74.5 Torr
Oxygen concentration (N_{O_2})	$4 \times 10^{17} \text{ cm}^{-3}$
Concentration of iodine molecules ($N_{O_2} = 0.02 N_{O_2}$)	$8 \times 10^{15} \text{ cm}^{-3}$
Concentration of water molecules ($N_{H_2O} = 0.01 N_{O_2}$)	$4 \times 10^{15} \text{ cm}^{-3}$
Concentration of helium atoms ($N_{He} = 5N_{O_2}$)	$2 \times 10^{18} \text{ cm}^{-3}$
Flow velocity in sections (1) and (2) (V_1) (Mach number M_1)	300 m s^{-1} (0.45)
Length of section (1) (z_A)	10 cm
Length of section (2) (z_B)	12 cm
Photodissociation rate of iodine molecules (Γ_A)	500 s^{-1}
Probability of induced transition between the $2P_{1/2}$ and $2P_{3/2}$ in the iodine atom (Γ_B)	$2 \times 10^5 \text{ s}^{-1}$

The numerical solution to Eqn (1) shows that, at a distance $z_A = 10$ cm from the point where illumination by radiation of type A begins, the concentration of iodine atoms is $n_{1A} = 2.4 \times 10^{15} \text{ cm}^{-3}$ (with about 14% iodine molecules dissociated). The radiation energy absorbed in a unit volume is $E_A \approx 0.5 \text{ mJ cm}^{-3}$.

Let us now consider the change in the component concentrations in section (2). To this end, we will simplify the system

of Eqns (4)–(8) to two equations for the concentration of iodine atoms and relative content Y . The inequalities $\Gamma_{1_2}^* > 10^7 \text{ s}^{-1}$, $\Gamma_b > 4 \times 10^4 \text{ s}^{-1}$, and $\Gamma_{1_2}^* > 10^6 \text{ s}^{-1}$ are satisfied for the gas mixture under consideration. The times corresponding to these frequencies, as will be shown below, are much shorter than the characteristic times for which the concentrations of iodine atoms and singlet oxygen change significantly. Therefore, assuming that $dn_1^*/dz \approx 0$, $dn_b/dz \approx 0$, and $dn_{1_2}^*/dz \approx 0$, we obtain the following quasi-steady-state approximations for the component concentrations and inversion density:

$$n_1^* = n_1 \left[\frac{k_{1f} n_a + 0.5 \Gamma_B}{1.5 \Gamma_B + \Gamma_{1_2}^*} \right], \quad g = 0.5 n_1 \frac{3k_{1f} n_a - \Gamma_{1_2}^*}{1.5 \Gamma_B + \Gamma_{1_2}^*}, \quad (9)$$

$$n_b \approx \frac{k_{6a} n_a n_1}{\Gamma_b} \left[\frac{k_{1f} n_a + 0.5 \Gamma_B}{1.5 \Gamma_B + \Gamma_{1_2}^*} \right], \quad n_{1_2}^* = \frac{k_3 n_{1_2} n_1}{\Gamma_{1_2}^*} \left[\frac{k_{1f} n_a + 0.5 \Gamma_B}{1.5 \Gamma_B + \Gamma_{1_2}^*} \right]. \quad (10)$$

Under the conditions considered here, the following inequality is satisfied: $n_b \ll N_{O_2}$; therefore, $N_{O_2} \approx n_a + n_X$ and $Y \approx n_a/N_{O_2}$. Let us substitute expressions (9) and (10) into Eqns (4) and (6). Taking into account that $\Gamma_B \ll \Gamma_{1_2}^*$ and $\Gamma_{1_2}^*/(k_{1f} n_a + k_{1b} n_X) \approx 1$, we obtain the equations for the concentration of iodine atoms,

$$V_1 \frac{dn_1}{dz} = 2n_1 n_{1_2} Y \times \left\{ \frac{k_{1f} Y N_{O_2} + 0.5 \Gamma_B}{k_{1b} [(K_e - 1) Y + 1]} \left[\frac{k_2 k_{6a}}{\Gamma_b} + \frac{k_4 k_3}{\Gamma_{1_2}^*} \right] - (2K_{10} - k_{10}^2 n_1) n_1^2 \right\}, \quad (11)$$

and for the relative content of $O_2(a)$ molecules:

$$V_1 \frac{dY}{dz} = - \frac{0.5 n_1}{N_{O_2}} \frac{\Gamma_B}{(K_e - 1) Y + 1} \left\{ [(2K_e + 1) Y - 1] + \frac{2 Y K_e \Gamma_Y}{\Gamma_B} \right\}, \quad (12)$$

where

$$K_e = K_e(T_1); \quad \Gamma_Y = \frac{(1-Y) K_5 N_{O_2}}{K_e} + Y K_6 N_{O_2} + k_9 N_{H_2O} + n_{1_2} \left(k_3 + \frac{N_{O_2} Y k_4 k_3}{\Gamma_{1_2}^*} + \frac{N_{O_2} Y k_2 k_{6a}}{\Gamma_b} \right).$$

The energy of B-type radiation, absorbed in a unit flow volume, is found by solving the equation

$$V_1 \frac{dE_B}{dz} = - \Gamma_B \varepsilon_{BG}, \quad (13)$$

where $\varepsilon_B = 1.51 \times 10^{-19} \text{ J}$ is the energy of a photon with a wavelength $\lambda = 1315 \text{ nm}$. The initial conditions for Eqns (11)–(13) are, respectively, $n_{1A} = 2.4 \times 10^{15} \text{ cm}^{-3}$, $Y = 0$ and $E_B = 0$.

Let us consider the stationary solutions to Eqns (11) and (12). In the zero approximation, having neglected the de-excitation of excited particles ($\Gamma_Y = 0$) and recombination of iodine atoms ($K_{10} = 0$, $k_{10}^2 = 0$), we obtain stationary values $Y_{th} = (2K_e + 1)^{-1} = 0.15$ for the relative content of $O_2(a)$ and $n_1 = 2N_{1_2}$ for the concentration of iodine atoms. The value $(2K_e + 1)^{-1} = 0.15$ is equal to the limiting attainable relative content of $O_2(a)$. Equating the right-hand side of Eqn (12) to zero and assuming that $\Gamma_Y = (1 - Y_{th}) K_5 N_{O_2} / K_e + Y_{si} K_6 N_{O_2} + k_9 N_{H_2O}$, we find a stationary value for the relative content of singlet oxygen in the first-order approximation:

$$Y_s = \frac{1}{2K_c + 1} \left(1 + \frac{2K_c \Gamma_Y}{\Gamma_B(2K_c + 1)} \right)^{-1}. \quad (14)$$

Let us now find Y_s for the conditions listed in Table 2. For the gas mixture under consideration, $\Gamma_Y \approx Y_{th} K_6 N_{O_2}$. The rate constant K_6 was determined with a rather large spread (from $2.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [16] to $6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [18]). At $K_6 = 6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $\Gamma_B \approx 2 \times 10^5 \text{ s}^{-1}$ (values from Table 1), one can obtain Y_s as high as ~ 0.13 . At the same time, if $K_6 = 2.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, the same Y_s value can be reached at $\Gamma_B \approx 7 \times 10^4 \text{ s}^{-1}$.

Then we estimate the stationary value of the molecular iodine fraction, with allowance for the fact that iodine atoms recombine mainly on oxygen molecules and helium atoms. Equating the right-hand side of (11) to zero and assuming that $Y = Y_{th}$, we find a stationary value for the fraction of undissociated iodine:

$$\frac{n_{I_2}}{N_{I_2}} = 4(k_{10}^{O_2} N_{O_2} + k_{10}^{He} N_{He}) \frac{(K_c - 1) Y_{th} + 1 \left[\frac{k_2 k_{6a}}{\Gamma_b} + \frac{k_4 k_3}{\Gamma_{I_2}^*} \right]^{-1}}{Y_{th}^2 K_c N_{O_2}}.$$

Based on this value, we reveal that $n_{I_2}/N_{I_2} \ll 1$ for the gas mixture under consideration. Thus, for a sufficiently long section (2), one can obtain a relative content of $O_2(a)$ molecules close to $Y_s(T_1)$ and a high degree of iodine dissociation.

The dependences of Y , n_1 and g on the coordinate along the flow direction, obtained by solving numerically Eqns (11) and (12), are presented in Fig. 2. It can be seen that a value $Y = 0.125$, close to Y_s , is reached at a distance of ~ 12 cm, and that iodine completely dissociates at a distance of 8 cm from the point where flow illumination by B-type radiation begins. Obviously, it is expedient to locate nozzle array (3) at a distance $z = 12$ cm, where $Y \approx Y_s$. It follows from the solution to (13) that, for the residence time of the gas in section (2), the radiation energy absorbed in a unit volume is $E_B = 17.5 \text{ mJ cm}^{-3}$.

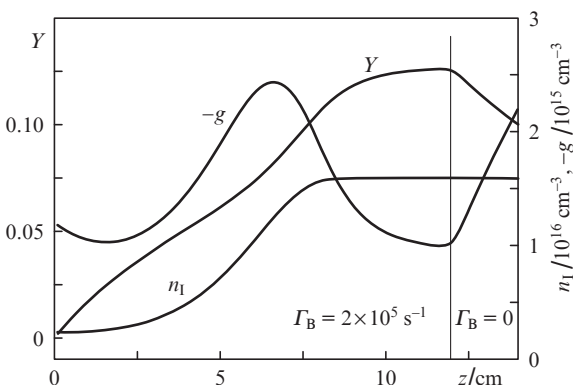


Figure 2. Changes in the concentration of iodine atoms, inverse population density on the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition and relative content of $O_2(a)$ along the flow direction, beginning with the instant of flow irradiation at a wavelength of 1315 nm.

Let us now consider as an example the formation of an OPOIL active medium by a nozzle array with equal sizes (1 cm) of the subsonic and supersonic parts along the gas flow. Primarily, we will estimate the energy loss in the subsonic region of the array, where optical pumping is absent. Figure 2 presents the calculated dependences of Y , n_1 and g on the coordinate along the flow direction (in the range $z \gg$

12 cm) at $\Gamma_B = 0$ and a constant flow velocity V_1 . One can see that the fraction of $O_2(a)$ molecules decreases to $Y_0 \approx 0.11$ by the end of the subsonic part of the nozzle; however, since the flow velocity increases in the subsonic region, the fraction of $O_2(a)$ molecules will be larger.

We assume that the total pressure loss and the increase in the stagnation temperature in the expanding part of the nozzle array are insignificant (i.e., the flow regime is close to isentropic) and that a supersonic flow with a Mach number $M_2 = 3$ and stagnation temperature of about 300 K is formed at the nozzle array output. According to the formulas of gas dynamics [22], the supersonic flow under these conditions will have a velocity $V_2 = 1100 \text{ m s}^{-2}$, a temperature $T_2 = 86 \text{ K}$ and a pressure $p_2 = 2.65 \text{ Torr}$, and the flow cross-sectional area in the supersonic region will be larger by a factor of 2.23 than in section (2). The concentration of iodine atoms, helium and oxygen molecules in the supersonic flow will be, respectively, $n_I^s \approx 2 \times 10^{15} \text{ cm}^{-3}$, $n_{He} \approx 2.5 \times 10^{17} \text{ cm}^{-3}$ and $n_{O_2} \approx 5 \times 10^{16} \text{ cm}^{-3}$.

The residence time of the gas mixture in the expanding part of the nozzle array is $\tau_{res} \approx 10^{-5} \text{ s}$. The increase in the flow temperature for this time, which is caused by the relaxation of accumulated energy in the fastest reactions 6a–6d is $\Delta T^* \approx \epsilon_A \tau_{res} Y_0 n_{O_2} n_I^s K_6 / [(2.5 n_{He} + 3.5 n_{O_2}) / k_B] \approx 10 \text{ K}$ [$\epsilon_A = 1.56 \times 10^{-19} \text{ J molecule}^{-1}$ is the excitation energy of the $O_2(a)$ molecule and k_B is the Boltzmann constant], which is much smaller than the initial value ($\sim 300 \text{ K}$). Along with the assumption about small loss of total pressure in nozzles, this fact justifies the calculations of the active-medium parameters using the formulas for an isentropic flow with an initial stagnation temperature of 300 K.

The maximum specific laser power that can be obtained from unit flow cross-sectional area in the cavity is $\epsilon_B V_2 n_{O_2} (Y_0 - Y_{th}) \approx 86 \text{ W cm}^{-2}$, where $Y_{th} = (2K_c(T_2) + 1)^{-1} \approx 0.005$. Under these conditions, the optical efficiency $\epsilon_B N_{O_2} (Y_0 - Y_{th}) / (E_A + E_B) \approx 0.35$, where $E_B = 0.5 + 17.6 \text{ mJ cm}^{-3} = 18.1 \text{ mJ cm}^{-3}$ is the absorbed light energy. In the centre of the emission line on the ${}^2P_{1/2}(F = 3) \rightarrow {}^2P_{3/2}(F = 4)$ transition, the small-signal gain is

$$n_I^s \frac{7}{12} \sigma \frac{(K_c(T_2) + 0.5) \Delta Y_e}{(K_c(T_2) - 1) Y_0 + 1} \approx 2.5 \times 10^{-2} \text{ cm}^{-1},$$

where $\sigma(\text{cm}^2) = 2.3 \times 10^{-16} (T_2)^{-0.5}$ is the stimulated-emission cross section on this transition under conditions of Doppler broadening.

4. Conclusions

In this study, we did not intend to determine the optimal compositions of the O_2 – I_2 – He – H_2O medium and OPOIL operation conditions. The initial data were chosen to demonstrate only the possibility of optical pumping of the oxygen–iodine medium. For example, the temperature of the medium (300 K) was chosen only based on the reliability of known rate constants at this temperature to make the calculation results reliable. We showed that successive illumination of an O_2 – I_2 – He – H_2O mixture flow by blue-green light ($\lambda = 500 \text{ nm}$) and IR radiation ($\lambda = 1315 \text{ nm}$) provides a high degree of dissociation of iodine molecules and a large fraction of singlet oxygen (above 10%).

Gas-dynamic cooling of the mixture obtained leads to the formation of an inversely populated medium. No minor products are formed in the working medium, and, after the recombination of iodine atoms, its composition is recovered

to the initial state. When recirculating the working mixture, iodine molecules may adsorb on the working surfaces of the gas-flow channel; however, using special coatings of the surfaces and choosing their appropriate temperatures, one can minimise this effect.

Let us find the radiation intensities providing the optical pumping rates considered here. Molecular iodine has a wide photodissociation band in the blue-green spectral region. In the wavelength range of 500 ± 20 nm, the absorption cross section of iodine molecules is $\sigma_A \approx 3 \times 10^{-18}$ cm², and the quantum photodissociation yield at pressures of several tens of Torr is unity [23, 24]. The iodine molecule photodissociation rate $\Gamma_A = 500$ s⁻¹ will be obtained at the radiation intensity $J_A = \varepsilon_A \Gamma_A \sigma_A = 66$ W cm⁻². The optical length necessary for absorption of 95% radiation is $3/(\sigma_A N_{I_2}) \approx 300$ cm. At $J_A = 660$ W cm⁻² ($\Gamma_A = 5000$ s⁻¹), one can obtain a degree of iodine dissociation as high as approximately 87% and $n_{I_0} = 1.4 \times 10^{16}$ cm⁻³ at the output of section (1). It follows from the calculations that in this case the OPOIL optical efficiency at $\Gamma_B = 2 \times 10^5$ s⁻¹ can be increased to 60%, a value comparable with the alkali laser efficiency [3].

There are six lines near 1315 nm in the absorption spectrum of the iodine atom. At the flow parameters listed in Table 2, the spectral width of each line is ~ 400 MHz, and they are barely overlapped. In the centre of the strongest line [which is due to the $^2P_{1/2}(F=3) \leftarrow ^2P_{3/2}(F=4)$ transition], the absorption cross section $\sigma_B \approx 3.5 \times 10^{-18}$ cm². The induced-transition probability $\Gamma_B = 2 \times 10^5$ s⁻¹ will be obtained at $J_B = \varepsilon_B \Gamma_B / \sigma_B = 8.6$ kW cm⁻². A pump intensity of the same order of magnitude is necessary for alkali lasers [25]. For the B-type radiation, the absorption coefficient $\alpha = \sigma_B(-g) \approx (3.5 \times 10^{-18} \text{ cm}^2)(2 \times 10^{15} \text{ cm}^{-3}) = 7 \times 10^{-3} \text{ cm}^{-1}$. An optical length $33/\alpha \approx 450$ cm is necessary to absorb 95% radiation energy. For sections (1) and (2) with transverse sizes of about 1 m, this degree of radiation absorption is obtained for three or four passes. The spectral width of the absorption band of B-type radiation can be increased to a certain extent by diluting the mixture with a large amount of the buffer gas. The absorption spectrum can also be broadened due to the Zeeman splitting of iodine atom lines by applying a magnetic field to the active medium in section (2) [26]. However, in both cases this broadening reduces the absorption coefficient of B-type radiation.

The issue of the possibility of providing (with expected progress in the development of diode laser arrays) necessary radiation intensities in the blue-green spectral region and at a wavelength of 1315 nm remained open in this study.

Acknowledgements. The part of the work performed at the Samara State Aerospace University was supported by the Ministry of Education and Science of the Russian Federation within the State Contract for Research at Institutions of Higher Education (No. 3.161.2014/K), and the work carried out at the Lebedev Physics Institute (Samara Branch) was supported by the Russian Foundation for Basic Research (Grant No. 14-05-97013).

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