ACTIVE MEDIA

Effect of vibrationally excited O_2 $(a\,{}^1\!\varDelta_g)$ molecules on the parameters of the active medium of an oxygen – iodine laser

V.N. Azyazov, I.O. Antonov, S.Yu. Pichugin, N.I. Ufimtsev

Abstract. **A comparison of the experimental and theoretical results shows that quenching of one singlet oxygen molecule leads to the formation of 4.5 vibrational quanta of the O_2 molecule on the average in the active medium of an oxygen – iodine laser. The dependence of threshold yield of singlet oxygen and of the gain on the relative concentration of vibrationally excited O_2 $(a\,{}^1\!\varDelta_g)$ molecules are studied. The threshold yield of singlet oxygen increases with the relative concentration of vibrationally excited O_2 molecules and may be several percent higher than the value assumed earlier. The gain depends weakly on the relative concentration of vibrationally excited oxygen molecules.**

Keywords: *singlet oxygen, vibrational excitation, oxygen – iodine laser.*

1. Introduction

It has been shown experimentally that the average number of stored vibrational quanta of oxygen molecules in the active medium of a chemical oxygen – iodine laser (COIL) attains values of $0.3 – 0.4$ [1, 2]. Vibrationally excited O_2 molecules may play an important role in the processes involving the formation of the active medium of a COIL, especially during dissociation of I_2. It was proposed in [3 – 5] that vibrationally excited molecules of singlet oxygen (SO) may participate in the population of the lower excited electronic states of iodine:

$$O_2(a, v = 1) + I_2(X) \rightarrow O_2(X) + I_2(A'), \qquad (1)$$

$$O_2(a, v = 2) + I_2(X) \leftrightarrow O_2(X) + I_2(A). \qquad (2)$$
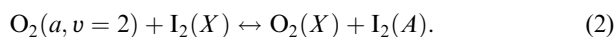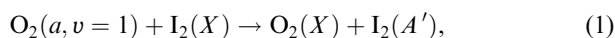
Hereafter, $O_2(X)$, $O_2(a)$ and $O_2(b)$ are oxygen molecules in the ground electronic state $X\,{}^3\varSigma_g^-$ and in the excited electronic states $a\,{}^1\!\varDelta_g$ and $b\,{}^1\varSigma_g^+$, respectively; I and I* are iodine atoms in the ground electronic state ${}^2P_{3/2}$ and in the excited state ${}^2P_{1/2}$, respectively; $I_2(X)$, $I_2(A')$ and $I_2(A)$ are iodine molecules in the ground state $X\,{}^1\varSigma_g^+$ and in the

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excited electronic states $A'\,{}^3\varPi_{2u}$ and $A\,{}^3\varPi_{1u}$, respectively. Figure 1 shows the energy levels corresponding to these electronic states and the energy levels corresponding to the vibrationally excited oxygen molecules $O_2(X)$, $O_2(a)$ and $O_2(b)$, and to three types of vibrations of the water molecule in the ground electronic state. It was proposed by several authors [3 – 7] that the excited electronic states $I_2(A')$ and $I_2(A)$ of iodine may be intermediate states during its dissociation. According to the hypothesis put forward in [8], the collision of an iodine molecule with the molecule $O_2(a, v \geqslant 3)$ may lead to its dissociation according to the process

$$O_2(a, v \geqslant 3) + I_2(X) \rightarrow O_2(X) + 2I. \qquad (3)$$
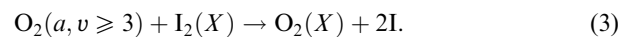
The operation of a COIL is based on the spin – orbit transition $I^* \rightarrow I$ at a wavelength of 1315 nm. This transition is inverted during quasi-resonance transfer of electronic energy from SO. It was assumed for a long time that the fraction of vibrationally excited oxygen molecules in the active medium of a COIL is negligible, and hence the laser transition inversion occurs mainly through the process

$$O_2(a, v = 0) + I \leftrightarrow O_2(X, v = 0) + I^* + 279\ \mathrm{cm}^{-1}. \qquad (4)$$
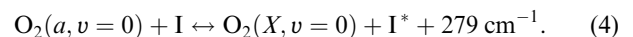
It was shown experimentally [1, 2] and theoretically [9] that the fraction of vibrationally excited oxygen molecules in the active medium of a COIL is significant. Hence, the vibrationally excited molecules $O_2(a, v = 1)$ and $O_2(a, v = 2)$ as well as $O_2(a, v = 0)$ molecules will participate in the laser transition inversion in a COIL in the processes
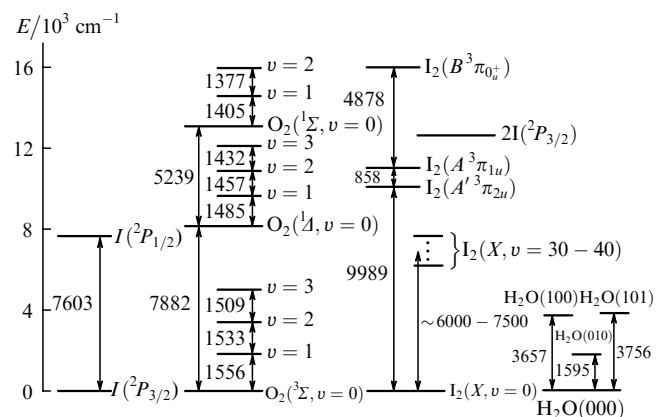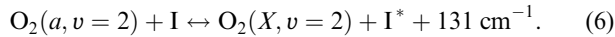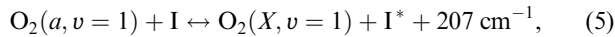

Figure 1. Energy level diagram of excited electronic and vibrational states of O_2, I_2, I and H_2O.

$$O_2(a, v = 1) + I \leftrightarrow O_2(X, v = 1) + I^* + 207\ \text{cm}^{-1}, \quad (5)$$

$$O_2(a, v = 2) + I \leftrightarrow O_2(X, v = 2) + I^* + 131\ \text{cm}^{-1}. \quad (6)$$

Due to the difference in the energies of vibrational excitation of an oxygen molecule in the singlet and triplet states, the energy defect in processes (5) and (6) decreases with increasing v (see Fig. 1). The equilibrium in these processes is displaced to the left. The equilibrium constants of processes (4)–(6) affect the threshold yield of SO as well as the gain of the active medium. An increase in the concentration of vibrationally excited SO molecules will lead to an increase in the threshold yield of SO and a decrease in the gain.

The main problem during the simulation of vibrational kinetics in the active medium of a COIL is the absence of data on the distribution of the energy released in the reactions over the reaction products. The fraction of energy passing to the vibrational degrees of freedom of oxygen during the deactivation of SO molecules is unknown. The probabilities of excitation of vibrational levels of O_2 in relaxation processes are also not known. In this work, the results of theoretical and experimental investigations are compared to estimate the average number of vibrational quanta formed as a result of quenching of a single SO molecule. Formulas are presented for calculating the threshold yield of SO and the gain as functions of the relative concentration of vibrationally excited O_2 molecules in the active medium of a COIL.
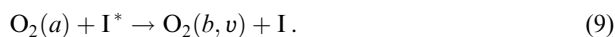
2. Formation of $O_2(v)$

Vibrationally excited O_2 molecules are formed at the stage of SO generation in the reaction zone of the SO generator (SOG) and during transportation of SO to the resonator in the processes

$$O_2(a) + O_2(a) \rightarrow O_2(b, v) + O_2(X, v'), \quad (7)$$

$$O_2(b) + H_2O \rightarrow O_2(a, v) + H_2O(v'). \quad (8)$$
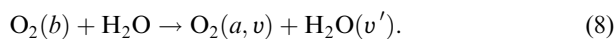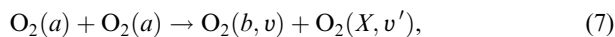
Vibrationally excited molecules $O_2(b, v)$ are formed in the pulling reaction (7) with yield probabilities $\gamma_{7,0} = 0.32$, $\gamma_{7,1} = 0.04$, $\gamma_{7,2} = 0.64$ [10]. Hereafter, $\gamma_{j,i}$ is the probability of formation of a vibrationally excited oxygen molecule in the jth reaction at the ith vibrational level. Simple formulas were obtained in [3] for calculating the relative population densities of oxygen over vibrational levels at the output from the SOG.

Addition of iodine to the oxygen flow leads to a sharp increase in the generation of vibrationally excited O_2 molecules through the process

$$O_2(a) + I^* \rightarrow O_2(b, v) + I. \quad (9)$$

The probabilities $\gamma_{j,i}$ of formation of vibrationally excited oxygen molecules are not known for reactions (8) and (9). The redistribution of vibrational energy quanta between three electron excited states $O_2(X)$, $O_2(a)$ and $O_2(b)$ of oxygen occurs most effectively during fast EE-exchange processes, e.g.,

$$O_2(a, v) + O_2(X, v') \leftrightarrow O_2(X, v) + O_2(a, v'). \quad (10)$$
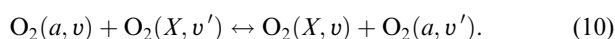
The redistribution of vibrational energy quanta between the vibrational levels of O_2 occurs during VV-exchange processes

$$O_2(v) + O_2(v') \leftrightarrow O_2(v - 1) + O_2(v' + 1). \quad (11)$$
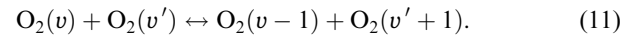
A distinguishing feature of the oxygen medium is the low VT-relaxation rate. The transformation of vibrational energy of O_2 into thermal energy occurs predominantly as follows [9]. At the first stage, oxygen imparts its vibrational energy to a water molecule during VV′ exchange

$$O_2(v) + H_2O(000) \leftrightarrow O_2(v - 1) + H_2O(010). \quad (12)$$
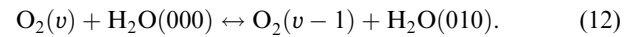
The energies of the vibrationally excited O_2 molecule and the bending mode of the H_2O molecule are close to each other (Fig. 1). As a result, the VV-exchange process between these molecules occurs quite rapidly. At the second stage, the vibrational energy is transferred to the translational degrees of freedom during the process

$$H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O. \quad (13)$$

Note that together with reaction (12), the vibrationally excited water molecules are formed in the course of the rapid process

$$I^* + H_2O \rightarrow I + H_2O(002). \quad (14)$$
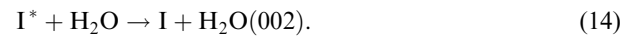
It was found experimentally that the mean content $\eta_v = N_v/N_{ox}$ of vibrational quanta of oxygen molecules is about $0.01 – 0.02$ at the output from the SOG [9] and $0.3 – 0.4$ in the active medium of the COIL [1, 2]. Hereafter, $N_v = \sum_i i N_i$ is the total number of vibrational quanta of oxygen molecules per unit volume, N_i is the population density of vibrationally excited O_2 molecules at the ith vibrational level, and N_{ox} is the total concentration of oxygen. Comparing the experimental values of η_v with the theoretical ones, we can estimate the average number $n_v = \sum_{j,i} i \gamma_{j,i}$ of vibrational quanta of O_2 molecules formed by quenching an SO molecule in the active medium of the COIL. The value of N_v is determined from the following balance equation:

$$\frac{dN_v}{dt} = (\gamma_{9,1} + 2\gamma_{9,2} + \gamma_{8,1} + 2\gamma_{8,2} + 3\gamma_{8,3})K_9 N_a N_{I^*}$$

$$- K_{12}N_v N_w + K_{12}^- N_{ox} N_{wv}, \quad (15)$$

where N_{I^*}, N_a and N_w are the concentrations of I^* atoms, $O_2(a)$ and H_2O molecules respectively; t is the time; K_j and K_j^- are the rate constants of the jth direct and inverse processes. The first term on the right hand side of Eqn (15) effectively takes into account the rate of formation of vibrational quanta during the processes (8) and (9).

The total number of vibrational quanta of water molecules per unit volume N_{wv} appearing in Eqn (15) is determined from the balance of their formation in processes (12) and (14) and quenching in process (13). Note that the VV exchange

$$H_2O(001) + H_2O(000) \leftrightarrow H_2O(000) + H_2O(020)$$
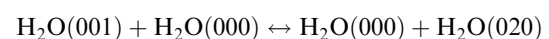
of energy between bending $[H_2O(010)]$ and stretching $[H_2O(001)]$ modes occurs much more rapidly than the VT relaxation of vibrational valence modes [11]. Consequently, vibrational quanta of water molecules are accumulated predominantly at the bending mode. It can also be assumed that four vibrational quanta are eventually formed at the bending mode of the H_2O molecule during the process (14). Taking this fact into account, we arrive at the following equation for N_{wv}:

$$\frac{dN_{wv}}{dt} = 4K_{14}N_wN_{I^*} + K_{12}N_vN_w$$
$$- K_{12}^- N_{ox}N_{wv} - K_{13}N_{wv}N_w. \tag{16}$$

Transformation of balance equations (15) and (16) under quasistationary conditions ($dN_v/dt = dN_{wv}/dt = 0$) leads to the following expressions for the average energy content of vibrational quanta of oxygen molecules (η_v) and water molecules ($\eta_{wv} = N_{wv}/N_{ox}$):

$$\eta_v = \frac{n_v K_9 \eta_a \eta_{I^*} + K_{12}^- \eta_{wv}}{K_{12}\eta_w}, \tag{17}$$

$$\eta_{wv} = \frac{4K_{14}\eta_w\eta_{I^*} + K_{12}\eta_v\eta_w}{K_{12}^- + K_{13}\eta_w}, \tag{18}$$

where $n_v = \gamma_{9,1} + 2\gamma_{9,2} + \gamma_{8,1} + 2\gamma_{8,2} + 3\gamma_{8,3}$; $\eta_{I^*} = N_{I^*}/N_{ox}$; $\eta_a = N_a/N_{ox}$; and $\eta_w = N_w/N_{ox}$.

By substituting (18) into (17), we arrive at the following expression as a result of simple transformations:

$$\eta_v = \frac{n_v K_9 \eta_a \eta_{I^*}(1 + \eta_w K_{13}/K_{12}^-) + 4K_{14}\eta_w\eta_{I^*}}{K_{eq12}K_{13}\eta_w^2}, \tag{19}$$

where K_{eqj} is the equilibrium constant of the jth process. In the experiments carried out in [1, 2], $\eta_v \approx 0.3$, $\eta_a \approx 0.5$, $\eta_{I^*} \approx 0.01$, $\eta_w \approx 0.03$, and the gas temperature is $T \approx 400$ K. The rate constants K_9, K_{12}, K_{13} and K_{14} of the reactions are 1.8×10^{-13} cm^3 s^{-1} [12], 1.7×10^{-12} cm^3 s^{-1} [13], 5×10^{-11} cm^3 s^{-1} [11] and 2.3×10^{-12} cm^3 s^{-1} [14], respectively. Substituting these values into (19), we obtain the average number $n_v \approx 4.5$ of vibrational quanta formed by quenching one SO molecule.
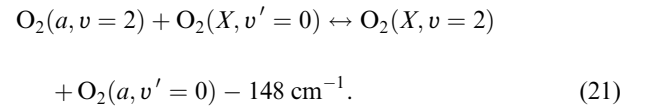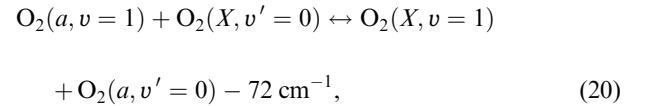
3. Threshold yield of $O_2(a)$

In the active medium of a COIL working on the spin–orbit transition $I^* \to I$, the gain $g = 7\sigma(N_{I^*} - N_I/2)/12$ is more than zero if the relative population density η_a of SO is higher than a certain threshold value $\eta_a^{th} = N_a^{th}/N_{ox}$ [where N_a^{th} is the threshold concentration of $O_2(a)$ and σ is the cross section of induced emission for the transition $I(^2P_{1/2}, F = 3) \to I(^2P_{3/2}, F = 4)$]. The threshold yield of SO is determined from the condition $g = 0$. If the population densities of the $O_2(v = 1)$ and $O_2(v = 2)$ molecules are close to equilibrium values, the contributions from processes (5) and (6) can be neglected. In this case, the threshold yield of SO depends only on the gas temperature T and is calculated by using the formula $\eta_a^{th} = 1/(2K_{eq4} + 1)$, where $K_{eq4} = 0.75 \exp[\Delta E_4/(kT)]$; and ΔE_4 is the energy defect of process (4). In this case, the threshold yield of $O_2(a)$ at room temperature is 0.15.

It was shown experimentally that $O_2(a, v)$ has a non-equilibrium concentration in the active medium of the COIL. An increase in the fraction of vibrationally excited oxygen molecules in the active medium of the COIL leads to an increase in the threshold yield of SO. Laser transition in the iodine atom at $T = 300$ K will be inverted during the process described by (5) if the relative population density of SO at the first vibrational level $\eta_{a1} = 0.2$, and during the process described by (6) if $\eta_{a2} = 0.26$. The total threshold yield η_a^{th} of $O_2(a)$ depends not only on the gas temperature, but also on the relative concentration of vibrationally excited oxygen molecules in the mixture.

Redistribution of vibrational quanta between $O_2(a)$ and $O_2(X)$ molecules occurs most effectively in the following EE-exchange processes:

$$O_2(a, v = 1) + O_2(X, v' = 0) \leftrightarrow O_2(X, v = 1)$$
$$+ O_2(a, v' = 0) - 72 \text{ cm}^{-1}, \tag{20}$$

$$O_2(a, v = 2) + O_2(X, v' = 0) \leftrightarrow O_2(X, v = 2)$$
$$+ O_2(a, v' = 0) - 148 \text{ cm}^{-1}. \tag{21}$$

Processes (4)–(6), (20) and (21) are much faster than the other processes. Hence, the population densities N_{I^*} and N_I of iodine atoms at the upper and lower levels, as well as the population density N_{ai} of SO at the ith vibrational levels can be expressed with a fairly high degree of accuracy in terms of the equilibrium constants of these processes and the relative population density of oxygen at the levels with $v = 0$, 1 and 2. The population density N_{ai} can be determined from the following balance equations:

$$\frac{dN_{a0}}{dt} = K_4^- N_{X0}N_{I^*} + K_{20}N_{a1}N_{X0} + K_{21}N_{a2}N_{X0}$$
$$- K_4 N_{a0}N_I - K_{20}^- N_{a0}N_{X1} - K_{21}^- N_{a0}N_{X2}, \tag{22}$$

$$\frac{dN_{a1}}{dt} = K_5^- N_{X1}N_{I^*} - K_5 N_{a1}N_I + K_{20}^- N_{X1}N_{a0}$$
$$- K_{20}N_{a1}N_{X0}, \tag{23}$$

$$\frac{dN_{a2}}{dt} = K_6^- N_{X2}N_{I^*} - K_6 N_{a2}N_I + K_{21}^- N_{X2}N_{a0}$$
$$- K_{21}N_{a2}N_{X0}, \tag{24}$$

where N_{Xi} is the oxygen concentration in the ground electron state at the ith vibrational level. In the present study, we confine ourselves to an analysis of population densities of SO for levels with $v = 0$, 1 and 2 only, assuming that the contribution of population densities of levels with $v \geqslant 3$ can be neglected in calculations of the threshold yield and the gain. It should be observed that the vibrationally excited molecules of SO ($v \geqslant 3$) may play a significant role in the I_2 dissociation processes, for example, in reaction (3) [8]. The rate constants of EE-exchange processes (20) ($K_{20} = 5.6 \times 10^{-11}$ cm^3 s^{-1}) and (21) ($K_{21} = 3.6 \times 10^{-11}$ cm^3 s^{-1}) are of the same order of magnitude as similar rate constants of processes (4)–(6) [15]. The relative concentration of iodine atoms in the active medium of the COIL is a few percent of the relative concentration of oxygen molecules. Hence, the contribution from the first two terms on the right-hand sides of Eqns (23) and (24) can

be neglected. For quasi-stationary conditions, we obtain from Eqns (23) and (24) the relative population density of $O_2(a)$ at the levels with $v = 1$ and 2, respectively:

$$\eta_{a1} = \frac{\eta_1 \eta_{a0}}{K_{eq20}(\eta_0 - \eta_{a0}) + \eta_{a0}}, \tag{25}$$

$$\eta_{a2} = \frac{\eta_2 \eta_{a0}}{K_{eq21}(\eta_0 - \eta_{a0}) + \eta_{a0}}. \tag{26}$$

In the following, we shall use the normalised gain

$$g_n = \frac{24g}{7\sigma N_{I_0}} = 3\theta - 1, \tag{27}$$

where $N_{I_0} = N_{I^*} + N_I$; $\theta = N_{I^*}/N_{I_0}$. For a relative $O_2(a)$ concentration equal to the threshold yield, the normalised gain $g_n = 3\theta - 1 = 0$, and hence $\theta = 1/3$. Summing the right-hand sides of Eqns (22)–(24), we obtain for quasistationary conditions $(dN_{ai}/dt = 0)$ the following expression for the threshold yield η_{a0}^{th} of SO molecules at the zeroth vibrational level:

$$\eta_{a0}^{th} = \frac{\eta_0 - 2\beta_1 K_{eq5}\eta_{a1} + \beta_1(\eta_1 - \eta_{a1})}{2K_{eq4} + 1}$$
$$- \frac{2\beta_2 K_{eq6} + \beta_2(\eta_2 - \eta_{a2})}{2K_{eq4} + 1}, \tag{28}$$

where $\beta_1 = K_5^-/K_4^-$ and $\beta_2 = K_6^-/K_4^-$. The threshold fraction of SO molecules $O_2(a, v)$ at the levels with $v = 0, 1, 2$ were calculated by iteration from the system of equations (25), (26) and (28). Figure 2 shows the dependence of the total threshold yield $\eta_a^{th} = \sum \eta_{ai}^{th}$ of SO on the relative concentration of vibrationally excited oxygen $\eta_1 + \eta_2$ (where η_1 and η_2 are the relative population densities of the first and second vibrational levels of the O_2 molecule) for three gas temperatures. The ratio η_1/η_2 was assumed to be equal to 7/3. It can be seen from Fig. 2 that the threshold yield increases with the fraction of vibrationally excited O_2 molecules and may be several percent higher than the generally accepted value. The quantities β_1 and β_2 were assumed equal to unity in Fig. 2. Variation of β_1 and β_2 from 0.2 to 2 shows that the threshold yield depends weakly on them.

4. The COIL gain

Only processes (4)–(6) were included in the balance equation for the concentration N_{I^*} of excited iodine atoms since the rates of other processes in the active medium of a COIL are lower by several orders of magnitude. The relative steady state concentration θ of excited iodine atoms obtained from the balance equation can be defined by the expression

$$\theta = (K_{eq4}\eta_{a0} + K_{eq5}\beta_1\eta_{a1} + K_{eq6}\beta_2\eta_{a2})[K_{eq4}\eta_{a0}$$
$$+ K_{eq5}\beta_1\eta_{a1} + K_{eq6}\beta_2\eta_{a2} + (\eta_0 - \eta_{a0}) + \beta_1(\eta_1 - \eta_{a1})$$
$$+ \beta_2(\eta_2 - \eta_{a2})]^{-1}, \tag{29}$$

where $\eta_{a0} = \eta_a - \eta_{a1} - \eta_{a2}$. It follows from formula (29) that the normalised gain g_n for a COIL depends not only on temperature, but also on the relative concentration of vibrationally excited O_2 molecules and the ratio of rate constants of processes (4)–(6). The values of η_{a1} and η_{a2} were determined from Eqns (25) and (26). Figure 3 shows the dependences of g_n on the relative concentration $\eta_1 + \eta_2$ of vibrationally excited oxygen (the ratio η_1/η_2 was assumed equal to 7/3). One can see that g_n depends weakly on $\eta_1 + \eta_2$. The quantities β_1 and β_2 were assumed to be equal to unity while calculating these dependences.
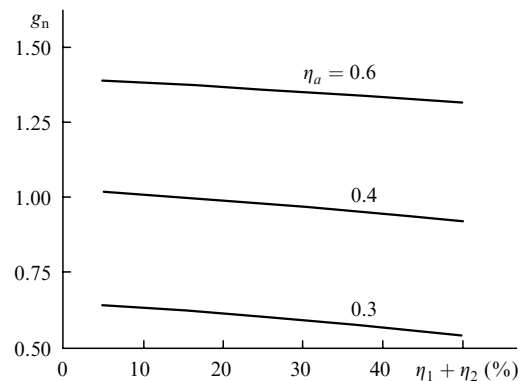
Figure 3. Dependence of the normalised gain g_n on the relative concentration of vibrationally excited oxygen molecules $\eta_1 + \eta_2$ at $T = 300$ K, relative concentration of I_2 in oxygen flow $\eta_{I_2} = 0.01$, $\eta_1/\eta_2 = 7/3$ for various relative concentrations of $O_2(a)$.

The rate constants of Eqns (5) and (6) are not known. Figure 4 shows how the ratio of the rate constants of processes (4)–(6) affects the gain of the active medium in a COIL. The values of β_1 and β_2 were varied between 0.1 and 5.0. For $K_4 \gg K_5, K_6$, the contribution from the vibrationally excited SO molecules is insignificant during laser transition. However, it does not lead to a decrease in the value of the gain. In this case, the vibrationally excited SO molecules serve as a sort of energy reservoir. In the laser radiation generation mode, a decrease in the population density of $O_2(a, v = 0)$ results in an effective pumping of electron energy from $O_2(a, v = 1)$ and $O_2(a, v = 2)$ to $O_2(a, v = 0)$ through fast EE-exchange processes (20) and (21). For $K_4 < K_5, K_6$, the contribution from processes (5) and (6) leads to a decrease in the value of the gain due to a relative
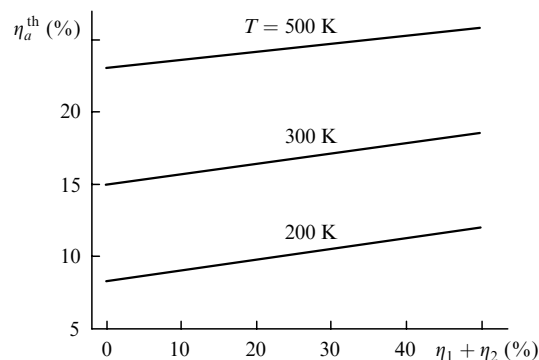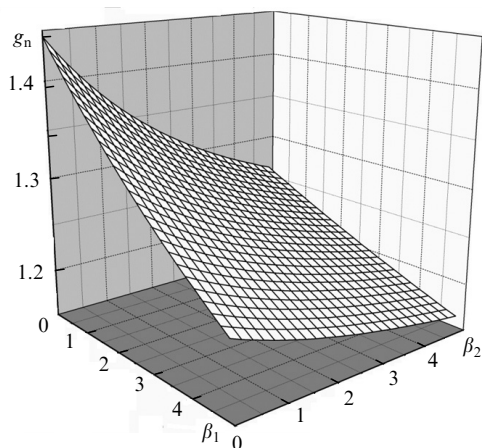
Figure 2. Theoretical dependences of the threshold yield of $O_2(a)$ on the relative concentration of vibrationally excited oxygen molecules $\eta_1 + \eta_2$ at various temperatures for $\eta_1/\eta_2 = 7/3$.

Figure 4. Dependence of the normalised gain g_n on the ratios β_1 and β_2 of rate constants for $\eta_a = 0.6$, $\eta_1 + \eta_2 = 0.3$, $\eta_1/\eta_2 = 7/3$, $\eta_{I_2} = 0.01$.

increase in the rates of these processes in the reverse direction.

5. Conclusions

A comparison of the theoretical values of the average store of vibrational quanta in the active medium of a COIL with those measured in [1, 2] shows that quenching of an $O_2(a)$ molecule in processes (8) and (9) results in the formation of $n_v \approx 4.5$ vibrational quanta of oxygen on the average. A higher value of n_v in an oxygen–iodine medium than $n_v \approx 4$ at the output from a SOG [9] can be attributed to additional generation of vibrational quanta of H_2O molecules in process (14). The increase in the concentration of $H_2O\,(010)$ molecules in Eqn (12) leads to a decrease in the quenching rate of the vibration energy stored in oxygen. The rate of pulling process (9) increases with temperature [16]. It is well known that together with the thermal energy, the vibrational energy may lead to an increase in the rate of reaction (9) [17]. This may be the reason behind an exaggerated value of n_v.

The absence of data on rate constants of processes (5) and (6) and the probability of the energy defect distribution over the products of reactions (8) and (9) complicates the simulation of kinetic processes in a COIL. Calculations show that the threshold yield of SO in the active medium of a COIL depends on gas temperature as well as the relative concentration of vibrationally excited oxygen molecules in it. The threshold yield of $O_2(a)$ may be several percent higher than the previously assumed value. The gain of the medium depends weakly on the concentration of vibrationally excited oxygen molecules in the active medium of a COIL.

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