

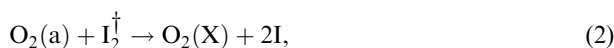
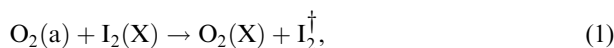
Probabilities of the production of vibrationally excited iodine molecules in the reaction $I(^2P_{1/2}) + I_2(X) \rightarrow I(^2P_{3/2}) + I_2(X, v > 10)$

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Abstract. Vibrational distributions of $I_2(X, v)$ ($0 \leq v \leq 45$) molecules are calculated and analysed in the active medium of an oxygen–iodine laser. It is found by comparing the calculated values with the experimental data that during the $I(^2P_{1/2}) + I_2(X) \rightarrow I(^2P_{3/2}) + I_2(X, v > 10)$ reaction the probability of the production of $I_2(X, v > 23)$ molecules is 0.1 and the total probability of the direct excitation of iodine molecules at the vibrational levels from 15 to 23 is 0.9. Based on the data obtained, the dissociation mechanisms of iodine molecules in the active medium of the oxygen–iodine laser are analysed.

Keywords: vibrational excitation of molecules, oxygen–iodine laser, dissociation of I_2 .

One of the unsolved problems of kinetics of processes in a chemical oxygen–iodine laser (COIL) is the dissociation of molecular iodine in the presence of singlet oxygen. Hereafter, $O_2(X)$, $O_2(a)$ and $O_2(b)$ are oxygen molecules in the electronic $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ states; I , I^* are the iodine atoms in the $^2P_{3/2}$ and $^2P_{1/2}$ states; $I_2(X)$, $I_2(A')$ and $I_2(A)$ are the iodine molecules in the $X^1\Sigma_g^+$, $A'^3\Pi_{2u}^+$ and $A^3\Pi_{1u}^+$ states. It is established at present that the dissociation processes has the initiating and chain stages and the intermediate excited state of I_2 is involved in this process. However, it has not been found which of the excited states of I_2 is the intermediate one, and the pump mechanism of this state has not been determined. In a standard kinetic package (SKP) of the chemical oxygen–iodine laser [1], the dissociation of I_2 at the initiating stage is described by the sequence of reactions



where I_2^\dagger are the iodine molecules in the ground $I_2(X)$ state, which are at the levels with the vibrational quantum numbers $v > 20$. The initiating stage is followed by the chain stage, which is described by the sequence of reactions



Hereafter, we will call this model the standard dissociation model. Experimental data [2–4] cast doubt on the reliability of this model. In particular, it was shown in paper [2] that the deactivation kinetics of vibrationally excited I_2 molecules does not correspond to the relaxation kinetics of the intermediate state of I_2^\dagger in the SKP. Moreover, the rate constants of deactivation reactions of I_2^\dagger by components of the COIL active medium (O_2 , Ar, He, H_2O) presented in the SKP are more typical of the relaxation of the excited electronic state [2, 3]. Besides, the rate constant of $O_2(a)$ quenching by $I_2(X)$ molecules [reaction (1)], which was measured in [4], is at least an order of magnitude lower than that accepted in the SKP.

On the other hand, the authors of the standard dissociation model [1, 5–9] present data in favour of their model. In particular, it was shown experimentally in paper [4] that vibrationally excited iodine molecules $I_2(X, 25 < v < 43)$ are produced in reaction (4). The excited iodine atoms were generated upon the photolysis of I_2 –Ar mixtures at 475 nm or CF_3I – I_2 –Ar mixtures at 266 nm. The $I_2(X, v)$ molecules were detected by using the laser-induced fluorescence (LIF) at the $I_2(B \leftarrow X)$ transition. In papers [6, 7], vibrationally excited $I_2(X, v)$ molecules were found in the I_2 – $O_2(a)$ – O_2 mixture also by using the LIF method. In these experiments, $O_2(a)$ was produced in a discharge singlet-oxygen generator at the output of which I_2 pairs were injected in the oxygen flow. The dissociation of I_2 molecules took place in the presence of $O_2(a)$. The excited atomic iodine was produced during the EE energy transfer in reaction (3). Authors of paper [6] managed to detect vibrationally excited molecules $I_2(X, 33 \leq v \leq 44)$ appearing in reaction (3). In papers [7, 8], the distribution of the absolute concentrations of iodine molecules over the vibrational levels was experimentally determined in the range $5 \leq v \leq 45$.

The probabilities γ_v of the production of $I_2(X)$ molecules at the v th vibrational level in reaction (4) are important parameters in the standard dissociation model. Unfortunately, they have not been measured so far. Paper [10] presents the distribution γ_v in relative units for the vibrational levels with v from the range $24 \leq v \leq 47$, which was obtained by analysing the results of measurements of relative populations of $I_2(X, v)$. In this paper, we attempt to determine the values of γ_v by comparing the calculated

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Received 7 February 2008; revision received 6 May 2008
Kvantovaya Elektronika 38 (12) 1101–1104 (2008)
Translated by I.A. Ulitkin

and experimental [5–8] values of populations of the vibrationally excited levels of iodine molecules and dissociation rates of I_2 .

First of all, by using data borrowed from paper [6], we will estimate the total probability $\Gamma_{v \geq 33}$ of the production of $I_2(X, v \geq 33)$ molecules in reaction (4). In paper [6], during the injection of the molecular iodine in the oxygen flow containing 6 % of $O_2(a)$, $I_2(X)$ molecules excited at the vibrational levels with $v = 33$ and higher were detected. In this case, the quasi-stationary ratio of these molecules $N_{v \geq 33}$ to the concentration of excited iodine atoms N_{I^*} was 4×10^{-4} . The quasi-stationary value of $N_{v \geq 33}$ is determined from the balance of production rates of $I_2(X, v \geq 33)$ molecules in reaction (4) and their decrease in dissociation reactions (2) and vibrational VT relaxation of $I_2(X, v) + O_2 \rightarrow I_2(X, v - 1) + O_2$. Based on this assumption, we obtain

$$\Gamma_{v \geq 33} K_4 N_{I^*} N_{I_2} = N_{v \geq 33} (K_d N_a + K_{v \geq 33} N_{O_2}).$$

Here, N_{I^*} , N_{I_2} , N_a , N_{O_2} are the concentrations of I^* , I_2 , $O_2(a)$ and $O_2(X)$; $K_4 = 3.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is the rate constant of reaction (4) [1]; K_d is the rate constant of reaction (2); $K_{v \geq 33}$ is the effective deactivation rate constant of $I_2(X, v \geq 33)$ molecules in collisions with the O_2 molecules. It follows that

$$\Gamma_{v \geq 33} = \frac{N_{v \geq 33}}{N_{I^*}} \frac{N_{O_2}}{N_{I_2}} \left(\frac{K_d}{K_4} \frac{N_a}{N_{O_2}} + \frac{K_{v \geq 33}}{K_4} \right).$$

By substituting $N_{v \geq 33}/N_{I^*} \approx 4 \times 10^{-4}$, $N_{O_2}/N_{I_2} \approx 10^3$, $N_a/N_{O_2} = 0.06$ from [6] and $K_{v \geq 33} \approx 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [10], $K_d \approx 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [11] in this expression, we obtain $\Gamma_{v \geq 33} \approx 0.08$.

We also calculated the populations of vibrational levels of $I_2(X, v)$ molecules under conditions of experiments [5]. In paper [5], the production of vibrationally excited iodine molecules was studied during the interaction of $I_2(X)$ with I^* atoms produced upon photodissociation of CH_3I in a preliminary mixed CH_3I-I_2-Ar mixture. In experiments [5], vibrationally excited $I_2(X, v = 26 - 42)$ molecules were recorded and the concentration of iodine molecules excited at the level with $v = 40$ was measured. We assumed in our calculations that during the quenching of I^* by $I_2(X)$ molecules, the $I_2(X, v)$ molecules were produced with the probability $\gamma_v = a_v \Gamma_{v > 23}$ at levels with $v > 23$, where $\Gamma_{v > 23}$ is the total probability of the production of $I_2(X, v > 23)$ molecules in reaction (4) and a_v is the relative probability of the production of $I_2(X)$ molecules at the v th vibrational level (the values of a_v for $v > 23$ were borrowed from paper [10], Fig. 1). In calculations of the concentrations of $I_2(X, v)$ molecules, the quantity $\Gamma_{v > 23}$ was varied. Good agreement with the experimental data [5] was achieved for $\Gamma_{v > 23} \approx 0.1$, while, for example, for $\Gamma_{v > 23} \approx 0.9$ the calculated concentrations of $I_2(X, v = 40)$ molecules exceeded the experimental concentrations by an order of magnitude. In this case, the above estimate of $\Gamma_{v \geq 33} \approx 0.08$ agrees with the quantity $\Gamma_{v > 23} \approx 0.1$, because the total probability of the production of $I_2(X, v = 24 - 32)$ molecules in reaction (4) is small compared to $\Gamma_{v \geq 33}$ (see Fig. 1). It follows from Fig. 1 that the position of the maximum in the distribution γ_v in the range $23 < v < 48$ is at the level with $v = 40$.

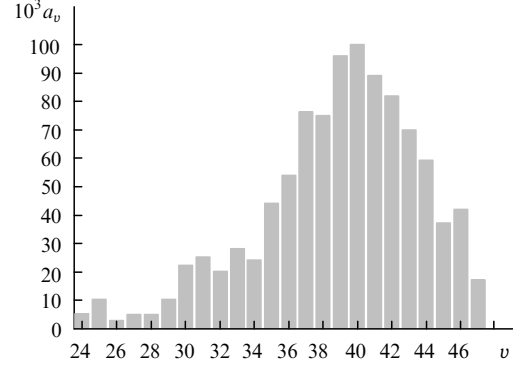
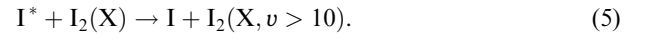


Figure 1. Dependence of relative probabilities a_v of the production of $I_2(X, v > 23)$ molecules in reaction (4) on the number of the vibrational level v [10].

Thus, we have shown that the total probability $\Gamma_{v > 23}$ of the production of $I_2(X, v > 23)$ molecule upon quenching I^* by $I_2(X)$ molecules is 0.1. The standard dissociation model for $\Gamma_{v > 23} \approx 0.1$ cannot provide the observed decay rates of I_2 . In this case, if this model is valid, the number of singlet-oxygen molecules required for dissociation of one I_2 molecule should exceed 20, which contradicts the experiment. It was shown in [12] that under the experimental conditions of this paper, 4.2 molecules of $O_2(a)$ were spent on the dissociation of one iodine molecule.

It was found in experiments described in [7, 8] that the concentration of $I_2(X, v = 11 - 23)$ molecules produced within $t \approx 10^{-3} \text{ s}$ after the injection of molecular iodine into the oxygen flow with the singlet-oxygen concentration of about 10 % considerably exceeds the concentration of vibrationally excited iodine molecules with $v \geq 30$. Such large populations of vibrational $I_2(X, v)$ levels for $10 < v \leq 23$ for small t can be explained only by their direct pumping during the reaction



We calculated the populations of vibrational levels of $I_2(X, v = 0 - 45)$ molecules for the experimental conditions of paper [8]: the initial composition of the mixture was $O_2(X):O_2(a):I_2 = 0.92:0.08:0.0475 \text{ Torr}$, the initial rate of the flow was $U_0 = 10.8 \text{ m s}^{-1}$, the initial temperature of the gas mixture was $T_0 = 300 \text{ K}$. In this case, the equations were numerically solved for relative concentrations $\eta_v = n_v/N_{O_2}$, $\eta_{I^*} = [I^*]/N_{O_2}$, $\eta_{I_2} = [I_2]/N_{O_2}$ and $\eta_a = [O_2(a)]/N_{O_2}$:

$$\frac{d\eta_v}{dx} = \frac{(N_{ox})_0}{U_0} \left(\frac{T_0}{T} \right)^2 (K_{v+1 \rightarrow v}^{O_2} \eta_{v+1} + K_{v-1 \rightarrow v}^{O_2} \eta_{v-1}$$

$$- K_{v \rightarrow v-1}^{O_2} \eta_v - K_{v \rightarrow v+1}^{O_2} \eta_v) \quad (v < 8),$$

$$\frac{d\eta_v}{dx} = \frac{(N_{ox})_0}{U_0} \left(\frac{T_0}{T} \right)^2 (\gamma_v K_4 \eta_{I_2} \eta_{I^*} + K_{v+1 \rightarrow v}^{O_2} \eta_{v+1}$$

$$+ K_{v-1 \rightarrow v}^{O_2} \eta_{v-1} - K_{v \rightarrow v-1}^{O_2} \eta_v - K_{v \rightarrow v+1}^{O_2} \eta_v) \quad (8 \leq v < 25),$$

$$\frac{d\eta_v}{dx} = \frac{(N_{ox})_0}{U_0} \left(\frac{T_0}{T} \right)^2 (\gamma_v K_4 \eta_{I_2} \eta_{I^*} + K_{v+1 \rightarrow v}^{O_2} \eta_{v+1} +$$

$$+ K_{v-1 \rightarrow v}^{O_2} \eta_{v-1} - K_{v \rightarrow v-1}^{O_2} \eta_v - K_{v \rightarrow v+1}^{O_2} \eta_v - K_d \eta_v \eta_a) \quad (v \geq 25),$$

where $K_{v \rightarrow v'}^{O_2}$ is the rate constant of the $I_2(X, v) + O_2 \rightarrow I_2(X, v') + O_2$ reaction. In this case we assumed that $K_{v \rightarrow v-1}^{O_2} = v(2.7 \times 10^{-12}) \text{ cm}^3 \text{ s}^{-1}$ [10] and the rate constants of inverse reactions were determined from the detailed balance relations. In the above equations, N_{ox} is the concentration of oxygen molecules in all electronic states; n_v is the concentration of $I_2(X)$ molecules at the v th vibrational level; U is the gas flow velocity; the subscript 0 corresponds to the initial values of the parameters. For brevity, the equation for the variables T , η_1^* , η_a and η_{i_2} are not presented. Their explicit form is presented, for example, in paper [13].

We found that the satisfactory agreement between the calculated and experimental values of $I_2(X, v)$ populations was achieved when the total excitation probability of vibrational levels from the range $15 \leq v \leq 23$ in reaction (5) was 0.8–0.9. Figure 2 presents the calculated values of populations of $I_2(X, v)$ molecules for $\Gamma_{v>23} = 0.1$ and $\Gamma_{15 \leq v \leq 23} = \sum_{i=15}^{23} \gamma_i = 0.9$, where $\gamma_{15} = \dots = \gamma_{19} = 0$, $\gamma_{20} = \dots = \gamma_{23} = 0.225$, and experimentally measured concentrations of $I_2(X, v)$. One can see that the results of calculations well agree with the experimental data. In this case, if we assume in calculations that $\Gamma_{15 \leq v \leq 23} = 0$, the calculated concentrations of $I_2(X, 15 \leq v \leq 23)$ molecules (dashed curve in Fig. 2) will be an order of magnitude smaller than those in experiments. Figure 2 shows the calculation results of populations of $I_2(X, v)$ molecules for the uniform distribution of the total probability $\Gamma_{20 \leq v \leq 23} = 0.9$ over the vibration levels v from 20 to 23. We performed calculations with different distributions γ_v over the levels in which the top coincided with one of the vibrational levels from the range $v = 20 - 22$. The results of calculations showed that the final distribution n_v weakly depends on the selected distribution γ_v and strongly – on the total probabilities $\Gamma_{v>23}$ and $\Gamma_{15 \leq v \leq 23}$.

This extraordinary distribution γ_v with two maxima can be explained by two different mechanisms in reaction (5):

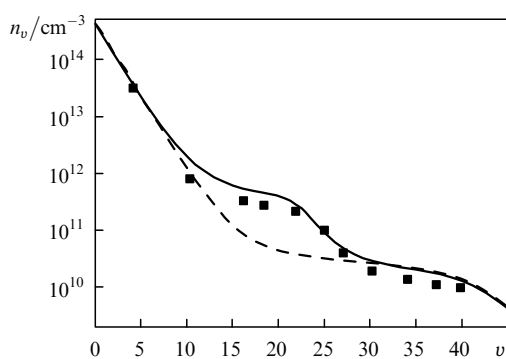
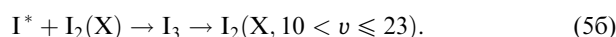
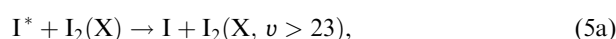
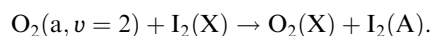
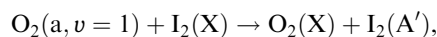


Figure 2. Populations of $I_2(X, v)$ molecules at a distance of 3 cm from the injection of iodine into the oxygen flow. The solid curve is the results of calculations for $\Gamma_{v>23} = 0.1$ and $\Gamma_{15 \leq v \leq 23} = 0.9$, the dashed curve – for $\Gamma_{v>23} = 0.1$ and $\Gamma_{15 \leq v \leq 23} = 0$; points are the experimental data from paper [8].

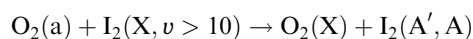
In reaction (5a), the EV energy transfer is accompanied by the production of vibrationally excited $I_2(X, v > 23)$ molecules with the same distribution over the vibrational levels with the maximum at $v = 40$ as that presented in Fig. 1. Chemical reaction (5b) proceeds by producing an intermediate I_3 complex [14]. The heat fraction of the chemical reaction spent on the vibrational excitation of products is, as a rule, smaller than during the EV process [15]. The obtained two-maximum distribution allows one to suppose that for reactions (5a) and (5b) the branching ratio are approximately equal to 0.1 and 0.9, respectively.

Thus, we have found in this paper that the total probability of the production of $I_2(X, v > 23)$ molecules in the $I^* + I_2(X) \rightarrow I + I_2(X, v > 10)$ reaction is 0.1. The standard model for $\Gamma_{v>23} \approx 0.1$ fails to explain the observed dissociation rate of I_2 in the oxygen–iodine laser medium. The experimentally observed large populations of the vibrational $I_2(X, v)$ levels for $v = 11 - 23$ can be explained only by their direct pumping during the quenching of I^* atoms by $I_2(X)$ molecules. It was found that satisfactory agreement between the calculated populations of $I_2(X, v)$ molecules and experimental data is achieved when the total excitation probability of vibrational levels with $v = 15 - 23$ in reaction (5) is 0.9.

The results of this paper indicate that the standard dissociation model, in which the intermediate state is the ground electronic $I_2(X, v > 20)$ state of the vibrationally excited iodine molecule, cannot explain high dissociation rates of iodine in the COIL active medium. One should pay attention to the iodine dissociation model proposed in papers [16–18], in which lower excited electronic states of $I_2(A')$ and $I_2(A)$ iodine serve as the intermediate state. These states are populated during the excitation energy transfer from vibrationally excited single-oxygen molecules in reactions



It was shown in recent papers [19–21] that in the COIL active medium, the average number of vibrational quanta per oxygen molecule can achieve 0.3–0.4. Note that the total energy of particles participating in the collision in reaction



is also sufficient to excite lower excited electronic states of molecular iodine. This reaction can considerably contribute to the iodine dissociation at high concentrations of I_2 [22].

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