Deactivation rate of I₂ molecules (X, $v \geqslant 30$) in the medium of a chemical oxygen – iodine laser

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Abstract. **The effective deactivation rate constants are calculated for I₂(X) molecules at vibrational levels with $v \geqslant 30$ colliding with N₂ and O₂ molecules in the medium of a chemical oxygen – iodine laser. The calculated constants $(4 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}}$ and $3 \times 10^{-12}\ \mathrm{cm^3\ s^{-1}})$ are less by half plus than the corresponding constants found earlier in the paper of Lawrence et al., where the dissociation of I₂ was neglected in calculations.**

The relaxation of the electronic energy in the active medium of a chemical oxygen – iodine laser (COIL) emitting at the $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ transition in atomic iodine leads to the nonequilibrium population of the vibrational levels of oxygen and iodine molecules [1 – 11]. The energy stored at the vibrational levels of O₂ and I₂ molecules can be involved in the dissociation of molecular iodine. The dissociation mechanism in which the intermediate states are excited electronic states I₂(A′, A) populated in collisions with vibrationally excited singlet oxygen was described in papers [4, 6, 12]. The energy of singlet oxygen excited to the third vibrational level is sufficient for dissociation of the I₂ molecule per collision [9]. In the model of Heidner et al. [13], the intermediate states in the dissociation process are excited vibrational states of molecules I₂(X). It is known that iodine atoms in the $^2P_{1/2}$ state, which we denote below by I^*, are rapidly quenched by I₂(X) molecules in the reaction $I^* + I_2(X) \rightarrow I + I_2^*$. The probability of vibrational excitation of I₂(X) molecules to levels with $v \leqslant 45$ in this reaction is quite high [14]. Therefore, it is reasonable to expect that iodine molecules in the COIL medium will be vibrationally excited to a great extent. The population of vibrational levels of I₂(X) molecules in mixtures containing oxygen in the a¹Δ state [which we denote below by O₂(a)] was experimentally studied in papers [2, 3]. It was found that the population of vibrational levels of iodine molecules in such media was substantially nonequilibrium. In this

case, I₂(X, v) molecules occupying vibrational levels above some threshold value v_{th} can dissociate in collisions with O₂(a) molecules:

$$O_2(a) + I_2(X, v \geqslant v_{th}) \rightarrow O_2(X) + 2I.$$
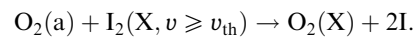
The minimal value of v at which the sum of the vibrational and electronic energies of molecules I₂(X, v) and O₂(a) exceeds the dissociation energy of I₂(X), is 23. It is often assumed that $v_{th} = 30$, and in this case the I₂(X, $v \geqslant v_{th}$) molecules colliding with singlet oxygen molecules occupy at once the dissociation term of I₂. Thus, to find the dissociation rate of iodine in the COIL medium, it is important to determine the deactivation rate of I₂(X, $v \geqslant v_{th}$) molecules in the medium. The aim of this paper is to calculate the effective deactivation rate constants of I₂(X, $v \geqslant v_{th}$) molecules in the COIL medium taking into account the vibrational excitation, relaxation, and dissociation of iodine molecules.

Let us denote the total concentration of I₂(X, v) molecules with $v \geqslant v_{th}$ by $N_{I_2}^+$. It is obvious that the rate of changing $N_{I_2}^+$ due to the VT exchange in collisions of iodine molecules with molecules of the component M of the COIL medium will be determined by the rate of changing the concentration of I₂(X, v_{th}) due to exchange by vibrational quanta with I₂ molecules occupying the $v_{th} - 1$ vibrational level,

$$\frac{dN_{I_2}^+}{dt} = \sum_M [K_M(v_{th} - 1 \rightarrow v_{th})N_{I_2}(v_{th} - 1)$$

$$- K_M(v_{th} \rightarrow v_{th} - 1)N_{I_2}(v_{th})]N_M. \qquad (1)$$

Here, $K_M(v \rightarrow w)$ is the rate constant of the process I₂(X, v) + M → I₂(X, w) + M. Let us denote by K_M^+ the effective deactivation rate constant of I₂(X, $v \geqslant v_{th}$) molecules in collisions with molecules M:

$$\frac{dN_{I_2}^+}{dt} = -K_M^+ N_{I_2}^+ N_M.$$

Taking (1) into account, we find

$$K_M^+ = \qquad\qquad\qquad\qquad\qquad\qquad (2)$$

$$\frac{K_M(v_{th} \rightarrow v_{th} - 1)N_{I_2}(v_{th}) - K_M(v_{th} - 1 \rightarrow v_{th})N_{I_2}(v_{th} - 1)}{N_{I_2}^+}.$$

Because

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$$K_{\mathrm{M}}(v_{\mathrm{th}} - 1 \rightarrow v_{\mathrm{th}}) = K_{\mathrm{M}}(v_{\mathrm{th}} \rightarrow v_{\mathrm{th}} - 1) \exp\left(-\frac{\Delta E_{\mathrm{th}}}{kT}\right),$$

where ΔE_{th} is the difference of the energies of molecules I$_2$(X, v) occupying the v_{th} and $v_{\mathrm{th}} - 1$ levels and T is the gas temperature, we obtain

$$K_{\mathrm{M}}^{+} =$$

$$\frac{K_{\mathrm{M}}(v_{\mathrm{th}} \rightarrow v_{\mathrm{th}} - 1)[N_{\mathrm{I}_2}(v_{\mathrm{th}}) - \exp(-\Delta E_{\mathrm{th}}/kT)N_{\mathrm{I}_2}(v_{\mathrm{th}} - 1)]}{N_{\mathrm{I}_2}^{+}}.$$

In particular, for $v_{\mathrm{th}} = 30$ and $T = 300$ K, we have

$$K_{\mathrm{M}}^{+} = \frac{K_{\mathrm{M}}(30 \rightarrow 29)[N_{\mathrm{I}_2}(30) - 0.42N_{\mathrm{I}_2}(29)]}{N_{\mathrm{I}_2}^{+}}. \tag{3}$$

The main processes proceeding in the COIL medium, which are considered in our paper, and the corresponding rate constants K_j ($j = 1 - 9$) are taken from [7] (Table 1). It is assumed that a gas flow entering a laser reactor consists of molecular oxygen in the electronic states X$^3\Sigma$, a$^1\Delta$, and b$^1\Sigma$ at concentrations N_{X}, N_{a}, and N_{b}, respectively, water vapour at the concentration N_{w}, and molecular iodine in the ground electronic state I$_2$(X) at the concentration N_{I_2}. We also assume that the flow has a constant cross section and the components of the mixture are mixed instantly. The equations describing the dependences of relative concentrations η of components (concentrations divided by the oxygen concentration) and temperature T on the distance x along the flow have the form

$$\frac{\mathrm{d}\eta_{\mathrm{a}}}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2(-2K_1\eta_{\mathrm{a}}^2 - K_2\eta_{\mathrm{a}}\eta_{\mathrm{I}^*} - K_3\eta_{\mathrm{a}}\eta_{\mathrm{I}}$$

$$+ K_4\eta_{\mathrm{X}}\eta_{\mathrm{I}^*} + K_5\eta_{\mathrm{b}}\eta_{\mathrm{w}} + K_9\eta_{\mathrm{b}}\eta_{\mathrm{I}_2} - K_{\mathrm{d}}\eta_{\mathrm{I}_2}^{+}\eta_{\mathrm{a}}),$$

$$\frac{\mathrm{d}\eta_{\mathrm{b}}}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2(K_1\eta_{\mathrm{a}}^2 + K_2\eta_{\mathrm{a}}\eta_{\mathrm{I}^*} - K_5\eta_{\mathrm{b}}\eta_{\mathrm{w}}$$

$$- K_8\eta_{\mathrm{b}}\eta_{\mathrm{I}_2} - K_9\eta_{\mathrm{b}}\eta_{\mathrm{I}_2}),$$

$$\frac{\mathrm{d}\eta_{\mathrm{I}^*}}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2(-K_2\eta_{\mathrm{a}}\eta_{\mathrm{I}^*} + K_3\eta_{\mathrm{a}}\eta_{\mathrm{I}} - K_4\eta_{\mathrm{X}}\eta_{\mathrm{I}^*}$$

$$- K_6\eta_{\mathrm{I}_2}\eta_{\mathrm{I}^*} - K_7\eta_{\mathrm{w}}\eta_{\mathrm{I}^*}),$$

Table 1.

No	Reaction	Reaction rate constant K_j/cm^3 s^{-1}
1	O$_2$(a) + O$_2$(a) $\rightarrow$ O$_2$(b) + O$_2$(X)	$9.5 \times 10^{-28} T^{3.8} \exp(700/T)$
2	O$_2$(a) + I* $\rightarrow$ O$_2$(b) + I	$4 \times 10^{-24} T^{3.8} \exp(700/T)$
3	O$_2$(a) + I $\rightarrow$ O$_2$(X) + I*	7.8×10^{-11}
4	O$_2$(X) + I* $\rightarrow$ O$_2$(a) + I	2.7×10^{-11}
5	O$_2$(b) + H$_2$O $\rightarrow$ O$_2$(a) + H$_2$O	6.7×10^{-12}
6	I* + I$_2$(X) $\rightarrow$ I + I$_2^*$	3.5×10^{-11}
7	I* + H$_2$O $\rightarrow$ I + H$_2$O	2.3×10^{-12}
8	O$_2$(b) + I$_2$(X) $\rightarrow$ O$_2$(X) + 2I	3.3×10^{-11}
9	O$_2$(b) + I$_2$(X) $\rightarrow$ O$_2$(X) + I$_2^*$	2.5×10^{-11}

$$\frac{\mathrm{d}\eta_{\mathrm{I}_2}}{\mathrm{d}x} = -\frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2(K_8\eta_{\mathrm{b}}\eta_{\mathrm{I}_2} + K_{\mathrm{d}}\eta_{\mathrm{I}_2}^{+}\eta_{\mathrm{a}}),$$

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{(C_p^{\mathrm{O}_2} + C_p^{\mathrm{M}}\eta_{\mathrm{M}})U_0}\left(\frac{T_0}{T}\right)^2(q_1K_1\eta_{\mathrm{a}}^2 + q_2K_2\eta_{\mathrm{a}}\eta_{\mathrm{I}^*}$$

$$+ q_5K_5\eta_{\mathrm{b}}\eta_{\mathrm{w}} + q_6K_6\eta_{\mathrm{I}_2}\eta_{\mathrm{I}^*} + q_7K_7\eta_{\mathrm{w}}\eta_{\mathrm{I}^*} + q_9K_9\eta_{\mathrm{b}}\eta_{\mathrm{I}_2}).$$

Here, K_{d} is the rate constant of the reaction O$_2$(a) + I$_2$(X, $v \geqslant v_{\mathrm{th}}$) $\rightarrow$ O$_2$(X) + 2I; the subscripts I* and I refer to iodine atoms in the electronic states ^{2}P$_{1/2}$ and ^{2}P$_{3/2}$; M denotes N$_2$ or He; 0 denotes the initial value of the corresponding parameter; N_{ox} is the total concentration of oxygen molecules; U_0 is the gas flow velocity; q_j is the energy effect of the jth reaction; $C_p^{\mathrm{O}_2}$ and C_p^{M} are the molar heat capacities of O$_2$ and the buffer gas M.

Equations for the relative population η_0 of iodine molecules at the vth vibrational level have the form:

for $1 \leqslant v < v_{\mathrm{th}}$,

$$\frac{\mathrm{d}\eta_v}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2\left\{\gamma_vK_6\eta_{\mathrm{I}_2}\eta_{\mathrm{I}^*} + \sum_{\mathrm{M}}[K_{\mathrm{M}}(v + 1 \rightarrow v)\eta_{v+1}\right.$$

$$+ K_{\mathrm{M}}(v - 1 \rightarrow v)\eta_{v-1} - K_{\mathrm{M}}(v \rightarrow v - 1)\eta_v$$

$$\left. - K_{\mathrm{M}}(v \rightarrow v + 1)\eta_v]\eta_{\mathrm{M}}\right\}, \tag{4}$$

for $v \geqslant v_{\mathrm{th}}$,

$$\frac{\mathrm{d}\eta_v}{\mathrm{d}x} = \frac{(N_{\mathrm{ox}})_0}{U_0}\left(\frac{T_0}{T}\right)^2\left\{\gamma_vK_6\eta_{\mathrm{I}_2}\eta_{\mathrm{I}^*} + \sum_{\mathrm{M}}[K_{\mathrm{M}}(v + 1 \rightarrow v)\eta_{v+1}\right.$$

$$+ K_{\mathrm{M}}(v - 1 \rightarrow v)\eta_{v-1} - K_{\mathrm{M}}(v \rightarrow v - 1)\eta_v$$

$$\left. - K_{\mathrm{M}}(v \rightarrow v + 1)\eta_v]\eta_{\mathrm{M}} - K_{\mathrm{d}}\eta_v\eta_{\mathrm{a}}\right\}. \tag{5}$$

Here, γ_0 is the probability of producing vibrationally excited I$_2$(X, v) molecules in the reaction I* + I$_2$(X) $\rightarrow$ I + I$_2$.

It was assumed that I$_2$(X, v) molecules were produced only at levels with $v > 23$ during the quenching of I* by I$_2$(X) [14], while the lower levels were populated during vibrational relaxation. The probabilities of producing vibrationally excited I$_2$(X, v) molecules in the reaction I*+ I$_2$(X)$\rightarrow$I + I$_2$ were assumed equal to $\gamma_v = a_v\gamma$, where γ is the total probability of producing I$_2$(X, $v > 23$) molecules in this reaction, and the values of the coefficient a_v were found from Fig. 7 in paper [14]. According to different estimates, the value of γ can be $0.05 - 0.2$. Note, however, that the values of K_{M}^{+} calculated in this paper were almost independent of the value of γ used in calculations.

By using relations (2) and (3), we calculated the effective deactivation rate constants for I$_2$(X, $v \geqslant 30$) molecules in collisions with O$_2$ and N$_2$ molecules in the typical COIL medium: O$_2$:N$_2$ = 1:1 Torr, $\eta_{\mathrm{a}0} = 0.6$, $\eta_{\mathrm{I}_20} = 0.01$, $\eta_{\mathrm{w}} = 0.03$, and $T_0 = 300$ K. The above equations were calculated numerically for the relative concentrations of the components of the COIL medium together with equations (4) and (5). The rate constants of the VT relaxation of I$_2$(X) in collisions with O$_2$ and N$_2$ molecules were taken from [14]. As a result, the populations of iodine molecules at different

vibrational levels, in particular, at levels with $v = 29$ and 30 were found and the total concentration of $I_2(X, v)$ molecules with $v \geqslant 30$ was determined at distances x where molecular iodine begins rapidly to dissociate. By using expression (3), we obtained the rate constants $K_{O_2}^+ \approx 3 \times 10^{-12}$ cm^{3}s^{-1} and $K_{N_2}^+ \approx 4 \times 10^{-12}$ cm^3 s^{-1}. These values are smaller by a factor of 2.2 than the values obtained for these constants in [14]. Note that the values of $K_{O_2}^+$ and $K_{N_2}^+$ depend on the dissociation rate constant K_d used in calculations (we assumed that $K_d = 3 \times 10^{-11}$ cm^{3}s^{-1}). In particular, if we assume that $K_d = 0$, the values of $K_{O_2}^+$ and $K_{N_2}^+$ will increase by a factor of 1.6.

Thus, expressions have been obtained for the effective deactivation rate constants of $I_2(X, v \geqslant v_{th})$ molecules in the COIL medium and these constants have been calculated for $v_{th} = 30$ in collisions with O_2 and N_2 molecules. These constants $(K_{N_2}^+ \approx 4 \times 10^{-12}$ cm^3 s^{-1} and $K_{O_2}^+ \approx 3 \times 10^{-12}$ cm^3 s^{-1} are smaller by a factor of 2.2 than the effective deactivation rate constants of $I_2(X, v \geqslant 30)$ molecules calculated in [14]. This discrepancy is mainly explained by the fact that K_M^+ was calculated in [14] by neglecting the dissociation of I_2.

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