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DISSOCIATION OF MOLECULAR IODINE DURING MIXING WITH SINGLET OXYGEN FLOW

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Abstract. The analytical model of the molecular iodine dissociation in the singlet oxygen(SO) media is considered. The mean number of SO molecules, which are spent to dissociate one iodine molecule, is evaluated, depending on the initial iodine, singlet and ground state oxygen, and water vapor concentrations. The two-dimensional numerical modeling of mixing of SO and iodine containing flows was done to investigate the influence of mixing on the process of the iodine dissociation and gain distribution.

1. ANALYTICAL CONSIDERATION.

The main processes which determine the gain in the active media of the Chemical Oxygen Iodine Laser (COIL) are known [1] today (see Tab.1,2). It allows to make numerical analysis in order to improve the operational characteristics of COIL. The exception is the mechanism of the molecular iodine dissociation including the role of electronically-excited states $I_2(A, A', B)$ and the number of SO molecules, which are spent to dissociate one iodine molecule.

The rate constants of the processes, which govern the population and depopulation of the electronically excited states $I_2(A, A')$ are poorly known, so it is difficult to estimate their role during dissociation.

The first rate-limiting step of the dissociation is the population in collisions with $O_2(a)$ or I^* of highly-excited vibrational levels of the ground state iodine molecule $I_2^*(X, 20 < v < 40)$. Then I_2^* can dissociate in the second collision with them. The population of electronically excited states $I_2(A, A')$ in collisions of vibrationally thermalised $I_2(X)$ molecules with $O_2(a)$, I^* is impossible, because their energies $E_{A'} = 9989 \text{ cm}^{-1}$, $E_A = 10846 \text{ cm}^{-1}$ are sufficiently higher than energies of $O_2(a)$ and I^* which are 7882 and 7603 cm^{-1} respectively. The iodine dissociation can also occur in collisions of $I_2(X)$ with $O_2(b)$, but the sequential mechanism is more effective in the COIL active medium. The excited iodine atom I^* is much more effective than $O_2(a)$ for the ground state $I_2(X, v)$ excitation, so the rate of dissociation increases during the molecular iodine dissociation, and the dissociation has a chain-like character. In [2] the sequential model of I_2 dissociation in SO medium with one intermediate excited state of I_2 molecule was suggested, which can satisfactorily explain experimental results [2,3]. For premixed case assuming steady-state conditions for all excited species and neglecting $O_2(a)$ concentration change during I_2 dissociation in [2] it was obtained an equation for the temporal behavior of I_2 concentration and its analytical solution. This equation and its solution can be written in the form

$$d[I_2]/dt = -k_c[I_2]\{(1+\delta)[I_2]_0 - [I_2]\} \quad (1); \quad [I_2(t)] = [I_2]_0(1+\delta)/(1+\delta \exp(t/\tau))$$

where $k_c = a(\eta k_3 + \eta k_9)$ —effective value of the rate constant for the chain dissociation $\delta = (\eta k_2 + \eta k_8)[O_2(a)]/k_c[I_2]_0$ —the ratio of dissociation rates for $O_2(b)$ and sequential dissociation which is typically of order 10^{-2} , $\eta = k_{10}[O_2(a)]/(\Sigma k_{12}^i[Q_i] + k_{10}[O_2(a)])$ and $\theta = k_7[O_2(a)]/\Sigma k_{41}^i[Q_i]$ are related to the efficiency of the sequential and $O_2(b)$ dissociation $a = 2k_{11}[O_2(a)]/(k_1[O_2(a)] + k_{-1}[O_2(x)])$ —the mean number of the excited iodine atoms which appear after one iodine molecule dissociation $\tau = \{(1+\delta)K_c[I_2]_0\}^{-1}$ —characteristic time of I_2 dissociation

The time it takes the iodine concentration to decrease N times as a result of dissociation equals $t_{ds} = \tau[\ln(1+1/\delta - 1/N\delta) + \ln N]$. One can distinguish two stages of dissociation. During the initiation period $t_i = \tau \ln 1/\delta$ the initial iodine concentration $[I_2]_0$ decreases approximately twice, then during the period $t_n = \tau \ln N$ it becomes $[I_2]_0/N$.

As the result of the fast energy exchange reaction (1) the I^* atoms and SO molecules form a united pool of electronically-excited particles. The rate of its relaxation depends significantly on the current I^* atoms concentration and consequently on the current $I_2(X)$ concentration. So using Heidner's approximations [2] one can obtain the equation for $O_2(a)$ relaxation during I_2 dissociation

$$d/dt[O_2(a)] = P[I_2]^2 - M[I_2] - L \quad (2)$$

The r.h.s. of (2) as that of (1) has a quadratic dependence on the current I_2 concentration. P , M , L — are complicated expressions, depending on $O_2(a, X)$ and quenchers concentrations.

Assuming that relative change of $O_2(a)$ concentration is small, one can solve equations (1) and (2) together to obtain the analytical solution for the $O_2(a)$ concentration change during I_2 dissociation. During the I_2 dissociation the decrease of $O_2(a)$ concentration equals

$$[O_2(a)]_0 - [O_2(a)] = (\alpha + n)[I_2]_0(1 - 1/N) + W_i t_i + W_q t_n$$

The last two terms account for quenching of excited particles during dissociation and $W_q \gg W_i$, where

$$W_q = \{\Sigma k_6^i [Q_i] + k_2 [O_2(a)]\} [O_2(a)] + \alpha \{\Sigma k_6^i [Q_i] + k_3 [O_2(a)]\} [I_2]_0;$$

$$W_i = \{q_a + k_2 [O_2(a)] + (1 + \delta) k_8 [I_2]_0\} [O_2(a)] - \alpha \delta \{\Sigma k_6^i [Q_i] + k_3 [O_2(a)] + (1 + \delta) k_9 [I_2]_0\} [I_2]_0$$

are the quenching rates on the chain and initial stages of dissociation.

The main quenching process is the excited iodine atom quenching on the chain stage of dissociation so one can obtain the following expression for the mean number of SO molecules, spent to dissociate one iodine molecule.

$$\Delta = ([O_2(a)]_0 - [O_2(a)]) / [I_2]_0 = \alpha + n + q \quad (3)$$

where α SO molecules are spent to excite iodine atoms, n molecules, $n = 1 + k_9 / (\delta k_3 + \eta k_9) \approx 1 + 1/\eta$, are spent for I_2 dissociation $q = \alpha t_n \{\Sigma k_6^i [Q_i] + k_3 [O_2(a)]\} -$ the number of excited particles which are quenched during dissociation. Since t_n inversely proportional to the initial iodine concentration the quenching term in (3) has the same dependence $q \sim [I_2]_0^{-1}$. Water vapor is a significant quencher of the excited particles in the active medium of COIL. The dependence of Δ on relative water vapor concentration $h = [H_2O] / \{[O_2(a)] + [O_2(x)]\}$ is plotted on fig.1 for different $I = [I_2]_0 / \{[O_2(a)] + [O_2(X)]\}$ — initial iodine concentrations for typical COIL conditions: $\{[O_2(a)] / [O_2(X)] = 1, h < 0.05, I < 0.01\}$. Dots are results of our and [4] modelling, cross — experimental results [4]. They are in satisfactory agreement with the results of our analytical prediction.

2. INFLUENCE OF MIXING WITH SINGLET OXYGEN ON THE I_2 DISSOCIATION.

From the analytical consideration it follows that the characteristic time of the iodine dissociation is inversely proportional to the initial iodine concentration. This can lead to sufficient difference in the experimental results and one-dimensional modelling predictions when a premixed flow approximation is used. Typically the averaged over the cross section of the COIL channel iodine concentration is $(5-10) \cdot 10^{14} \text{ cm}^{-3}$ and calculated for the premixed case dissociation time is of order $t_{ds} = (2-5) 10^{-4} \text{ s}$. In real devices in the region of the iodine injection its concentration can be an order of magnitude higher. This leads to sufficiently faster dissociation if dissociation time is smaller than the diffusion one and changes the place of the maximum gain respectively to the premixed case. In the typical COIL conditions the iodine molecular diffusion coefficient is $D = (1-2) 10^2 \text{ cm}^2 \text{ s}^{-1}$ [4] and the characteristic diffusion time $t_{df} = L^2 / D = (1-5) 10^{-3} \text{ s}$ where $L = 0.5-1 \text{ cm}$ is a typical distance between the holes through which iodine is injected. Since t_{df} is sufficiently greater than t_{ds} the iodine dissociation will proceed in highly inhomogeneous conditions and the gain will strongly vary across the SO flow depending on the distance from the place of the iodine injection [6].

Here we report the results of numerical modeling which was done in order to investigate the influence of mixing on the iodine dissociation and gain distribution in the COIL medium. The stationary two-dimensional parabolic approximation of gas dynamic was used [7]. The kinetic scheme accounted for all the processes 1-12 (see tab.1,2).

The gain was calculated on the $I(2P_{1/2}, F=3 \rightarrow 2P_{3/2}, F=4)$ transition assuming equilibrium population of superfine structure components and Doppler line width.

The geometry of mixing and initial parameters of the mixing flows were chosen to approximate the conditions of experimental device [8] because overall diagnostics in this device is planned [9] including the iodine distribution in the flow. In this device the iodine is injected at a 45° angle to the flow direction through the holes in the tubes placed at a distance of 19 mm from each other. In our modeling the gas flow is calculated between two symmetry axes placed at a distance $L=9.5$ mm (see fig.2). The SO flow F_1 contains $O_2(a):O_2(X):O_2(b):H_2O:Cl_2=0.6:0.4:3 \cdot 10^{-5}:0.03:0.04$ torr, has a temperature $T_1=233$ K⁰ and velocity $u_1=55$ m/s. Flow F_2 contains $I_2:Ar=0.19:0.88$ torr, has temperature $T_2=330$ K⁰ and velocity $u_2=1.42 \cdot u_1$. It is injected through the hole $h=0.5$ mm at a 45° angle to the main flow. The ratio of the averaged over the channel cross section iodine concentration to the total oxygen one $I=[I_2]_{av}/\{[O_2(a)]+[O_2(X)]\}=0.007$. The results of calculations are shown on fig.2-4. Fig.2 shows the isolines of total iodine concentration $I_t=2 \cdot [I_2]+[I^*]+[I]$. One can see that mixing occurs at the distance of order $L_m=7$ cm after injection. Fig.3 shows the gain distribution in several cross sections. It is highly inhomogeneous in the region of maximal gain and becomes near uniform only at the distance $\approx L_m$. On fig.4 the averaged over the channel cross section results of the above mentioned calculations are compared with the results for the premixed case with equal averaged parameters. Full lines show the distribution of averaged gain along the flow for the inhomogeneous (1) and premixed (2) cases. Broken lines show the ratio of the averaged undissociated molecular iodine concentration to the initial one for inhomogeneous (1) and premixed (2) cases. One can see that in the inhomogeneous case the dissociation proceeds in the region of high local iodine concentration noticeably faster than in the premixed case which leads to marked difference in the position of maximal averaged gain and inhomogeneous gain distribution across the COIL channel. So the mixing effects play significant role in the COIL active medium and should be accounted for in realistic COIL modelling.

Table.1 The kinetic scheme of COIL active medium.

N	process	$k_i(\text{cm}^3/\text{s})$
1	$O_2(a) + I \longrightarrow O_2 + I^*$	$k_1=7.6 \cdot 10^{-11}$
	$k_{-1}=k_1 \cdot (4/3) \exp(-400/T)$	
2	$O_2(a)+O_2(a) \longrightarrow O_2(b)+O_2(X)$	$k_2=2 \cdot 10^{-17}$
3	$O_2(a) + I^* \longrightarrow O_2(b)+I$	$k_3=7.8 \cdot 10^{-14}$
4	$O_2(b) + Q \longrightarrow O_2(a)+Q$	see tab.2
5	$O_2(a) + Q \longrightarrow O_2(X)+Q$	see tab.2
6	$I^* + Q \longrightarrow I + Q$	see tab.2
7	$O_2(b) + I_2^+ \longrightarrow O_2 + 2I$	$k_4=4 \cdot 10^{-12}$
8	$O_2(a) + I_2^+ \longrightarrow O_2 + I_2$	$k_8=7 \cdot 10^{-15}$
9	$I^* + I_2 \longrightarrow I + I_2^+$	$k_9=3.5 \cdot 10^{-11}$
10	$O_2(a) + I_2^+ \longrightarrow O_2 + 2I$	$k_{10}=3 \cdot 10^{-10}$
11	$I^* + I_2^+ \longrightarrow 3I$	$k_{11}=5 \cdot 10^{-10}$
12	$I_2^+ + Q \longrightarrow I_2 + Q$	see tab.2

$I=I(^2P_{3/2})$, $I^*=I(^2P_{1/2})$, $I_2^+=I_2(X, 20 < v < 40)$.

Table.2 Quenching rate constants

Q	k^1_4	k^1_5	k^1_6	$K^1_{I_2}, \text{cm}^3/\text{s}$
Ar	$5.8 \cdot 10^{-18}$	$2.1 \cdot 10^{-19}$	$2.0 \cdot 10^{-18}$	10^{-13}
O ₂	$4.6 \cdot 10^{-17}$	$1.7 \cdot 10^{-18}$	$4.6 \cdot 10^{-14}$	$5 \cdot 10^{-12}$
I ₂	$2.0 \cdot 10^{-11}$	$7.0 \cdot 10^{-15}$	$3.1 \cdot 10^{-11}$	$5 \cdot 10^{-10}$
I		$3.0 \cdot 10^{-14}$	$1.7 \cdot 10^{-13}$	—
H ₂ O	$6.7 \cdot 10^{-12}$	$5.6 \cdot 10^{-18}$	$1.9 \cdot 10^{-12}$	$3 \cdot 10^{-10}$
Cl ₂	$4.5 \cdot 10^{-16}$	$6.3 \cdot 10^{-18}$	$2.0 \cdot 10^{-14}$	—

Fig.1 Δ versus h for different I

Fig.2 The iodine concentration distribution

Fig.3 Distribution of the gain across the flow

Fig.4 Distribution of the gain and I_2 along the flow

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