MECHANISM OF GENERATION TERMINATION AT THE $5^2P_{1/2}$–$5^2P_{3/2}$ TRANSITION IN IODINE

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The study of alkyl and perfluoro-alkyliodide lasers[1-5] showed that the generation at the atomic iodine transition of $\lambda \approx 1.3\ \mu$ usually terminates much earlier than the pumping pulse. In order to determine the causes of this effect the contribution from the so-called recombination mechanism toward deactivation of excited iodine atoms ($5^2P_{1/2}$) is analyzed. A numerical computation of the time dependence of the output emission was made for this purpose, taking into account the rate constants k_r and k_T of the processes $I + I + M \rightarrow I_2 + M$ (M = RI, I_2) and $I(^2P_{1/2}) + I_2 \rightarrow I(^2P_{3/2}) + I_2^*$ that were determined experimentally in [6-12]. The obtained results and their comparison with experimental data[1-5] show that the accumulation of molecular iodine through recombination in triple collisions can be the cause of a power drop and premature termination of generation provided special measures are taken to prevent excessive heating of the working gas by the "hot" products of photodissociation (addition of buffer gas, selection of working gases with a high specific heat, and a relatively low photodissociation degree). The failure to meet this condition leads to a still sharper drop of the laser emission pulse.

THE generation of a pulse at the $5^2P_{1/2}$–$5^2P_{3/2}$ iodine transition in the photodissociation of CF_3I and some other molecules terminates in many cases much earlier than the pumping pulse.[1-5] In some cases (strong pumping) generation termination is observed even before the maximum illumination of the active medium.[1,3,4] At the same time both the experiment and elementary computation show that never more than 10–20% of the working medium (see below) undergoes decomposition through photodissociation in the course of the generation process. Some assumptions on the mechanism of the observed generation termination (pyrolysis, recombination of iodine atoms, splitting reaction of the type $CF_3I + I(^2P_{1/2}) \rightarrow CF_3 + I_2$) are given in [3] and [4] [1)] although without adequate proof, with the exception of experiments revealing the effect of pyrolysis as reported in [3].

In the present work we attempted to explain the observed time dependences of generation power on the basis of available experimental data.

We consider the following set of processes:

$$2I(^2P_{1/2,3/2}) + M \rightarrow I_2 + M, \quad (1)$$

$$2I(^2P_{1/2,3/2}) + I_2 \rightarrow 2I_2, \quad (2)$$

$$I(^2P_{1/2}) + I_2 \rightarrow I(^2P_{3/2}) + I_2^*. \quad (3)$$

Processes (1) and (2) describe the recombination of iodine in triple collisions where the working-medium molecules (M) participate in process (1) and I_2 molecules participate in process (2). The process rates are characterized by tri-molecular constants k_r' for process (1) and k_r for process (2).

As is shown below, the role played by these processes in premature termination of generation is mainly determined by the accumulation of iodine molecules, underlying the effective development of the rapid process (3), rather than by the depletion of the atoms $I(^2P_{1/2})$ (as is suggested in [4] for example). The "quenching" rate of the atoms of $I(^2P_{1/2})$ in process (3) is characterized by the bimolecular constant k_q. In the course of recombination of iodine atoms the effectiveness of iodine molecules as the "third" body is anomalously large[7,8] which is why process (2) must be taken into account. A similar situation is observed in the deactivation of the $I(^2P_{1/2})$ atoms: process (3) is by 3–4 orders more effective than the analogous process occurring with the participation of CF_3I molecules.[9-12] The contribution of the latter is thus neglected. (Under conditions of generation this contribution is small as a rule in comparison to the frequency of stimulated transitions.) At the same time it is clear that process (1) cannot be neglected in a similar situation, because with a well purified working medium it is the only process responsible for the accumulation of iodine molecules in the initial stage of generation.

To obtain a quantitative measure of the effect of the above mechanism we performed a numerical computation of the time dependences of the generation power, using the following assumptions that to some extent idealize the normal experimental conditions.

1. The working medium absorbs radiation only within a single rectangular absorption band that is bounded by the wavelengths of 2440 and 2900 Å ($\Delta\nu_a = 6500\,cm^{-1}$). The absorption in this band is characterized by the cross section $\sigma = 4 \times 10^{-19}\ cm^2$ and is accompanied by photodissociation of the working medium molecule with a 100% yield of $I(^2P_{1/2})$ atoms. By using pump sources with a continuous spectrum and a given brightness temperature we can readily determine the pumping rate ($cm^{-3}\ sec^{-1}$) from the above characteristic of the working medium:

[1)] The complete ineffectiveness of an analogous splitting reaction in CH_3I is proved in /6/ by the tagged atom method. The ineffectiveness of this reaction also in the case of CF_3I follows directly from /10,14/.

$$R(t) = \bar{\sigma} n(t) I_\nu(t) \Delta\nu_a, \quad (4)$$

This value approximately corresponds to the case of CF_3I vapor as the working medium (n is the molecular concentration and $I_\nu \Delta\nu_a$ is the photon flux density in $cm^{-2}sec^{-1}$ in the elementary volume of active medium under consideration).

2. The function R(t) is approximated by the expression

$$R = \bar{\sigma} k n_0 I_{max} e^{-\gamma' t}(1 - e^{-\gamma'' t}), \quad (5)$$

where $k = (1+\alpha)^{1+\alpha/\alpha^\alpha}$, $\alpha = \gamma'/\gamma''$, n_0 is the initial concentration of the working medium, $I_{max} = (I_\nu \Delta\nu_a)_{max}$ is the maximum value of $I_\nu \Delta\nu_a$, and γ' and γ'' are constants determining the shape of the pumping pulse. As we noted n(t) varies negligibly during generation and therefore the approximation used here is close to the customary approximation $I_\nu(t)\Delta\nu_a = kI_{max} \exp(-\gamma' t)(1 - \exp -\gamma'' t)$ for flash lamps. For the same reason the functions R(t) are practically similar in various regions of the active medium volume and it is not necessary to take the "bleaching" kinetics into account.

3. The output power of stimulated emission is determined from the condition

$$N(t) = N_{th} \quad \text{for} \quad t_s < t < t_f, \quad (6)$$

where $N(t) = N_2(t) - N_1(t)g_2/g_1$; $N_1(t)$ and $N_2(t)$ are the populations of the lower and upper working levels of the iodine atom, g_1 and g_2 are the corresponding statistical weights, t_s and t_f are times determining the start and finish of generation, $N_{th} = 8\pi\Delta\nu L/\lambda^2 A_{21}$ is the value of threshold inversion, $\Delta\nu$ is the width of the contour line, L are resonator losses in cm^{-1}, λ is the wavelength, and A_{21} is the Einstein coefficient for spontaneous transition $I(^2P_{1/2}-{}^2P_{3/2})$. Satisfaction of (6) corresponds to high intensities of stimulated emission achievable in lasers of this type, a large number of generating modes (large volume of the active medium), and a near-rectangular emission line contour (achieved if an $I(^2P_{1/2})$ atom in formation receives translational energy $\Delta E_{kin} \gg kT$). The first two factors tend to bridge the dips in the contour of lines corresponding to neighboring modes; the last stabilizes the width of the generating region of the contour. It is also clear that with moderate N_{th} the correct (within several per cent) evaluation of the time dependence of stimulated emission intensity does not require an exact satisfaction of (6) except for times close to t_s and t_f. This conclusion is supported by the results of computation (see below) of the output power for various values of N_{th}.

4. The effects of all processes on the value of N(t) are neglected with the exception of photodissociation of the working gas discussed above and processes (1)–(3).

5. The value of k_r is considered independent of the electronic state of the recombining iodine atoms ($^2P_{1/2}$ or $^2P_{3/2}$). This conclusion is at variance with the assumption held in [10] but it does not contradict the Bunker and Davidson recombination theory[13] that best agrees with experimental data.

6. We neglect gas heating during the generation pulse and the corresponding change in the constants k_r, k_r', and k_q. Taking the above assumptions into account we obtain the following expressions from the kinetic equations describing the variation of working level populations in an elementary volume dV of the active medium:

$$dN/dt = R(t) - \Phi_1(t, N_c) - N[\Phi_2(t, N_c) + Kw(t, N_c)] \quad (7)$$

($\omega = 0$ when $N < N_{th}$)

$$dN_c/dt = -\tfrac{1}{2}k_p N_c^2[(1+a)n_0 - n(t) - N_c] + R(t). \quad (8)$$

Here $N = N_2 - \frac{1}{2}N_1$ (since $g_1 = 4$ and $g_2 = 2$), $N_c = N_1 + N_2$, $\Phi_1(t, N_c) = \frac{1}{4}k_T N_c(t)[n_0 - n(t) - N_c(t)]$ (it is clear that the quantity in square brackets in the expression for Φ_1 represents double concentration of iodine molecules $2n_i$),

$$\Phi_2 = \tfrac{1}{2}k_p N_c(t)[(1+a)n_0 - n(t) - N_c(t)] + \tfrac{1}{2}k_\tau[n_0 - n(t) - N_c(t)],$$

$$n_0 - n(t) = \int_0^t R(t')dt', \quad a = \frac{2k_p'}{k_p}, \quad K = \frac{3A_{21}\lambda^2}{16\pi\Delta\nu\tau h\nu}$$

ω is output power from 1 cm^3 of the active medium, $h\nu$ is the energy of a stimulated emission photon, and τ are useful losses of the resonator in cm^{-1}. Equations (7) and (8) account for the fact that so long as the quantity $an(t)/(n_0 - n(t))$ is not too small in comparison to unity it is close to the quantity $an_0/(n_0 - n(t))$ and the corresponding substitution cannot introduce significant errors.

When (6) is taken into account we obtain from (7)

$$w(t) = \frac{2}{3}h\nu\frac{\tau}{L}[R(t) - \Phi_1(t, N_c) - N_{th}\Phi_2(t, N_c)]. \quad (9)$$

In the absence of the resonator $N_{th} = \infty$. For this case, assuming that $\omega = 0$, we obtain from (7)

$$dN/dt = R(t) - \Phi_1(t, N_c) - N\Phi_2(t, N_c), \quad (10)$$

that determines together with (8) the function N(t)[2] and the starting time of generation (when $N_{th} < N_{max}$ and (6) is taken into account).

The functions $\omega(t)$, N(t), $N_c(t)$, and R(t) were calculated by the Ural-2 computer using equations and formulas (5), (8)–(10) and varying four parameters: I_{max}, n_0, k_r', and N_{th}. In all cases we assumed that $\tau \approx L$ in (9) (Brewster windows, relatively high mirror transmission, and a short length of cell with the working gas).

The selection of values for a number of the parameters requires some explanation. The values of I_{max} presented in the table are typical, for example, of conditions in an optically thin active medium and a 4π geometry of an equilibrium source whose temperatures are (in the order of increasing I_{max}) 4500, 4900, 7200, 8800, and 10 600°K. Under these conditions $I_{max} = \rho(T)c$ if $\rho(T)$ is the number of photons per 1 cm^3 of an equilibrium source within a corresponding spectral interval and at a corresponding temperature. In practice, however, it is very difficult to approach this limit. For example, if $I_{max} = \frac{1}{8}\rho(T)c$ (apparently a still realistic case), the temperatures of the equilibrium pumping source corresponding to these values of I_{max} are equal to (in the same order) 5600, 6070, 10 000, 13 000, and 18 000°K.

[2] In [4] the time dependence of N(t) was identified with the function $\omega(t)$. This lack of precision was not observed upon comparison with experimental data only because a sufficiently large number of arbitrary parameters used in the analysis allowed for a transformation of the theoretical curves within wide limits.

Computed data						Experimental data								
	pumping		generation		%			pumping		generation				
p, Torr	$I_{max}\cdot10^{-20}$ cm^{-2} sec^{-1}	Δt^{*}_{pe}, μsec	ϵ_e, mj/cm^3	Δt_{ge}, μsec	$\left(\frac{\Delta n}{n_0}\right)^{**}_{phg}$	Reference	p, Torr	E^{***}_p, kj	Δt^{*}_{ma}, μsec	ϵ_e, mj/cm^3	ϵ'^{****}_e mj/cm^3	Δt_{ge}, μsec	V, cm^3	h^{*****}, cm
10.7	0.59	1450	0.57	970	1.86	[5]	10	6.25	1500	0.048	0.061	1500	8340	7
10.7	1.18	1450	0.88	750	3.0	[5]	10	40.5	1500	0.90	1.15	1500	44400	8.2
10.7	1.18	112	0.14	340	0.49	[1]	10	4	45	0.054	0.22	10	14	0.5
10.7	38.8	112	4.0	111	12.5	[1]	80	4	45	0.32	1.35	10	14	0.5
32	1.18	112	0.44	220	0.47	[2]	43	1.22	27	0.11		24	23	0.7
32	38.8	112	6.8	59	7.9	[4]	110	2	30			20		0.7
107	1.18	112	1.19	120	0.40	[3]	81	2.6	40	0.14	0.59	10	14	0.5
107	38.8	112	10.6	32	3.9									
107	141	55.5	19.5	17	7.4									
107	443	55.5	34.0	11	12.5									

*Corresponds to the level of 0.35 I_{max} (approximately in the case of Δt_{pe}).

**$(\Delta n/n_0)_{phg}$ is the portion of working gas molecules that dissociated at the termination of generation only by photodissociation, obtained from computed data.

***Electrical energy of charged capacitor bank.

****$\epsilon'_e = \epsilon_e L_e/\tau_e$ (L_e and τ_e were roughly evaluated from the conditions of the corresponding experiment).

*****Characteristic thickness of the exposed layer of active medium (equals cell diameter for data of [1,2,4]).

The value of $\kappa_r = 0.025\ \kappa_r$ was used in the computation; experimental data are given for CF_3I.

We can assume that if the first values of I_{max} are to some extent typical of the pumping conditions in [5] (soft discharge regime in Xe 1.5 msec long), the last two appear to match approximately the conditions in [1-4] (hard discharge regimes in He with a duration up to 100 μsec). A sufficiently low ($\lesssim 0.3$) optical density of the active medium is assumed in all cases lest the values of I_{max} turn out to be considerably below the theoretical values for a portion of the active medium.

The computed value of $k_r = 4.7\times10^{-30}$ cm^6/sec was taken from [7]. The computed values of k'_r (0.005 k_r; 0.025 k , and 0.075 k) were selected from the most probable range of values based on data presented in [13]. The value of $k_q = 5\times10^{-12}$ cm^3 sec^{-1} was taken from [9]. The computation was performed for three values of N_{th}: 2.5×10^{13}, 3.8×10^{14}, and 1.14×10^{15} cm^{-3}. Considering that $\lambda = 1.315$ μ and $A_{21} = 7.7$ sec^{-1} the value of $N_{th} = 3.8\times10^{14}$ cm^{-3} (apparently the most realistic) corresponds, say, to $\Delta\nu = 6\times10^8$ sec^{-1} (additional kinetic energy of iodine atoms of ~0.1 eV) and to mirror reflection of 100 and 50% for a length of active medium of 1 m. It seems that the last of the above values of N_{th} is more acceptable when the hyperfine splitting of iodine levels is large enough. The computation results are given in Fig. 1-3. According to Figs. 1a and c, in the laser model under consideration, the generation pulse becomes shorter when initial pressure (p) and pumping pulse amplitude (I_{max}) are increased (without changing the pulse shape). A similar tendency is manifested by the functions N(t) (when $N_{th} = \infty$) shown in Figs. 1b and d. A substantial difference in the functions ω(t) compared for high and low values of p and I_{max} (Fig. 1a, curves 2–5 and Fig. 1c, curves 5 and 6) consists in the fact that the generation pulse drop in the first case is due to the above deactivation mechanism of $I(^2P_{1/2})$ atoms, and in the second case the cause is a drop of the pumping pulse. The functions ω(t) practically coincide on the scale used in Figs. 1a and c for all the computed values of N_{th}. A slight deviation of these curves can be detected only in the case of low values of p and I_{max} and only with a 10-fold increase of scale along the ordinate axis (Fig. 1d, curves 5′, 5″, and 5‴). This indicates that the curves ω(t) are

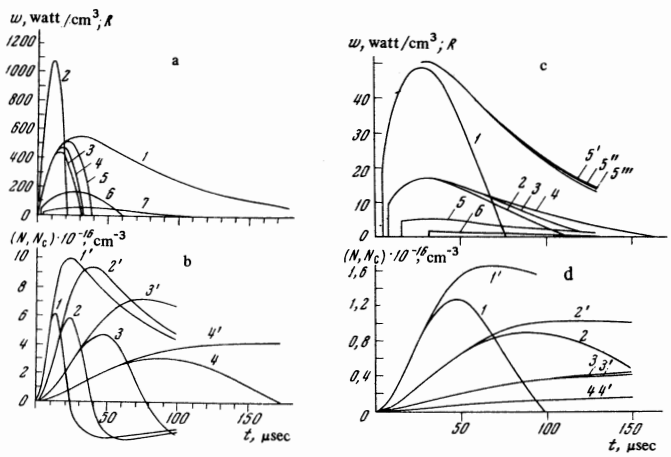

FIG. 1. Computation results for pumping pulse length of 112 μsec at the level of 0.35 R_{max}; $R(t) = R_{max}$ when t = 30 μsec ($\gamma' = 1.54\times10^4$ sec^{-1}, $\alpha = 1/3$). (a) 1–R(t) in relative units, 2-7–the functions ω(t) for $I_{max} = 3.88\times10^{21}$ cm^{-2} sec^{-1} (T = 10,000°K) and $N_{th} = 3.8\times10^{14}$ cm^{-3}, with different values of pressure (2–320 Torr, 3, 4, 5–107 Torr, 6–32 Torr, and 7–10.7 Torr at the temperature of 20°C) and the coefficient α (2, 4, 6, 7–0.05; 3–0.15; 5–0.01). (b) the functions N(t) and $N_c(t)$ for $I_{max} = 3.88\times10^{21}$ cm^{-2} sec^{-1} (T = 10,000°K) and α = 0.05; 1-4–the functions N(t) ($N_{th} = \infty$) for pressures of 320 Torr (1), 107 Torr (2), 32 Torr (3), and 10.7 Torr (4); 1′-4′–the functions $N_c(t)$ for pressures in the same sequence. (c) 1-6–the functions ω(t) for $I_{max} = 1.18\times10^{20}$ cm^{-2} sec^{-1} (T = 6070°K) and $N_{th} = 3.8\times10^{14}$ cm^{-3} with different values of pressure (1–320 Torr, 2,3,4–107 Torr, 5–32 Torr, and 6–10.7 Torr at the temperature of 20°C) and the coefficient α (1,3,5,6 –0.05, 2–0.15, 4–0.01); 5′, 5″, 5‴–the functions ω(t) × 10 computed for the same values of N_{th} and p as curve 5 and having different N_{th}(5′–2.5×10^{13} cm^{-3} 5″–3.8×10^{14} cm^{-3}, 5‴ –1.14×10^{15} cm^{-3}). (d) the functions N(t) and $N_c(t)$ differing from those shown in Fig. 1b by the value of $I_{max} = 1.16\times10^{20}$ cm^{-2} sec^{-1}.

not critical with respect to the values of N_{th} and that the direct effect of recombination processes (1) and (2) on the generation power is negligible (since the process rates are accounted for only by a part of the small quantity $\Phi_2(t, N_c)$). At the same time their indirect effect (via Φ_1, which depends on n_i) is obviously large.

Figure 2 shows the functions $\omega(t)$ and $R(t)$ computed for p = 10 Torr and approximately corresponding to the conditions obtained in [5].

Figure 3 shows computed curves of $\omega(t)$ for p = = 107 Torr and approximations of R(t) typical of [1-4].

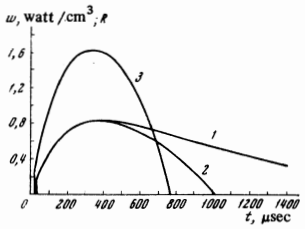

FIG. 2. Computation results for pumping pulse length of 1450 μsec at the level of 0.35 R_{max}. R(t) = R_{max} when t = 400 μsec; 1–R(t) in relative units; 2 and 3–the function $\omega(t)$ for p = 10.7 Torr (20°C), $\alpha = 0.05$; $N_{th} = 2.5 \times 10^{13}$ cm^{-3}; I_{max} equals 5.9×10^{19} cm^{-2} sec^{-1} in the case of curve 2 (T = 5600°K) and 1.18×10^{20} cm^{-2} sec^{-1} in the case of curve 3 (T = 6070°K).

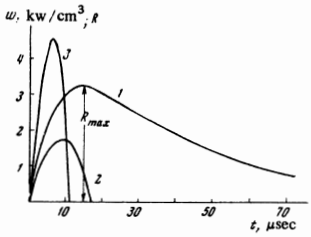

FIG. 3. Computation results for pumping pulse length of 55.5 μsec at the level of 0.35 R_{max}, t_{max} = 15 μsec ($\gamma' = 3.08 \times 10^4$ sec^{-1}, $\alpha = 1/3$). 1–R(t) in relative units; 2, 3–the functions $\omega(t)$ for p = 107 Torr (20°C), $\alpha = 0.05$; $N_{th} = 3.8 \times 10^{14}$ cm^{-3}; I_{max} equals 1.4×10^{22} cm^{-2} sec^{-1} in the case of curve 2 (T = 13,000°K) and 4.43×10^{22} cm^{-2} sec^{-1} in the case of curve 3 (T = 18,000°K).

The table can give some idea on the correlation between the theoretical and experimental data. Curve 3 in Fig. 2 yields the computed value of the specific energy output $\varepsilon_c = 0.88$ mJ/cm^3 which is fairly close to its full experimental value $\varepsilon'_e = 1.15$ mJ/cm^3 obtained in [5] for a capacitor bank energy of 40.5 kJ. The computed duration of generation was $\Delta t_{gc} = 750$ μsec, i.e., approximately half of the corresponding experimental value Δt_{ge}. Going over to curve 2 (Fig. 2), Δt_{gc} increases to 970 μsec but ε_c decreases to 0.57 mJ/cm^3. This deviation from experimental data might be caused by the fact that the computation neglected two factors tending to decrease the concentration of I_2 molecules: their dissociation in the visible portion of the spectrum and heating of active medium (up to 100–200°C for $(\Delta n/n_0)_{ph} \sim 3\%$) leading to a reduction of k_r. Under the conditions obtained in [1-4] at high values of p correlation with respect to Δt_g (see the table) is reached only when $\varepsilon_c \gg \varepsilon'_e$. In part this seems to be caused by a depressed value of the factor L_e/τ_e due to the possibility of unaccounted-for losses (vignette effect in long thin tubes, incomplete collection of the laser emission by the sensitive surface of the detector, etc.). In the case of small p and large I_{max} no correlation with respect to Δt_g is reached. This discrepancy can possibly be due to pyrolysis.[3] The quenching of generation due to this effect is difficult to evaluate at this time. It seems that it is more pronounced in the case of CF_3I than in molecules with greater "heat capacity" such as C_2F_5I, C_3F_7I, etc. Since with increasing pressure and constant value of I_{max} the magnitude of Δt_{gc} decreases significantly, the relative contribution from pyrolysis should decrease in comparison to the contribution from the above mechanism. The effectiveness of pyrolysis strongly depends on

$$\left(\frac{\Delta n}{n_0}\right)_{ph} = \frac{1}{n_0}\int_0^t R(t')\,dt'$$

and thus on t. The contribution from pyrolysis can be reduced, probably to a negligible value, by an appropriate addition of buffer gas increasing the heat capacity of the active medium, as it was done in [3]. If the gas admixture is not active with respect to the deactivation and recombination of iodine (inert gases, nitrogen, C_2F_6, etc.[1]) the duration of generation and its power are mainly limited by the mechanism determined by the processes (1)–(3) and also by the deactivation and recombination of iodine with the participation of buffer gas molecules or atoms. (In the computation this factor is readily accounted for by an appropriate increase of the coefficient a.) Termination of generation due to this mechanism is clearly much more difficult to prevent than that due to pyrolysis.

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