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KINETICS OF A CF_3I *PHOTODISSOCIATION LASER*

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The first part of this paper contains a critical analysis of literature data on elementary processes taking place in the photolysis of CF_3I (Sec. 1) and a description of a kinetic model of CF_3I laser based on this analysis (Sec. 2). This part also contains a discussion of the assumptions underlying a number of kinetic laser models[3,6,8]. The second part describes the laser model and presents the results of numerical computations of the characteristics of actual experimental lasers and a comparative analysis of computed and experimental data. The proposed model is based on rate constants of the elementary processes determined independently of the laser. A sufficiently good agreement of these data is obtained for an initial CF_3I pressure of about 100 Torr. The model is inadequate at low pressures of ~ 20 Torr apparently because of the slow relaxation of "hot" particles, significant contribution from neglected elementary processes, and inaccurate data on rate constants for processes employed in the model.

THERE are many published papers[1-8] that discuss in a varying degree of detail the kinetic model of an iodine photodissociation laser using trifluoromethyl iodide at the 1315 nm wavelength. Typically, however, the majority of authors propose different and as a rule poorly coordinate interpretations of the observed laser characteristics and mainly of the time dependence of laser emission and its energy yield. To approach the correct interpretation of the operation of a given laser it is first necessary to analyze the basic assumptions and conclusions concerning the kinetic laser model presented in the published literature. To simplify the task we try to avoid photodissociative lasers based on other iodides.

1. ELEMENTARY PROCESSES

Laser generation at the 1315 nm wavelength was first observed in 1964 by Kasper and Pimentel[1] in pulsed photolysis of CH_3I and CF_3I. In particular their work contains the most reasonable proposition regarding liable products of photolysis. According to[1] the operation of CF_3I laser is described by the following:

$$CF_3J + h\nu_1 \rightarrow CF_3 + \begin{cases} f_1^* I^* \\ (1 - f_1^*)\, I \end{cases}, \tag{1}$$

$$I^* + h\nu_2 \rightarrow I + 2h\nu_2, \tag{2}$$

$$I^* \rightarrow I + h\nu_2, \tag{2$'$}$$

$$2J^{(*)} + M \rightarrow I_2 + M, \tag{3}$$

$$2CF_3 \rightarrow C_2F_6. \tag{4}$$

Here $h\nu_1$ and $h\nu_2$ are photon energies in the working absorption band and laser emission line respectively and f_1^* is the quantum yield of iodine atoms in the $^2P_{1/2}$ state in process (1) from photodissociation of CF_3I molecules. The quantum yield is close to unity[9,10] although it is not precisely determined. The asterisk in parentheses in (3) means that this process includes all possible combinations of I and I* atoms.[1)]

In contrast to process (3) the recombination of radicals in process (4) is a second-order process at pressures above 5–10 Torr due to the large number of degrees of freedom of the activated C_2F_6 molecule. This follows from the corresponding data on the recombination of methyl radicals ([14], p. 209). The rate constant k_4 of process (4) at T = 400°K was measured by the sector method in[17] ($k_4 = 3.88 \times 10^{-11}$ cm^{3}sec^{-1}).[2)] It turned out that it depends very weakly on temperature (the activation energy $E_4 \sim 1$ kcal/mole[18]).

In their next work, Kasper, Pimentel and Parker[2] considered some mechanism that would limit the generation time and the number of photons in a laser pulse in comparison to the corresponding parameters of the pumping pulse. The authors assume that this limitation

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[1)] The third order of process (3)(or more precisely its first order relative to the concentration of "third bodies") in the case when the "third body" M is represented by the CF_3I molecule at the pressure of 50–220 Torr and T = 373°K is subject to doubt in [11] based on data from an indirect experiment that determined the exchange rate R_{ex} of I^{131} and I^{127} atoms in a mixture of CF_3I^{127} and I_2^{131} vapors illuminated by λ = 5461 Å emission. The above work however apparently failed to consider the possibility of increasing the effective coefficient of extinction of iodine molecules with increasing pressure [12] at λ = 5461 Å. This could have caused the observed deviation from $R_{ex} \propto \sqrt{n}$ (n is the concentration of CF_3I molecules). Much more reliable are data of other papers, such as [13], where the third order of the iodine recombination process is established by direct experiments for a large number of gases and at sufficiently high pressures. There is no reason to consider CF_3I an exception. It seems that (3) can be considered a third-order process up to ~100 Torr.

[2)] Process (4) is described in [15] by a third-order rate constant at particle (argon) concentrations of 10^{18}-10^{19} cm^{-3} and T ~ 2000°K. However the value of the constant used in that work was not determined independently, as we understand from [16], but was obtained from [17] by a simple conversion. The value of k_4 according to [18] is approximately one-half of that given in the text. The latter value seems to be more suitable to laser conditions if we consider the complexity of the "third bodies" used in [17,18].

is due to the rise in the active medium temperature causing a rapid decomposition of the initial molecules in pyrolysis processes. Here in the case of the CF_3I molecule the main role falls to the process

$$CF_3I + I^* \rightarrow I_2 + CF_3 \qquad (5)$$

and the lesser role to the process

$$CF_3I \rightarrow CF_3 + I. \qquad (6)$$

The conclusion that pyrolysis proceeds effectively is supported by data from two experiments given in[2].

1. Analysis of photolysis products based on infrared spectra showed that the degree of decomposition of CF_3I molecules increases from 3 to 75% when the discharge energy in the excitation lamps is increased from 320 to 2600 J. This increase of the degree of decomposition cannot, it seems, be attributed solely to the shift of the spectral peak of the excitation lamps towards the shortwave region.

2. Dilution with argon (376 Torr) or C_2F_6 (31 Torr) at 10 Torr CF_3I lengthens the generation pulse and somewhat increases the energy yield (approximately 1.3 and 1.8 times).

No quantitative description of laser operation is given in[2]. The first attempt to provide such a description is published in Pollack's paper[3]. However it cannot be considered successful in spite of the tempting agreement between his experimental and theoretical relationships.

According to Pollack[3] in alkyl- and perfluoroalkyl-iodide lasers generation terminates due to the direct effect of process (3) on the population excess N of laser levels ($N = N_2 - N_1/2$, where N_1 and N_2 are the populations of the lower and upper laser levels), assuming equiprobable recombinations of the I and I* atoms. It is further emphasized in[3] that among the possible "third bodies" M the I_2 molecule is distinguished by the greatest effectiveness in process (3)[19,20]. In this special case process (3) is written as follows:

$$2I^* + I_2 \rightarrow 2I_2. \qquad (7)$$

According to Christie, Harrison, et al.,[19] $k_7 = 4.7 \times 10^{-30}$ cm^{6}sec^{-1} at room temperature. Bunker and Davidson[20] give a somewhat larger value of k_7 for T = 300°K and the temperature dependence of $k_7(T)$ (see Table I below). Nevertheless even an elementary computation shows that the lifetime of I* atoms is determined to a much larger extent by double collisions with I_2 molecules, i.e., by the process

$$I^* + I_2 \rightarrow I + I_2, \qquad (8)$$

established by Donovan and Husain[21]. According to these authors, $k_8 = 5 \times 10^{-12}$ cm^{3}sec^{-1} for T ~ 300°K. Hence the ratio of population excess N decay rates in processes (8) and (7) for T ~ 300°K is in the order of magnitude

$$\dot{N}(8)/\dot{N}(7) \approx 3k_8/2k_7N_{thr} \approx 10^2 - 10^3,$$

where N_{thr} is the threshold population excess ($10^{15}-10^{16}$ cm^{-3}). The ratio N(8)/N(7) increases even faster with temperature. Furthermore if iodine atoms recombine primarily in an unexcited state, which is in better agreement with the luminescence damping curves for I* atoms[10], then processes (3) and (7) increase rather than decrease N.

Table I

Process	A	q	E	Q	Reference
			kcal/mole		
(3′)	$1.1 \cdot 10^{-32}$ *	0	−1.7	36	[13]
(3″) **	$9.5 \cdot 10^{-34}$	0	−1.27	36	[16,19,20]
(4)	$3.88 \cdot 10^{-11}$	0	~1	96.5	[17,18,28]
(6)	10^{13}	0	54	−54	[14], pp. 257–265
(7)	$1.23 \cdot 10^{-37}$	$^3/_2$	−5.33	36	[19,20]
(8)	$2.9 \cdot 10^{-13}$	$^1/_2$ ***	0	21.6	[21]
(9)	$1.22 \cdot 10^{-10}$	0	17,8	−17.8	[25,26]
(11)	$4 \cdot 10^{-18}$	$^1/_2$ ***	0	21.6	[10]
(−3) (−7) ****	10^{24}	0	—	−36	[14], p. 293
(−6)	$2 \cdot 10^{-26}$	0	—	54	[26,30]
(9)	$3.52 \cdot 10^{-2}$	0	—	17.8	[26,30]

*M = CF_3I; evaluated from boiling point (T_b) and empirical relation $k_3(T_b)$ determined in [13].

**M = Ar; in the region T = 300–1000°K k_3 computed from data in Table I coincides with an accuracy of 11% with the interpretation of V. N. Kondrat'ev [16] (q = −1.3; E = 0).

***In processes (8) and (11) the effective cross section is assumed independent of T.

****The rate of reverse processes is computed from parameters determining the equilibrium constant $K_i = k_{-i}/k_i = B_iT^{\Delta q_i}\exp(-Q_i/kT)$; $B_i = A_{-i}/A_i$, $\Delta q_i = q_{-i} - q_i$, and $Q_i = E_{-i} - E_i$ are given in columns 2, 3 and 5 respectively.

Passing over other significant faults of the model proposed in[3] we merely note that the good agreement between the computed and experimental curves in[3] is due to the "excessively" good fitting of the theoretical curves to the experimental data. This was pointed out before in[4]. Normalization of theoretical parameters with respect to the experimental curves can determine the rate constants of the dominant processes (or their combinations) from laser characteristics only if these processes have been correctly determined. In this approach an independent criterion is obviously necessary to evaluate the degree to which the last condition has been met.

A more valid approach appears to be based on determination methods that are independent of the laser to find rate constants for processes of significance in a given situation. In such a case the degree of agreement between computed and experimental characteristics of the laser is a true criterion of the validity of description. While inadequately studied, this approach may turn out to be merely insufficient (but not basically incorrect, as may happen in the first case). The obvious precondition for such a conclusion is the elimination of data derived from an excessively rough theoretical analysis (whose accuracy does not go beyond an order of magnitude) and from indirect experiments (whose accuracy is limited by assumptions that have not been proved and are not obvious).

A number of faults of Pollack's model[3] have been taken into account in the model proposed in[4]. This model takes into account only processes (1), (2), (3) (where M represents CF_3I molecules), (7), and (8). The model does not take into account changes of the active-medium temperature during pumping and the effect of this factor on the constants of the processes that are allowed for. This essentially limits the applicability of this model almost to the isothermal case (relatively weak pumping and strong dilution with buffer gas). This conclusion is confirmed by a comparison of theoretical and experimental data for generation time Δt and specific energy yield ϵ performed in[4] for various published experiments with CF_3I lasers. If (for rough calculations) the pumping rate in the experiments is characterized by the value of electrical energy of charged capacitors per pumping pulse length and active medium volume of the laser, a satisfactory agreement between the computed and experimental data occurs simultaneously in Δt and ϵ only for the laser described by Maria and Ultee[22] where this quantity amounts to a mere ~ 600 W/cm^3 (for other CF_3I lasers reported in the literature (see[1-3,7,23] for example) this quantity was larger by 3–4 orders of magnitude).

In the case of high-power pumping corresponding to the conditions reported in[1-3,7,23] and CF_3I pressures $\lesssim 100$ Torr, the generation damping mechanism proposed in[4] is not effective enough to explain the observed values of Δt and ϵ even without accounting for the reduction of k_3 and k_7 with increasing temperature. Computation yields excessive values of Δt or ϵ (or both Δt and ϵ) as the theoretical pumping rate is varied (within the limits of indeterminacy of the corresponding experimental value, which is fairly high as a rule). Consequently this model also fails to reflect significant processes that accelerate sharply with increasing temperature of the active medium. We can assume that these are processes (5) or (6) suggested, as indicated, in[2] on the basis of qualitative experimental data.

Process (5) was assumed to be fairly fast in the laser model considered by O'Brien and Bowen[6]. In addition this model takes into account processes (1), (2), (2′), and (8). The effect of temperature change is neglected. The value of k_5 used in[6] is not supported by any argument or citation by the authors. For the same reason as in[3] the agreement between the computation results and experimental data serves as a convincing argument neither in favor of the adopted value of k_5 nor in favor of the model itself.

According to Husain and others[24] and especially[10] the value of k_5 is small ($\leq 2 \times 10^{-18}$ cm^{3}sec^{-1}[10]) for $T \sim 300$°K. According to[10] it does not exceed 3×10^{-18} cm^{3}sec^{-1} for $T = 480$°K. Hence it follows that process (5) could be significant in the case of a high activation energy E_5. Data on E_5 are not available. However[24,25] present a thorough study of the process

$$I + CF_3I \rightleftharpoons I_2 + CF_3, \qquad (9)$$

for which according to Amphlett and Whittle[26], who effectively confirmed the data of Boyd, Downs, and others[25], the value of k_9 is determined by the expression $k_9 = A_9 \exp(-E_9/RT)$ for $A_9 = 1.22 \times 10^{-10}$ cm^{3}sec^{-1} and $E_9 = 17{,}800$ cal/mole (R is the universal gas constant in cal/mole · deg). Hence for $T = 480$°K the value of $k_9 = 2 \times 10^{-18}$ cm^{3}sec^{-1}, i.e., it is of the same order as the upper limit for k_5. Therefore the effect of process (5) could be commensurable with that of process (9) at any temperature only if $E_5 \approx E_9$. It can be readily shown that in this case the main role of processes (5) and (9) in CF_3I laser kinetics is determined by their contribution to the accumulation of molecular iodine, while the direct effect of both processes on redistribution of laser level populations is relatively small. Most probably, however, E_5 is much smaller than E_9. The same conclusion can be reached by comparing the thermal effects of these processes (Q_5 and Q_9). Considering the bond energy D of pair C–I in the CF_3I molecule, or D(C–I), the most reliably determined in[25] (54 kcal/mole), we obtain $Q_5 = -4$ kcal/mole, and $Q_9 = 18$ kcal/mole (from[26], $E_9 \approx Q_9$). For $E_5 < 15$–18 kcal/mole process (5) can be neglected at any temperature.

Nevertheless, in addition to O'Brien and Bowen[6], Skorobogatov and Khomenko[8] also made an attempt to describe the operation of the CF_3I laser assuming a high effectiveness of process (5)[3]. The analysis of various laser mechanisms led these authors to the conclusion that the only mechanism in good agreement with experimental data is that defined by process (7) and an unbranched chain reaction with a link consisting of two stages: process (5)[4] and the process

$$CF_3^{\bullet} + CF_3I \rightarrow C_2F_6 + I^{\bullet}. \qquad (10)$$

The latter was first proposed by Andreeva, Malyshev, et al.[5] to explain the observed quantity of iodine atoms formed in pulsed CF_3I photolysis as a function of xenon admixture. It was assumed that in the presence of a large quantity of xenon hot CF_3^* radicals will be quickly deactivated, reducing the effectiveness of process (10). However the results of various experiments reported in[10] are not a direct proof of process (10) and can be partially explained by a variation in the thermal regime of the laser (i.e., variation in the dependence of T(t) and $k_i(T(t))$, where t is the time) upon the addition of buffer gas or change in pumping emission spectrum rather than by a difference in the behavior of hot and thermallized CF_3 radicals. In particular the possibility of such an interpretation of experimental results involving laser excitation in the spectral region of 240–300 nm was shown in[7]. The curves shown in Figs. 2 and 3 of[5] (broadening of the absorption band, particularly in the direction of the long-wave wing) also indicate the presence of thermal deformation of the absorption band that is considerable in experiments performed without the addition of xenon, and that is weak is experiments with CF_3I diluted with xenon. This deformation directly reflects the increase in vibrational temperature in valence and deformation vibrations of the C–I bond (frequencies $\nu_3 = 284$ cm^{-1} and $\nu_6 = 265$ cm^{-1}[28]). In the central portion of the absorption band (260–270 nm) the deformation effect is indistinguishable in sign from the effect of decay of CF_3I molecules in process (10).

Not having any data from direct experimental measurements of the rate of process (10) we merely note that the procedure described in[10] compared the amplitude

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[3] A process differing from (5) by the replacement of radical C_3F_7 for the radical CF_3 is proposed in [27] to explain the inverse relationship between the Q of the resonator and the quantity of molecular iodine accumulated after the laser pulse. According to [10] such explanation of experimental results is not possible if the degree of dissociation of C_3F_7I molecules due to photolysis $\lesssim 2.5\%$ (i.e., iodine is determined completely without losses) and the heating of the active medium is relatively low, or is not uniquely possible if the degree of dissociation is large (see below).

[4] The formed CF_3 radicals are assumed vibrationally excited.

values of luminescence signal of I^* atoms; in one experiment I^* atoms were formed in the photolysis of pure CF_3I (0.5–5 Torr), and in another CF_3I was diluted with argon in the ratio of 1 : 30. The gas temperature in both experiments was 300–330°K. On the average the amplitudes relative to CF_3I pressure turned out to be larger in the first experiment than in the second by a factor of 1.2. Taking the total number of radicals and the competing process (4) into account, this means that k_{10} cannot be larger than 10^{-13} cm^{3}sec^{-1}. Since $Q_{10} > 20$ kcal/mole[5)] we can hardly expect a considerable increase of k_{10} with increasing "temperature" of CF_3I molecules. On the other hand, the constant k_{10} was taken in[8] as equal to 10^{-11} cm^{3}sec^{-1} to bring the "chain" model into agreement with a real CF_3I laser. Consequently, since the values of k_5 and k_{10} used in[8] appears strongly exaggerated, the agreement of this computation with real laser data has no more meaning than that of the preceding cases[3,6].

As one of the arguments in favor of the "chain" model of the CF_3I laser, Skorobogatov and Khomenko[8] propose that according to this model the instantaneous quantum yield of the laser at the peak of laser emission intensity is close to 2. Referring to[1-3] these authors maintain that this quantity also approaches 2 in the experiments. However none of the cited experimental papers leads to such a conclusion because the measurement accuracy of the total laser emission power and particularly that of the pumping energy absorbed by the laser volume per unit of time are too low without special experimental measures. As far as we can judge the problem of measuring quantum yield was not posed in any of the above papers except for[7]. In the latter the integral quantum yield was determined with a relative standard error of ~ 30% and turned out to be close to 1/3. It was close to unity in the beginning of the generation pulse (see[7] Fig. 4). In view of the above the CF_3I laser model developed in[8] is erroneous.

The thermal regime of the laser and process (6) were considered in[7]. In particular it was shown there that heating of the active medium can be readily accounted for in the description of laser kinetics in terms of the equilibrium model; the faster thermal equilibrium is established among the various vibrational, rotational, and translational degrees of freedom the more accurate the model. The vibrational-translational and vibrational-rotational relaxations of "hot" particles, mainly $C_2F_6^*$ and CF_3^*, are the slowest. Considering that the "exchange" of one vibrational quantum in the interval 700–1250 cm^{-1} requires not more than 1000 collisions on the average we can conclude that the equilibrium model is accurate for an initial pressure of CF_3I vapor of the order of $p_I \sim 100$ Torr or, in the case of lower p_I, for a considerable dilution with buffer gas. We were not able to find any data on k_6 in the form $k_6 = A_6 \exp(-E_6/RT)$ in the literature. There is only a rough theoretical calculation of the rate constant of the CF_3I dissociation process represented as a bimolecular reaction with the participation of argon atoms[15]. Based on the considerations presented in[14] (pp. 257–265) we can assume that A_6 is close to 10^{13} sec^{-1} and $E_6 = D(C-I) = 54$ kcal/mole. In the absence of experimental verification these values of A_6 and E_6 may be considered the most probable. Incidentally, as we show below, if the true value of E_6 is not much less than the above (35–40 kcal/mole) or A_6 is not much more than the above (~ 10^{15}–10^{16} sec^{-1}) process (6) cannot affect the laser generation.

2. THE KINETIC LASER MODEL

We consider the results of an attempt to define CF_3I laser kinetics restricted to the most reliably determined or the most convincing processes. In addition to the obviously important processes[6)] (1)–(4) and (7)–(9) the proposed kinetic model includes the following to make the situation more precise: process (6), processes reverse to (3), (6), (7), and (9)[7)] (denoted by (–3), (–6), (–7), and (–9)), the process

$$I^* + CF_3I \to I + CF_3I \qquad (11)$$

and finally the photodissociation of iodine molecules yielding I and I^* atoms ($\lambda < 499.0$ nm) [process (12)] and two I atoms ($\lambda > 499.0$ nm) [process (13)]. The model does not take into account questionable processes ((5), (10), $CF_3^* + CF_3I \to C_2F_6 + I$—process (14), $I^* + CF_3 \to I + CF_3$—process (15), and others), known weak processes (spontaneous emission, heat exchange across the laser cell surface, deactivation of I^* atoms at the wall), and high-temperature processes ($CF_3 \rightleftarrows CF_2 + F$—process (16), $CF_3 + F \to CF_4$—process (17), $2CF_2 \rightleftarrows C_2F_4$—process (18), and others).

The time dependences of specific output power (w) of the laser, concentration of molecules of CF_3I (n), I_2 (n_i). and CF_3 radicals (n_r), total concentration (N_s) of iodine atoms excess population (N) of laser levels, and finally temperature (T) were calculated on the BÉSM-4 computer as solutions of a system of six balance equations[8)] solved for dn/dt, dn_i/dt, dn_r/dt, dN_s/dt, dN/dt, and dT/dt, taking into account the equation[9)]

$$w = C\chi(N - N_{\text{thr}})F(N_{\text{thr}}),$$

where $C = 10^{-12}$ if all quantities are measured in CGS units,

$$\chi(N - N_{\text{thr}}) = \begin{cases} 0 \text{ for } N < N_{\text{thr}} \\ 1 \text{ for } N \geqslant N_{\text{thr}} \end{cases},$$

$F(N_{thr})$ is the value of F(N) for $N = N_{thr}$, and F(N) is a function of N and other variables (n, n_r, n_i, N_s, and T). To save space we write only the equation for N:

[5)] Q_{10} should be 20 kcal/mole in the case of unexcited CF_3 [25,29].

[6)] According to [10] recombination of I and I^* atoms as well as of I^* and I^* in processes (3) and (7) is considered slow and is neglected in the computation.

[7)] The constants of reverse processes were either determined experimentally (k_9 [29]), or were computed from the known equilibrium constants (K_{-3}, K_{-6}, K_{-7} [30]).

[8)] The equation $n_0 = n + N_s + n_i/2$ following from the conservation of iodine atoms was used to check the accuracy of the computation.

[9)] The equations for w and dN/dt are written in the approximation of saturated laser transition and quasistationary concentration of photons in the resonator. This is permissible if we are interested only in the value of w averaged over the coordinates, spectrum and time (within an interval long enough to average spikes but short in comparison to the length of the processes under consideration).

$$\frac{dN}{dt}=\begin{cases}F(N) \text{ for } N<N_{\text{thr}} & (w=0)\\ 0 \quad\text{ for } N\geqslant N_{\text{thr}} & (w\geqslant 0)\\ F(N) \text{ for } w<0.\end{cases}$$

This representation of the right-hand side has a formal character (w < 0 does not occur), yet it is convenient for numerical integration with a sufficiently small increment (5×10^{-8} sec). It is not difficult to find F(N) and to derive the remaining equations.

For the case of the real laser under investigation the probability γ_1 (sec^{-1}) of CF_3I molecule dissociation (process 1) is well approximated by the curve

$$y=(xe^{1-x})^4,\quad y=\gamma_1/\gamma_{1max},\\ x=t/t_{max}$$

(without taking the thermal deformation of the absorption band into account). Measurements showed that $\gamma_{1\,max}$ = 2220 sec^{-1} and t_{max} = 75 μsec with a relative standard error of 20–30%. The relative probabilities of iodine molecule dissociation for the same source were computed as 1.1 (γ_{12}/γ_1) and 4.3 (γ_{13}/γ_1).

Table I shows the utilized values of parameters for the rate constants in the form

$$k_i=A_iT^{q_i}\exp(-E_i/RT)$$

and equilibrium constants K_i (in the same form except for Q replacing E). The values of A refer to the same particle (an atom or a radical in the case of recombination); the units of measurement used are cm, sec, °K.

For the investigated laser within a range of CF_3I pressures p_I = 20–100 Torr and Ar pressures p_{II} = 0–500 Torr the values of N_{thr} are well described by the expression[10] $N_{thr} = 10^{13}\,(7.5\,p_I + 1.5\,p_{II})$, where N_{thr} is expressed in cm^{-3} and p_I and p_{II} in Torr. The stationary heat capacity c_{vI} of gaseous CF_3I according to[30] increases with T fairly quickly at first (from 14.9 cal/mole · deg for T – 300°K to 20 cal/mole · deg for T = 600°K) and then slower (23 cal/mole · deg for 1500°K). In the computation for p_I = 100 Torr and p_{II} = 0, the results of which are given in Fig. 1, we assumed c_{vI} = 17 cal/mole · deg.

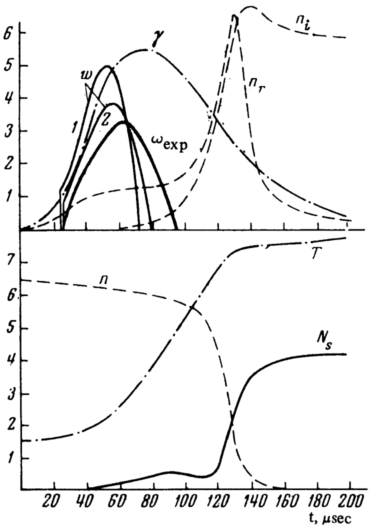

FIG. 1. Time characteristics of a CF_3I laser; p_I = 100 Torr, p_{II} = 0 (without argon). Units of measurement: w–0.1 kW/cm^3, γ–400 sec^{-1}, n_i–10^{17} cm^{-3}, n_r–10^{16} cm^{-3}, n–5 × 10^{17} cm^{-3}, N_S–5 × 10^{17} cm^{-3}, T–200°K. For computed curves (except curve 2) c_{vI} = 17 cal/mole·deg, γ_{1max} = 2.22 × 10^3 sec^{-1}, N_{thr} = 7.5 × 10^{15} cm^{-3}; for curve 2: γ_{1max} = 1.55 × 10^3 sec^{-1}, N_{thr} = 5.26 × 10^{15} cm^{-3}. Heavy line denotes experimental data.

The computed value of specific energy yield for curve 1 in Fig. 1 is ϵ_1 = 16.5 mJ/cm^3 for a laser emission pulse length of Δt_1 = 49 μsec. The corresponding experimental values are ϵ_e = 14 mJ/cm^3 and Δt_e = 73 μsec. The nature of the deviation ($\epsilon_1 > \epsilon_e$, $\Delta t_1 > \Delta t_e$) points to the inaccuracy of the computed value of γ_{1max} as the cause (excessive due to the hard-to-account-for reduction in the transparency of the laser cell in prolonged use). In fact curve 2 obtained for γ_{1max} amounting to 0.7 of the previous value appears to be in better agreement with the experiment (ϵ_2 = 13.9 mJ/cm^3, Δt_2 = 55 μsec).

In order to establish the cause of generation termination for this model at p_I = 100 Torr (p_{II} = 0) we consider the ratio of inputs to laser emission from various processes for time t = 70 μsec close to the generation termination time t_{ter} = 73 μsec. According to Table II the cause of termination (in all investigated cases) is quenching of the I* atoms apparently in process (8). To investigate the cause of the high effectiveness of process (8) we analyze data on the contributions to the rate dn_i/dt of iodine molecule accumulation:

time, μsec:	$t=70$	$t=90$	$t=120$
dn_i/dt:	$+0.41$	$+0.154$	$+0.044$

We find that in this case the rate of molecule accumulation is due to the processes of tri-molecular recombination of iodine atoms (process (9) turns out useful here since it proceeds in the reverse direction).

At relatively low pressures ($p_I \sim$ 20 Torr) the usefulness of this model is not evident because of the insufficient rate of the vibrational-translational relaxation. However even in this case we observe a qualitative agreement between the computed and experimental characteristics of the laser (see Fig. 2) if we introduce the concept of effective heat capacity $(c_v)_{eff} < c_v$. This

Table II

Process	Process rate v × 10^{-21} [$\text{cm}^{-3}\,\text{sec}^{-1}$] at time t		
	$p_I = 100$ $p_{II} = 0$ t_{end} = 73 $t = 70$	$p_I = 20$ $p_{II} = 0$ t_{end} = 100 $t = 90$	$p_I = 20$ p_{II} = 100 (Ar) t_{end} = 129 $t = 120$
Pumping (1)	+6.71	+1.20	+0.73
Quenching (8), (11)	--6.26	–0.33	–0.49
Splitting (9), (–9)	–0.22	+0.08	0.00
Iodine photodissociation (12, (13)	–0.07	–0.01	–0.01
Iodine recombination (3), (7)	+0.95	+0.01	+0.05
Pyrolysis (6), (–6)	+0.15	+0.02	+0.03
Generation of laser emission (2)	1.25	0.98	0.31
Iodine recombination	+0.95	+0.015	+0.046
Iodine splitting	–0.44	+0.151	+0.007
Iodine photodissociation	–0.10	–0.012	–0.009
dn_i/dt	+0.41	+0.154	+0.044

Note: p is in Torr, t and t_{end} in μsec.

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[10] With an accuracy of the above value of γ_{1max} = 2220 sec^{-1} and the equality f_1^* = 1.

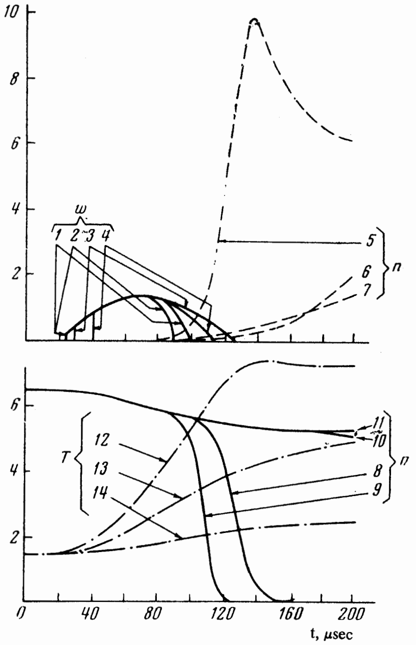

FIG. 2. Time characteristics of CF_3I laser for $p_I = 20$ Torr and $p_{II} = 0$, and $p_{II} = 500$ Torr (Ar). Units of measurement are w—0.1 kW/cm³, n_I—10^{16} cm^{-3}, n—10^{17} cm^{-3}, T—200°K. In the computations, for curves 1, 5, 8, 12—$p_{II} = 0$, $\gamma_{1\max} = 2.22 \times 10^3$ sec^{-1}, $N_{thr} = 1.5 \times 10^{15}$ cm^{-3}, $c_{vI} = 13$ cal/mole·deg; for curves 2, 9—$p_{II} = 0$, $\gamma_{1\max} = 2.22 \times 10^3$ sec^{-1}, $N_{thr} = 1.5 \times 10^{15}$ cm^{-3}, $c_{vI} = 10$ cal/mole·deg; for curves 3, 6, 10, 13—$p_{II} = 100$ Torr, $\gamma_{1\max} = 2.22 \times 10^3$ sec^{-1}, $N_{thr} = 3 \times 10^{15}$ cm^{-3}, $c_{vI} = 16$ cal/mole·deg, $c_{vII} = 2$ cal/mole·deg; for curves 4, 7, 11, 14—$p_{II} = 500$ Torr, $\gamma_{1\max} = 2.22 \times 10^3$ sec^{-1}, $N_{thr} = 9 \times 10^{15}$ cm^{-3}, $c_{vI} = 16$ cal/mole·deg, $c_{vII} = 3$ cal/mole·deg.

approach is based on the following considerations.

The main portion of energy is emitted in the form of vibrational excitation of $C_2F_6^*$, CF_3^*, and I_2^* molecules and radicals (processes (4), (1), (3), (7), (−9)). Fairly probable is the transfer of energy from directly excited modes to other modes of the same particles, with the exception of I_2^* (due to anharmonicity at large amplitudes), then to other particles, in particular CF_3I molecules (due to the proximity of resonance at a number of vibrational frequencies[28,31]), and finally to vibrational frequencies ν_3 and ν_6 of the CF_3I molecule by virtue of both factors. The last two modes determine the effectiveness of processes (9) and (6). On the other hand as p_I decreases (with $p_{II} = 0$) the relative role of process (9) increases since its contribution (at $T \gtrsim 800$°K) is approximately proportional to p_I^2 and rapidly rises with temperature; at the same time the contribution of processes (3) and (7), mainly significant at low temperature, decreases approximately as p_I^3. In such an energy transfer the translational and rotational degrees of freedom may remain uninvolved allowing us to assume, at low p_I and p_{II}, that $(c_v)_{eff}$ is less than c_v by a few (up to 6) cal/mole · deg.[11]

Data computed for $p_I = 20$ Torr and $p_{II} = 0$, 100, and 500 Torr shown in Fig. 2 give a qualitatively true picture of the lagging of laser pulse w(t), first a slight rise and then a decrease of ϵ, as argon dilution of CF_3I is increased. (For example these data can be compared with the corresponding oscillograms in[7]). However for $p_I = 20$ Torr and $p_{II} = 0$ (the case of the highest nonequilibrium) the excess in ϵ and Δt is eliminated only for $(c_v)_{eff} \sim 6$–8 cal/mole · deg. This casts a doubt on the adequacy of this model of laser operation at low p_I. We can merely assert that as p_I decreases (and $p_{II} = 0$) the role of limiting the values of ϵ and Δt gradually shifts from processes (3) and (7) to process (9) (see Table II, columns 3 and 4) in the absence of any other limitations, and that other processes (6), (12), and (13) included in the model are in no case significant for generation.

Another inaccuracy of the model consists in the description of the last phase of the photolysis pulse when the temperature of the active medium approaches 1500°K.[12] This is due to the omission of processes ((16)—(18), etc.) studied with the aid of shock tubes[15,32] that accumulate CF_4, CF_2, CF, and C instead of C_2F_6 if the temperature exceeds 1500—1800°K[15,32]. The high degree of heating ($T \gtrsim 1500$—1800°K) was determined by V. M. Smirnov from mass-spectrometric analysis of gaseous products of pulsed photolysis of CF_3I. For an initial CF_3I pressure of 60 Torr, photodissociation degree of 20—40%, and pumping pulse length of ~60 μsec, the following distribution was established with a high-Q resonator: CF_4—70%, C_2F_6—8—8.5%, and C_2F_4—5% (the determined quantity of CF_3I was taken as 100%). In both cases the walls of the laser cell were coated with soot after the passage of the pulse. The frequently observed increase of optical density of the medium at $\lambda \sim 260$ nm in the last stage of CF_3I photolysis seems to be the sought indication of the appearance of CF_2 radicals (see[7] Fig. 3) that are absorptive at this wavelength[33].

It is not difficult to take processes (16)—(18) into account within the equilibrium approximation since the rate constants of these processes are known.

If we are not interested in the fate of CF_3 radicals, in the addition to the above we can find also other experimental verifications of the CF_3I laser kinetics model discussed above.

1. Experiment shows[5] a multiple reduction of iodine content in the end products of photolysis following a multiple dilution of CF_3I with buffer gas. In our model a similar result follows from Fig. 2 for example:

$$n_0 - n(\infty)\big|_{p_I=20\ \text{Torr},\ p_{II}=0} \gg n_0 - n(\infty)\big|_{p_I=20\ \text{Torr},\ p_{II}=500\ \text{Torr}};$$

($n_I(t) = \frac{1}{2}(n_0 - n(t)$ for $t \to \infty$).

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[11] We should also not exclude the possibility of a reverse variant of energy transfer, i.e., that via translational and rotational degrees of freedom without involving many modes. This is also favored by the anharmonicity of the "hot" particle modes and in addition by the low frequencies ν_3 and ν_6 of the CF_3I molecule ($\nu_3 = 284$ cm^{-1}, $\nu_6 = 265$ cm^{-1}).

[12] The prolonged action of intense ultraviolet pumping radiation on CF_3I and apparently many other iodide vapors can be conveniently divided into three stages according to Figs. 1 and 2: laser stage (for our case of $p_I = 100$ Torr the interval is t = 0–90 μsec), pyrolysis stage (90–140 μsec), and quasi-equilibrium stage (t > 140 μsec). The indicated inaccuracy appears at the end of the pyrolysis stage and therefore does not affect the accuracy of the laser generation description.

2. We have noted the dependence of $n_i(\infty)$ on the resonator Q; although it was determined in experiments with another perfluoroalkyl iodide[27], it follows from our model, in view of the fact that a situation similar to a thermal explosion occurs in the pyrolysis stage and is characterized (within a certain range of pumping pulse energies) by an extremely strong dependence of the decomposition of the initial iodide on the emitted thermal energy. In the case of CF_3I the thermal explosion occurs at $T \sim 1200$°K[13)] thanks to a sequence of three rapid processes, (6), (9), and (4), provided of course that the loss of CF_3 radicals in processes (16) and (17) is still insignificant. Self-acceleration is due to the liberation of $54 - 18 + 96 = 25$ kcal/mole for each sequence of these three elementary acts. The pyrolysis stage of the phenomenon should obviously be coordinated with the end of the pumping pulse if the energy carried away by the laser emission is to affect the I_2 content in the photolysis products.

3. The appearance of thermal explosion in the form of a sharp drop in the value of n(t) for $t \sim 140\ \mu$sec (from the beginning of photolysis) was determined in[7] where the laser cell was exposed to radiation at $\lambda = 285$ nm ([7], Fig. 3 c). The thermal deformation of the absorption band contour is relatively small for this wavelength. Similar dependencies of n(t) in this model are shown in Fig. 1 and Fig. 2 (curves 8 and 11).

4. The oscillogram obtained by exciting C_3F_7I laser (45 Torr) in the absorption band of molecular iodine of $\sim$490 nm ([34] Fig. 2d) clearly shows both the rapid rise of $n_i(t)$ apparently corresponding to the pyrolysis stage (processes analogous to (9) and (6)) and the following slow decrease of n_i. According to Fig. 1 (curve $n_i(t)$ and Fig. 2 (curve 5) the latter effect is also described by this model and corresponds to thermal dissociation of iodine molecules. In this model the accumulation of iodine molecules in excess over the equilibrium is due to the fact that they are the direct product of thermal explosion (see above). Obviously their recombination accumulation cannot result in excess over equilibrium concentration.

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[13)] If the iodine atom concentration is significant the acceleration of heat emission should commence at $T \sim 800$°K due to (9) and (4)(gross process $2I + 2CF_3I \rightarrow 2I_2 + C_2F_6 + 60$ kcal/mole).

Translated by S. Kassel
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