Accumulation of iodine molecules in flash photolysis of CF_3I and *n*-C_3F_7I vapor

I. M. Belousova, N. G. Gorshkov, O. B. Danilov, V. Yu. Zalesskiĭ, and I. L. Yachnev

(Submitted March 15, 1973)
Zh. Eksp. Teor. Fiz. 65, 517–523 (August 1973)

It is established experimentally that no recombination accumulation of iodine molecules occurs after flash photolysis of CF_3I and C_3F_7I vapor before the initiation of pyrolysis. Removal of iodine atoms at this stage of photolysis occurs in the rapid reverse recombination reaction. Pyrolysis is accompanied by a fast increase of the concentration of I_2 and stops the stimulated emission on the $^2P_{1/2}$-$^2P_{3/2}$ transition in the iodine atoms.

1. INTRODUCTION

It is commonly assumed[1-3] that the premature termination of oscillation in perfluoroalkyliodide photodissociation lasers, which is usually observed at not too low initial active-gas pressures and not too weak pumping, results from quenching of excited iondine atoms by I_2 molecules. This follows from experiments described in[4]. Under the conditions that characterize these experiments, with simultaneous oscillography of the laser radiation (1315 nm) and probe radiation (465 nm), in the cases of both CF_3I and n-C_3F_7I the oscillation terminates at practically the same moment when the rapid accumulation of iodine molecules begins. The causes of iodine molecule accumulation have been discussed in the literature.[2-5] On the basis of[5] we select as the two most probable causes:

1) Recombination of iodine atoms.

2) Rising temperature of the active medium, accompanied by pyrolysis of the original molecules:

$$RI \to R + I, \quad I + RI \to R + I_2, \qquad (1)$$

where R is either the CF_3 or the C_3F_7 radical.

The two processes differ sharply with respect to the characteristic accumulation rate of iodine molecules, as well as its dependence on the initial gas pressure and on temperature. Numerical calculations in[5] show that in the case of recombination the accumulation rate of iodine molecules is relatively small and that it increases for higher initial gas pressures and lower temperatures. In the case of the second accumulation mechanism the temperature dependence becomes of threshold character. Before a certain threshold temperature is reached, $T_{thr} \approx 1000$ K, the pyrolysis processes resulting in the accumulation of iodine molecules develop very rapidly. The threshold character and high rate of accumulation are clearly apparent in the experiments of[4], at least in the case of C_3F_7I photodissociation lasers (PDL). It may be inferred that under the given conditions iodine molecules are formed in a fast process whose "switching-on" time practically coincides with the termination of oscillation and depends on the state of the gaseous medium. It was reasonable to identify this process as pyrolysis, i.e., to assume that under the conditions of[4] the second of the aforementioned accumulation mechanisms was responsible for the termination of oscillation. It was then natural to attempt the realization of conditions under which oscillation would be terminated by the first mechanism of iodine molecule accumulation, i.e., by the recombination of iodine atoms. An obvious means of delaying the onset of pyrolysis after the termination of oscillation is effected by iodine molecules formed through atomic recombination, is to increase the concentration of the buffer gas (the inactive diluent gas). It was of decided interest to achieve such conditions, because in this way alone an attempt could be made to influence the iodine molecule accumulation rate by adding impurities that would react with the iodine atoms.

In addition to investigating the mechanism that terminates oscillation, we have in this work, which is a continuation of[4], endeavored to achieve the aforementioned conditions by diluting the active gas (CF_3I or C_3F_7I) with tetrafluoroethylene or tetrafluoromethane. We also proposed to test the efficiency with which the first of these diluents could be iodized to finally form a saturated $C_2F_4I_2$ molecule in competition with the recombination of iodine atoms and thus to retard the accumulation of I_2 molecules. It will be shown that the experimental results were somewhat unexpected.

2. EXPERIMENT

A calorimeter and the registration channel of a 465-nm reference signal were added to the apparatus used in[4]. Our technique enabled us to register simultaneously: 1) the accumulation of molecular iodine, in time, according to absorption at $\lambda = 465$ nm, 2) the shape of the stimulated emission pulse ($\lambda = 1315$ nm), 3) the shape of the pump pulse ($\lambda = 270$ nm), and 4) the energy of the stimulated emission pulse.

It should be noted that the sensitivity of molecular iodine registration in several of the described experiments corresponded to 5×10^{15} cm^{-3} concentration. This was achieved by registering the difference between the probe and reference signals using an S1-42 oscillograph with a differential amplifier.

3. EXPERIMENTAL RESULTS

Figure 1 shows typical oscillograms of pulses of (a) stimulated emission, (b) pump radiation, (c) the probe light signal ($\lambda = 465$ nm) passing through the vessel containing the active medium, and (h) the corresponding reference signal at the same wavelength, for pure C_3F_7I (30 Torr). The pulse oscillograms of stimulated emission (d) and the probe signal (e) in the same figure correspond to a mixture of C_3F_7I and C_2F_4 in the initial concentration ratio 1 : 5 at 30 Torr initial pressure of C_3F_7I. A comparison of the oscillograms shows that the dilution of C_3F_7I vapor with tetrafluoroethylene delays the time when oscillation terminates and rapid accumulation of molecular iodine begins. It

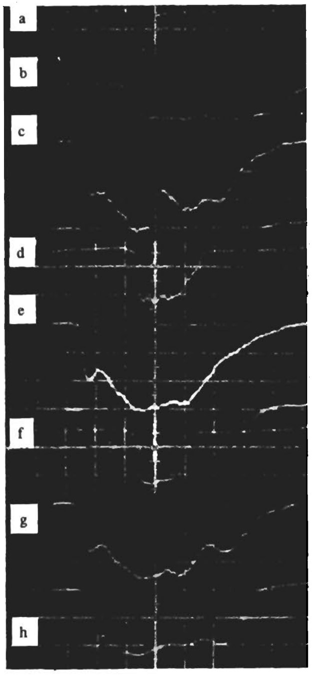

FIG. 1. Oscillograms of pulses: (a) emission, (b) pumping, and (c) the probe signal for C_3F_7I at 30 Torr; (d) emission and (e) the probe signal for a mixture of C_3F_7I and C_2F_4 at the partial pressures 30 Torr and 150 Torr, respectively; (f) emission, (g) the probe signal, and (h) the reference signal for a mixture of C_3F_7I and CF_4 at the partial pressures 30 Torr and 150 Torr, respectively.

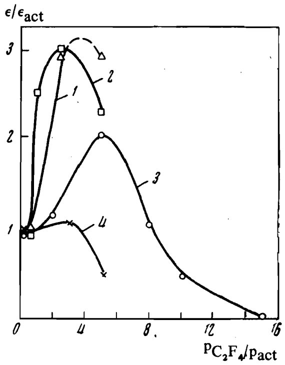

FIG. 2. Dependence of the energy density of stimulated emission on C_2F_4 pressure with: 1—CF_3I, 30 Torr; 2—CF_3I, 60 Torr; 3—C_3F_7I, 30 Torr; 4—C_3F_7I, 60 Torr. ϵ_{act} and p_{act} are the energy density and the pressure of the active gas.

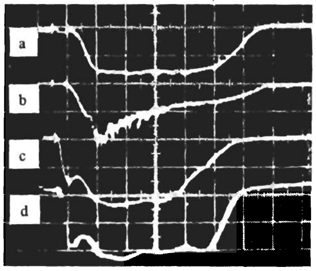

FIG. 3. Oscillograms of pulses: (a) pumping, (b) emission, (c) the probe signal, and the probe reference signal for a mixture of C_3F_7I and C_2F_4 at the partial pressures 30 Torr and 300 Torr, respectively. The pedestal of the emission pulse was caused by noise induction.

is characteristic that these two effects are observed simultaneously, independently of the dilution. The same pattern is observed qualitatively when the active gas is CF_3I.

Thus, dilution with tetrafluoroethylene delays the termination of oscillation and delays molecular iodine accumulation, while these two effects remain simultaneous. The only difference lies in the fact that the addition of tetrafluoroethylene to CF_3I produces a greater effect than in the case of C_3F_7I at the same initial pressure. This is seen especially clearly in the dependence of ϵ (the energy density of stimulated emission) on C_2F_4 pressure (Fig. 2). The left wings of the bell-shaped curves in Fig. 2 are considerably steeper for CF_3I than for C_3F_7I. This result can be attributed to considerable difference between the specific heats of these molecules and hence to a different "sensitivity" of the medium's pre-pyrolytic heating time to the addition of the buffer gas.[5] It might appear that $p_{C_2F_4}$ could increase until the duration of oscillation begins to be limited by recombination accumulation of molecular iodine (the rise of temperature is slowed and both the pressure and recombination rate of atomic iodine are increased). Accordingly, as $p_{C_2F_4}$ is further increased, the value of ϵ, having passed through its maximum, should begin to decrease; this is actually observed in Fig. 2. However, the experiments showed that the decrease of ϵ represented by the right wings of the curves in Fig. 2 resulted mainly not from the recombination accumulation of molecular iodine but from the quenching of excited iodine by molecules of tetrafluoroethylene and whatever impurities were present. This is clearly seen in Fig. 3 for C_3F_7I vapor, initially at 30 Torr, which had been diluted in a 1 :12 ratio with tetrafluoroethylene. Here the slow damping of oscillation is not accompanied by appreciable accumulation of iodine molecules.

The recombination mechanism of oscillation stoppage (unlike the pyrolytic mechanism) should be characterized by a decreasing duration of oscillation as the buffer gas pressure is increased. This did not occur in the described experiments, and three hypotheses can be stated in explanation. The conditions for oscillation termination by "recombination" molecular iodine might not have been achieved because: 1) The formed iodine atoms iodized the tetrafluoroethylene; 2) a too strongly "quenching" buffer gas had been selected; or 3) there exists a "natural" and quite strong mechanism for removing the formed iodine atoms. We shall now discuss these hypotheses.

4. DISCUSSION OF RESULTS

The first hypothesis was tested in experiments where C_2F_4 was replaced by tetrafluoromethane (CF_4) as the diluent of the active gas. The possibility of iodizing this molecule (CF_4) is obviously excluded because it is a saturated compound. On the other hand, there should be little difference between the buffering effects of CF_4 and C_2F_4. Curves g and f of Fig. 1 show that dilution of the active gas with tetrafluoromethane produces the same result as dilution with tetrafluoroethylene in the channels registering the stimulated emission and the changing concentration of iodine molecules. Therefore the first explanation of failure to achieve recombination-induced termination of oscillation must be dropped. However, from the fact that recombination accumulation of iodine molecules does not occur with CF_4, it cannot be concluded definitely that C_2F_4 is not iodized efficiently. For example, such a conclusion would have no basis if the last of the three hypotheses should be confirmed for the evident inefficiency of iodine atom recombination.

The second and third hypotheses were tested by means of a numerical calculation based on the kinetic model of the CF_3I PDL that was proposed in[5]. The appropriate equations contained an additional term to account for quenching of excited iodine atoms by CF_3 radicals. We used numerical values given in[6] for the rate constants of iodine atom quenching by C_2F_4 molecules, and values of the constants for iodine recombination assisted by these molecules that are given in Kondrat'ev's book[7]. A basis for the third hypothesis (removal of the atomic iodine formed in photolysis) is given in[8], where experimental results were accounted for by introducing the idea of an extremely high rate of reverse recombination (i.e., $CF_3 + I \rightarrow CF_3I$).

The value obtained in[8] for this rate constant $[(4-6.5)\times 10^{-11}\ cm^3/sec]$ is two or three orders greater than the value obtained by a computation using the pyrolysis constant (the reverse process), assuming that the ratio of these constants is the same as in thermodynamic equilibrium. A possible explanation of this discrepancy is that the rate of vibrational relaxation limits the rate of pyrolysis. In that case the calculated reverse recombination rate constant utilized in[5] is very low and the discussion in[2] must be considerably amplified. Calculations performed with several values of the reverse recombination constant showed that for a correct description of molecular iodine accumulation in the active medium of PDL we must assume that the reverse recombination process is highly efficient. Otherwise, the probe signal (Fig. 1) would necessarily reflect relatively slow recombination accumulation of iodine molecules in the pre-pyrolysis stage, especially in the case of dilution with a buffer gas (curve 11 of Fig. 4). This does not actually occur, i.e., molecular iodine is not accumulated before pyrolysis (curves 9 and 10 of Fig. 4).

A calculation based on the assumption of a high rate of reverse recombination yielded high overestimates of the emission energy density, which were brought into consistency with experiment simply by taking into account the aforementioned quenching of iodine by CF_3 radicals. (For the model described in[5] this was not essential because of the rapid accumulation of strongly quenching molecular iodine.) For the rate constant of iodine quenching by CF_3 radicals we used the value $1.5\times 10^{-11}\ cm^3/sec$, which follows from the work of[9] if the reverse recombination of metastable iodine atoms is neglected.

The data represented in Fig. 4 enable us to judge how closely the kinetic model approaches a correct description of the action of a CF_3I photodissociation laser. The calculations depended very critically upon the value chosen for the reverse recombination constant. The closest agreement between the experimental and calculated time dependences of the laser power output, iodine molecule concentration, and energy density for both undiluted and diluted CF_3I was attained when the value of the reverse recombination constant was taken to be $4\times 10^{-11}\ cm^3/sec$, which is quite close to the result obtained in[8]. The calculated results for this case are represented in Fig. 4 and in the table. The results correspond to the value determined in[10] for the recombination constant of radicals forming the C_2F_6 molecule. For a value of this constant that is about one-half smaller, in accordance with[9], the best agreement between calculations and experiment is found when the value of the reverse recombination constant is $\sim 3\times 10^{-11}\ cm^3/sec$. It must be kept in mind that because of somewhat weaker pumping when the initial pressure of CF_3I was 60 Torr, the calculation yielded a somewhat overestimated value of the pumping rate.

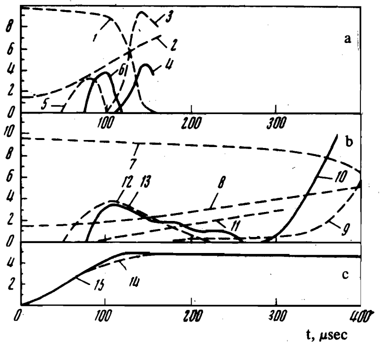

FIG. 4. Time dependences of the concentration of active molecules n and of iodine molecules n_i, of the temperature T, of emission power output w, and of pump intensity γ. a–for pure CF_3I at 30 Torr: 1–concentration of active molecules, 2–gas temperature, 3–calculated I_2 concentration, 4–measured I_2 concentration, 5–calculated power output, 6–registered power output. b–for CF_3I (30 Torr) mixed with C_2F_4 (150 Torr): 7–concentration of active molecules, 8–gas temperature, 9–calculated I_2 concentration, 10–measured I_2 concentration, 11–I_2 concentration calculated for the recombination mechanism of iodine molecule accumulation, 12–calculated power output, 13–measured power output. c–Pump intensity: 14–calculated, 15–registered. Scales: n–$10^{16}\ cm^{-3}$/div., w–0.1 kW-cm^{-3}/div., T–200 K/div., n_i–$10^{16}\ cm^{-3}$/div., γ–7 × $10^{-4}\ sec^{-1}$/div.

Relative values of some PDL parameters

p, Torr		$\epsilon \times 10^3$, J/cm³	Δt of oscillation, μsec	t of I_2 accumulation, μsec ($n_i = 0.05\ n_0$)
CF_3I	C_2F_4			
30	—	6,6 * 5	60 43	110 116
30	150	17,8 14,5	180 178	250 294
60	—	13,3 9,4	76 50	118 90
60	150	27 28	151 124	230 210

*Upper values—calculated; lower values—experimental.

5. CONCLUSIONS

1. We have established experimentally and explained the absence of recombination accumulation of molecular iodine before the onset of pyrolysis in photodissocation lasers operating with the simplest perfluoroalkyliodides, both when the active gas is pure and when it is diluted with a buffer gas.

2. Pyrolysis of the active molecules was shown to be the principal cause of both I_2 accumulation and the termination of oscillation in the simplest perfluoralkyliodides.

3. We confirmed the conclusion reached in[8] that in the kinetics of photodissociation lasers operating with perfluoroalkyliodides reverse recombination and the quenching of excited iodine atoms by CF_3 radicals have very important roles.

4. In accordance with the best agreement of calculated and experimental data on emission energy and power output, and consistent with the data on the accumulation of iodine molecules, the reverse recombination constant is chosen to be $4\times 10^{-11}\ cm^3/sec$.

5. It was shown that PDL energy output is considerably enhanced by diluting the active gas with C_2F_4 or CF_4 buffer gas.

The authors are indebted to L. A. Dmitrieva for computer calculations.

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Translated by I. Emin
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