Selective Pumping Effect of a Photodissociative Laser

L. K. Gavrilina[1], V. Ya. Karpov, Yu. S. Leonov[1], V. A. Sautkin[1], and A. A. Filyukov

Applied Mathematics Institute, USSR Academy of Sciences

Submitted September 15, 1971

Zh. Eksp. Teor. Fiz. **62**, 485–489 (February, 1972)

Additional selective pumping in a iodine perfluoralkyl photodissociative laser, which results in photolysis of molecular iodine, is studied experimentally and theoretically. A comparison of the theoretical conclusions and the experiments shows that in contrast to CF_3I, C_3F_7I photolysis involves a mechanism of storage of molecular iodine which resembles the recombination mechanism. Additional sources of molecular iodine production are essential for CF_3I.

IN the simple model of Zalesskiĭ and Venediktov[1], the quenching of the generation of a photodissociation laser based on perfluoralkyl-iodides is an unambiguous consequence of the deactivation of the excited atoms of the iodine by the iodine molecules; the kinetics of this deactivation is described by the scheme

$$RI + h\nu(\lambda \sim 3000\,\text{Å}) \xrightarrow{k_1} J(^2P_{1/2}) + R, \quad (1)$$

$$2I(^2P_{1/2}, {}^2P_{3/2}) + I_2 \xrightarrow{k_2} 2I_2, \quad (2)$$

$$2I(^2P_{1/2}, {}^2P_{3/2}) + M \xrightarrow{k_3} I_2 + M, \quad (3)$$

$$I(^2P_{1/2}) + I_2 \xrightarrow{k_4} I(^2P_{3/2}) + I_2 \quad (4)$$

(the notation is the same as in[1]).

If this model is valid for a certain concrete substance RI, then one of the methods of lengthening the generation and increasing the total energy output, other conditions being equal, may be the use of an additional selective source of radiation in the absorption band of the molecular iodine. Moreover, if this kinetic model is not complete in the concrete case, in the sense of describing the processes that lead to the accumulation of the molecular iodine, but the main mechanism of generation quenching still remains the reaction of quenching by the iodine molecule, then the effect of the additional selective pumping should also lead to an increase of the total energy output of the stimulated emission. The effect of the influence of selective pumping of the working medium subjected to strong pyrolysis, for example CF_3I as the working medium in the absence of strong dilution by a buffer gas, is precisely such a case. The effect of selective pumping supplements the kinetic scheme (1)—(4) by the process

$$I_2 + h\nu(\lambda \sim 5000\,\text{Å}) \xrightarrow{k_5} 2I(^2P_{1/2}, {}^2P_{3/2}), \quad (5)$$

which leads to a decrease in the concentration of the molecular iodine, and also to pumping of the iodine atoms to the excited level. When an iodine molecule absorbs a quantum of light, it dissociates and if the wavelength of the light is shorter than 4995 Å, the photolysis products are one iodine atom in the excited state $^2P_{1/2}$ and one iodine atom in the ground state $^2P_{3/2}$. Photolysis by light of wavelength longer than 4995 Å yields two iodine atoms in the ground state[2]. Incidentally, there are indications that the excited atoms are produced also by photolysis with light from the long-wave region of the absorption band[3].

We have experimentally established that selective pumping exerts a strong influence on the parameters of the generation pulse. The experimental setup consisted of an ordinary photodissociation laser with a pump source based on an IFP-5000 lamp and a resonator with flat mirrors (reflection coefficients $R_1 \cong 100\%$ and $R_2 \cong 8\%$), supplemented with an analogous lamp placed in a coaxial cavity filter of molybdenum glass, filled with chlorine at atmospheric pressure. The filtering chlorine layer was approximately 1 cm thick. The quartz cell was 30 cm long and had an inside diameter of 1 cm. The energy of the stimulated radiation was measured with an IÉK-1 calorimeter, and the shape of the generation pulse was registered with the aid of an FÉK-13 coaxial photocell and with an OK-17M oscilloscope, which simultaneously registered, through another FÉK-13 cell, the shape of the summary pulse of the pump and additional illumination lamps. Energies of 900 and 2500 J were fed to the pump and additional-illumination lamps, respectively, through a synchronizing block. A specially performed control iodometry has demonstrated the complete absence of decomposition of the perfluoralkly-iodides if only filtered radiation is used. The working media were CF_3I, C_3F_7I, and their mixtures with xenon.

Figure 1 shows the relative increase of the stimulated-emission energy yield, ΔE, due to turning on an additional selective illumination source, as a function of the pressure of the undiluted working medium (E is the energy output without additional illumination).

The net result of the experimental data is that for CF_3I (the points on curve 1 of Fig. 1) the relative contribution of the selective-illumination effect increases with increasing distance from the optimum-pressure region (70—100 Torr), where the absolute energy yield has a maximum under the experimental conditions without the additional selective illumination. It is interesting to note that we have observed in the region of large CF_3I pressures a number of cases when the registered generation occurred only in the presence of the selective additional illumination. In the case of C_3F_7I (points on curve 3 of Fig. 1), the increase of the relative energy yield, unlike in CF_3I, depended little on the pressure of the working medium and its average value was 20%. When the C_3F_7I was diluted by xenon in a ratio 1 : 4, the relative effect of selective pumping increased to 40%.

The presented typical oscillograms illustrate the dif-

[1]Physics Institute, USSR Academy of Sciences

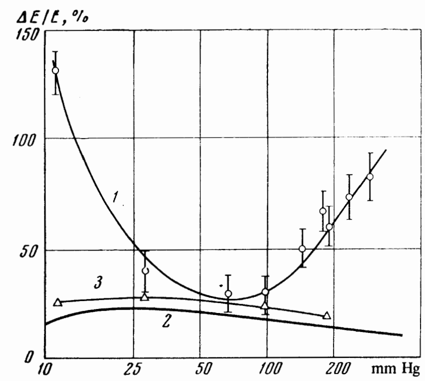

FIG. 1. Pressure dependence of the relative increase of the stimulated-emission energy yield: O–CF_3I, Δ–C_3F_7I.

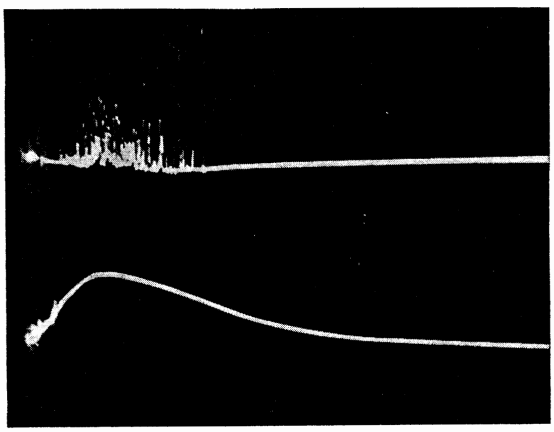

FIG. 2. Oscillograms of generation pulse and of pump pulse without selected additional illumination.

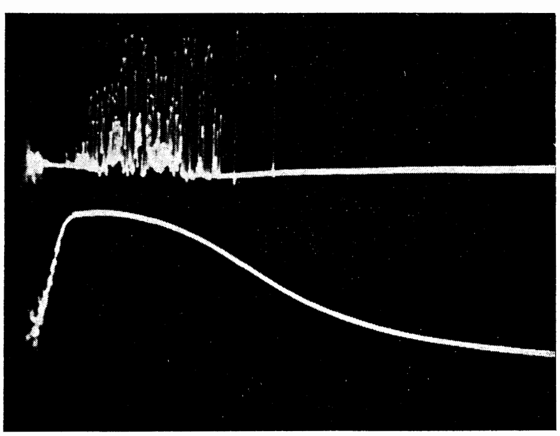

FIG. 3. Oscillograms of generation pulse and pump pulse with selective additional illumination.

ference in generation resulting from including the additional selective pumping, for C_3F_7I at 100 Torr.

For the generation pulse shown in Fig. 2, the output energy E was 0.25 ± 0.01 J. Figure 3 shows the generation pulse with additional selective pumping with energy $E + \Delta E = 0.32 \pm 0.01$ J. The lower curves characterize the change in the shape of the pump pulse in the region $\lambda \sim 5000$ Å.

The qualitative difference between the results of the experiments for CF_3I and C_3F_7I can be attributed to the symmetrical difference between the mechanisms of molecular-iodine accumulation and the photolysis of these substances. The power of the stimulated emission from a unit volume of the working medium W(t), is proportional to the difference between the rates of production and deactivation of the excited atoms. Assuming that in each act of the photolysis of the molecule I_2 there is produced one atom in the ground state and one atom in the excited state, we can write

$$W(t) = {}^2/_3 h\nu\{k_1[RI] - {}^1/_2 k_4[I][I_2] + {}^1/_2 k_5[I_2]\}, \qquad (6)$$

where $h\nu$ is the energy of the stimulated-emission quantum, and k_1, k_4, and k_5 are the rate constants of reactions (1), (4), and (5). Under identical photolysis conditions and under identical initial densities of the working medium, the value of W(t) depends significantly on the change of the molecular-iodine concentration in the system. A kinetic calculation of the recombination mechanism of I_2 production, determined by the reactions (2) and (3), leads to a dependence of the effective selective additional illumination on the pressure of the working medium, represented by curve 2 of Fig. 1. This dependence agrees well with the experimental data for C_3F_7I. It was assumed in the calculation that the source of the selective illumination has an intensity corresponding to black body radiation with temperature 10^4 °K.

From a qualitative comparison of the dependence of the average experimental data on the CF_3I pressure (curve 1 of Fig. 1) with the calculation (curve 2) it follows that for CF_3I the accumulation of I_2 does not have a pure recombination character. A similar dependence can be obtained by assuming that the quenching processes have the maximum possible rate[4]. The maximum rate of the de-activation processes corresponds to the minimum power of the stimulated emission.

Taking into account in (6) the law of conservation of the number of iodine atoms

$$[I] + 2[I_2] = [RI(0)] - [RI(t)],$$

we find that at a fixed instant of time t the radiation power is minimal if the kinetic curve showing the variation of the molecular iodine satisfies the equation

$$[I_2(t)] = {}^1/_4\{[RI(0)] - [RI(t)] - k_5/k_4\}.$$

Substituting this relation in (6) and integrating the resultant expression with respect to time from zero to the instant when the radiation power becomes equal to zero, we easily find that the effect of selective additional illumination does not depend on the pressure of the working medium and amounts to

$$\Delta E = \frac{2}{3} h\nu \frac{k_5}{k_4}.$$

In this case the ratio $\Delta E/E$ has a minimum in the pressure region where the absolute energy yield E without selective illumination is maximal and increases with increasing distance from this region, i.e., it has precisely the form of curve 1 in Fig. 1.

[1]V. Yu. Zalesskiĭ and A. A. Venediktov, Zh. Eksp. Teor. Fiz. **55**, 2088 (1968) [Sov. Phys. JETP **28**, 1104 (1969)].
[2]V. N. Kondrat'ev, Kinetika khimicheskikh gazovykh reaktsiĭ (Kinetics of Chemical Gas Reactions), Publ by An SSSR, 1958.
[3]A. B. Callear and J. F. Wilson, Trans. Faraday Soc. **63**, 1358 (1967).
[4]A. A. Filyukov and V. Ya. Karpov, Zh. Eksp. Teor. Fiz. **62**, 119 (1972) [Sov. Phys. JETP **35**, 000 (1972)].

Translated by J. G. Adashko
61