

Determination of the fraction of excited iodine atoms produced by dissociation of iodides in a self-sustained pulsed discharge

N.P. Vagin, I.V. Kochetov, A.P. Napartovich, N.N. Yuryshev

Abstract. Based on the measured absorption coefficient for the atomic iodine transition in the mixtures of iodides with helium we have determined the fractions of the excited atomic iodine produced by dissociation of CH_3I , CF_3I , $i\text{-C}_3\text{F}_7\text{I}$, $\text{C}_2\text{F}_5\text{I}$ and $\text{C}_2\text{H}_5\text{I}$ molecules in a self-sustained pulsed discharge. In the 1:(3–15) mixtures of iodides with helium at the pressure 133–400 Pa these fractions amount to 0.29 for CF_3I and CH_3I , 0.2 for $i\text{-C}_3\text{F}_7\text{I}$, and 0.31 for $\text{C}_2\text{F}_5\text{I}$ and $\text{C}_2\text{H}_5\text{I}$. The accuracy of determining the excited iodine fraction is 10%. The numerical modelling is carried out for the mixtures containing CF_3I . The calculated values of the excited iodine fraction for the mixture with CF_3I agree well with the experimental data.

Keywords: oxygen–iodine laser, pulsed discharge, dissociation of iodides, atomic iodine, excited iodine atoms.

1. Introduction

The processes of dissociation of alkyl iodides and perfluoroalkyl iodides have been studied for many years. These studied are stimulated by a wide application of these compounds as active media of photodissociation iodine lasers generating the radiation at the atomic iodine transition $\text{I}(^2\text{P}_{1/2}) \rightarrow \text{I}(^2\text{P}_{3/2})$ with the wavelength $\lambda = 1.315 \mu\text{m}$. In this connection, the information about the kinetic processes involved in the formation of inverted population in such lasers, in particular about the fraction of excited atoms in the total concentration of iodine atoms produced in the process of dissociation, becomes essentially important. As to the dissociation of iodides under the impact of UV radiation, which is the process mainly used to pump iodine lasers, we should note that besides the special papers, the specific features of the inverted population kinetics are presented in monographs [1, 2]. The fraction of excited iodine atoms produced by photodissociation of most of the above iodides amounts to 90% [1, 2], which facilitated the achievement of high radiation energy (1 kJ [1] and 400 kJ [3]) in photodissociation lasers. The his-

tory of the development of these lasers in the USSR is presented in detail in Ref. [4].

Ramirez et al. [5] reported the results of measuring the fraction of excited iodine atoms for the case of iodide molecules affected by a beam of fast electrons having an energy of a few hundred keV. The experiments were performed under the iodide pressure 66–4000 Pa and the buffer gas pressure 20–80 Pa. For all the studied iodides, a large fraction of excited atoms (0.65–0.8) was recorded. In particular, it amounted to 0.73 for CH_3I , 0.79 for CF_3I , and 0.76 for $i\text{-C}_3\text{F}_7\text{I}$. These values essentially exceed the values of 1/3, necessary to achieve the inversion in the laser transition of the atomic iodine. In this connection, the authors of Ref. [5] conclude that the application of electron beams is promising for pumping iodine lasers.

In the pioneering work [6] the authors considered the possibility of lasing under the dissociation of CF_3I molecules in a glow discharge.

Pleasance and Weaver [7] report the laser oscillation at the atomic iodine transition under the excitation by a transverse electric discharge in the mixture of CF_3I with nitrogen, and Wong and Beverly [8] obtained lasing in the mixture of $i\text{-C}_3\text{F}_7\text{I}$ with helium. The numerical simulation of the laser oscillation dynamics under pulsed discharge excitation, performed by Beverly and Wong [9], allowed the fraction of excited iodine atoms to be estimated, which amounted to 0.45 for CF_3I and 0.95 for $i\text{-C}_3\text{F}_7\text{I}$.

Earlier [10] we have measured the rates of the atomic iodine production in a self-sustained pulsed discharge in the mixtures of iodides with a buffer gas. As a buffer gas, we used helium and molecular nitrogen. The rate of production of iodine atoms was measured using the absorption spectroscopy method. We studied the dissociation of the iodides $\text{C}_n\text{F}_{2n+1}\text{I}$ and $\text{C}_n\text{H}_{2n+1}\text{I}$ ($n = 1, 2$) and determined the ‘energy costs’ of the atomic iodine production. The experimental data obtained for the mixture containing CF_3I were compared with the results of the numerical simulation. The comparison of calculated results with the experimental ones showed their reasonable agreement. The measurement of the iodine atom concentration after the termination of the discharge allowed the correction of our results [11, 12] related to the two-channel distribution (with the formation of excited iodine atoms and non-excited ones) in the process of predissociation of the electronically excited molecules CF_3I^{**} (the threshold of excitation by electrons 7.2 eV). The best agreement with the experiment is achieved at the fraction of iodine atoms in the excited state equal to 0.7, while in papers [11, 12] it was accepted to equal 1.0. Note that the main channel of the atomic iodine formation in the ground state is the predissociation of electronically excited molecules CF_3I^* (the threshold

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of excitation by electrons 4.7 eV) [10–12]. Therefore, the total fraction of the excited atomic iodine for all dissociation channels of the molecule CF_3I under the conditions of a pulsed self-sustained discharge in the experiment [10] amounted to 0.3.

The aim of the present work is to study experimentally the efficiency of the formation of excited iodine atoms due to the dissociation of CH_3I , CF_3I , $i\text{-C}_3\text{F}_7\text{I}$, $\text{C}_2\text{F}_5\text{I}$, and $\text{C}_2\text{H}_5\text{I}$ iodides in the longitudinal pulsed self-sustained electric discharge, to simulate the dynamics of the formation and loss of the iodine atoms in the excited and ground state in the mixture of CF_3I with helium, and to compare the experimental and calculated data.

Interest in these issues is additionally stimulated by the fact that in recent years the studies of the oxygen–iodine laser (OIL) have been carried out, in which the singlet oxygen was produced in an electric discharge rather than in chemical reactions (see, e.g., our paper [13] and references therein). The presence of additional channels of the excited iodine formation is important for the choice of the further direction of study.

2. Experiment

The excitation degree of the iodine atoms produced in the process of dissociation in the electric discharge was determined by measuring the absorption coefficient of the iodide mixture with the buffer gas at the wavelength of the $^2\text{P}_{3/2}(F=4) \rightarrow ^2\text{P}_{1/2}(F=3)$ transition between the hyperfine structure sub-levels of the iodine atom. The source of the probe radiation was a tunable external-cavity semiconductor laser. The tuning to the absorption line centre was implemented by means of a heated cell with crystalline iodine. In the cylindrical cell having the inner diameter 45 mm, a double-sectioned longitudinal electric discharge (in two discharge tubes) was ignited. The total length of two discharge sections amounted to 115 cm. The absorption path length for the double pass through the discharge zone equalled 230 cm. The absorption signal was recorded using an FD-10 germanium photodetector and a TDS 1012B oscilloscope.

The longitudinal pulsed self-sustained discharge was powered from the battery of capacitors having the capacitance 6.8–20.4 nF, charged to the voltage $U_0 = 10\text{--}22$ kV and discharged through a TGI-1000/25 thyatron. In each tube of the double-section discharge, the capacitors having the capacitance 3.4–10.2 nF were connected to the electrodes. A detailed description of the experimental setup is presented in our earlier paper [10].

Besides the electric discharge initiation, the setup allowed the studied mixture to be irradiated with the UV light from a self-made direct pulsed lamps. The duration of the UV pulse amounted to 3 μs at the half-maximum intensity level. The length of the absorption (gain) region in this case was equal to 80 cm for two passages. The yield of excited atoms under the dissociation induced by UV radiation is known for many iodides, so that the comparison of the signals for different ways of dissociation allowed certain conclusions on the operability of the registration system.

In the experiments, we used CF_3I and CH_3I produced by JSC SIA ‘P&M-Invest’ without additional purification. As a buffer gases the high purity nitrogen and brand B helium were used. The mixtures with the required composition were prepared in metal tanks and before the experiment were placed in a polyethylene bag, from which they were supplied to the dis-

charge chamber. The use of a soft bag allowed the pressure at the rotameter input to be maintained equal to the atmospheric one for the precise determination of the flow rate.

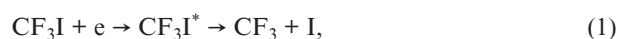
Unfortunately, the imperfection of the gas vacuum system did not allow its evacuation to the residual pressures below 10 Pa. Therefore, in the assumption that the residual pressure is determined by the inleakage of atmospheric air, the partial pressure of the residual oxygen amounts to 2 Pa. As shown below, the presence of oxygen affects the relaxation rate of the atomic iodine excitation.

3. Kinetics model

In the calculations for the mixtures containing CF_3I , we used the zero-dimensional kinetic model of a pulsed discharge elaborated by us [10–12]. The following plasma components were taken into account: e, I, I^* , I_2 , I^- , I^+ , CF_3I , $\text{CF}_3\text{I}(\text{vib})$, CF_3I^* , CF_3I^{**} , CF_3I^{3*} , CF_3I^{4*} , CF_3I^{5*} , CF_3 , CF_4 , CF_2I , CF_2 , C_2F_6 , IO, CF_3O , CF_3O_2 , F, COF_2 , $\text{C}_2\text{F}_6\text{O}_3$, IF, C_2F_6 , CF_3I^+ , CF_2I^+ , CF_3^+ , O_2 , $\text{O}_2(\text{vib})$, $\text{O}_2(a^1\Delta_g)$, $\text{O}_2(b^1\Sigma_g^+)$, O_2^* , O_2^- , O_2^+ , O_4^+ , O, $\text{O}(^1\text{D})$, O^- , O^+ , O_3 , O_3^- , He, He^* , He^{**} , He^+ , He_2^+ , N_2 , $\text{N}_2(\text{vib})$, N_2^* , N_2^{**} , N_2^+ , and N_4^+ . Here CF_3I^* , CF_3I^{**} , CF_3I^{3*} , CF_3I^{4*} , and CF_3I^{5*} are the electronically excited predissociation states of the CF_3I molecule with the excitation thresholds 4.7, 7.2, 8.1, 9.0, and 9.8 eV, respectively; He^* is the lowest excited electronic state of helium; He^{**} is the joint electronic state with the excitation threshold 20.5 eV, including all electronic states of the helium atom, except the lowest one; N_2^* is the lowest excited electronic state $\text{A}^3\Sigma_v^+$ of nitrogen; N_2^{**} is the joint electronic state with the excitation threshold 7.35 eV, including all electronic states of the nitrogen molecule except the lowest one; and the notation ‘vib’ means the vibrationally excited molecule. The model implies the simultaneous solution of the kinetic equations for the discharge plasma components and the Boltzmann equation for the electron energy distribution function (EEDF). The Boltzmann equation for the EEDF is solved using the two-term approximation. This equation takes into account the elastic collisions of electrons with atoms and molecules, the vibrational excitation in the approximation of the effective vibrational level, the excitation of electronic states, the dissociation of molecules by electron impact, the ionisation of atoms and molecules, and the dissociative attachment of electrons to the molecules of CF_3I .

Together with the kinetic equations, we solved the equations for the external electric circuit and the equation for the translational temperature of the gas. The modelled electric circuit consisted of a discharge gap and a series-connected capacitor and a parasitic inductor (4.18 μH). The value of the parasitic inductance was determined from the comparison of the calculated values of the discharge current and voltage with the experimentally measured ones. We assumed that the capacitor was initially charged to the specified voltage U_0 . In the experiment after the first half-period of the current pulse, the thyatron was turned off. In the model, this fact was taken into account. The gas heating in the discharge was calculated using the heat balance equation, in which all known channels of energy dissipation of the electrons and excited particles were included.

The atomic iodine can be produced in the following processes of dissociation of the CF_3I molecule caused by an electron impact:





where CF_3I^* and CF_3I^{**} are rapidly decaying predissociation states of the electronically excited CF_3I molecule; I^* is the excited state $^2\text{P}_{1/2}$ of the atomic iodine; and I is the ground state $^2\text{P}_{3/2}$ of the atomic iodine. The threshold is 4.7 eV for process (1) and 7.2 eV for process (2). In our papers [11, 12] it was assumed that the decay of CF_3I^{**} is accompanied by the formation of I^* , i.e., via channel (3b), while channel (3a) is absent. This conclusion followed from the measurements of the shape and the energy of the OIL pulse with the generation of iodine atoms in the pulsed glow discharge. Note also that in Refs [11, 12] the discharge was ignited in the active medium with a high (50%) content of singlet oxygen $\text{O}_2(^1\Delta_g)$. The presence of singlet oxygen reduces the sensitivity of laser characteristics to the relative contribution of channels (3a) and (3b). In our paper [10], the concentration of the iodine atoms in the pulsed discharge in the CF_3I –He mixture was measured using the absorption technique, which excludes the uncertainties due to the presence of singlet oxygen $\text{O}_2(^1\Delta_g)$ and the cavity characteristics. The fractions of the iodine atoms, produced via channels (3a) and (3b) have been determined again. They amounted to 0.3 and 0.7, respectively.

The formation of higher electronic states of CF_3I , excited by the electrons of plasma and denoted in the kinetic model as CF_3I^{*+} , CF_3I^{*+} , and CF_3I^{5*} with the thresholds 8.1, 9.0, and 9.8 eV, leads to the production of the CF_2I , CF_2 , and IF radicals and F atoms [12].

4. Results and discussion

In the experiments we measured the absorption coefficient at the atomic iodine transition $^2\text{P}_{3/2}(F=4) \rightarrow ^2\text{P}_{1/2}(F=3)$ and then the following parameter was determined from it [10]:

$$\Delta N = \frac{[\text{I}]}{2} - [\text{I}^*], \quad (4)$$

where $[\text{I}]$ and $[\text{I}^*]$ are the concentrations of atoms I and I^* . The values of ΔN were determined immediately after the termination of the discharge current pulse (ΔN_0) and after long time (ΔN_1), when the concentration of excited iodine atoms becomes negligibly small. For the iodides CH_3I and $\text{C}_2\text{H}_5\text{I}$ containing hydrogen, the rate of relaxation of the excited iodine atoms on the iodide molecules is high, which under the conditions of the experiment provided the relaxation during hundreds of microseconds. For the iodides containing fluorine CF_3I , $i\text{-C}_3\text{F}_7\text{I}$, and $\text{C}_2\text{F}_5\text{I}$, the rate of the excited iodine relaxation is considerably lower; therefore, in the experiment its relaxation was enhanced by adding molecular oxygen to the mixture. The excitation of the atomic iodine was transferred to the lower metastable electronic level of the molecular oxygen $\text{O}_2(a^1\Delta_g)$. Assuming iodine to be present only in the ground state at large times, we arrive at the expression

$$2\Delta N_1 = [\text{I}]_0 + [\text{I}^*]_0, \quad (5)$$

where $[\text{I}]_0$ and $[\text{I}^*]_0$ are the concentrations of the excited and unexcited iodine at the initial moment of time. Determining

from Eqn (5) the concentration $[\text{I}^*]_0$, we obtain the fraction of the excited iodine atoms, formed by the dissociation of iodides in the discharge:

$$Y = \frac{[\text{I}^*]_0}{[\text{I}^*]_0 + [\text{I}]_0} = \frac{1}{3} - \frac{1}{3} \frac{\Delta N_0}{\Delta N_1}. \quad (6)$$

To check the operability of the setup, we performed experiments with dissociation of iodides by the pulsed UV radiation. Figure 1 presents the time dependences of ΔN under the photodissociation of iodides in the $\text{CF}_3\text{I}:\text{He} = 1:4$ and $\text{CH}_3\text{I}:\text{He} = 1:4$ mixtures, the pressure of the iodides being 56 and 64 Pa, respectively. The rate constant of the excited iodine deactivation by the molecules of CH_3I amounts to $\sim 2.76 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [14], which under the above pressure of iodide corresponds to the characteristic relaxation time of the excited state, 240 μs . Therefore, the observed maximal value of ΔN corresponds to practical absence of the excited state, i.e., the concentration of iodine atoms produced by photodissociation of CH_3I is equal to $2\Delta N_{\text{max}} = 3 \times 10^{13} \text{ cm}^{-3}$. Extrapolating the dependence $\Delta N(t)$ to the point $t = 0$, we find that at the initial moment of time, $\Delta N_0 = -(2.0 - 1.5) \times 10^{13} \text{ cm}^{-3}$. Using the above values of the parameters, we obtain the concentration of the excited iodine atoms at the initial moment of time, $(2.0 - 2.3) \times 10^{13} \text{ cm}^{-3}$, which corresponds to the value of the so-called branching ratio, equal to 2.0–3.3 and defined as the ratio of the initial concentrations of excited and unexcited atoms: $[\text{I}^*]_0/[\text{I}]_0 = Y(1 - Y)$. Note that the determined values of Y are in the range of the data presented by other authors (Table 1).

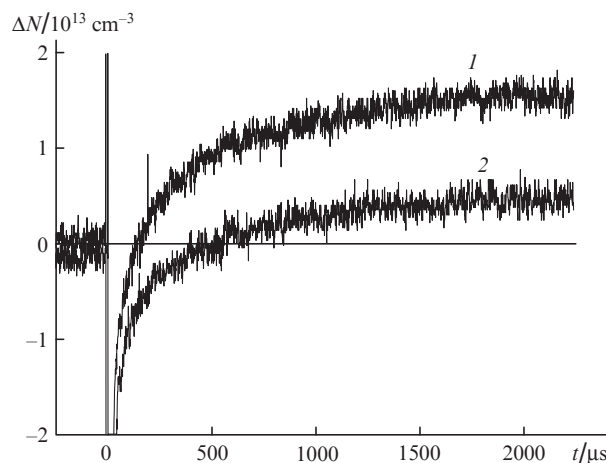


Figure 1. Time dependence of ΔN under the photolysis of iodides (1) CH_3I and (2) CF_3I in mixtures with helium.

Similar results for CF_3I cannot be obtained using dependence (2) in Fig. 1, because the deactivation of I^* atoms by the CF_3I molecules is considerably slower. The corresponding rate constant amounts to $\sim 3.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [14]; therefore, the measured value of ΔN includes the contribution of the excited atoms, the concentration of which in the present experiment was unknown.

The performed experiments on the photolysis of iodides have shown the possibility of using the considered technique for measuring the values of the branching ratio for iodine atoms in the process of the dissociation of iodides. Figure 2 presents for comparison the dependences of $\Delta N(t)$ in the cases

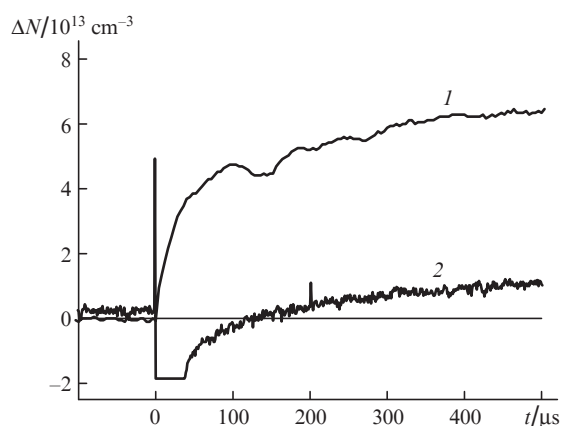
Table 1. Fractions of excited iodine atoms Y , produced using different methods of iodides dissociation.

Iodide	Pulsed discharge	Electron beam	Photolysis	Laser photolysis
CF ₃ I	0.3 [10] 0.29 [p. p.]* 0.45 [9]	0.79 [5]	0.91 [15] 0.9 [16]	–
CH ₃ I	0.29 [p. p.]	0.73 [5]	0.92 [15] 0.76 [17]	0.75 [18] 0.81 [19]
i-C ₃ F ₇ I	0.2 [p. p.] 0.95 [9]	0.76 [5]	0.90 [15]	–
C ₂ F ₅ I	0.31 [p. p.]	0.73 [5]	>0.98 [15]	–
C ₂ H ₅ I	0.31 [p. p.]	–	0.69 [15]	–

Notes: [p. p.] – present paper.

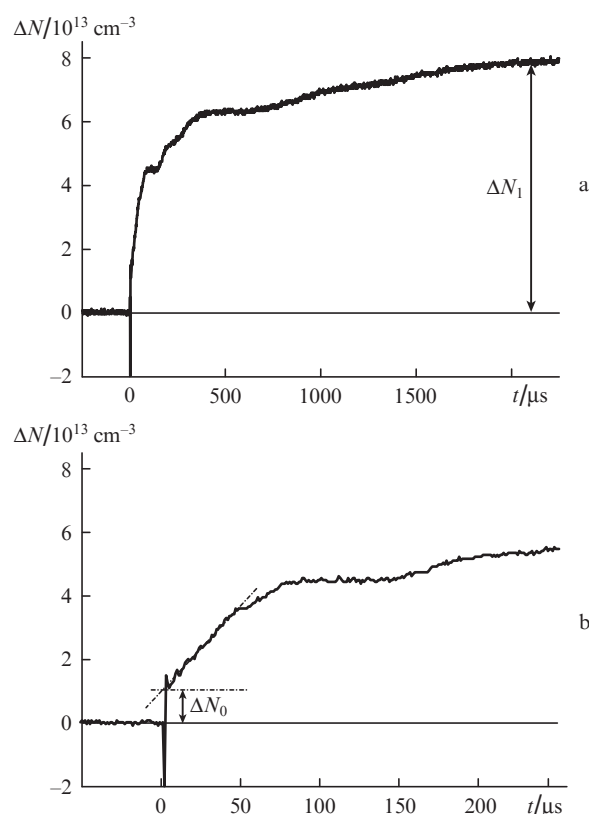
*The small difference from our earlier paper [10] for CF₃I lies within the measurement error.

of photodissociation and electric discharge dissociation of CF₃I. Recall that in iodine lasers the lasing mainly occurs at the strongest transition $^2P_{1/2}(F=3) \rightarrow ^2P_{3/2}(F=4)$ between the sublevels of the hyperfine structure of the iodine atom, where the gain takes place when the values of the branching ratio exceeds 0.5, which corresponds to the excited state yield $Y > 1/3$. As follows from Fig. 2, in the case of CF₃I in a discharge, the gain at this transition is not achieved, i.e., $Y \leq 1/3$.

**Figure 2.** Time dependences of ΔN under (1) the electric discharge dissociation and (2) photodissociation of CH₃I:He = 56:412 Pa and 64:253 Pa, respectively.

The procedure of measuring Y for different iodides consisted in the following. At the above transition of iodine, the absorption coefficients were analysed with different time resolutions. The low resolution (long-term measurements) allowed the total concentration of the produced iodine atoms to be determined. The high resolution (short-term measurements) yielded the value of ΔN immediately after the initiation.

Figure 3 presents the dependences $\Delta N(t)$ with different time resolutions. The moments of measuring ΔN_0 and ΔN_1 for the CH₃I–He mixture are indicated. As mentioned above, the high rate of relaxation of I* atoms at the CH₃I molecules leads to the situation, in which at large time intervals all iodine atoms are in the ground state (Fig. 3a). The value of Y and the concentration of excited iodine atoms produced by the electric discharge dissociation of CH₃I, calculated using formula

**Figure 3.** Time dependences of ΔN for the electric discharge dissociation of the iodide in the mixture CH₃I:He = 35:275 Pa, measured at (a) large and (b) small time intervals after the initiation. The discharge voltage is 22.3 kV, and the specific energy contribution is 90 J L⁻¹ atm⁻¹.

(6), are presented in Table 2. The measurements were carried out under different experimental conditions determined by the capabilities of the experimental setup.

Table 2. Concentrations of the excited iodine atoms produced by the electric discharge dissociation of CH₃I mixed with He, and the values of Y for the mixtures CH₃I:He = 1:7 at different pressures p and the voltages U_0 applied to the capacitance.

p /Pa	U_0 /kV	$[I^*]/10^{13} \text{ cm}^{-3}$	Y
310	22.3	4.7	0.29
310	15.7	3.4	0.31
160	15.7	2.4	0.28

One can see that in all experiments the yield of iodine atoms in the excited state for CH₃I did not exceed the gain threshold value. The value of the excited iodine yield remained similar (within the error of measurements) under all experimental conditions. After averaging over a large number of experiments, this value amounted to 0.29.

As mentioned above, due to the low efficiency of deactivation of I* atoms by the CF₃I molecules, in order to measure the total concentration of iodine atoms produced by the discharge we had to add oxygen that possesses high deactivation activity to the studied gas mixture. One can see from Fig. 4 that the amplitudes of $\Delta N(t)$, recorded in the presence and in the absence of the added oxygen, are essentially different. At short times (Fig. 4b) the added oxygen virtually does not affect the values of ΔN , observed at the initial moment of time. Assuming that at the moment of time corresponding to

the maximum of ΔN in the mixture with oxygen all atoms are not excited, one can find their concentration as $[I] = 2\Delta N_1 = 11.2 \times 10^{13} \text{ cm}^{-3}$ (Fig. 4a). From Fig. 4b it is seen that at the initial moment of time, $\Delta N_0 = 0.88 \times 10^{13} \text{ cm}^{-3}$, i.e., the value of Y under these experimental conditions is equal to 0.28. Within the error of the experiment, it is independent of the experimental conditions. The value of Y averaged over a large number of experiments amounted to 0.29.

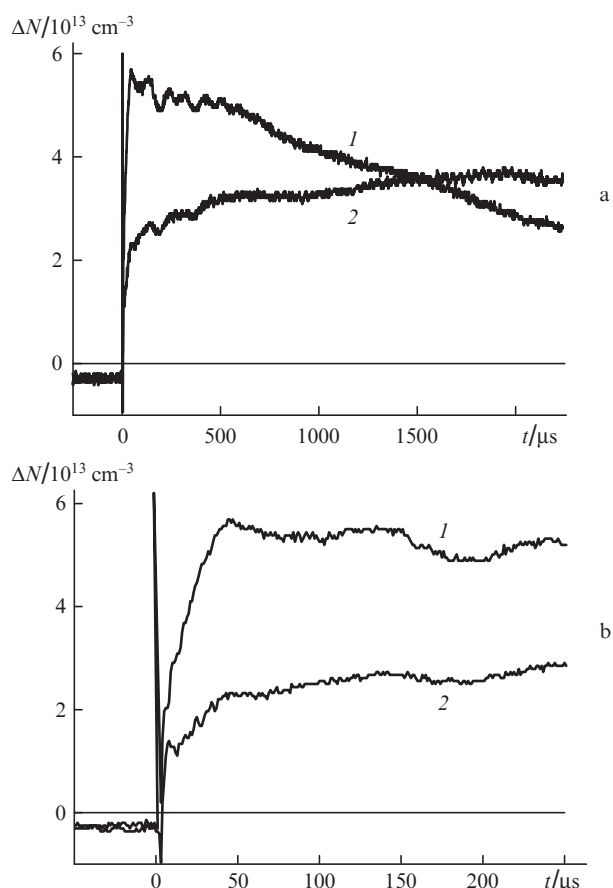


Figure 4. Time dependences of ΔN for the electric discharge dissociation of the iodide in the mixture $\text{CH}_3\text{I}:\text{He} = 39:286 \text{ Pa}$ with the addition of O_2 (27 Pa) (1) and in the absence of O_2 (2), measured at (a) large and (b) small time intervals after the initiation. The discharge voltage is 22.3 kV, and the specific energy contribution is $90 \text{ J L}^{-1} \text{ atm}^{-1}$.

Figure 5 shows the fraction η of the discharge power spent on the production of atomic iodine in the ground and excited states [processes (1), (3a), and (3b)] as a function of the magnitude of the reduced electric field E/N , where E is the discharge electric field strength, and N is the total concentration of particles in the mixture. The same Figure presents the dependence $Y(E/N)$. The vertical line indicates the magnitude of the reduced electric field at the maximum of the discharge current, calculated using the kinetic model. The dependence $Y(E/N)$ for the mixtures of CF_3I with different contents of He are presented in Fig. 6. The electron energy balance is calculated using the Boltzmann equation for the EEDF with the cross sections of electron scattering by the molecule CF_3I adopted from Ref. [10]. As follows from the analysis of the results calculated using the complete kinetic model, an increase in the helium content leads to a decrease in the reduced electric field at the maximum

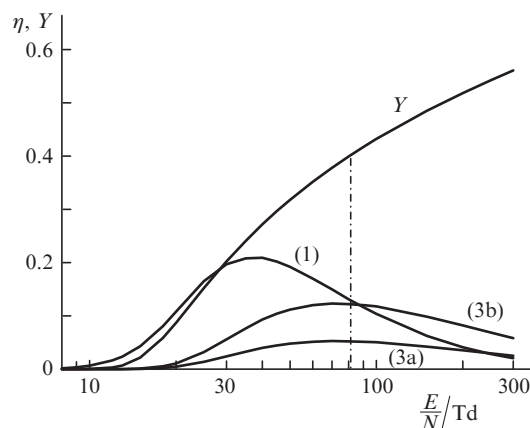


Figure 5. Calculated fractions η of the discharge power spent on the production of I and I^* in processes (1), (3a), and (3b), and the fraction Y as a function of magnitude of the reduced electric field E/N for the mixture $\text{CF}_3\text{I}:\text{He} = 1:7.5$.

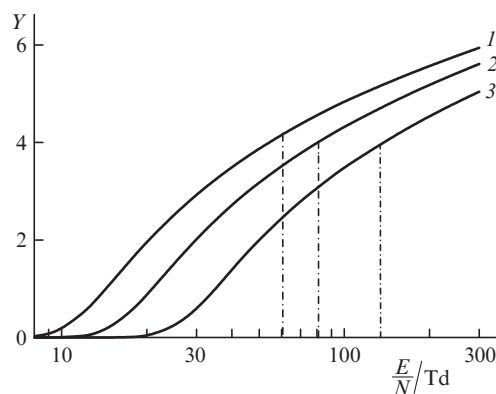


Figure 6. Calculated dependences $Y(E/N)$ for the mixtures $\text{CF}_3\text{I}:\text{He} =$ (1) 1:15, (2) 1:7.5 and (3) 1:3.

of the discharge current. In this case, the value of Y amounts to ~ 0.4 and does not depend on the buffer gas concentration.

It is clear that the calculation of the excited iodine fraction Y from the energy balance is approximate. To obtain more precise data one has to use the full kinetic model [10–12] for the calculation. The dependences $Y(t)$ calculated using this model for the pure mixture $\text{CF}_3\text{I}:\text{He} = 1:8$ and for the mixtures containing oxygen and air are shown in Fig. 7. At $t \approx 0.1 \mu\text{s}$ the fraction of the excited iodine grows and reaches its maximal value 0.37 before the achievement of the maximal discharge current. This is because at this moment the value of E/N is greater than at the maximum of the discharge current (which is reached at $t = 0.4 \mu\text{s}$). In the interval $0.4–10 \mu\text{s}$ the fraction of the excited iodine amounts to 0.29, which is smaller than the value 0.4, estimated from the energy balance of electrons and the value of the reduced electric field at the maximum of the discharge current. For the pure mixture $\text{CF}_3\text{I} - \text{He}$ at $t = 0.4–30 \mu\text{s}$, the fraction of the excited iodine remains unchanged. The inleakage of air or a small amount of oxygen into the cuvette with the gas causes a slight decrease in the excited iodine fraction at these times. The special addition of molecular oxygen (27 Pa) leads to the reduction of the excited iodine fraction at $t = 0.4–30 \mu\text{s}$. This is due to the energy transfer from the electronically excited iodine to the electronically excited state $\text{O}_2(a^1\Delta_g)$ of oxygen:

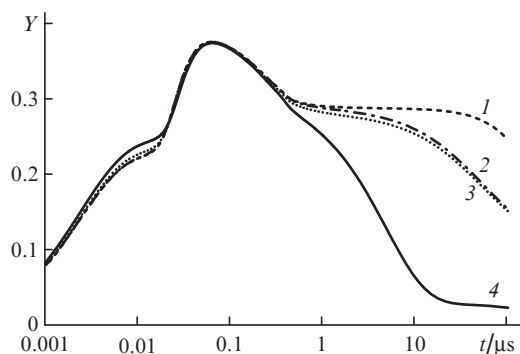


Figure 7. Calculated dependences of $Y(t)$ for the pure mixture $\text{CF}_3\text{I}:\text{He} = 1:8$ (1) and the mixture containing additional oxygen [(2), 2 Pa; (4), 27 Pa] and air [(3), 6.5 Pa]. The pressure of the mixture $p = 532$ Pa, $C = 6.8$ nF, $U_0 = 22.3$ kV, and the specific energy contribution is $40 \text{ J L}^{-1} \text{ atm}^{-1}$.



The calculated dependences of $\Delta N(t)$ for the pure mixture $\text{CF}_3\text{I} - \text{He}$ and for the mixture containing additional oxygen and air are presented in Fig. 8. In the same Figure the moments of measuring ΔN_0 and ΔN_1 are indicated. Unfortunately, in the experimental setup the atmospheric air leakage to the discharge zone takes place, making it interesting to estimate the measurement error caused by the uncertainty of the inleakage amount. For the $\Delta N(t)$ dependences presented in Fig. 8 such an estimate yields the error $\sim 10\%$.

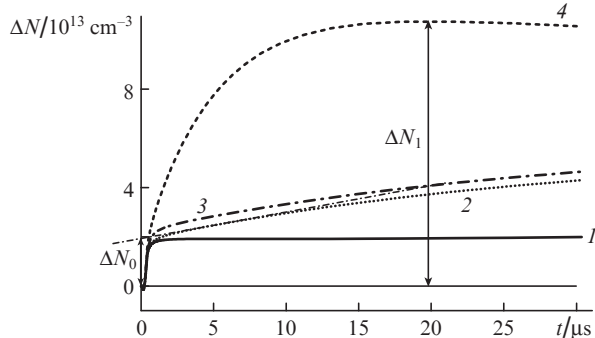


Figure 8. Calculated time dependences of ΔN for the pure mixture $\text{CF}_3\text{I}:\text{He} = 1:8$ (1) and for the mixture containing additional oxygen [(2) 2 Pa; (4) 27 Pa] and air [(3) 6.5 Pa]. The pressure of the mixture $p = 532$ Pa, $C = 6.8$ nF, $U_0 = 22.3$ kV.

From the results of the performed measurements, the following values of Y were determined: 0.2 for $i\text{-C}_3\text{F}_7\text{I}$ and 0.31 for $\text{C}_2\text{F}_5\text{I}$ and $\text{C}_2\text{H}_5\text{I}$.

The calculations using our model have shown that lasing observed in Ref. [7] occurs due to the population inversion of the working levels in the atomic iodine arising after the discharge in the process of recombination of the iodide dissociation products. The atoms of the unexcited iodine recombine faster than the excited ones. Beverly and Wong [9] simulated the experiment [7]. In contrast to Ref. [9] where in the kinetic model the total fraction of the excited iodine Y after the discharge was assumed equal to 0.45, in our model it amounted to 0.3 (Table 1). This difference can be explained by the fact that our kinetic model includes the process of the excited atomic iodine production in the collision of the CF_3I mole-

cules with electronically excited molecules of nitrogen [11], while in Ref. [9] this channel was not taken into account.

Beverly and Wong [9], using the results of simulation of atomic iodine lasing in the $i\text{-C}_3\text{F}_7\text{I}-\text{He}$ mixture in the pulsed electric discharge [8], determined the fraction of the excited iodine, $Y = 0.95$, after the discharge. The reasons for a strong difference from our result, $Y = 0.2$ (Table 1), are not clear for us; however, they could be related to a considerably higher pressure (about 9 kPa) used in Ref. [8].

5. Conclusions

The performed experiments show that the fraction Y of the excited iodine atoms produced by the dissociation of CH_3I , CF_3I , $i\text{-C}_3\text{F}_7\text{I}$, $\text{C}_2\text{F}_5\text{I}$, and $\text{C}_2\text{H}_5\text{I}$ in the self-sustained pulsed discharge does not exceed 0.31, which is somewhat smaller than the value required for the amplification at the transition $^2\text{P}_{1/2}(F=3) \rightarrow ^2\text{P}_{3/2}(F=4)$ of the hyperfine structure of the iodine atom. The accuracy of Y determination amounts to $\sim 10\%$. The obtained values of Y for CF_3I are in good agreement with the results of the numerical simulation. From the results of the work, it follows that the self-sustained electric discharge is not applicable for direct pumping of iodine lasers based on alkyl iodides and perfluoroalkyl iodides.

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