

ACTIVE MEDIA

PACS numbers: 32.50.+d; 42.55.Ks; 42.62.Fi; 52.80.–s
DOI: 10.1070/QE2013v043n07ABEH015078

Dynamics of production of iodine atoms by dissociation of iodides in a pulsed self-sustained discharge

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Abstract. **Absorption at the laser transition has been used for the first time to assess the evolution of concentration of iodine atoms in a pulsed self-sustained discharge in mixtures of iodides with a buffer gas such as molecular nitrogen and helium. Dynamics of the iodine atom production is studied by the method of absorption spectroscopy. The dissociation of $C_nF_{2n+1}I$ and $C_nH_{2n+1}I$ (n = 1, 2) iodides is investigated. The energy required to produce atomic iodine is evaluated. The experimental data obtained for CF_3I are compared with the results of numerical simulations, their reasonable agreement being demonstrated.**

Keywords: *oxygen–iodine laser, atomic iodine, iodide dissociation, pulsed discharge.*

1. Introduction

Iodine atoms needed for operation of a continuous-wave chemical oxygen–iodine laser (COIL) are traditionally produced by dissociation of iodine molecules in processes involving singlet oxygen (SO), which leads to the loss of some of its parts and reduction in the efficiency of a cw COIL. This drawback can be overcome by the use of external sources of iodine atoms. The gain medium of the laser is formed in this case by mixing the gas flows from the external source of iodine atoms and the SO generator. Both chemical [1] and the electric-discharge [2–4] methods of dissociation of iodides were studied to produce atomic iodine. Mikheyev et al. [2] investigated the possibility of atomic iodine production for COILs by decomposing CH_3I in a dc glow discharge in a vortex gas flow. In this case, the concentration of iodine atoms reached 3.6×10^{15} cm^{-3}. The use of a vortex flow made it possible to stabilise the glow discharge in a strongly electronegative halogen-containing gas mixture at pressures up to 2600 Pa. For the dissociation of iodide use was also made of microwave and RF discharges [3, 4].

For the practical implementation of the COIL it is important to minimise the energy needed to produce iodine atoms in the discharge. The energy needed for an iodine atom to be produced was estimated in [4] to vary from 30 to 130 eV per atom with an increase in the specific energy input in CF_3I mixtures with Ar and He.

The authors of [5, 6] used a pulsed self-sustained discharge to ensure the pulsed operation of the COIL. In this case, the discharge is produced in the active medium at output of the chemical SO generator at a typical SO concentration of 50%. Vagin et al. [6] managed to obtain the pulse energy (reduced to the volume of the medium) of 0.5 J L^{-1} at the oxygen pressure of 133 Pa in the laser with a sparger SO generator. Kochetov et al. [7] developed a numerical model for a pulsed laser triggered by a pulsed discharge in the active medium CF_3I–He–$O_2(a^1\Delta_g)$–O_2. The results of calculations of the pulse energy and shape corresponded to the experimental data [6].

A pulsed self-sustained discharge allows one to vary the discharge parameters (voltage, input energy, duration) in a wide range and seems to be promising as a source of iodine atoms for both pulsed and continuous-wave oxygen–iodine lasers. The typical duration of the laser pulse is usually hundreds of microseconds. In the case of using a discharge in the external source of iodine atoms, the times of transportation and mixing of the atoms produced are added to the required lifetime of iodine atoms. As a result, we obtain the time, a typical value of which is ~10 ms. This makes it important to study experimentally the evolution of atomic iodine at large times and leads to the need for modification of the model developed in [7, 8].

The aim of this paper is to study the evolution of the iodine atom concentration in a pulsed self-sustained discharge in buffer gas–iodide mixtures for determining the energy needed for producing atomic iodine and to compare the results of measurements with the results of numerical calculations.

2. Experimental setup

To measure the concentration of atomic iodine, we used the absorption method. The source of the probe radiation was a tunable narrow-band external-cavity semiconductor laser developed and manufactured at the P.N. Lebedev Physics Institute. The spectral width of laser radiation was 10 MHz, the diameter of the probe beam did not exceed 3 mm. The width of the frequency tuning range overlapped the spectral region corresponding to the hyperfine structure of the I ($^2P_{3/2}$) → I ($^2P_{1/2}$) transition. The emission wavelength of the probe laser was kept at the centre of the most intense line $F = 4 \rightarrow F' = 3$ of the I ($^2P_{3/2}$) → I ($^2P_{1/2}$) transition by controlling the signal absorbed in a cell with thermally dissociated molecular iodine. A sealed-off quartz tube with quartz windows contained 200 mg of molecular iodine. The cell temperature was maintained through its heating by a nichrome coil wound around the outer surface of the cell. For thermal insulation the tube was covered with asbestos. This design made it

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Received 7 December 2012; revision received 11 February 2013
Kvantovaya Elektronika **43** (7) 610–615 (2013)
Translated by I.A. Ulitkin

possible to heat the cell up to 700 °C. In practice, the temperature of about 330 °C is sufficient for measurements.

The optical scheme for measuring the concentration of iodine atoms in the laser cell is shown in Fig. 1. The probe beam of the tunable laser diode LD, reflected from the mirror M1 (reflectivity $R_1 = 90\%$), falls into the laser cell containing the medium under study. The intensity of the radiation passing through the medium was detected with a photodetector PD2 and a TDS 1012B digital oscilloscope. The lens in front of the detector PD2 was used to eliminate the modulation of the radiation power incident on the detector. Vibration of the mirror M3 caused by the operation of the vacuum pumps and cooling fans of the thyratron resulted in the deviation of the probe beam. Even at small angular displacements the radiation spot was markedly displaced in the detector plane. Because the diameter of the detector input was small, this resulted in a significant modulation of the PD2 signal.

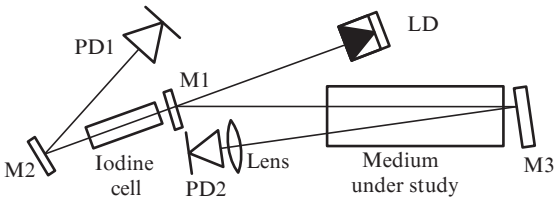

Figure 1. Optical scheme for measuring the concentration of atomic iodine.

Part of probe radiation (10%) passed through the heated cell and was detected by the photodetector PD1 and the TDS 1012 oscilloscope. Figure 2 shows a fragment of the absorption spectrum of the cell with crystalline iodine, showing the tuning range of the probe radiation. Measurements were performed at a cell temperature of 300 °C. In this case, the linewidth at half intensity was ~700 MHz. The uncertainty in the frequency tuning of the probe radiation in the experimental conditions was determined by the thickness of the rays in the oscilloscope, the stability of the screen image being no worse than 50 MHz. Such an uncertainty leads to inaccuracies (~6%) in determining the concentrations of iodine atoms. This value is within the statistical scatter in the experimental data of 10%.

To measure the concentration of iodine atoms, the laser radiation frequency was tuned to the centre of the line $F = 4 \rightarrow F' = 3$ by successively reducing the scanning range and the subsequently adjusting the radiation frequency with the laser diffraction grating built into the control unit.

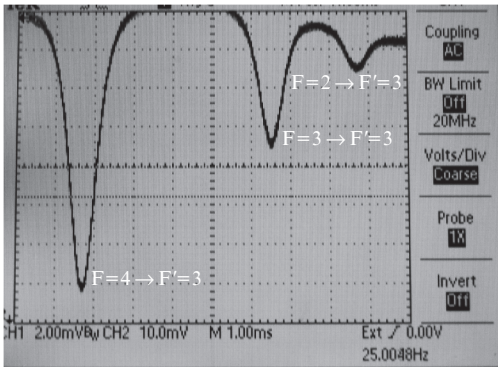

Figure 2. Fragment of the absorption spectrum of a cell with heated iodine; $T = 300$ °C, the sweep is 0.029 cm^{-1} div^{-1}.

In a cylindrical cell with an inner diameter of 45 mm, a two-section longitudinal electric discharge was produced. The total length of the two sections of the discharge was 115 cm. Thus, the probe signal passed the distance of 230 cm through the medium. The discharge was fed from the battery of low-inductance capacitors through the TGI-1000/25 thyratron, the battery capacity ranging from 6.8 to 20.4 nF and the voltage – from 10 to 22 kV. It should be noted that the formation of a uniform discharge in a mixture with electronegative gases is a difficult task, especially when the pressure increases. This imposes restrictions on the pressure range and the composition of the mixtures investigated. The parameters of the electrical discharge (current and voltage) were recorded with a TDS 2014B oscilloscope, the value of the input energy was calculated as the integral of the product of voltage and current.

The gas mixtures of the desired composition were prepared by mixing the initial components, the flow rate of which was controlled by rotameters. To maintain the air pressure at the rotameter input, the initial components were fed from plastic bags filled from bottles with the prepared mixtures of the desired composition. We failed to decrease the residual pressure in the system below 10 Pa, which was caused by inleakage of air. Therefore, the pressure of oxygen in all the experiments was no less than 2 Pa. Control of many parameters that affect the measured values (mixture composition, precision the absorption line centre tuning, etc.) allowed us to achieve repeatability of the results of experiments carried out under the same conditions at a level of ~10%. Because the diameter of the probe beam was 3 mm, the value of the transmitted signal can be affected by the gas-dynamic inhomogeneity caused by the pulsed discharge. In our case, these inhomogeneities were not controlled, and their influence manifested itself at high energy inputs into the discharge.

To find the concentration of iodine atoms, we used the absorption technique. The low-intensity signal passed through the medium is given by

$$I = I_0 \exp(-\kappa L), \tag{1}$$

where I_0 is the intensity of incident radiation; L is the path length in an absorbing medium; κ is the absorption coefficient, which can be represented as $\kappa = -(7/12)\sigma\Delta N$; σ is the stimulated emission cross section at the transition of the hyperfine structure of the iodine atom ($^2P_{1/2}$, $F' = 3$) → ($^2P_{3/2}$, $F = 4$); $\Delta N = (n^* - 0.5n)$; n^* and n are the concentrations of excited and unexcited iodine atoms, respectively. In the presence of excited iodine atoms the total concentration of iodine atoms is $(n + n^*) = -2\Delta N + 3n^*$. The measured absorption coefficient allows one to find ΔN, and the total concentration of iodine atoms can be assessed if we know n^*. As shown in [7], dissociation of CF_3I in the discharge is accompanied by the partial production of iodine atoms in the excited $^2P_{1/2}$ state. If an independent method for detecting the excited atoms is not used, the absorption measurements should be carried out under conditions when the excited atoms are absent. To achieve this goal in the mixtures for which quenching of the upper level is inefficient, molecular oxygen was added. In this case, rapid transfer of energy from the upper level of iodine to molecular oxygen in the ground state results in a rapid decrease in the concentration of excited iodine.

The frequency dependence of the cross section σ is described by the expression

$$\sigma(\nu) = \frac{A\lambda^2}{8\pi} f(\nu), \tag{2}$$

where A is the Einstein coefficient for the transition in question, and $f(\nu)$ is the function that describes the shape of the transition line.

In the case of the Doppler line broadening mechanism, which takes place at low working pressures, we have

$$f(\nu) = \sqrt{\frac{\ln 2}{\pi}} \frac{2}{\Delta\nu_D} \exp\left\{-\left[\frac{2(\nu-\nu_0)}{\Delta\nu_D}\sqrt{\ln 2}\right]^2\right\}, \tag{3}$$

where $\Delta\nu_D = (2/\lambda)\sqrt{2kT\ln 2/m}$; $\nu_0 = c/\lambda_0$ is the frequency of the line centre; and m is the mass of the iodine molecule. Hence

$$\sigma(\nu) = \frac{A\lambda^3}{8\pi}\sqrt{\frac{M}{2\pi RT}} \exp\left[-\frac{Mc^2}{2RT}\left(\frac{\Delta\nu}{\nu_0}\right)^2\right], \tag{4}$$

where $\Delta\nu = \nu_0 - \nu$; $M = 126.9$ is the atomic weight of iodine; T is the temperature in Kelvin; $R = 8.314$ J mol^{-1} K^{-1}; and $A = 5$ s^{-1} [9]. In the centre of the line

$$\sigma(\nu_0) = \sqrt{\frac{M}{2\pi RT}} \frac{A\lambda^3}{8\pi}. \tag{5}$$

At room temperature, $\sigma(\nu_0) = 1.3\times10^{-17}$ cm^2. The values of $\sigma(\nu)$ and $\sigma(\nu_0)$ depend on temperature, which should be known to determine the concentration of iodine atoms by the measured absorption. Temperature was found by comparing $I(\nu_0)$ and $I(\nu_0 - \Delta\nu)$ – intensities of the transmitted radiation at the line centre frequency and the frequency detuned from the line centre by a known quantity $\Delta\nu$. The gas temperature was determined from the expression

$$T = -[(Mc^2)/2R\ln(Q)][(\Delta\nu)^2/(\nu_0)^2], \tag{6}$$

where $Q = [\ln(I(\nu_0 - \Delta\nu)/I_0)]/[\ln(I(\nu_0)/I_0)]$. The insufficient accuracy of measuring $\Delta\nu$ did not allow us to determine the temperature at low energy inputs into the discharge. In this case, the temperature of the medium was assumed to be ambient. The maximum temperature can be estimated by assuming that all the input energy is spent on breaking the bond R – I, which requires 226.8 kJ mol^{-1}, and on heating the mixture. In this limit, the temperature T may be determined by the formula

$$T[K] = \frac{\varepsilon - ([I]/N_A)226800}{C_V/N_A} + 298, \tag{7}$$

where ε is the value of specific energy input (J cm^{-3}); [I] is the concentration of the iodine atoms produced (cm^{-3}); C_V is the specific heat at a constant volume (J mol^{-1} K^{-1}), N_A is Avogadro's number; and the initial temperature of the mixture is 298 K. The value of C_V depends on the mixture temperature, composition and pressure; at an initial temperature $C_V = 12.5$[He] + 62.6[CF_3I] + 36[CH_3I] + 20.8[N_2] (J mol^{-1} K^{-1} cm^{-3}). For a typical mixture composition CF_3I (36 Pa) + I (266 Pa) used in the experiment, the estimate yields a maximum temperature of 495 at an energy input of 1 J.

3. Theoretical model

In the calculations, we used the previously developed zero-dimensional kinetic model of a pulsed glow discharge [7, 8] in mixtures containing CF_3I. For other iodides information about the cross sections of electron scattering is far from complete, which makes it impossible to build a complete model. Our model includes a joint solution of the kinetic equations for the components of the discharge plasma in conjunction with the Boltzmann equation for the electron energy distribution function (EEDF). The Boltzmann equation for the EEDF is solved in two-term approximation, which takes into account elastic collisions of electrons with atoms and molecules, excitation of vibrational levels in the effective vibrational level approximation, excitation of the electronic states, dissociation of molecules by electron impact, ionisation of atoms and molecules and dissociative attachment of electrons to CF_3I molecules.

Together with the kinetic equations we solved equations for the external electric circuit and the equation for the translational temperature of the gas. The simulated electric circuit consisted of a discharge gap and a series-connected capacitor and 'stray' inductance (4.18 μH), the value of which was determined by comparing the calculated and experimentally measured discharge current and voltage. The capacitor was initially charged up to the voltage U_0. In the experiment, after the first half-period of the current pulse the thyratron was 'locked', which was accounted for in the model. Heating the gas in the discharge was calculated by the heat balance equation, which included all the known channels of energy dissipation of electrons and excited particles.

In the mixtures, where the buffer gas was helium, atomic iodine may be produced in the following processes of dissociation of CF_3I molecules by electron impact:

$$CF_3I + e \rightarrow CF_3I^* \rightarrow CF_3 + I, \tag{8}$$

$$CF_3I + e \rightarrow CF_3I^{**}, \tag{9}$$

$$CF_3I^{**} \rightarrow CF_3 + I, \tag{10a}$$

$$CF_3I^{**} \rightarrow CF_3 + I^*, \tag{10b}$$

where CF_3I^* and CF_3I^{**} are the CF_3I molecules in a rapidly decaying predissociation states, and I^* are the excited iodine atoms. Process (8) is a 4.7-eV energy threshold, process (9) – 7.2 eV. In our previous work [7], we assumed that the decomposition of CF_3I^{**} is accompanied by the production of I^*, i.e., through channel (10b). This conclusion was based on the measurements of shape and energy of the COIL pulse with the generation of iodine atoms in a pulsed glow discharge. Note also that in [7] the discharge was formed in an active medium with a high (50%) content of singlet oxygen O_2 ($^1\Delta_g$). The presence of singlet oxygen reduces the sensitivity of the laser characteristics to the ratio of energy inputs from channels (10a) and (10b). In the present work the concentration of iodine atoms produced in the pulsed discharge is measured by using the absorption technique that eliminates the uncertainties associated with the characteristics of the resonator. Therefore, the distribution in the channels (10a) and (10b) was re-determined by comparison with experiment.

4. Results and discussion

We studied mixtures of various iodides RI with the buffer gas with a concentration ratio of 1:7.5 at pressures 180–550 Pa.

The specific energy input varied in the range 0–2 mJ cm^{-3}. It should be noted that when nitrogen was used as a buffer gas, the discharge instability led to poor reproducibility of data, which made us employ helium and nitrogen mixtures as a buffer gas and study the $RI:He:N_2 = 1:3.75:3.75$ mixture.

4.1. CF_3I mixture with helium and nitrogen

The components of the working mixture $CF_3I–He–N_2$ poorly quench the excited iodine atoms. Therefore, to reduce the concentration of excited atoms, molecular oxygen with a partial pressure of 27 Pa, removing excitation from iodine atoms in the rapid process of energy exchange that is reverse to the process of inversion in an oxygen–iodine laser, is added to the mixture.

Figure 3 shows the experimentally measured and calculated time dependences of $2|\Delta N|$. In calculations, the ratio of the rates in channels (10a) and (10b) was varied to obtain the best agreement between the calculated fraction of the radiation passed through the medium under study and the experimentally measured radiation in the time interval from 0 to 20 μs. The best agreement is achieved when the ratio of energy inputs from channels (10a) and (10b) in the production of iodine atoms is equal to 3:7. Reasonable agreement can be reached at short times. This figure also shows the calculated time dependences of the total concentrations of excited and unexcited iodine atoms. The shape of the curves and the maximum values of $2|\Delta N|$ and $n + n^*$ differ, which in view of the relation $n + n^* = -2\Delta N + 3n^*$ is due to the nonzero value of n^*. The maximum total concentration of iodine $(n + n^*)_{max}$ exceeds $2|\Delta N|_{max}$ and is attained at shorter times. Figure 3 shows the results of calculations for two pressures of molecular oxygen –27 and 1.3 Pa (residual pressure of oxygen in the system). In the case of low concentrations of O_2, the energy of the excited states of iodine does not have time to be transmitted to O_2 molecules, and the value of $2|\Delta N|$ at times considered is significantly less than $n + n^*$. In the calculations the account for addition of molecular nitrogen at a pressure of 5 Pa into the mixture is due to inleakage of air into the system and has little effect on the results. The ratio $(n + n^*)_{max} \times (2|\Delta N|_{max})^{-1}$ (Fig. 4) is plotted as a function of the molecular oxygen pressure. At pressures of 13, 26 and 40 Pa, the ratio is 1.38, 1.18 and 1.11, respectively. This figure also shows how the value of the energy input into the discharge E_{in} changes when molecular oxygen is added to the $CF_3I:He = 1:7.5$ mixture. For convenience, it is normalised to the value $E_{in}[O_2] = 0$ of the energy input into the discharge in the absence of O_2 in the gas mixture. The energy input increases monotonically with increasing O_2 pressure and grows by 8% at a pressure of 40 Pa. The total concentration of atomic iodine at small additions of O_2 slightly increases and then decreases.

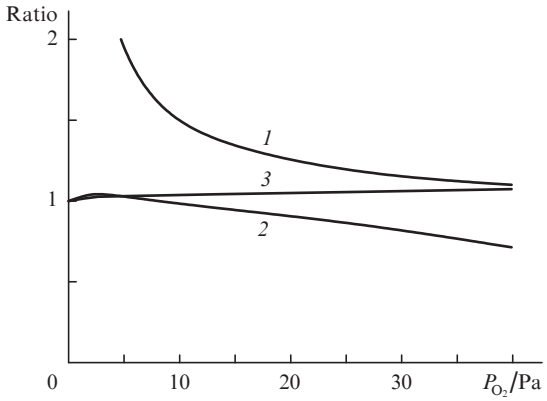

Figure 4. Calculated dependence of the ratios (*1*) $(n + n^*)|_{max}/(2|\Delta N|_{max})$, (*2*) $(n + n^*)|_{max}/(n + n^*)|_{[O_2]=0,max}$ and (*3*) $E_{in}/E_{in}|_{[O_2]=0}$ on the oxygen pressure. The mixture $CF_3I:He = 1:7.5$ at 350 Pa; $U_0 = 22.3$ kV.

Figure 5 shows the measured and calculated values of $2|\Delta N|$ as functions of the specific energy input for the mixture of CF_3I with He at different pressures of the gas mixture. It can be seen that pressure has little effect on the value of $2|\Delta N|$. A reasonable agreement between the experimental and theoretical results is observed for the 550-Pa pressure. At pressures of 200 and 350 Pa, the theory predicts lower values of $2|\Delta N|$ than those found in the experiment.

For the $CF_3I:He=1:7.5$ mixture at a pressure of 350 Pa and the energy input of 1 J into the discharge, the maximum concentration of iodine atoms was 2×10^{14} cm^{-3} (see the data in Fig. 5, marked by triangles) and the discharge volume was

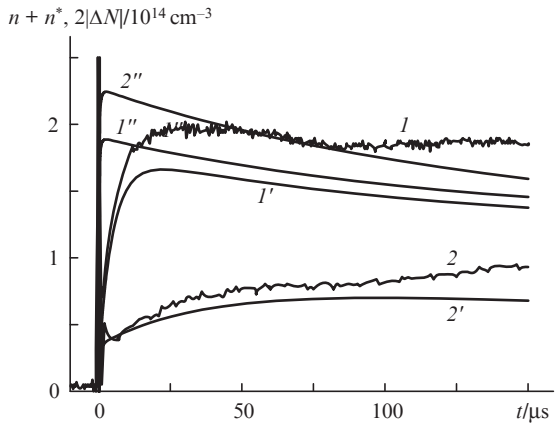

Figure 3. Temporal evolution of (*1*, *2*) measured and (*1′*, *2′*) calculated $2|\Delta N|$ values, as well as of (*1″*, *2″*) calculated $n + n^*$ values. The $CF_3I:He = 1:7.5$ mixture at a pressure of 350 Pa and pressures of oxygen (*1*) 27 and (*2*) 1.3 Pa; $U_0 = 22.3$ kV.

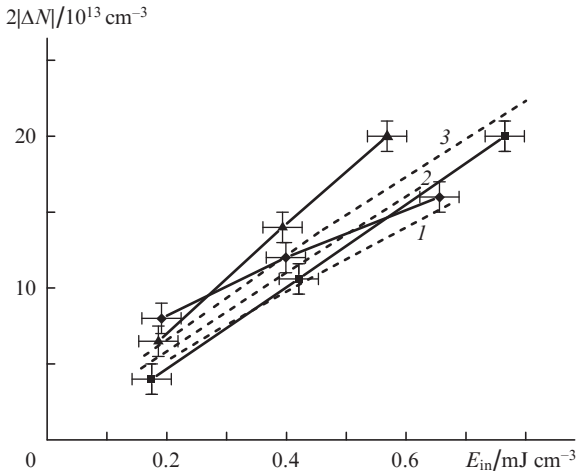

Figure 5. Dependences of $2|\Delta N|$ on E_{in} in the $CF_3I:He = 1:7.5$ mixture at pressures of (♦, *1*) 200, (▲, *2*) 350 and (■, *3*) 550 Pa; dashed lines represent the calculation results.

1830 cm^3. Therefore, the energy needed to produce an iodine atom in this case is approximately 17 eV per atom. Note that the theoretical calculation (see Fig. 4) predicts for these conditions $(n + n^*)_{max}/(2|\Delta N|_{max}) = 1.18$. Thus, the energy needed to produce an iodine atom with the account for the influence on the measurement results of excited iodine atoms is slightly lower than in the case of simple evaluation. For the $He:O_2:O_2(a^1\Delta_g):CF_3I = 10:1:1:1$ mixture at a pressure of 670 Pa, Kochetov et al. [7] predicted the energy of the iodine atom production to be equal to 30 eV per atom, in good agreement with the experiment [6]. Special calculations were carried out [7] to elucidate the reason of this difference in the energy needed to produce an iodine atom. It was found that a higher concentration of oxygen, half of which is the singlet state, leads to a significant increase in energy of the iodine atom production. This increase is due to a decrease in the proportion of the discharge energy that allows dissociation of CF_3I to produce iodine. A significant contribution to the energy balance of the electrons is made by the processes of excitation, including cascading, of oxygen molecules.

Figure 6 shows the dependences of $2|\Delta N|$ on the specific energy input at different pressures of the $CF_3I:He:N_2 = 1:3.75:3.75$ mixture. The energy of the iodine atom production, when half helium in the mixture is replaced by nitrogen, is higher than the initial mixture. This may indicate differences in the mechanisms of production of iodine atoms in these mixtures. Let us estimate the energy needed to produce an iodine atom, using the experimental data. Since the dependence of the concentration of iodine atoms on the input energy in Fig. 6 is approximately linear, the energy needed to produce an iodine atom in the investigated range of the discharge parameters is virtually constant.

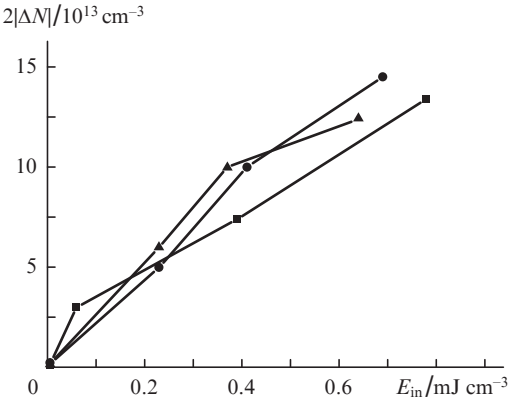

Figure 6. Dependences of $2|\Delta N|$ on E_{in} in the $CF_3I:He:N_2 = 1:3.75:3.75$ mixture at pressures of (●) 180, (▲) 350 and (■) 450 Pa.

When replacing half helium by nitrogen in the mixture, the energy needed for an iodine atom to be produced, estimated from experimental data, is higher by more than half. The theoretical model from work [8], developed for describing the dissociation of CF_3I in the mixture with N_2 in a pulsed glow discharge, predicts for experiments of this work the same energy of the iodine atom production, as in the case, when use is made of helium as a buffer gas. Reasons for the discrepancy between theory and experiment remain unidentified. One of them may be the assumption [8] that in collisions of CF_3I molecules with electronically excited nitrogen molecules, the result of dissociation is the detachment of the iodine atom, although precise data on CF_3I dissociation channels are not available.

4.2. CH_3I mixture with helium and nitrogen

The rate constant for quenching of excited iodine atoms by CH_3I molecules is five orders of magnitude higher than by CF_3I molecules. Therefore, the experimentally observed absorbance corresponds to the situation when the total concentration of iodine atoms is equal to $2|\Delta N|$. Experiments were carried out using the mixtures of the same composition as in the case of CF_3I. Figure 7 shows the dependences of the concentration of iodine atoms on E_{in} at various pressures of the CH_3I–He mixture. As in the case of CF_3I, these dependences are virtually linear, and an increase in pressure causes a reduction in the dissociation efficiency. It is worthy of note that the energy needed to produce an iodine atom at a pressure of about 300 Pa is 17.6 eV per atom, which is almost identical to the value obtained for mixtures with CF_3I. This situation does not seem strange, given that the binding energy of the iodine atom in the CH_3I (2.33 eV [10]) and CF_3I (2.32 eV [11]) are virtually identical.

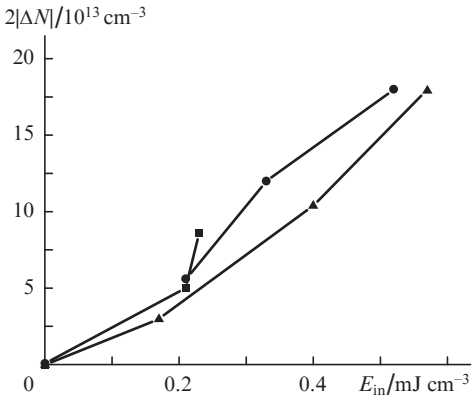

Figure 7. Measured dependences of the concentration of production of iodine atoms on E_{in} in the $CF_3I:He = 1:7.5$ mixture at pressures of (■) 150, (●) 350 and (▲) 460 Pa.

As in the experiments with CF_3I, use of nitrogen as a buffer gas reduces the efficiency of production of iodine atoms. Figure 8 shows the waveforms of intensity of probe radiation

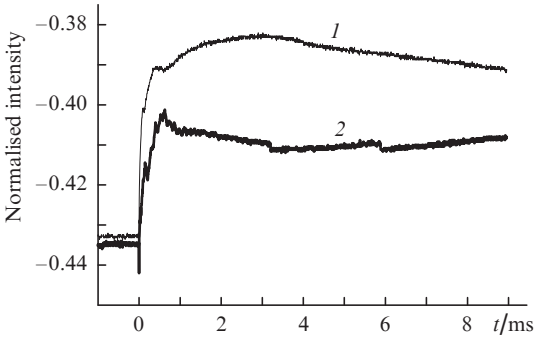

Figure 8. Waveforms of intensity of probe radiation transmitted through the CH_3I (36 Pa) mixture with (*1*) He (270 Pa) and (*2*) N_2 (270 Pa) at energy inputs of 0.96 and 1.35 J, respectively.

transmitted through the medium under investigation when nitrogen and helium are employed as a buffer gases. It can be seen that absorption in the nitrogen mixture is much lower, although the energy input is substantially greater when use is made of nitrogen.

4.3. C_2H_5I and C_2F_5I mixtures with helium and nitrogen

We also examined mixtures of more complex iodides, C_2F_5I and C_2H_5I, with helium and nitrogen under similar experimental conditions. Despite the fact that these iodides have a low saturated vapour pressure, especially C_2H_5I, and are unlikely to be of interest as iodine donors for use in chemical oxygen–iodine lasers, their study is important for understanding the processes of dissociation of complex organic compounds in a low-temperature plasma. We studied the composition of the mixture RI : buffer gas = 1 : 15. High content of the buffer gas is necessary for the convenient work with these compounds. As is the case of simple iodides, the dependences of concentration of iodine atom production on the value to the input energy are almost linear. However, the energy needed to produce an iodine atom in this case is much higher: 40 and 41.6 eV per atom for C_2F_5I and C_2H_5I, respectively. Since the binding energies of $I-CF_3$ and $I-C_2F_5$ are very close (2.32 and 2.27 eV, respectively), this fact indicates the presence of additional channels of discharge energy dissipation in mixtures of complex organic compounds.

In experiments with C_2H_5I we found the effect of the discharge pulse duration on the efficiency of production of iodine atoms, characterised by the energy needed to produce an iodine atom. The duration was varied by changing the discharge capacity and selecting the charging voltage, providing the same energy input into the discharge. Evolution of the $2|\Delta N|$ value for the C_2H_5I : He = 1 : 15 mixture at a pressure of 400 Pa is presented in Fig. 9. At a low voltage and high capacity (i.e., at a high discharge duration) the energy of the iodine atom production is lower.

A similar effect of the parameters of the discharge circuit on the efficiency of production of iodine atoms was observed in C_3F_7I : He=1 : 7.5 mixtures. As in the case of other iodides, we have here a linear dependence of the concentration of iodine atoms produced by the discharge on the input energy. The energy needed to produce an iodine atom is 42 eV per atom at a pressure of 220 Pa and 45 eV per atom at a pressure of 340 Pa, which is close to the values obtained for C_2F_5I.

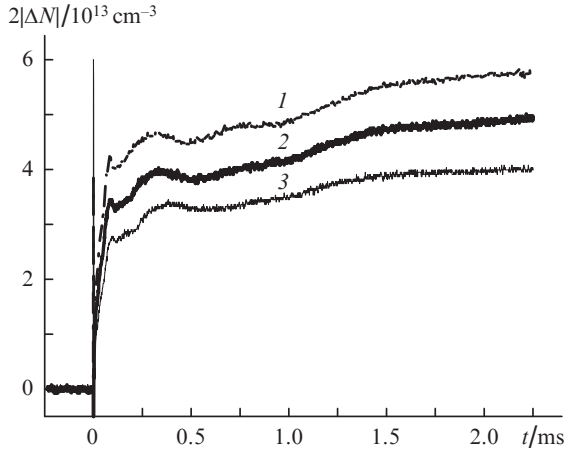

Figure 9. Temporal evolution of the concentration of iodine atoms at various discharge circuit parameters: (*1*) C = 20.4 nF, U_0 = 12.8 kV; (*2*) 13.6 nF, 15.8 kV; and (*3*) 6.8 nF, 22.3 kV. The energy needed to produce an iodine atom is equal to 30, 38 and 43 eV per atom, respectively.

5. Conclusions

In the work on absorption at the laser transition we have studied the evolution of concentration of iodine atoms in the afterglow of a pulsed self-sustained discharge in mixtures of iodides with a buffer gas. Experimental evaluation of the energy needed to produce atomic iodine depends on the type of iodide, and for the simplest iodides in different conditions it varies between 17–30 eV per atom.

The measured dynamics of the concentration of iodine atoms after the discharge termination has made it possible to introduce changes in the ratio of the efficiencies of two channels of the CF_3I^{**} pre-dissociation process. The best agreement with the experiment is achieved if the contribution to the pre-dissociation in the channel of production of ground state iodine atoms is 30%. Note that in paper [7] by comparing the calculated and experimental values of the pulse delay and the duration after the discharge in a mixture flowing from the chemical SO generator, this value was assumed equal to zero.

Our studies have shown that the use of a pulsed self-sustained discharge for production of iodine atoms in the COIL is as effective as other methods of dissociation of iodides, and the simplicity of technology and the ability to vary the discharge parameters make it even more advantageous as compared to other methods. The relatively low values of the energy needed to produce iodine atoms obtained in a pulsed discharge permit to operate at low energy inputs, providing a slight increase in the temperature of the active medium, which allows one to reduce the threshold concentration of singlet oxygen and improve the chemical efficiency of the laser.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (Grant Nos 10-02-00152-a and 11-02-00613-a).

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