*ACTIVE MEDIA*

PACS numbers: 42.55.Ks; 52.80.Hc
DOI: 10.1070/QE2002v032n01ABEH002115

# Atomic iodine production in a gas flow by decomposing methyl iodide in a dc glow discharge

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***Abstract*. The production of atomic iodine for an oxygen–iodine laser is studied by decomposing methyl iodide in a dc glow discharge in a vortex gas flow. The concentration of iodine atoms in discharge products was measured from the atomic iodine absorption of the radiation of a single-frequency tunable diode laser at a wavelength of 1.315 μm. Atomic iodine concentrations sufficient for the operation of an oxygen–iodine laser were obtained. The concentration of atomic iodine amounted to $3.6 \times 10^{15}$ cm$^{-3}$ for a pressure of the carrying argon gas of 15 Torr. The discharge stabilisation by a vortex gas flow allowed the glow discharge to be sustained in a strongly electronegative halogen-containing gas mixture for pressures up to 20 Torr.**

***Keywords***: *oxygen–iodine laser, atomic iodine, glow discharge.*

## 1. Introduction

The production of atomic iodine with an atomic concentration of $\sim 10^{15}$ cm$^{-3}$ at a pressure of a medium (including the carrying gas) $p \geqslant 10$ Torr is of interest for the optimisation of characteristics of chemical oxygen–iodine lasers (COILs). In lasers of this type, electronic-excited singlet oxygen $O_2(a\,^1\Delta)$ is employed as the energy carrier. This energy is resonantly transferred to the upper laser level of iodine atoms. It also ensures the dissociation of iodine molecules.

Arguments in favour of using atomic iodine in chemical lasers were presented in Refs [1, 2] and are as follows. The number of singlet-oxygen molecules required for the dissociation of one iodine molecule ranges from 3 to 6. Chemical generators usually produce a stream of oxygen containing $\sim 50$ % of $O_2(a\,^1\Delta)$ molecules. At room temperature, inversion is achieved at the concentration of the $O_2(a\,^1\Delta)$ molecules of about 20 %, and when gas-dynamic cooling is used (a supersonic flow), it is of about 10 %. At the optimal relative concentration $[I_2]/[O_2] \sim 2$ %, no less than 10 % of the $O_2(a\,^1\Delta)$ molecules is spent for the dissociation of iodine. Therefore, by using iodine atoms prepared in advance and by mixing them with the gas carrying singlet oxygen, one would expect an increase in the output COIL power up to 25 %. In this case, the lower the initial percentage of singlet oxygen in the medium delivered to the active region, the higher the increase in the output laser power.

In Refs [1, 2], an attempt was made to obtain iodine atoms in the plasma of a continuous microwave discharge in a mixture of He with $I_2$ and subsequently use them in an COIL. Attempts to attain the optimal iodine concentration did not meet with success in this experiment. The degree of $I_2$ dissociation was 40 % to 20 % and lowered with increasing iodine content. Nevertheless, the output COIL power was observed to increase in Refs [1, 2].

The production of iodine atoms in a pulsed discharge directly in the active medium of an OIL was studied in papers [3, 4]. According to estimates of the authors of paper [4], the achieved atomic iodine concentration was of the order of $1.8 \times 10^{15}$ cm$^{-3}$.

The aim of this work is to investigate the possibility of obtaining the required atomic iodine concentrations [1] in a dc glow discharge by using methyl iodide $CH_3I$ as a donor. Halogen-containing gas mixtures are strongly electronegative, and the volume discharge in them is known to become unstable with increasing pressure and/or the energy input. For this reason, we used in our experiments a discharge in a vortex gas flow. Such a discharge features improved stability and can exist at high pressures and a high energy input [5].

The use of iodine-containing $CH_3I$ molecules instead of $I_2$ molecules offers a significant advantage: in the products of decomposition of the former, the concentration of $I_2$ molecules is known to be low, because they are produced only by recombination. In this case, the recombination of iodine atoms involving a $CH_3I$ molecule as the third particle proceeds with a significantly lower rate than the recombination involving $I_2$. In addition, the use of $CH_3I$ does not require an additional heating of the medium, as in the case of $I_2$, because the saturated $CH_3I$ vapour pressure at room temperature is of about 400 Torr.

## 2. Experimental

The scheme of the experimental setup is shown in Fig. 1. The dc glow discharge was ignited in a vortex gas flow in a quartz tube with an internal diameter of 17 mm between cooled copper electrodes. The anode was a solid cylinder 12 mm in diameter and the cathode was a hollow cylinder with an internal diameter of 10 mm. The interelectrode

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Received 13 August 2001; revision received 31 October 2001
*Kvantovaya Elektronika* **32** (1) 1–4 (2002)
Translated by E.N.Ragozin

spacing was varied from 6 to 2.2 cm. The carrier gas was supplied near the cathode tangentially to the circumference of the cross section of the tube. Methyl iodide was admixed to the discharge on the anode side. The discharge products were removed to the diagnostics region through the opening in the cylindrical cathode. We studied the efficiency of decomposition of methyl iodide in the glow discharge plasma of Ar, He, $O_2$, and $N_2$ gases and the air.

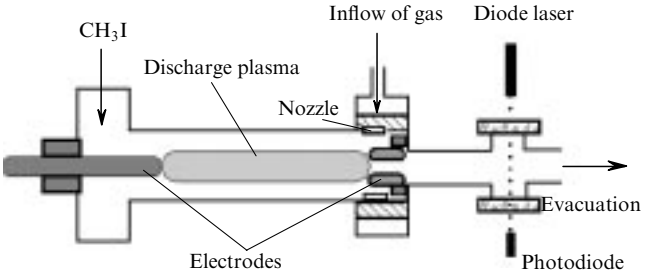


**Figure 1.** Schematic of the experimental setup.

The concentration of iodine atoms was determined from the absorption of probe laser radiation at a wavelength $\lambda = 1.315$ μm by atomic iodine. In the diagnostics region the gas flew perpendicular to the probe beam. The resonance absorption at the $^2P_{3/2}(F = 4) \rightarrow {}^2P_{1/2}(F = 3)$ atomic iodine transition was recorded using a measuring complex based on a single-frequency tunable semiconductor laser. The absorption coefficient was measured as a function of the probre radiation frequency. Every value was measured for 10–15 s, which corresponded to averaging the results of 200–300 cycles of laser radiation frequency scanning. The data processing involved the approximation of the absorption line shape by the Voigt profile. In this case, the Gaussian ($W_G$) and Lorentzian ($W_L$) linewidths (for I atoms and $\lambda = 1.315$ μm) were related by the expressions $T = (W_G/14.49)^2$ and $W_L = W_{las} + \gamma p(300/T)^{0.87}$, where $T$ is the temperature of the medium; $p$ is the gas pressure; $W_{las} = 8$ MHz is the width of a Lorentzian emission line of the semiconductor laser; and $\gamma = 3.6$ MHz Torr$^{-1}$ is the corresponding impact broadening coefficient for argon; the widths $W_G$ and $W_L$ are taken in megahertz. The approximation of the absorption line shape by the Voigt profile also made it possible to determine the gas temperature.

The concentration of atomic iodine was determined from the integral $S$ over the absorption line. The optical path of the laser beam in the medium containing atomic iodine was assumed to be known. In this case, the following relation is valid:

$$S = \frac{7}{12}\left([\mathrm{I}]^* - \frac{1}{2}[\mathrm{I}]\right)\frac{A_{34}\lambda^2}{8\pi},$$

where $[\mathrm{I}]^*$ is the concentration of iodine atoms in the excited state and $A_{34} = 5.1$ s$^{-1}$ is the transition probability.

To estimate the error of measurements of [I] caused by the presence of excited iodine atoms, we measured the concentration $[\mathrm{I}]^*$ from the spontaneous emission at the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition. When recording $[\mathrm{I}]^*$, the calibration was performed against the blackbody radiation (the measuring technique was described in detail in paper [6]). The measurements showed that $[\mathrm{I}]^*$ amounts to ~2 % of [I], and therefore the corresponding error can be neglected in our experiments.

Estimates show that no appreciable atomic-to-molecular iodine recombination should occur under our experimental conditions. The recombination rate coefficients for atomic iodine in the reaction $\mathrm{I} + \mathrm{I} + \mathrm{M} \rightarrow \mathrm{I}_2 + \mathrm{M}$ at a temperature of ~500 K were [7, 8]: $3 \times 10^{-31}$ cm$^6$ s$^{-1}$ for $\mathrm{M} = \mathrm{I}_2$, $8 \times 10^{-32}$ cm$^6$ s$^{-1}$ for $\mathrm{M} = \mathrm{CH_3I}$, and $3 \times 10^{-33}$ cm$^6$ s$^{-1}$ for M = Ar. The absence of significant recombination was experimentally verified by measuring [I] at two points along the flow spaced 15 mm apart. As expected, we revealed no difference in the concentration [I] at these points. At a distance of ±7 mm from the flow centre in the direction perpendicular to the flow velocity, the concentration [I] was lower by 10 %, indicating to the presence of the concentration maximum on the axis. Therefore, the measured [I] values are averaged over the optical path.

## 3. Results of measurements

Our measurements showed that the highest concentrations [I] were obtained using argon as the carrier gas. When helium and oxygen were used, the values of [I] were two times lower, and when nitrogen and air were used, they were lower by an order of magnitude. The discharge glow was not uniform over its cross section: a bright region was observed at the centre, which occupied ~1/3 of the discharge tube diameter. In oxygen (and especially in nitrogen and air), the discharge tube and the electrodes were strongly contaminated after several minutes of operation to impair the discharge stability.

The results of measurements of the concentration [I] as a function of the discharge current are given in Fig. 2 for an argon pressure of 6 Torr and an interelectrode spacing of 6 cm. One can see that the maxima of concentration [I] are observed for a current value independent of the $CH_3I$ flow rate. The decrease in the concentration [I] with increasing current is probably caused by the gas heating. As the flow rate of methyl iodide was increased from 0.04 to

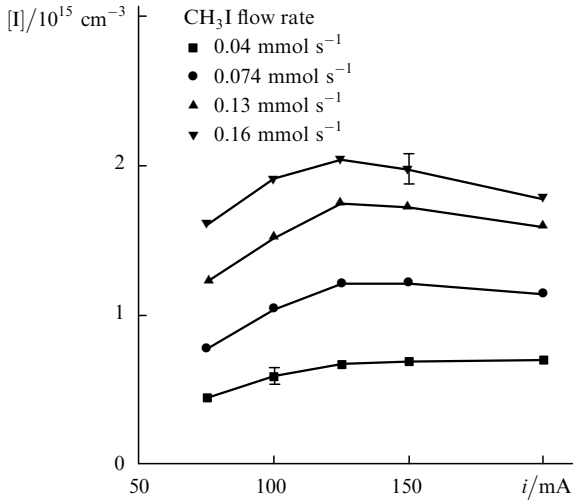


**Figure 2.** Dependences of the atomic iodine concentration [I] on the discharge current $i$ for different $CH_3I$ flow rates for an argon pressure of 6 Torr, an argon flow rate of 3 mmol s$^{-1}$, and an interelectrode spacing of 6 cm.

0.16 mmol $s^{-1}$, the maximum concentration of atomic iodine increased linearly.

As the current increased from 75 to 200 mA, the discharge voltage changed from 450 to 500 V for a methyl iodide flow rate of 0.04 mmol $s^{-1}$ and from 800 to 880 V for a flow rate of 0.16 mmol $s^{-1}$. The overall potential drop at the electrodes estimated from measurements for different interelectrode spacings was of about 300 V. For maximum concentrations [I], the fraction of iodine atoms relative to the initial number of methyl iodide molecules ranged from 40 % for a methyl iodide flow rate of 0.04 mmol $s^{-1}$ to 30 % for a flow rate of 0.16 mmol $s^{-1}$.

As the Ar pressure was increased at a fixed current and also as the current was increased at a fixed pressure, the concentration [I] dropped sharply at some instant, indicating to the onset of the discharge instability. In this case, a characteristic change in the absorption line $J$ was observed (Fig. 3). For low discharge currents, the absorption line shape was smooth, and for high currents it became noisy.

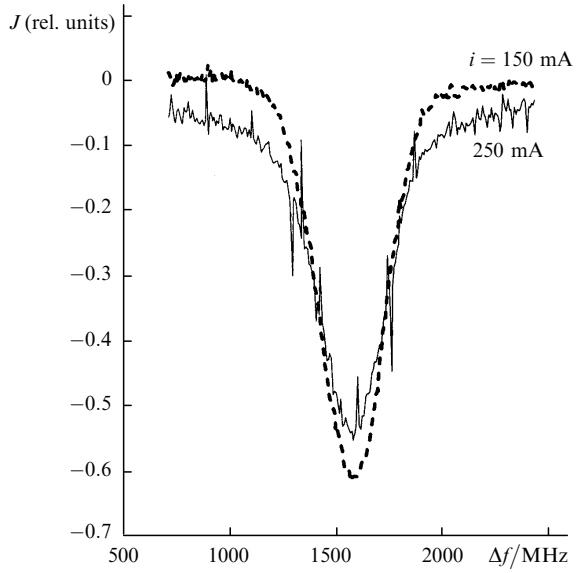


**Figure 3.** Absorption line shape of the $^2P_{3/2}(F=4) \rightarrow {}^2P_{1/2}$ $(F=3)$ transition in atomic iodine for two values of the discharge current $i$.

By decreasing the interelectrode spacing, we increased the argon pressure, the discharge stability being retained. By reducing this spacing from 6 to 2.2 cm, we obtained a stable discharge for a pressure up to 20 Torr. In this case, atomic iodine concentration as high as $2 \times 10^{15}$ $cm^{-3}$ was achieved. Fig. 4 shows the typical dependences of [I] on the discharge current for two interelectrode spacings for an argon pressure of 15 Torr and different argon flow rates.

The maximum concentration [I] equal to $3.6 \times 10^{15}$ $cm^{-3}$ was obtained in a discharge with an interelectrode spacing of 2.2 cm for an argon pressure of 15 Torr and an argon flow rate of 2.2 mmol $s^{-1}$. In this case, the temperature determined from the absorption line width was 570 K. The fraction of iodine atoms amounted to 20 % of the initial number of methyl iodide molecules.

## 4. Discussion of results

It is known that one of the main parameters determining the discharge processes is the ratio $E/N$ between the electric

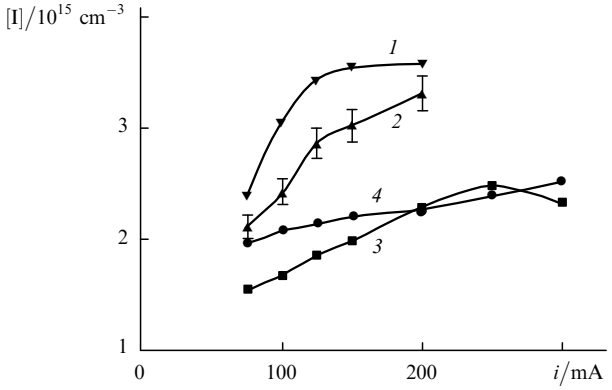


**Figure 4.** Typical dependences of the concentration [I] on the discharge current $i$ for a methyl iodide flow rate of 0.14 mmol $s^{-1}$ and an argon pressure of 15 Torr for an argon flow rate of 2 (*1, 2*) and 3 mmol $s^{-1}$ (*3, 4*) and an interelectrode spacing of 2.2 (*1, 3*) and 3 cm (*2, 4*).

field intensity and the concentration of particles. In our experiments, $E/N$ in the positive column of the glow discharge was equal to $(1.5-8) \times 10^{-16}$ V $cm^{-2}$. For these $E/N$ values, the average electron energy in argon is $\sim 8$ eV [9]. Under these conditions, atomic iodine in the discharge plasma is produced by the reaction of electron-impact dissociation of methyl iodide $CH_3I + e \rightarrow CH_3 + I + e$ and also as a result of the dissociative attachment $CH_3I + e \rightarrow CH_3 + I^-$ with subsequent recombination of $I^-$ ions. It seems likely that the dissociative recombination of $CH_3I^+$ with electrons and $I^-$ ions is also possible.

The data for these reactions are presently unavailable in the literature, but the rate constants of similar reactions are of the order of $10^{-7}-10^{-9}$ $cm^3$ $s^{-1}$ [9–11]. The $CH_3 + I \rightarrow CH_3I$ recombination rate is low [12]. Because the probability of recombination of iodine atoms at walls is equal to $\sim 10^{-3}-10^{-4}$ [13], this process can also be neglected. Therefore, for an average electron density $n_e \sim 10^{12}$ $cm^{-3}$ used in our experiments, the characteristic production time of atomic iodine did not exceed $\sim 1$ ms. Estimates showed that the $Ar - CH_3I$ mixture stayed in the discharge region for 2–3 ms and over, and therefore one would expect an almost complete dissociation of methyl iodide. However, the fraction of iodine atoms in the experiments was no higher than 40 % of the initial number of $CH_3I$ molecules. Increasing the interelectrode spacing did not result in an increase in the concentration [I], despite the fact that the mixture was in the discharge longer by a factor of 1.5–2.

The incomplete dissociation of methyl iodide can be explained by a nonuniform filling of the discharge tube with the plasma. It seems likely that a part of the gas mixture in this case does not manage to interact with the discharge plasma for a sufficiently long time, which eventually results in the incomplete dissociation of $CH_3I$. Other loss mechanisms are also possible, for instance the production of some iodine-containing molecules.

Of significance for a COIL is the question of whether it is possible to transport iodine from the discharge region to the region of mixing with singlet oxygen. The recombination rate of atomic iodine was estimated using the kinetic model. Calculations performed for our experimental conditions (considering that immediately after the discharge $[I] = 3.6 \times 10^{15}$ $cm^{-3}$, $T = 500$ K, and that about 20 % of methyl

iodide dissociated and the argon pressure was 15 Torr), showed that [I] decreases by 1 % in 1 ms and by 5 % in 5 ms. Under these conditions, the main contribution to the recombination of atomic iodine is made by the reaction $I + I + CH_3I \rightarrow I_2 + CH_3I$. Therefore, under our experimental conditions there is enough time for atomic iodine to be transported to the region of mixing with singlet oxygen.

Note that a characteristic feature of a COIL is the low gain determined by the optimal concentration [I]. Higher densities of atomic iodine reduce the laser efficiency due to the quenching of excited atoms. In this case, it is the iodine molecules, which are always present in the active medium along with the atoms, that are the strongest quenchers. The use of the preliminary prepared atomic iodine will increase its optimal density and, hence, increase the gain of the active medium.

## 5. Conclusions

We have produced atomic iodine by the electric-discharge technique at concentrations sufficient for the operation of a COIL. The required concentrations equal to $3.6 \times 10^{15}$ $cm^{-3}$ obtained upon the decomposition of methyl iodide in a vortex argon flow at an argon pressure of 15 Torr. This pressure is sufficient for the subsequent injection of atomic iodine into the active region of the COIL.

The discharge stabilisation by the vortex gas flow allowed the dc glow discharge to be sustained in a strongly electronegative halogen-containing gas mixture at pressures up to 20 Torr.

When methyl iodide is used as the donor of atomic iodine, its incomplete dissociation should not prevent the transportation of atomic iodine to the region of mixing with oxygen, unlike the case where $I_2$ is employed as the donor. According to theoretical estimates, the decrease in the atomic iodine concentration in our experiments was no more than $\sim$5 % in 5 ms. The possibility of increasing the optimal concentration of atomic iodine with the consequential increase in the gain of the COIL active medium may prove to be an additional advantage of employing atomic iodine instead of molecular iodine.

***Acknowledgements.*** The authors thank the US Air Force Laboratory for providing the spectroscopic measuring complex with a tunable semiconductor laser, and also V.D.Nikolaev, M.V.Zagidullin, and M.I.Svistun for their assistance in operating the above complex and helpful discussions. This work was supported by the European Office of Aerospace Research and Development (the ISTC Contract No. 1826) and the 'Integration' Federal Dedicated Programme (Contract No. A0056).

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