Quantum Electronics **32** (7) 609 – 613 (2002)

PACS numbers: 42.55.Ks; 42.60.Lh
DOI: 10.1070/QE2002v032n07ABEH002255

A pulsed oxygen – iodine chemical laser excited by a longitudinal electric discharge

N.P. Vagin, N.N. Yuryshev

***Abstract*. The dependence of the energy parameters of an oxygen – iodine chemical laser with a bulk generation of iodine atoms in a longitudinal electric discharge on the length of the discharge gap is studied for various discharge energies and voltages and various working mixture compositions (at constant oxygen and iodine pressures). Analyses of the results suggests that temperature effects account for a twofold decrease in the specific energy yield for the lasing initiated by a longitudinal electric discharge compared to the photolytic initiation.**

Keywords: *chemical oxygen – iodine laser, electric discharge, singlet oxygen.*

1. Introduction

The pulse bulk generation of iodine atoms in a mixture containing singlet oxygen is the most efficient method for providing a pulse operating mode of a chemical oxygen – iodine laser (COIL) from the viewpoint of obtaining the maximum ratio between the output powers in the pulse and cw modes at the same consumption of reagents. This method was implemented for the first time in a pulse photolysis for producing iodine atoms from CF_3I [1]. Subsequently, the initiation of lasing by pulse photolysis made it possible to achieve a specific energy yield of 3 J L^{-1} at an oxygen pressure of 3 Torr [2].

The possibility of using a transverse electric discharge for initiating the lasing of a pulsed COIL laser with a bulk generation of iodine atoms was demonstrated in paper [3]. Such a discharge allows for the operation at elevated pressures of the working mixture and requires certain efforts for providing the discharge homogeneity especially for a discharge chamber of increased dimensions. The initiation of lasing by a longitudinal discharge is limited by a certain working-mixture pressure, but it is easy to implement, and ensures a high lasing efficiency of a pulsed COIL. An electric efficiency of such a laser close to 100 % was reported in paper [4].

The aim of this work is to study the dependence of the laser energy characteristics on the discharge-gap length. The results of this study can be used in constructing electric-discharge-initiated pulsed COILs. In contrast to a transverse discharge, a longitudinal discharge in the transverse-flow scheme has an additional degree of freedom that can be used, for example, for placing a system for gain modulation using the Zeeman effect.

In our case, when speaking about a longitudinal discharge, we mean such a discharge geometry in which the distance between the electrodes appreciably exceeds the transverse size of the discharge column. Decreasing the discharge gap leads to a discharge geometry that better corresponds to a transverse discharge.

The use of a pulse glow discharge for generating iodine atoms in a gas mixture containing singlet oxygen is a nontrivial problem. Indeed, electrons, ions, excited molecules, and products of dissociation of molecular components of the mixture are produced in the electric discharge. The form and number of these components generally depend on the discharge parameters, mainly on the discharge energy and the reduced electric-field strength E/N. In addition, the discharge-gap length determines the resistance of the plasma channel and, consequently, the electric energy deposited into the laser active medium.

Thus, the optimisation of the discharge parameters aimed at the improvement of the laser output energy characteristics is an important task, and varying the discharge-gap length makes it possible to change these discharge parameters, while the voltage across capacitors remains unaltered.

2. Experimental

A schematic of the experiment is shown in Fig. 1. The discharge chamber is mounted in one of the arms of the experimental setup, which was previously used in experiments with a pulsed laser excited by a longitudinal discharge [4]. The inner diameter of this chamber manufactured of polymethyl methacrylate is 39 mm. Five holes in which electrodes were installed were drilled in the chamber with a 10-cm spacing along its length. Electrode sections of IFP-20000 flash lamps 20 mm in diameter contained tungsten electrodes and served as cathodes. These sections were inserted into the holes of the discharge chamber and sealed. The same electrode was used as the anode. In order to exclude the effect of near-electrode processes on the measurement results, the electrodes were positioned outside of the laser resonator volume. Hence, only the processes in the positive column participated in the production of the active laser medium. A system with

N.P. Vagin, N.N. Yuryshev P.N. Lebedev Physics Institute, Leninskii prosp. 53, 119991 Moscow, Russia; e-mail: yuryshev@mail1.lebedev.ru

Received 24 January 2002
Kvantovaya Elektronika **32** (7) 609 – 613 (2002)
Translated by A.S. Seferov

movable ring electrodes was also tested. However, it was rejected, because unstable results were obtained. An electric discharge produced by a capacitor bank was initiated by a TGI-25/1000 thyratron ensuring the operation at voltages of up to 25 kV. The capacitor bank was assembled from ceramic low-inductance 3.4-nF capacitors. The discharge energy was varied by changing both the operating voltage and the number of capacitors in the bank. Singlet oxygen was produced in a sparger generator of singlet oxygen [3, 4].

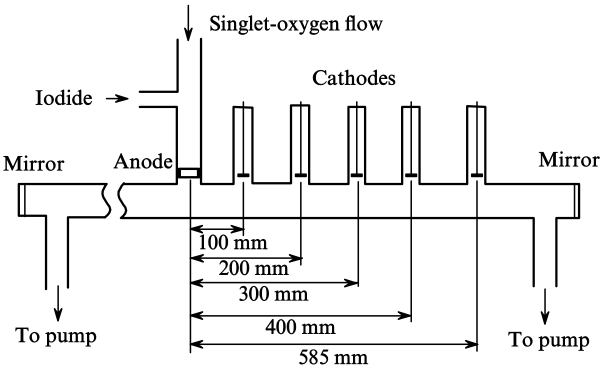

Figure 1. Schematic of the discharge chamber.

The specific output energy and efficiency are the criteria of the laser operation efficiency. However, the laser output energy depends on the degree to which the threshold gain is exceeded, which, in its turn, is a function of the amplification length. In order to reduce the influence of the amplification length on the specific output lasing parameters, a resonator with a 0.8 % transmission of the output mirror was used (in most of experiments, the optimal transmission is ~ 4 %). A spherical mirror with a 0.05 % transmission served as the second reflector. The laser output energy was bounded by an external diaphragm 30 mm in diameter set at a distance of 45 cm from the output mirror.

All experiments were performed at oxygen and CF_3I partial pressures of 1 and 0.5 Torr, respectively. Helium, nitrogen, and sulphur hexafluoride (SF_6) were employed as buffer gases. The experimental parameters were varied within the following ranges: 10 – 58.5 cm (the discharge-gap length), 10 – 20 kV (the discharge voltage), and 2 – 8 Torr (the buffer-gas pressure). The laser radiation energy was measured with an IMO-2N calorimeter, and the laser pulse shape was recorded by an FD-10G germanium photodiode and storage oscilloscope and was photographed by a digital camera.

3. Results and discussion

In contrast to the photolysis, which is a selective tool for the dissociation of iodides, an electric discharge interacts with all components of the working mixture and leads to the formation of electrons, ions, molecular fragments, etc., that may have a significant effect on the inversion formation kinetics in a pulsed COIL. Therefore, interpreting the results becomes a fairly complex problem. Nevertheless, we tried to expose the general properties of the behaviour of a pulsed COIL excited by a longitudinal discharge.

The output energy is one of the key parameters characterising the laser efficiency. Fig. 2 shows the laser output energy as a function of the discharge length at various initiation conditions (discharge voltage, storage capacitance) for helium used as a buffer gas. As we see, the output energy increases linearly with the initiation length at least in the cases where the lasing occurs at an appreciable excess of the threshold gain. In the first approximation, this means that the specific output energy weakly depends on the initiation energy and reduced electric-field strength. The aforementioned parameters exert a more significant effect on the generation of iodine atoms. Note that the initiation energy affects mainly through thermal effects, i.e., through an increase in the threshold concentration of singlet oxygen and decrease in the weak-signal gain. A deviation from the linearity at initiation lengths of 600 mm may be associated with both a decrease in the singlet-oxygen content during the filling of the active volume and a discharge inhomogeneity.

In the case of a longitudinal discharge, the energy of the capacitive storage is almost fully deposited into the active medium. This circumstance results in a less noticeable influence of the buffer-gas pressure on the output energy and on the laser pulse duration compared to the lasing initiated by a transverse discharge with resistive stabilisation. This effect manifests itself when helium serves as a buffer gas and is virtually independent on the discharge length.

Another situation is observed for nitrogen. When the threshold gain is exceeded by an appreciable value, an increase in the nitrogen pressure at short discharge-gap lengths at first leads to a slight and then to an abrupt output-energy decrease. As the discharge-gap length increases, an appreciable energy decrease is observed at lower nitrogen pressures. These facts indicate that the buffer gas not only changes the specific heat of the active mixture, but also modifies the plasma parameters and, probably, the discharge homogeneity.

This effect is more pronounced with SF_6 used as a buffer gas. Being highly electronegative, SF_6 strongly affects the lasing even at low concentrations. Nevertheless, short discharge-gap lengths allow for the operation with SF_6 as a buffer gas and thus ensure a chemically induced generation of iodine atoms using HI as a donor of these atoms.

In the first experiments with a discharge-initiated pulsed COIL, it was noticed that the specific output radiation energy achieved in it is lower than that obtained in the photolysis-initiated lasing. Various factors can be responsible for the difference observed: a discharge-induced breakdown of singlet oxygen, the formation of components that actively quench singlet oxygen and excited iodine, and the heating of the active medium leading to a decrease in the fraction of the energy that can be extracted.

A typical energy value required for the breakage of the C – I bond in alkyliodides and perfluoroalkyliodides is ~ 210 kJ mol^{-1} (53 kcal mol^{-1} for CF_3I and 54 kcal mol^{-1} for CH_3I). For the photolytic production of iodine atoms from these iodides, which have absorption peaks at a wavelength of 270 nm, the energy expenditure for one atom is 7.4×10^{-19} J (446 kJ mol^{-1}). Thus, the exothermality of the photodissociation process is characterised by 225 kJ mol^{-1}. In reality, the reaction is slightly less exothermic, since a certain fraction of iodine atoms forms in the

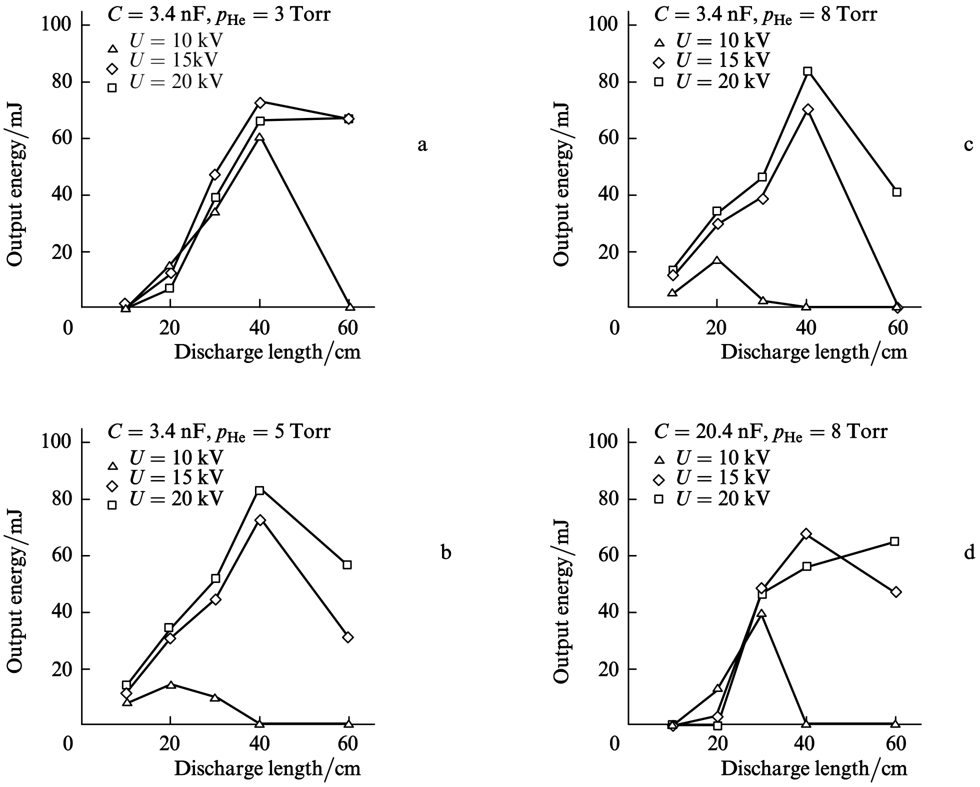

Figure 2. Laser output energy as a function of the discharge-gap length at various discharge voltages U, charging capacitances C, and helium pressures p_{He}.

$I(^2P_{1/2})$ excited state (92 kcal mol^{-1}). The yield of the excited state strongly depends on the sort of iodide and is set equal to zero in this consideration. In order to obtain a concentration of iodine atoms of 10^{18} L^{-1}, which corresponds to a pulse duration of $\sim$ 10 μs, a specific energy deposition of UV radiation of 0.74 J L^{-1} is required. However, only a half of this energy can be converted into translational degrees of freedom (i.e., into heat).

Another situation takes place when the lasing is initiated by an electric discharge. In this case, comparable pulse durations are achieved at specific stored energies of 8 J L^{-1}. In view of the energy expenditure for the breakage of the CF_3-I bond, the specific energy that can be converted into heat is 7.63 J L^{-1}, which 20 times higher than the value obtained for the photolysis.

Since the active medium is virtually motionless during the laser pulse, its temperature is determined by the specific heat capacity at constant volume c_V. For different mixture components at their partial pressures of 1 Torr, we have: $c_V = 3.3 \times 10^{-3}$ J L^{-1} K^{-1} for CF_3I, 1.12×10^{-3} J L^{-1} K^{-1} for O_2, 0.67×10^{-3} J L^{-1} K^{-1} for Ar and He, 1.11×10^{-3} J L^{-1} K^{-1} for N_2, and 4.72×10^{-3} J L^{-1} K^{-1} for SF_6.

For a mixture with a typical composition $O_2 : CF_3I : He = 1 : 0.5 : 3$ Torr, the specific heat is $c_V = 4.78 \times 10^{-3}$ J L^{-1} K^{-1}. In this case, the specific energy that can be converted into heat is 8.23 J L^{-1}, which corresponds to a temperature increase by $\Delta T = 1722$ K. This ΔT is the upper bound of the temperature rise. The actual value is expected to be lower because of the excitation of vibrational and rotational degrees of freedom and losses for the ionisation and formation of molecular fragments. A temperature rise leads to an increase in the threshold content of singlet oxygen and, consequently, to a reduction of the fraction of the energy extracted from the active medium. In fact, the threshold yield of singlet oxygen

$$Y_{th} = \frac{1}{1.5\exp(401\mathrm{K}/T) + 1}$$

tends to a limiting value of 0.4 at an unbounded temperature rise. At $T = 2048$ K $(300 + \Delta T)$, we have $Y_{th} = 0.35$ instead of $Y_{th} = 0.15$ at room temperature. Earlier studies of a sparger generator of singlet oxygen have shown that the yield of singlet oxygen is $Y = 0.5 \pm 0.05$. The specific extracted energy of laser radiation is $E_{extr} = (Y - Y_{th})[O_2]h\nu_{las}$. Thus, for the electric-discharge initiation, $Y - Y_{th} = 0.1 - 0.2$ instead of $Y - Y_{th} = 0.3 - 0.4$ for the photolytic initiation. The temperature rise can account for the observed difference between the specific output energy obtained at the lasing-initiation methods considered.

The threshold yield of singlet oxygen and the temperature were measured in special experiments. Unexcited oxygen was added to the active medium until the lasing was quenched. It is easy to show that

$$Y_{th} = \frac{Y_0}{1 + \Phi_{O_2}/\Phi_{Cl_2}},$$

where Y_0 is the initial yield of singlet oxygen; Φ_{Cl_2} is the consumption of chlorine; and Φ_{O_2} is the consumption of unexcited oxygen corresponding to the lasing quenching. The experiments were carried out with almost totally reflecting mirrors of the resonator. A mixture with a composition $O_2 : CF_3I : N_2 = 1 : 0.5 : 3$ Torr was used, and the discharge-gap length was 40 cm. At a storage capacitance $C = 20.4$ nF and a voltage $U = 20$ kV, we have $\Phi_{Cl_2} = 83.2$

Torr L s^{-1} and $\Phi_{O_2} = 62$ Torr L s^{-1}. Assuming that $Y_0 = 0.45 - 0.55$, we easily obtain $Y_{th} = 0.26 - 0.31$. Such threshold yields of singlet oxygen correspond to temperatures of 326 – 716 K. Under our experimental conditions, the energy input was 8.6 J L^{-1}. At a specific heat of the active medium $c_V = 6.1 \times 10^{-3}$ J L^{-1} K^{-1}, this energy input must result in a temperature increase by $\Delta T = 1419$ K, which is twice as large as ΔT obtained from the threshold content of singlet oxygen. This may mean that the deposited energy was not fully converted into the translational degrees of freedom. Note that the energy expenditure for the production of iodine atoms (i.e., for the iodide dissociation) is negligible and is neglected.

In a similar experiment performed at a stored energy of 1.4 J ($C = 3.4$ nF and $U = 20$ kV), $\Delta T = 280$ K was obtained. An estimate based on the deposited energy and specific heat yields $\Delta T = 240$ K, which is in satisfactory agreement with the above value. Note that, as a consequence of a weak temperature dependence of the threshold content at high temperatures, the accuracy of temperature measurements from the singlet-oxygen threshold yield decreases with increasing temperature.

It follows from the above reasoning that, under our conditions, the chemical efficiency of a discharge-initiated laser has a limit of 20 % ($Y_0 = 0.45 - 0.55$ and $Y_{th} = 0.26 - 0.31$). However, in experiments on the lasing initiation by a transverse discharge, a specific energy yield of 0.5 J L^{-1} was attained at a partial oxygen pressure of 1 Torr. This energy yield corresponds to a 10% chemical efficiency of the laser. This fact demonstrates a high efficiency of energy extraction from the active medium of a pulsed COIL with a bulk generation of iodine atoms.

Hence, a pulsed electric-discharge-initiated COIL operates under specific conditions. In contrast to a supersonic cw COIL in which the active medium is at a comparatively low temperature (180 K), a pulsed COIL with discharge-initiated lasing operates at an active-medium temperature close to 1000 K. This situation requires new information on the temperature dependences of the rate constants of processes governing the inversion behaviour. The first one is the temperature dependence of the rate constant K of the energy exchange between singlet oxygen and atomic iodine. Much attention was paid to the study of this process at low temperatures typical of a cw supersonic COIL operation, whereas the temperature range of > 300 K was poorly studied.

Different temperature dependences of these rate constants are available in the literature (in cm^3 s^{-1}): $K(T) = 2.3\times 10^{-8}/T$ [5], $K(T) = 5.12 \times 10^{-12}\sqrt{T}$ [6] (T is measured in Kelvins). A correct temperature dependence is necessary for an adequate description of the pulsed COIL operation. Determining the concentration of iodine atoms from the laser pulse duration adopted in our work is based on the use of the energy-exchange rate at room temperature. It is obvious that, if the inversely proportional dependence of the rate on the temperature is valid, then the actual concentrations of iodine atoms produced in the discharge are several times higher.

The high-temperature active medium in a pulsed COIL with discharge-initiated lasing is, in a certain approximation, a model of the active medium that, as can be expected, will be formed in an COIL with an electric-discharge generator of singlet oxygen [7]. In fact, obtaining singlet oxygen with a concentration of 40 % in pure O_2 with a concentration of 10^{21} L^{-1} (corresponds to a pressure of 30 Torr at room temperature) requires a specific energy input of 125 J L^{-1}. Up to 62 J L^{-1} can be expended to the active-medium heating, if the singlet-oxygen excitation efficiency is 50 % [7]. The specific heat capacity of oxygen at a pressure of 30 Torr is 34×10^{-3} J L^{-1} K^{-1}. A temperature increase by $\Delta T = 1823$ K is probable. The temperature can be reduced at the expense of an adiabatic expansion in a supersonic nozzle. However, even if a Mach number $M = 3$ is reached, the temperature decreases only to 764 K, and the flow density falls by more than an order of magnitude, to 8×10^{19} cm^{-3}. The similarity of the situations also consists in the presence of atomic particles, metastable states, etc. in the active medium.

The time parameters of the laser pulse are determined mainly by the specific energy input to the active medium. Comparing the data obtained for initiation lengths of 20 and 60 cm shows that rather close pulse durations (38 and 44 μs) are observed at the same specific energy input of 1.6 J L^{-1}. Note that, in this case, the reduced electric-field strengths differ by a factor of ~ 3 (5.2×10^{-15} and 1.8×10^{-15} V cm^2, respectively).

The pulse duration depends on the energy input similar to the case of the initiation by a transverse discharge,. When a transverse discharge with resistive stabilisation is used, the energy accumulated in the storage is distributed between the stabilising resistors and discharge plasma. If the data on the discharge current – voltage characteristics is absent, it is impossible to determine the energy deposited into the active medium. In a longitudinal discharge without ballast resistors, the stored energy is almost entirely deposited into the active medium, making it possible to estimate the energy expenditure per iodine atom. For example, the specific energy input for a 10-μs pulse is 8.6 J L^{-1} (53×10^{18} eV L^{-1}), and the concentration of iodine atoms determined from the pulse duration is 1.3×10^{18} L^{-1}. Hence, it follows that the energy ‘cost’ of one iodine atom is 41 eV.

The use of SF_6 allows us to reduce the pulse duration to 5 μs at the same energy input. This testifies to the influence of the plasma parameters on the processes of iodine atoms formation or to the presence of a chemical mechanism stimulating their production.

4. Conclusions

The investigation of the influence of the discharge-gap length on the energy characteristics of a pulsed COIL with a bulk generation of iodine atoms has shown that, within the range of experimental conditions studied, the specific lasing energy yield is virtually independent of the energy input and is determined by the specific energy stored in the active medium.

It is shown that a twofold decrease (compared to photolytic initiation) in the specific energy yield observed in the discharge-initiated lasing can be explained by an increase in the medium temperature. This fact is indirectly confirmed by the measurement of the threshold yield of singlet oxygen $Y_{th} = 31$ %, which is appreciably higher than the corresponding value at room temperature $Y_{th} = 15$ %.

Acknowledgements. This work was supported in part by the European Office of Aerospace Research and Development (EOARD) within the framework of a partner project of the International Science and Technology Centre (No. 1864)

References

1. Basov N.G., Vagin N.P., et al. *Kvantovaya Elektron.*, **11**, 1893 (1984) [*Sov. J. Quantum Electron.*, **14**, 1275 (1984)].
2. Yuryshev N.N. *Proc. SPIE Int. Soc. Opt. Eng.*, **1397**, 221 (1991).
3. Vagin N.P., Yuryshev N.N. *Kvantovaya Elektron.*, **31**, 127 (2001) [*Quantum Electron.*, **31**, 127 (2001)].
4. Vagin N.P., Pazyuk V.S., Yuryshev N.N. *Kvantovaya Elektron.*, **22**, 776 (1995) [*Quantum Electron.*, **25**, 746 (1995)].
5. Copeland D.A., Bauer A.H. *IEEE J. Quantum. Electron.*, **29**, 2525 (1993).
6. Marter T, Heaven M.C., Plummer D. *Chem. Phys. Lett.*, **260**, 201 (1996).
7. Carroll D.L., Solomon W.C. *Proc. SPIE Int. Soc. Opt. Eng.*, **4184**, 40 (2001).