LASERS

Efficient generation in a chemical oxygen – iodine laser with a low buffer-gas flow rate

V.N. Azyazov, V.S. Safonov, N.I. Ufimtsev

Abstract. The efficient generation in a chemical oxygen – iodine laser (COIL) with a low buffer-gas flow rate for Mach numbers $M \leqslant 1$ is demonstrated. The maximum output power of the COIL was 415 W for a molecular chlorine flow rate of 20 mmol s^{-1}, which corresponds to a chemical efficiency $\eta_{ch} = 23\,\%$. It is shown that the substitution of the buffer gas CO_2 for N_2 does not cause any significant variation in the dependence of the output power on the degree of dilution of the active medium.

The energy in a chemical oxygen – iodine laser (COIL) is transported by the electronically excited singlet oxygen $O_2(^1\Delta)$, which is obtained by chlorination of the alkaline aqueous solution of hydrogen peroxide in gas – liquid generators. One of the disadvantages of this method for obtaining $O_2(^1\Delta)$ is the presence of water vapour in the oxygen flow, which leads to relaxation of the excited electronic state. The partial pressure p_{H_2O} of water vapour at the output of the singlet-oxygen generator (SOG) is approximately equal to the saturated vapour pressure of water over the surface of the working solution and usually amounts to a few Torr. The admissible relative concentration of water vapour in oxygen is $\eta_{H_2O} = p_{H_2O}/p_{O_2} \leqslant 0.05$ [1].

In the first COILs, singlet oxygen was generated in a bubbling SOG [2 – 6] where the output pressure p_{O_2} of oxygen did not exceed a few Torr. To reduce the concentration of water vapour to an acceptable level, a cryogenic water vapour trap was installed at the outlet of the SOG. Another method of attaining an acceptable value of η_{H_2O} involves an increase in the oxygen pressure at the SOG outlet [7]. A successful operation of a COIL without a water-vapour trap was realised for the first time by using a jet SOG [8] in which the output oxygen pressure may be as high as 100 Torr [9].

The water-vapour trap considerably complicates the construction of a COIL; however, the highest chemical efficiency $\eta_{ch} \approx 30\,\%$ was attained in experimental setups with a water vapour trap [5, 6] for relatively low subsonic velocities of gas flow through a resonator with a low flow rate of the buffer gas. In order to attain a high chemical efficiency (25 % – 28 %) in a COIL without water vapour traps, a supersonic flow of the active medium is used, after a preliminary (single or multiple) dilution of the active medium by the buffer gas [10]. This also complicates the construction of the laser and requires high flow rates of the buffer gas and additional energy expenditure on flow of the gas and its exhaust into the atmosphere. In this connection, it should be certainly interesting to find such regimes of COIL operation without a water vapour trap that do not require large flow rates of the buffer gas or supersonic velocities of the active medium flow through the resonator. The first results of such investigations were reported in Refs [11 – 13].

In these regimes, the maximum chemical efficiency $\eta_{ch} = 18\,\%$ was realised in setups with a gain length of 5 cm for supersonic velocities of the active medium flow [11, 12]. An increase in the gain length leads to a decrease in the optimal concentration of iodine and retards the relaxation processes. As a result, the optimal velocity of the gas may become subsonic if other conditions remain unchanged. The results of testing of a COIL without a water vapour trap and with a gain length of 10 cm are presented in Ref. [13] for a low buffer gas flow rate. The velocity of gas flow in these experiments was 125 m s^{-1} being limited by the capacity of the pumping system, and the chemical efficiency was $\eta_{ch} = 12\,\%$. The lower value of η_{ch} compared to that for lasers with a smaller gain length can be explained the fact that the gas velocity in the resonator is not optimal.

We present here the results of experiments aimed at finding an efficient and economical regime of operation of an COIL without a water vapour trap and with a gain length of 10 cm for a low buffer gas flow rate in the region of transonic velocities of the active medium flow.

Experiments were carried out on a setup whose schematic diagram is shown in Fig. 1. Singlet oxygen was generated in a counterflow jet singlet-oxygen generator (*6*), which was identical to the one used in [11, 12] and has a reaction zone cross section of 5×1.2 cm. Molecular chlorine was introduced into the lower part of the generator from two ports in the side walls of the generator. The alkaline solution of hydrogen peroxide was prepared in a thermally insulated vessel (*1*) using 3 litres of 37 % hydrogen peroxide solution and 2 litres of KOH solution at a concentration 14.5 mol L^{-1}. A heat exchanger (*2*) was used for removal of the heat released during the preparation of the solution and in the course of the chemical reaction between chlorine

V.N. Azyazov, V.S. Safonov, N.I. Ufimtsev P.N. Lebedev Physics Institute, Samara Branch, Russian Academy of Sciences, ul. Novo-Sadovaya 221, 443011 Samara, Russia; e-mail: asu@fian.smr.ru

and the solution components. Ethyl alcohol, which was circulated continuously through the system consisting of heat exchanger (2) and refrigerator (3), served as the coolant. Stirrer (5) facilitated a more efficient cooling of solution. The solution temperature was maintained at $-15\,^{\circ}C$. Pump (4) ensured a continuous flow of the working solution. The pressure of the solution over the jet injector (10) was maintained at 2 atm.
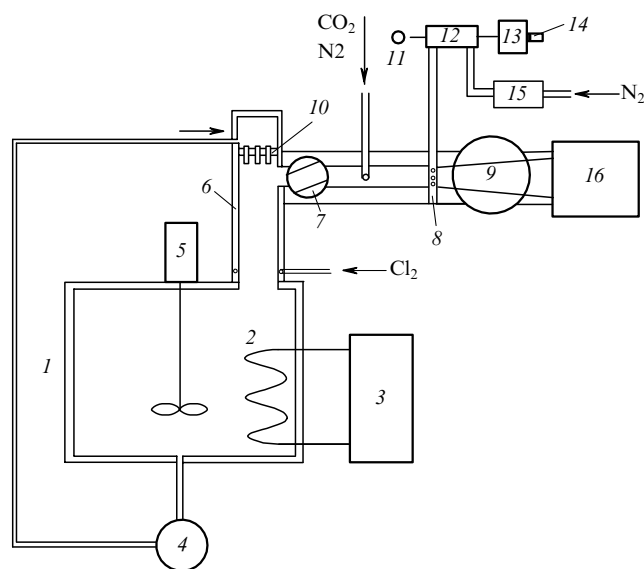
Figure 1. Schematic of the COIL: (1) thermally insulated tank; (2) heat exchanger; (3) refrigerator; (4) liquid gear-type pump; (5) stirrer; (6) jet singlet-oxygen generator; (7) slit valve; (8) iodine injector; (9) resonator; (10) jet injector; (11) light source; (12) cell for measuring concentration of I_2; (13) monochromator; (14) photodiode; (15) molecular iodine vapour generator; (16) gas evacuation system.

Singlet oxygen was produced in a narrow surface layer of the solution in the chemical reaction of molecular chlorine absorbed from the gaseous phase with HO_2^- ions. The gas–liquid interface was created by injecting a jet of the solution into the reaction chamber of the SOG through injector (10) consisting of 93 stainless steel tubes of length 27 mm and an internal diameter 0.8 mm. The height of the reaction chamber from the chlorine inlet point to the outlet hole was 15 cm. In all experiments, the chlorine flow rate was 20 mmol s^{-1}. The slit valve (7) regulated the volumetric pumping rate in the reaction chamber of the SOG.

The SOG and the resonator were connected through an organic glass channel of length 10.5 cm and cross section 1.2×10 cm. Gaseous N_2 or CO_2 (primary buffer gas) could be injected into the oxygen flow at a distance of 3 cm from the slit valve. Molecular iodine vapour was introduced into the oxygen flow by a rake-type injector (8) consisting of 16 vertical copper tubes of diameter 2.8 mm, the separation between centres of adjacent tubes being 6 mm. Ten holes of diameter 0.5 mm were drilled at an interval of 1 mm on both sides of the tubes at right angles to the oxygen flow. Gaseous molecular iodine produced in vapour generator (15) passed together with the carrier secondary buffer gas through the measuring cell (12) with quartz windows. The concentration of I_2 was determined by measuring the absorption of light from the incandescent lamp (11) passing through the cell at a wavelength of 500 nm. The light passing through the measuring cell (12) and monochromator (13) was transformed into an electric signal by photodiode (14).

We used a 64-cm long stable resonator consisting of two spherical mirrors with a radius of curvature 5 m and an overall transmittance of 1.19 %. The diameter 4.5 cm of the mirrors determined the downstream length of the active zone. The mirrors were purged with a buffer gas at a flow rate of 6 mmol s^{-1}. The length of the active zone along the optical axis was 10 cm. The gas evacuation system (16) ensured a maximum pumping rate of 1500 L s^{-1}. For such a volumetric pumping rate, the cross section of the gas channel in the I_2 injector, which is not cluttered by tubes in our setup, is critical for the supersonic nozzle. The gas pressure in the SOG, intermediate chamber, measuring cell, resonator and the Pitot tube installed at the resonator outlet was measured by 'Sapfir' pressure gauges. We studied two regimes of the COIL operation with different pumping rates and different configurations of the gas channel in the resonator. In the first mode, the volumetric pumping rate was 1500 L s^{-1}, while the gas channel in the resonator, which follows the iodine injector with a cross section 1.4×10 cm, changed its dimensions due to a divergence of 6° between the upper and lower walls. Three positions of the optical axis, characterised by the distance $L = 5.5$, 7.5, and 8.5 cm from the point at which iodine was introduced, were used in our experiments. The radiation power always decreased with increasing L. The maximum power was observed for the minimum possible distance $L = 5.5$ cm used in our experiments. Table 1 shows the COIL parameters for which the maximum chemical efficiency was attained in the first regime. The high dissociation rate of iodine is worth noting. A low

Table 1. Results of COIL testing.

Gas flow rate/mmol s^{-1}			p_g/Torr	p_r/Torr	M	W/W	η_{ch} (%)	Reference
G_{Cl}	G_2	G_{I_2}						
20	4.8	0.65	32	0.54	1.3	280	15.5	Our work (first regime)
20	5.8	0.27	23	1.25	~ 1	415	23	Our work (second regime)
11.6	0.5	0.2	20	1	1.4	190	18	[11]
10	5	0.37	20	1	1.6	163	18	[12]
13.4	–	0.1	25	1.9	0.4	150	12	[13]

N o t e : $G_1 = 0$ and G_2 are the flow rates of the primary and secondary buffer gas; G_{I_2} and G_{Cl} are the molecular iodine and chlorine vapour flow rates; p_g and p_r are the gas pressures in the SOG and the resonator; M is the Mach number, and W is the output power of the COIL.

pressure in the resonator (0.54 Torr) and a small characteristic scale of mixing (~ 1 mm) led to a high mixing rate, which is comparable with the iodine dissociation rate and even exceeds it. According to our estimates, the dissociation time for I_2 in this regime is a few tenths of a millisecond, i.e., much shorter than the value predicted by the well-known dissociation model proposed in [14].

In the second regime, the pumping rate was lowered to 500 L s^{-1}, and the gas channel in the resonator was modified. In contrast to the first regime, the initial cross section of the channel was 1.1×10 cm. The divergence between the upper and lower walls was $3°$. The channel height along the optical axis was 1.4 cm. In this regime, the pressure in the resonator increased from 0.54 Torr (first regime) to 1.25 Torr. The relative concentration of molecular iodine reduced from 3.2 % (first regime) to 1.3 %. The maximum output power in this regime was 415 W, which corresponds to a chemical efficiency of 23 % (see Table 1). For comparison, Table 1 also contains the parameters corresponding to an COIL investigated under similar conditions in Refs [11–13]. No primary buffer gas was used in these investigations, and the secondary buffer gas (nitrogen) was introduced in small amounts. The chemical efficiency in the second regime was 5 % higher (when the relative concentration of I_2 was half the value in the first regime) than the efficiency values attained in Refs [11, 12]. Compared to Ref. [13], the chemical efficiency was almost doubled, thus indicating that the optimal gas velocity was in the transonic region.

When the gas velocity in the resonator was reduced to ~ 200 m s^{-1} in the second regime, the output power decreased only by a factor of 1.12. For a gas velocity of ~ 150 m s^{-1}, the output power was 1.86 times lower than for velocities in the transonic range (Mach number $M \leqslant 1$). The gas velocity decreased for a constant chlorine flow rate, and hence the pressure in the resonator increased.

We used N_2 or CO_2 as the buffer gas, which was added to the oxygen flow at the SOG output. On the one hand, CO_2 molecules weakly quench the electronically excited molecules of $O_2(^1\Delta)$ and $I(^2P_{1/2})$. On the other hand CO_2 molecules efficiently quench the electronically excited oxygen $O_2(^1\Sigma)$, which may play an active role in the process of dissociation of I_2 [15] because its excitation energy is sufficient to dissociate an iodine molecule in a single collision. Experiments reveal that the dependences of the COIL output power on the degree of dilution of oxygen by primary nitrogen or carbon dioxide gas are identical (up to two-fold dilution).

Fig. 2 shows the dependence of the COIL output power on a total flow rate of the buffer gas CO_2 for the second regime. The flow rate of the secondary buffer gas CO_2 remained constant in these experiments: $G_2 = 5.8$ mmol s^{-1}. One can see that the output power depends weakly on the degree of dilution of oxygen by carbon dioxide gas. This fact indicates that the role of $O_2(^1\Sigma)$ in the process of dissociation of I_2 is insignificant.

Thus, the results of our experiments show that a COIL with a low flow rate of the buffer gas and iodine can efficiently produce emission for $M \leqslant 1$. The maximum output power of the COIL was 415 W for a molecular chlorine flow rate of 20 mmol s^{-1}, corresponding to a chemical efficiency $\eta_{ch} = 23$ %, and was attained in runs in which a uniform and complete filling of the active medium by the intracavity radiation field was observed. Dilution of oxygen
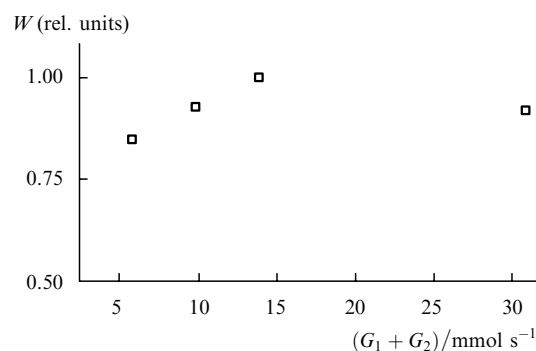
Figure 2. Dependence of the output power W of the COIL on the total flow rate of the primary and secondary CO_2 buffer gas for the second regime for $p_g = 27$ Torr, $G_{I_2} = 0.24$ mmol s^{-1}, $M \approx 1$, and $G_2 = 5.8$ mmol s^{-1}.

by a primary buffer gas did not enhance the output power, as unlike the case of a COIL in which molecular iodine was injected into the subsonic flow region in front of a slit nozzle [12] or the Cassedy grating [16]. A similar conclusion was drawn in Ref. [11]. The replacement of the buffer gas N_2 by CO_2 did not lead to any significant variations in the dependence of the output power on the degree of dilution of the active medium by these gases. A decrease in the gas velocity in the resonator to 200 m s^{-1} lowered the output power only by 12 %.

The small scale of mixing (~ 1 mm) in our setup and a low pressure in the resonator ensured a high mixing rate for oxygen and iodine flows. The estimated time of dissociation of iodine in the first regime was a few tenths of a millisecond, which is much smaller than the value predicted by the iodine dissociation model proposed in Ref. [14] and used frequently at present.

The increase in the energy efficiency in the COIL operating regimes studied here is caused mainly by an increase in the gain length of the active medium from 5 cm [11, 12] to 10 cm. The optimal values of the main laser parameters depend strongly on the gain length of the active medium. For example, the optimal gas velocity and the relative concentration of molecular iodine decreased with increasing L from 5 cm [11, 12] to 10 cm. An increase in the gas velocity from 125 m s^{-1} [13] to ~ 300 m s^{-1} for the same value (10 cm) of the gain length led to a doubling of the chemical efficiency.

It should be interesting to study the operation regimes of a COIL without water vapour trap and with a low flow rate of the buffer gas for even larger gain lengths. An increase in the gain length leads to a decrease in the optimal relative concentration of iodine in oxygen. This reduces the rates of relaxation processes, thus making it possible to increase the pressure of oxygen in the resonator. Such a regime has the advantage that it allows a decrease in the relative energy expenditure on flow of the medium and also lowers the dominance of Doppler broadening over collision broadening with the help of the working gas rather than the buffer gas.

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