Pulsed COIL with Volume Generation of Iodine Atoms in Electric Discharge.

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ABSTRACT

The method of volume generation of iodine atoms to obtain the pulsed mode of COIL is the most effective by the ratio of pulsed power to cw one at the same flowrate of chemicals. The electric discharge is a very convenient tool to produce iodine atoms in an active medium. The electrical efficiency close to 100% was obtained when longitudinal glow discharge was used.

The investigation of both influence of the discharge gap length on the performance of pulsed COIL initiated with longitudinal discharge and transverse discharge initiated pulsed COIL based on the Jet Singlet Oxygen Generator were performed. The lasing of Jet SOG based pulsed COIL has been obtained for the first time. The operation pressure of 17 Torr at oxygen partial pressure of 7 Torr in the laser cavity has been obtained.

The temperature parameters of active medium being under electric discharge initiation were analyzed. The active medium temperature growth was shown to be responsible for decrease of specific output energy in discharge initiated COIL unlike that for photolytic initiation.

Keywords: gas laser, chemical oxygen-iodine laser, pulsed mode, singlet oxygen generator, iodide

1. INTRODUCTION

Application of the transverse self-sustained electric discharge to initiate pulsed chemical oxygen-iodine laser (COIL) with volume generation of iodine atoms was successfully demonstrated in [1]. This kind of electric discharge makes it possible to work at higher active medium pressure but at the same time it requires significant efforts to make this discharge to be uniform. In its turn, longitudinal glow discharge, having limitation by operation pressure, is a very simple in realization and provide the laser to have high electrical efficiency. The value of close to 100% efficiency (ratio of laser output energy to that stored in capacity) was reported [2].

The goal of this work is investigation of the influence of the length of the longitudinal discharge gap on the pulsed COIL output parameters. The results obtained can be useful for designing the pulsed COIL with electric discharge initiation. Unlike that for transverse initiation geometry the longitudinal one reserve the degree of freedom which can be used, for example, to mount the Q-switch system based on the Zeeman effect.

Saying on longitudinal discharge we have in mind the discharge geometry where the distance between the electrodes significantly exceed the electrode size. So one can see that shortening the discharge gap results in discharge geometry more close to transverse one.

As it was shown in the works carried out in Lebedev Physical Institute the application of such a discharge to initiate the pulsed COIL with volume generation of iodine atoms makes it possible the laser to operate with a high electrical efficiency close to 100% at specific output energy of 0.5 J/1 per 1 Torr of O2. The laser operation at a length of discharge gap of 60 cm was demonstrated. The application of a glow discharge to generate iodine atoms in the gas mixture containing the singlet oxygen to form COIL active medium is not a trivial task. Indeed, the electrical discharge produces electrons, ions, and molecular fragments. The sort and concentration of these components, in general, depend on discharge parameters - mainly discharge energy and reduced strength of electric field E/N. Besides, the length of the discharge gap determines the resistance of plasma channel and, hence, the energy deposition into the active medium.

Thus the optimization of discharge parameters to improve the energy parameters of the laser is a crucial task and variation of the length of the discharge gap allows one to vary latter parameter keeping the voltage constant.

2. EXPERIMENTAL
The schematic diagram of experiment with longitudinal discharge is shown in Fig.1. The discharge chamber is mounted in one of the shoulders of experimental facility used in investigations of a pulsed COIL initiated with a longitudinal discharge [2].

The discharge chamber, 39-mm i.d., is made of PMMA. The chamber has 5 electrode holes. The electrode section of typical flash lamp, 20-mm o.d., is chosen as a cathode. These sections are inserted into electrode holes and sealed. The annular electrode is a common anode. To eliminate the influence of near electrode regions the electrodes are carried out the laser cavity area. Thus, the discharge positive column processes only form the laser active medium.

The discharge chamber with a moving annular cathode was investigated too. But this design was abandon due to instability of results obtained.

The electrical discharge fed by a capacitor bank is triggered with a thyratron TGI-25/1000 operating at a voltage up to 25 kV. The capacitor bank is assembled of several disk ceramic capacitors. Variation of both the voltage and the number of capacitor makes it possible to change the discharge energy.

The singlet oxygen is produced in the sparger type SOG packed with Rushig rings to, firstly, intensify the mass-transfer and, secondly, to prevent ejection of BHP from SOG. The buffer gases (N\textsubscript{2}, Ar, SF\textsubscript{6}) is fed through the SOG in a mixture with chlorine. The typical pump capacity in experiment is 80 l/s. The previously made measurements of the dependence of singlet oxygen yield on pump capacity allow us to evaluate the value of SO yield under different experiment conditions.

The laser operation at different length of the discharge gap is compared by output specific energy and efficiency, i.e. ratio of output specific energy to specific deposition energy. But output laser energy depends on the level of threshold exceeding, which, in its turn, depends on the gain length, i.e. length of the discharge gap. The 0.8 % transmission of the output spherical mirror of laser cavity is chosen to minimize this effect (the transmission of about 4 % is optimal for majority of experimental conditions). The 0.05 % transmission spherical mirror is chosen as a totally reflecting one. The laser output energy is limited with an external 30-mm diameter diaphragm installed 45 cm from output mirror.

The output laser energy emitted from aperture of 30 mm is measured with IMO - 2N, the pulse shape is recorded with a store oscilloscope and then is recorded with a digital camera Kodak DC-240.

The traditional design counter flow jet singlet oxygen generator of 4 cm internal diameter was used in experiments with pulsed COIL initiated with transverse discharge (Fig.2). The jets were formed with an assembly of 120 tubes of 0.7 mm i.d. The length of jets or reaction zone (distance from jets injector edge to the point of chlorine injection) was as long as 14 cm. The calculated value of specific surface area for smooth jet was 2 cm\textsuperscript{-1}. The working BHP solution was prepared in a separate vessel providing mixture cooling during the dilution process. Before utilization the working mixture was cooled down to -10\textdegree C. Medicine purity hydrogen peroxide of 38 % concentration and 12 N water solution of high purity KOH were used to prepare 4 l of working BHP. The jets were driven with atmospheric pressure. This volume was enough to provide the runtime of 17 s. The operation parameters of jet SOG were optimized to minimize the content of residual chlorine in the SOG effluents. It was necessary to avoid instability of the mixture of singlet oxygen with iodide due to reaction

\[
\text{C}_6\text{H}_{13}+\text{I} + \text{O}_2(\Delta) + \text{Cl}_2 \rightarrow 1 + \text{products}
\]

3. RESULTS AND DISCUSSION

3.1. Pulsed COIL initiated with longitudinal discharge
All experiments were carried out with an operation mixture of 1 Torr O₂ and 0.5 Torr CF₃I. Helium, nitrogen and sulfur hexafluoride are used as buffer gases. The experimental parameters were varied within 10 – 58.5 cm for discharge gap, from 10 to 20 kV for discharge voltage and from 2 to 8 Torr for partial buffer gas pressure.

Unlike photolysis, which is a very selective tool for iodide decomposition, the electric discharge interacts with all components of active medium. Forming electrons, ions and different molecular fragments, electric discharge modifies the active medium composition. In its turn, the initial composition of an active medium is a factor determining the discharge parameters: breakdown voltage, electron distribution by energy, discharge resistance, etc. Thus, the interpretation of the results obtained is a very difficult task. Nevertheless, we tried to evaluate the general rules in the behavior of the pulsed COIL with longitudinal discharge initiation.

The term “transverse” usually applies to the discharge geometry when discharge gap is appreciably less the cross-size. In this case the discharge resistance is low. When resistant loaded pins electrode is used for discharge stabilization the energy stored in capacitor bank is distributed between the plasma and load proportionally to their resistance. So, the variation of plasma resistance due to buffer gas, for example, results in change of energy deposition into active medium.

In the case of longitudinal geometry, when electrode separation is long enough, the capacitor energy is wholly deposited into active medium. So, the energy deposition is governed by capacitor only. It results in less influence of buffer gas pressure on laser output energy and pulse duration as compared with that for transverse excitation. This effect is most strongly marked for He as a buffer gas.

Another situation takes place when nitrogen N₂ is used as a buffer gas. In this case the pattern of buffer gas influence depends on the length of the discharge gap. Considering only the situations when the laser operates highly over the threshold one can see that for short discharge length the increase of nitrogen partial pressure results in initially weak and then sharp drop of output energy. At longer discharge length the sharp drop of output energy arrives at less nitrogen pressure. It means the buffer gases not only increases the heat capacity of active medium but also significantly change the plasma parameters and, may be, the discharge uniformity.

This effect is more demonstrated for sulfur hexafluoride. Being very electronegative, SF₆ affects very strongly even at low concentration. Nevertheless, at short discharge length longitudinally excited COIL can operate with SF₆ as a buffer gas and, hence, chemical generation of iodine atoms due to reaction of fluorine atoms produced in a discharge with hydrogen iodide as an iodine donor is possible.

\[
F + HI = I + HF
\]

It was observed in the first experiments with electric discharge initiated pulsed COIL the output specific energy of such a laser is at disadvantage in relation to photolytically initiated one. The different factors can be the reason of such a phenomenon. They are decrease of the singlet oxygen yield, forming the effective quenchers of excited states, heating of active medium and, hence, decrease of extractable fraction of energy stored in singlet oxygen. As it was shown the latter reason is the most possible.

The typical value of energy required to break the bond C-I in alkyl iodides or perfluoro-alkyl iodides is about 210 kJ/mol (53 kcal/mol for CF₃I, 54 kcal/mol for CH₃I). When photolysis is used to produce iodine atoms from these species which have a maximum absorption at the wavelength of about 270 nm the energy absorbed to produce one iodine atom is 7.4·10⁻¹⁹ J (446 kJ/mol). Thus, the photo dissociation process is 225 kJ/mol exothermic. In fact the reaction is somewhat less exothermic because the fraction of iodine atoms is produced in excited state I (³P₁/₂) (92 kcal/mol). The yield of excited state strongly depends on the sort of iodine donor and assumed to be zero in this consideration. If one produces the iodine concentration of 1·10¹⁸ 1³ that corresponds to the COIL pulse duration of about 10 μs, the UV energy absorbed in the active medium is 0.74 J/l. But only half of this quantity of energy (0.37 J/l) is transferred to translation degrees of freedom i.e. to heat.

Another situation takes place when electric discharge is used instead of photolysis. In this case the comparable pulse duration is obtained when specific energy stored in the capacitor bank exceeds 8 J/l. When longitudinal discharge without ballast resistor is used, all energy stored in the capacitor bank is deposited into active medium. Thus, subtracting the energy consumed for breaking the CF₃–I bond, one can evaluate the value of energy to be transferred to heat (7.63 J/l) twenty times as much as that in photolysis.

As soon as the active medium is practically immovable during the short pulse its temperature is governed by heat capacity C_v. The values of C_v for different components of the mixture at partial pressure 1 Torr are:

- CF₃I: 3.3·10⁻³ J/l K
- O₂: 1.12
- Ar, He: 0.67
Thus, for the typical mixture composition \( O_2 : CF_3I : He = 1 : 0.5 : 3 \) Torr one has \( C_v = 4.78 \times 10^{-3} \) J/\( \ell \) K. The energy that can be theoretically transferred to heat is \( 8.23 \) J/\( \ell \). Being wholly transferred to translation degrees of freedom this energy results in \( \Delta T = 1722 \) K of temperature growth. This value is an upper limit of temperature growth. In fact, the real value of temperature is somewhat less because of excitation of rotation and vibration degrees of freedom of mixture components and formation of ions and different fragments. Such a great growth of temperature results in growth of threshold yield of singlet oxygen and, thus, in significant decrease of extractable energy. Indeed, the value of threshold yield

\[
Y_{th} = l/1.5 \exp(401/T) + 1,
\]

has a limit \( Y_{th} = 0.4 \) when temperature tends to infinity. Thus, at the temperature \( T = 2022 \) K (\( T_0 + \Delta T \)) the value of threshold yield is \( Y_{th} = 0.35 \) instead of \( Y_{th} = 0.15 \) at room temperature. A previously made investigations of sparger SOG used in experiments shows the yield of singlet oxygen \( Y = 0.5 \pm 0.05 \). One can derive that the extractable energy \( E_{extrac} \) under discharge initiation is \( E_{extrac} = (0.10 - 0.20)\text{[O}_2\text{]}hV_{\text{laser}} \) instead of \( E_{extrac} = (0.3 - 0.4)\text{[O}_2\text{]}hV_{\text{laser}} \). Having in mind that the real temperature growth is not so high one can conclude this effect is a primary reason of output energy drop when discharge is used instead of photolysis to initiate.

The special experiments were performed to evaluate the threshold yield and, thus, the real temperature of active medium. Unexcited oxygen was admixed to the active medium up to the concentration resulting in quenching of lasing. It is easy to show

\[
Y_{th} = Y_0/(1 + \Phi_{C12}/\Phi_{C12}),
\]

where \( Y_0 \) is an initial singlet oxygen yield, \( \Phi_{C12} \) is a chlorine flowrate, \( \Phi_{C12} \) is an additional oxygen flowrate resulting in quenching of lasing. It is obvious, these experiments were carried out with totally reflecting mirrors of laser resonator. The mixture composition \( O_2 : CF_3I : N_2 = 1 : 0.5 : 3 \) Torr and discharge length of 40 cm were used. For the cases of 20.4 nF capacitor bank, 20 kV of operation voltage and \( \Phi_{C12} = 83.2 \) Torr/s the value \( \Phi_{C12} = 62 \) Torr/s was obtained. Thus, assuming \( Y_0 = 0.45 - 0.55 \) one can evaluate \( Y_{th} = 0.26 - 0.31 \). Such values of \( Y_{th} \) correspond to the growth of temperature due to initiation energy deposition within the range of 326K - 716K. The conditions of experiments correspond to that of run 56.4, where the specific energy deposition is as large as 8.6 J/\( \ell \). At the heat capacity of active medium \( C_v = 6.1 \times 10^{-3} \) J/\( \ell \) K this value of energy deposition corresponds to the temperature growth of \( \Delta T = 1410 \) K. This value is twice as much as that obtained via threshold yield. It may signify that not all energy deposited into active medium is transferred to translation degrees of freedom. Note, that energy consumed to produce iodine atoms is too small to be account.

The similar experiment made for the energy stored in capacitor bank of 1.4J ( \( C = 3.4 \) nF, \( U = 20 \) kV) gives the growth of temperature \( \Delta T = 280 \) K. The same parameter evaluated from deposited energy and heat capacity is \( \Delta T = 240 \) K. It is seen both values are in a good agreement.

Note, that because of a weak dependence of threshold yield on temperature at high values of temperature the accuracy of temperature measurement via threshold yield drops with temperature increase.

As it follows from aforesaid, at high energy deposition the chemical efficiency has a theoretical limit of about 20% (\( Y_0 = 0.45 - 0.55, Y_{th} = 0.26 - 0.31 \)). But it was shown in experiments with transverse discharge the specific output energy of 0.5 J/\( \ell \) is obtainable at oxygen pressure 1 Torr. This value of specific energy corresponds to 10% of chemical efficiency. This fact demonstrates a very high efficiency of laser energy extraction from active medium.

Thus, the electric discharge initiation of pulsed COIL creates specific conditions of its operation. Unlike CW supersonic mode of COIL operation when the active medium temperature is low, the pulsed COIL with discharge initiation works under high temperature (close to 1000K) of active medium. This situation requires the new kinetic information on rate constants of processes which are critical for laser operation. The first of them is temperature dependence of energy exchange between singlet oxygen and iodine atom. In application to supersonic cw operation this process was under deep investigation for temperatures below room ones. As to temperature region above 300K, it is not investigated so deeply. The different temperature dependences are reported in literature, \( K(T)=2.3 \times 10^{-8}T \) [3], \( K(T) = 5.12 \times 10^{-12}T \) [4]. The correct temperature dependence of rate constant is necessary for adequate modeling of laser operation. Our evaluations of iodine atom concentration from duration of a laser pulse were made using the room temperature value for energy transfer constant. One can see the real concentration can be several times higher.

The high temperature active medium being produced in the electric discharge initiated COIL, is a model of active medium which, one can expect, can be produced in Electri COIL, i.e. oxygen-iodine laser with electrical SOG. Indeed, production of 40% yield of singlet oxygen in pure oxygen with concentration of \( 10^{21} \) cm\(^{-3} \) (corresponds to 30 Torr at
room temperature) requires the energy deposition of 125 J/l. At the efficiency of the excitation process of 50% [5] the energy transferred to translation degrees of freedom is 62 J/l. The heat capacity of oxygen at pressure 30 Torr is about 34-10^3 J/l K. Thus, the growth of active medium temperature can achieve ΔT = 1823K. To drop this high temperature the adiabatic expansion in supersonic nozzle is used. But even Mach number M=3 makes it possible to drop temperature to only T=764K. Note, the density of oxygen at this Mach number drops to 8-10^16 cm^-3.

The output energy is one of the key parameters defining laser operation. Figures 3 - 6 demonstrate the influence of initiation length (discharge gap length) on the laser output energy for He as a buffer gas and for different initiation conditions (voltage, bank capacity). One can see the output energy grows proportionally with initiation length, at least for lengths over the threshold one. It means, as a first approximation, the output energy doesn't depend on initiation energy and reduced electric field strength. These parameters can be more essential for iodine atom generation. The influence of initiation energy on laser output brings mainly via heat effects i.e. grows of a threshold yield and gain drop. The fact the dependence falls off linear for initiation length of 600 mm can be explained as a mutual influence of singlet oxygen relaxation, low specific initiation and, may be, discharge nonuniformity. (Note, the uncontrolled breakdown to the flange of the discharge cell can be the source of possible error for the 60 cm gap length.)

The temporary laser pulse behavior is governed by mainly the specific energy deposited into active medium. The comparison of results obtained for discharge length 20 cm and 60 cm shows the pulse durations of 38 μs and 44 μs are obtained for specific deposition energy of 8.6 J/l. Note, the values of reduced electric field strength differs about three times (521 Td and 178 Td, respectively).

Like that observed under initiation with transverse electric discharge, the pulse duration depends on deposition energy. At the case of investigated earlier transverse resistively stabilized discharge the energy stored in capacitor bank shared between resistors and plasma. Having no information on volt-ampere characteristic of discharge, it is impossible to determine the value of energy deposited into active medium. In longitudinal discharge practically all energy is deposited into active medium. This fact makes it possible to evaluate the energy cost of iodine atom produced by discharge. Thus for the pulse duration of 10 μs energy deposition is 8.6 J/l = 53-10^18 eV/l and iodine atom concentration determined through pulse duration is 1.3-10^18 l^3. So the energy cost of iodine atom in experiment is about 41 eV/atom. Note, this value is one-fifth as large as that reported for transverse discharge initiation at the same pulse duration.

The same energy deposition into active medium with SF₆ resulted in pulse duration as short as 5 μs. This fact shows the influence of plasma parameters on process of iodine atom formation.

### 3.2. Pulsed COIL based on the Jet SOG

The motivations for investigation of the pulsed chemical oxygen-iodine laser based on the jet singlet oxygen generator are the promising results obtained in investigation of the features of pulsed COIL initiation with transverse discharge [1], as well as results of numerical analysis and experimental study of COIL with generation of singlet oxygen via photolytic ozone decomposition [6]. It was shown that pulsed COIL output energy increased linearly with the growth of the oxygen pressure.

The value of specific energy, that is energy obtained from the unit of the volume of the active medium, is a crucial factor, which governs the mass and dimension of laser. Thus the trend to increase the operation pressure is motivated. Recently, Japanese scientists attempted to get COIL operation using the porous high pressure SOG and method of volume generation of atomic iodine from CH₃I [7]. The experiments made at the pressure over 30 Torr results in 2.8 J/l of specific output energy and 2 ms of pulse duration. The results obtained are far from that one could expect. By the way, the similar result was obtained earlier when molecular iodine was used as iodine donor. It means, the authors failed to realize the method of volume iodine generation completely. The most possible reason why the low result was obtained, is a low efficiency of chlorine utilization and, hence, relatively high chlorine concentration. It was shown in works carried out earlier in LPI [8], the chlorine being mixed with singlet oxygen decompose molecules of alkyliodide and release the free iodine atoms thus forming the active medium one has when singlet oxygen is mixed with I₂. Note, the long pulse duration is evidence of more of cw operation than pulsed one.

The jet SOG is a source of high-pressure singlet oxygen too. The special preliminary experiments showed the operation conditions when chlorine utilization is rather high. So, one can expect the influence of release of free iodine atoms will be negligible.

When BHP jets are injected into low pressure medium of SOG the gas saturated liquid comes to the boil, thus producing the drops. The drops are carried out by gas flow from SOG to laser chamber thus resulting in experiment break-down. To avoid this effect the buffer gas is fed to the pressure of 10 Torr and then the chlorine flow is fed. The
oxygen pressure in the SOG is a sum of that for chlorine, nitrogen and iodide. At the same time, the oxygen partial pressure in the laser chamber is equal to total pressure divided by ratio of nitrogen flowrate to that of oxygen. As the flow velocity is subsonic the total pressure in the laser chamber is equal to that in the SOG.

Because of large idle volume of experimental set-up and low chlorine flowrate the transient period for gas flow is too long. One can assume this effect is responsible for degradation of laser pulse parameters during the run. The pulse amplitude decreases with time and, hence, with increase of oxygen pressure. Iodide methyl CH\textsubscript{3}I was used as an iodine atom donor. As it was shown [9], this iodide provides the better energy parameters of laser. But its merit takes place when active medium is free of chlorine. The experiments show that in spite the SOG operates under conditions when the chlorine utilization is maximal, the concentration of residual chlorine is enough to cause the active medium to be unstable. It is a reason why we could not increase the CH\textsubscript{3}I pressure and make a laser to work over the threshold.

The laser chamber used was previously designed to work in joint experiments with Samara branch of LPI and comparison of CW and pulsed modes of COIL operation. It governed the dimensions of laser chamber. But, as it follows from the analysis of the temperature working conditions of active medium in the case of discharge initiation, the chosen dimension of laser chamber is not enough to provide the laser operation over threshold. Indeed, the typical iodine atom concentration in supersonic cw COIL is about \(10^{15}\) cm\(^{-3}\). It follows from the experiments on the pulsed COIL initiated by the longitudinal electric discharge to create such a concentration needs to deposit into active medium energy of \(10\ J/l\). The specific heat capacity of the mixture of oxygen and nitrogen under 15 Torr is \(C_v = 16.8 \times 10^{-3}\) J/K. Thus the temperature increase is \(\Delta T = 600\) K. It means the temperature of active medium can achieve the value of 900K. Under such a temperature the small signal gain is \(G_0 = 7.8 \times 10^{-4}\) cm\(^{-1}\) at singlet oxygen yield \(Y=50\%\). So the total gain at the double pass length \(L= 10\ cm\) is \(G = 7.8 \times 10^{-3} = 0.78\%\).

The temperature of active medium in the case of supersonic cw COIL is but 150K. This value at the similar operation condition corresponds to the small signal gain of \(G_0 = 5.4 \times 10^{-3}\) cm\(^{-1}\) and total gain of \(G = 5.4\%\). Thus, pulsed laser with discharge initiation has a gain one order of magnitude less. So, the laser operation needs application of mirrors with high reflection. Such mirrors, as a rule, have relatively high level of losses.

It is not correct to say about any energy parameter when the laser operates with a totally reflecting mirrors. Nevertheless, we succeeded to get the laser operation under oxygen pressure in laser cavity of \(7\ Torr\), iodide pressure of \(1.8\ Torr\) and total pressure of \(17\ Torr\). Note the pulse duration obtained was as short as \(5\ \mu s\).

4. CONCLUSION

The experiments with pulsed COIL initiated with a longitudinal electric discharge showed the initiation length up to 60 cm is available in the active medium conditions close to that of cw laser. It is shown the active medium temperature growth after discharge can be responsible for the specific output energy drop as compared to photolytic initiation.

The laser effect is obtained for the first time with the pulsed COIL based on the jet singlet oxygen generator. The laser operation is obtained under the total pressure of \(17\ Torr\) and oxygen partial pressure of \(7\ Torr\). The laser operation under the high pressure makes it possible to reduce the pump rate and, thus, to minimize the weight and size of the laser.

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Fig. 1. Schematic diagram of the discharge chamber used in investigation of a pulsed COIL initiated with a longitudinal glow discharge.

Fig. 2. Schematic diagram of experiment with pulsed COIL based on a jet SOG
Fig.3.

Fig.4.

Fig.5.

Fig.6.