

# Dissociation of iodine molecules and singlet oxygen generation in $O_2-I_2$ mixture induced by 1315-nm laser radiation

M.V. Zagidullin, N.A. Khvatov, M.S. Malyshev, V.N. Azyazov

**Abstract.** It is observed that laser light at a wavelength of 1315 nm induces continuous stable fluorescence at the  $O_2(b^1\Sigma \rightarrow X^3\Sigma)$  and  $I_2(B^3\Pi_u \rightarrow X^1\Sigma)$  bands in a  $O_2-I_2$  mixture preliminarily irradiated at a wavelength of 532 nm to achieve partial photolysis of iodine molecules. This testifies to generation of iodine atoms and excited  $O_2(a^1\Delta)$ ,  $O_2(b^1\Sigma)$ , and  $I_2(B^3\Pi_u)$  molecules in the  $O_2-I_2$  mixture under irradiation at 1315 nm.

**Keywords:** fluorescence, laser radiation, singlet oxygen, iodine, dissociation.

At present, interest is paid to the development of high-power diode-pumped gas lasers, in particular, to lasers based on alkali metal vapours [1–2] and metastable atoms of noble gases [3, 4]. In this connection, it is worthwhile to search for other gas media in which radiation of IR and visible diode laser arrays could be transformed to high-power single-beam coherent radiation. The oxygen–iodine medium, in which an energy carrier is singlet oxygen  $O_2(a^1\Delta)$ , is very attractive for these purposes [5–7]. In work [5],  $O_2(a^1\Delta)$  molecules were obtained by E–E energy exchange between  $O_2(X^3\Sigma)$  molecules and light-excited fullerene molecules deposited on a solid surface. First experiments on optical pumping of oxygen molecules into the  $b^1\Sigma$  state by a laser diode array, which caused efficient generation of  $O_2(a^1\Delta)$  molecules, were performed in [6]. It was shown in [7] that partial dissociation of iodine in an  $O_2-I_2$  mixture and subsequent irradiation of the mixture at a wavelength of 1315 nm (for example, by InGaAs diode lasers) with sufficiently high intensities lead to almost complete dissociation of iodine, while the concentration of  $O_2(a^1\Delta)$  molecules at room temperature may reach  $\sim 15\%$ . After this, the population inversion on the  $^2P_{1/2}-^2P_{3/2}$  transition of the iodine atom can be obtained by gas-dynamic cooling of the obtained medium. Estimates show that the small-signal gain in this medium may reach  $\sim 10^{-2} \text{ cm}^{-1}$ .

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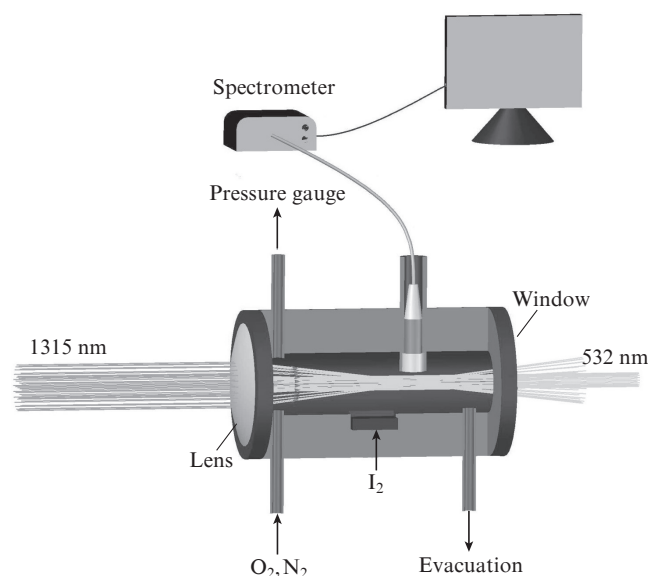
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In this work, we present experimental data demonstrating that 1315-nm irradiation of a  $O_2-I_2$  mixture with partial dissociation of iodine initiates energy-exchange and chemical processes, which lead to the formation of atomic iodine and electronically excited oxygen molecules.

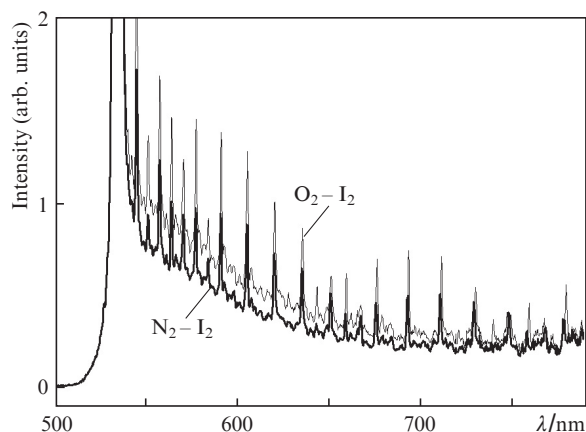
The irradiation of  $O_2-I_2$  and  $N_2-I_2$  mixtures at a wavelength of 1315 nm was performed in a fluorescence cell (FC). The scheme of the FC and the experiment is shown in Fig. 1. The cell was a hollow copper cylinder 140 mm long with an inner diameter of 27 mm. Iodine crystals were placed on the bottom of the preliminarily evacuated FC, which was then filled with oxygen (99.999%) or nitrogen (99.999%) from commercial tanks. Mixing of saturated iodine vapours with these gases resulted in the formation of  $O_2-I_2$  or  $N_2-I_2$  mixtures. For partial dissociation of iodine molecules, we used irradiation by the second harmonic ( $\lambda = 532 \text{ nm}$ ) of a cw Nd:YAG laser. The laser beam 2 mm in diameter with a power of 60 mW passed through a plane-parallel window and propagated in the FC along its axis. A chemical oxygen–iodine laser (COIL) with a power of  $\sim 30 \text{ W}$  was used as a source of radiation with  $\lambda = 1315 \text{ nm}$ . A lens with a focal length of 75 mm focused the COIL radiation into the region irradiated by the Nd:YAG laser. According to calculations, the COIL beam diameter was minimal (0.6 mm) at a distance of 77 mm from the lens and about 1 mm at a distance of



**Figure 1.** Experimental scheme for initiation and recording of laser-induced fluorescence.

$\pm 3$  mm from the waist. Thus, the COIL intensity within this range of distances changed from 3.8 to 10 kW cm<sup>-2</sup>. This irradiation of O<sub>2</sub>-I<sub>2</sub> or N<sub>2</sub>-I<sub>2</sub> mixtures caused laser-induced fluorescence (LIF). The LIF was directed from the region of the COIL beam waist through an optical fibre on the input slit of an Avantes-2048 spectrometer (Avantes, Holland). The absolute sensitivity of the spectrometer within the wavelength range 450–920 nm was calibrated using an AvaLight HAL-CAL light source (Avantes, Holland). The LIF spectrum with an exposure time of 1 s was displayed in real time on a computer monitor.

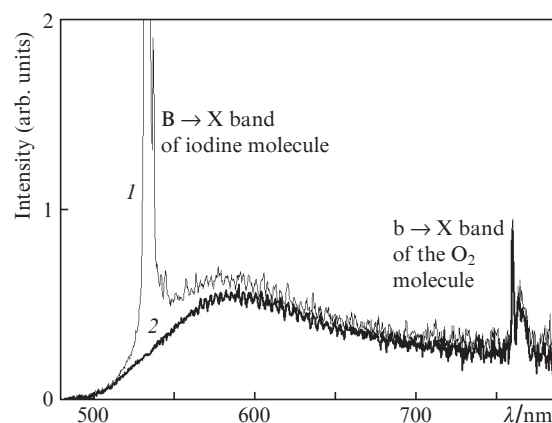
In the first set of experiments, we excited LIF on the B → X transition of iodine molecules (hereinafter, X is the ground term X<sup>1</sup>Σ and B is the excited term B<sup>3</sup>Π<sub>u</sub> of the iodine molecule) only by the Nd:YAG laser radiation. The bandwidth of the used laser was smaller than the spectral distance between the lines of the X → B transition of the I<sub>2</sub> molecule, because of which it was necessary to tune the laser frequency to achieve LIF. Slight variation in the laser wavelength due to a temperature drift of the active laser element led to coincidence of the laser wavelength with individual lines of the X → B transition and allowed us to achieve rather long LIF, the spectrum of which is shown in Fig. 2. The broad peak near λ = 532 nm is caused by the saturation of the CCD array by the Nd:YAG radiation scattered from the FC windows and walls. One can see that the profiles and intensities of the spectra for the O<sub>2</sub>-I<sub>2</sub> and N<sub>2</sub>-I<sub>2</sub> mixtures are almost the same. If the gases were irradiated only by radiation with a wavelength of 1315 nm, LIF in the range of 450–920 nm was not observed.



**Figure 2.** Fluorescence spectra induced by 532-nm light in O<sub>2</sub>-I<sub>2</sub> and N<sub>2</sub>-I<sub>2</sub> mixtures at a pressure of 24 Torr.

In the second set of experiments, gases were irradiated simultaneously at wavelengths of 532 and 1315 nm. The irradiation at λ = 532 nm was terminated as soon as a LIF spectrum appeared on the screen. The LIF spectrum in experiments with the N<sub>2</sub>-I<sub>2</sub> mixture was identical to the spectrum observed for this mixture in the first set of experiments, but immediately disappeared after switching off the Nd:YAG laser. The LIF spectrum of the O<sub>2</sub>-I<sub>2</sub> mixture before and after switching off the 532-nm radiation is shown in Fig. 3. One can see that it considerably differs from the LIF spectrum shown in Fig. 2. The short-wavelength LIF edge is close to λ = 490 nm, while in the first set of experiments it was close to λ = 530 nm. The occurrence of LIF with λ ≥ 490 nm indi-

cates that iodine molecules in the B state on vibrational-rotational levels are formed up to the dissociation limit (~20000 cm<sup>-1</sup>). The LIF spectrum near λ = 762 nm exhibits the b<sup>1</sup>Σ → X<sup>3</sup>Σ transition band of the oxygen molecule, which testifies to generation of O<sub>2</sub>(b) molecules in the mixture under irradiation at λ = 1315 nm. The LIF spectrum shown in Fig. 3 did not change during the entire time of irradiation at λ = 1315 nm. An increase in the oxygen pressure in the FC to 50 Torr caused no change in the amplitude of the b<sup>1</sup>Σ → X<sup>3</sup>Σ transition band. Observations at a small angle to the FC axis allowed us to estimate the diameter of the induced fluorescence region to be approximately 1 mm and its length along the FC axis in the COIL beam caustic region to be 10 mm.

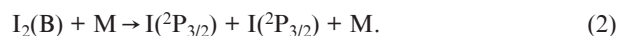


**Figure 3.** Fluorescence spectra induced by light with wavelengths of (1) 532 and 1315 nm and (2) 1315 nm in an O<sub>2</sub>-I<sub>2</sub> mixture at a pressure of 24 Torr.

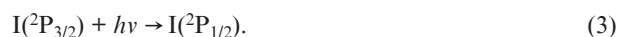
The formation of excited I<sub>2</sub>(B) and O<sub>2</sub>(b<sup>1</sup>Σ) molecules in the O<sub>2</sub>-I<sub>2</sub> mixture under irradiation only at λ = 1315 nm can be explained as follows. The excitation of a iodine molecule into the B<sup>3</sup>Π<sub>u</sub> state by radiation at λ = 532 nm leads to its predissociation



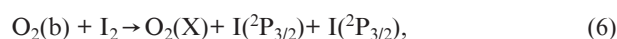
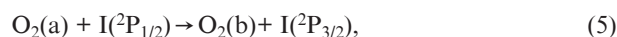
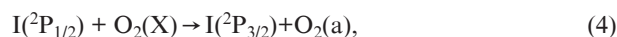
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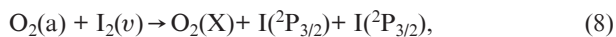
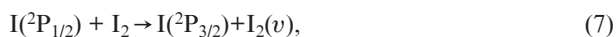


The radiation at a wavelength of 1315 nm excites iodine atoms:

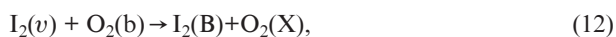
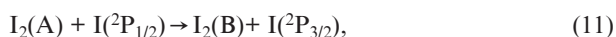
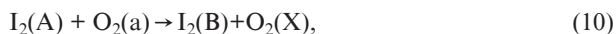
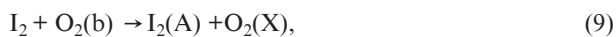


The appearance of excited iodine atoms initiates the following chain of secondary reactions causing iodine dissociation and generation of excited molecules:





where  $I_2(v)$  is the vibrationally excited iodine molecule in the ground electronic state,  $O_2(a) = O_2(a^1\Delta)$ ;  $O_2(b) = O_2(b^1\Sigma)$ ; and  $O_2(X) = O_2(X^3\Sigma)$ . The formation of  $I_2(B)$  molecules can occur as a result of the reactions [8, 9]:



where A denotes one of the two states  $A^3\Pi_u$  or  $A^3\Pi_{2u}$ , the energies of which are higher than the ground state of the iodine molecule by approximately  $10^4 \text{ cm}^{-1}$ . It is obvious that the concentration of iodine atoms and excited  $I_2(B)$  and  $O_2(b)$  molecules in the  $O_2-I_2$  mixture can remain unchanged under irradiation at  $\lambda = 1315 \text{ nm}$  only due to processes (3)–(12). According to our estimates, the concentrations of  $O_2(b)$  and  $I_2(^3\Pi_u)$  molecules in the induced fluorescence region are  $\sim 10^{14}$  and  $10^9 \text{ cm}^{-3}$ , respectively. An important role in the kinetic scheme (3)–(12) is played by singlet oxygen molecules  $O_2(a)$ . However, due to intense scattered radiation of the COIL at  $\lambda = 1315 \text{ nm}$ , we failed to separate the  $O_2(a \rightarrow X)$  emission band at a wavelength of  $1268 \text{ nm}$  using a monochromator and a narrow-band filter. The gas temperature in the region of LIF excitation, which is determined from the intensity ratio of the P and R branches in the  $b \rightarrow X$  emission band of the oxygen molecule [10], was estimated by us to be  $\sim 700 \text{ K}$ . The high local temperature leads to inhomogeneous gas density, negatively affects the kinetics of generation of excited molecules, and causes losses of iodine atoms and excited particles due to their diffusive and convective motion from the irradiated region.

Despite these negative factors, under our experimental conditions, reactions (3)–(12) in the  $O_2-I_2$  mixture irradiated at  $\lambda = 1315 \text{ nm}$  ensure continuous generation of iodine atoms and electronically excited iodine [ $I_2(B)$ ] and oxygen [ $O_2(b^1\Sigma)$  and  $O_2(a^1\Delta)$ ] molecules.

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