

An optical boiler generating singlet oxygen $O_2(a^1\Delta_g)$

N.I. Lipatov, A.S. Biryukov, E.S. Gulyamova

Abstract. An ecologically perfect generator of singlet oxygen $O_2(a^1\Delta_g)$ is proposed which fundamentally differs from existing singlet-oxygen generators. Excited $O_2(X^3\Sigma_g^-)$ molecules are generated due to interaction of the $O_2(X^3\Sigma_g^-)$ molecules with a quasi-monochromatic field, which is supplied from an external source to a closed volume – an optical boiler containing oxygen. It is shown that, by pumping continuously the optical boiler by the light field of power $\sim 3 \times 10^5$ W, it is possible to accumulate up to 40 % of singlet oxygen ($O_2(b^1\Sigma_g^+) + O_2(a^1\Delta_g)$) in the boiler volume during $\sim 10^{-2}$ s.

Keywords: singlet oxygen, quasi-monochromatic field, optical boiler.

Singlet oxygen $O_2(a^1\Delta_g)$ is an oxygen molecule in the lowest first excited electronic state with the radiative lifetime exceeding 10^3 s [1]. This circumstance motivates interest in singlet oxygen among researchers active in the fields of biochemistry of living tissues, atmospheric plasma chemistry, organic chemistry, and studying the quantum-mechanical properties of the homogeneous $E - E$, V , and T exchange in molecules [2, 3].

The methods of generating singlet oxygen attract special attention after the obtaining of cw lasing in atomic iodine [4], in which the population inversion was achieved due to energy transfer from singlet oxygen $O_2(a^1\Delta_g)$ [5, 6]. Among all the sources of $O_2(a^1\Delta_g)$ available at present, the most promising are a chemical generator [7] and a low-temperature high-frequency discharge plasma in the oxygen medium [8, 9]. Note that the chemical generator, in which the reaction of chlorine with the alkali solution of hydrogen peroxide is used, has the highest efficiency and can provide the $O_2(a^1\Delta_g)$ yield up to 50 %, whereas the high-frequency discharge gives only ~ 10 % at present. A comparatively low yield of $O_2(a^1\Delta_g)$ in the case of the high-frequency discharge is caused by the properties of a low-pressure oxygen plasma [8, 9]. The chemical generator has its own considerable

disadvantages: first, the irreversible consumption of one of the components and, second, the use of halogen makes it ecologically hazardous.

A singlet-oxygen generator proposed in our paper is essentially free of these disadvantages. The generator represents a closed optical boiler in which only two substances interact, namely, molecular oxygen and radiation with the spectrum lying within the $A(0-0)$ absorption band of the O_2 molecule at ~ 762 nm. By absorbing this radiation, the O_2 molecules undergo transitions from the ground $X^3\Sigma_g^-$ state to the excited $b^1\Sigma_g^+$ state. During collisions, the $O_2(b^1\Sigma_g^+)$ molecules can undergo efficient transitions to the $a^1\Delta_g$ state. Thus, the interaction of radiation with molecular oxygen provides the generation of singlet oxygen $O_2(a^1\Delta_g)$.

The optical boiler represents a hollow sphere (the analogue of the Ulbricht sphere) with the internal surface having the efficient specular or, which is better, diffusion reflection at 762 nm. The light field is coupled into the sphere volume, for example, through optical fibres. This field can be produced by a light emitting diode array*. Already after several reflections, a homogeneous isotropic light field is formed within the sphere volume.

As a result, two processes, positive and negative, which determine the photon loss, begin to act within the optical boiler volume. The positive process is the absorption of light by O_2 molecules, while the negative one is the loss of photons due to incomplete reflection from the internal surface of the sphere (reflectance $r \neq 1$).

The generation efficiency of $O_2(a^1\Delta_g)$ molecule in the optical boiler considerably depends on the relation between these losses. The photon loss $\Delta\rho_{\text{refl}}$ after one reflection from walls is $\sim \rho(1-r)$. At the same time, the absorption loss per passage in the boiler is $\Delta\rho_{\text{abs}} \sim \rho 2R\sigma N$ (where ρ is the photon density in the boiler volume, R is the boiler radius, N is the concentration of O_2 molecules in the boiler, and σ is the absorption cross section). It is obvious that the greater is excess of $\Delta\rho_{\text{abs}}$ over $\Delta\rho_{\text{refl}}$, the higher is the generator efficiency, i.e. the inequality $2R\sigma N(1-r)^{-1} > 1$ should be fulfilled. This means that it is necessary to increase the values of r and R . Then, for example, for $R = 5$ cm and $r \sim 0.999$, the losses $\Delta\rho_{\text{refl}}$ and $\Delta\rho_{\text{abs}}$ will be comparable already for the oxygen pressure in the boiler $p_{O_2} \leq 2$ atm (at the gas temperature 300 K). Therefore, we can expect that in this

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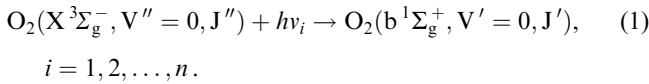
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* Note that diode array-optical fibre devices based on modern fibre lasers can provide light fluxes noticeably exceeding kilowatt powers [10]. A few tens of such fibreoptic inputs to an optical generator will provide the required radiation power.

case about 50 % of the light energy $P\tau_p$ supplied to the boiler will be spent to generate the O_2 ($b^1\Sigma_g^+$, $V=0$) molecules. Here, P is the light flux power supplied to the boiler and τ_p is the irradiation time.

If the light field in the boiler is a set of n individual monochromatic components at the frequencies corresponding to the intense absorption lines of the P, R, and Q branches of the $O_2(X^3\Sigma_g^-, V''=0) \rightarrow O_2(b^1\Sigma_g^+, V'=0)$ transition, the efficiency of excitation of O_2 molecules to the $b^1\Sigma_g^+$, $V'=0$ state can be increased in fact by a factor of n . A similar result, i.e. the increase in the excitation efficiency will be provided by the isotropic distribution of the light field in the boiler because in this case the negative influence of the Doppler effect on the absorption of light by O_2 molecules is excluded.

Figure 1 presents the scheme of transitions in the energy level diagram of the O_2 molecule, which is complete enough for the aim of our paper. The scheme includes five processes with substantially different rates. Consider each of these processes in detail. Process 1 is the absorption of radiation from the ground state:



Here, ν_i is the frequency of the $J'' \rightarrow J'$ line related to the P, R, and Q branches of the $X, V'' \rightarrow b, V'$ vibronic transition. These transitions are magnetic dipole transitions and, therefore, are forbidden by the corresponding selection rules, which is confirmed by their comparatively low absorption cross sections $\sigma_i \approx 2 \times 10^{-24} \text{ cm}^2$ [11]. However, the influence of this circumstance on the generation efficiency of excited $O_2(b^1\Sigma_g^+)$ molecules and, correspondingly, $O_2(a^1\Delta_g)$ molecules can be considerably reduced by providing the long enough interaction of O_2 molecules with the light field. This means in fact that the boiler should operate in the regime of accumulation of both photons, because the light flux is continuously supplied into the generator volume, and excited $O_2(a^1\Delta_g)$ molecules which rather slowly relax to the $X^3\Sigma_g^-$ ground state due to collisions with each other (process 3 in Fig. 1). For example, under normal conditions, we have $\tau_a p_{O_2} \approx 5 \times 10^{-2} \text{ s atm}$, where τ_a is the relaxation time of the $a^1\Delta_g$ state [12]. Of course, the interaction time τ_p of radiation with O_2 molecules in the boiler volume should satisfy the condition $\tau_p < \tau_a$.

We will consider the light field in the boiler as a set of fields with close frequencies and randomly varying phase

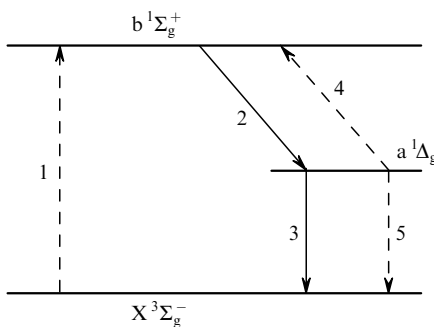


Figure 1. Energy level diagram of the O_2 molecule. The arrows and numbers indicate transitions and processes considered in the paper.

relations. In this case, the probability of the $(X, V''=0) \rightarrow (b, V'=0)$ transition can be represented as a sum of the probabilities of transitions induced by the monochromatic field components with the energy density $\rho_{\nu_i} hv_i$, where ρ_{ν_i} and hv_i are the photon density and energy, respectively. Accordingly, the balance of photons in the boiler volume can be described by the expression

$$\frac{d\rho}{dt} = \frac{P}{h\nu V} - \rho\tilde{\sigma}cN_X - \rho c \frac{3(1-r)}{R}, \quad (2)$$

where $\rho = \sum_i^n \rho_i$ is the total density of photons with the average energy $h\nu$ in the boiler volume; $P = \sum_{i=1}^n P_i$ is the light flux power supplied to the boiler from an external source through optical fibres; $V = 4\pi R^3/3$ is the boiler volume; $\tilde{\sigma} \approx n\sigma_i$ is the effective absorption cross section for the $X \rightarrow b$ band; c is the speed of light; and N_X is the concentration of O_2 molecules in the ground state.

We assume for simplicity that P is time-independent, i.e. a rectangular radiation pulse of duration τ_p is used. The rate of the reflection loss [the third term in the right-hand side of (2)] also remains constant, whereas the rate of loss caused by the absorption of light by O_2 molecules will continuously decrease in the time interval $0 < t < \tau_p$ because N_X decreases.

To find the rigorous solution of (2), it is necessary to know the function $N_X(t)$. At the same time, the model description of the behaviour of the photon density $\rho(t)$ at the initial stage of the interaction of light with gas inside the optical boiler can be obtained by neglecting the time dependence of N_X . In this case, the solution of Eqn (2) will have the form

$$\rho(t) = \rho_{\max} \left[1 - \exp\left(-\frac{t}{T}\right) \right], \quad (3)$$

where

$$T = \left[\tilde{\sigma}cN_X + \frac{3(1-r)c}{R} \right]^{-1}; \quad \rho_{\max} = \frac{PT}{h\nu V}.$$

Note that Eqn (2) was derived by neglecting the possible influence of the spontaneous radiative decay of the $b^1\Sigma_g^+$ state and induced emission at the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ transition on the photon balance.

Because the radiative lifetime τ_b of the $b^1\Sigma_g^+$ state exceeds 10 s [13], the radiative decay can be neglected in the photon balance. As for the induced emission process, its inclusion to the photon balance is justified if its rate greatly exceeds the resulting quenching rate of the $b^1\Sigma_g^+$ state, i.e. if the inequality

$$\rho\tilde{\sigma}c \gg \frac{1}{\tau_b} + W_b + k_{b \rightarrow a}^{O_2} N_X \quad (4)$$

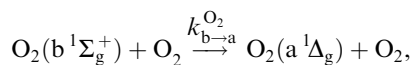
is fulfilled, where the empirical relation

$$W_b = \left(\frac{R^2}{6D} + \frac{2R}{v_T \gamma_b} \right)^{-1}$$

describes the diffusion loss of the $O_2(b^1\Sigma_g^+)$ molecules, which is accompanied by their heterogeneous relaxation at the boiler walls [14]. Here, D is the diffusion coefficient; v_T is the thermal velocity of molecules; and γ_b is the

accommodation coefficient. Under normal conditions and $R = 5$ cm, we have $W_b \approx 1/\tau_b$ for a glass boiler.

The third term in the right-hand side of (4) characterises the rate of process 2

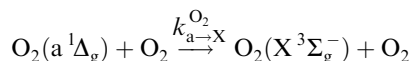


which exceeds the rates of spontaneous decay of O₂(b ¹Σ_g⁺) molecules and their heterogeneous relaxation. Moreover, it is known [15] that the b ¹Σ_g⁺ state is quenched by undergoing transition to the a ¹Δ_g state with the efficiency more than 90 % for most of the partners in collisions, including O₂. Accordingly, the estimate of the photon density at which inequality (4) can be fulfilled gives $\rho(t) \gg k_{b \rightarrow a}^{\text{O}_2} N / (\bar{\sigma} c) \approx 10^{16} \text{ cm}^{-3}$.

Note here that $\rho(t)$ denotes the current photon density, which is determined by expression (3) for any instant in the time interval $0 < t \leq \tau_p$.

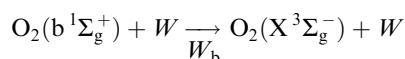
For the light flux power $P \approx 5 \times 10^5$ W in the boiler volume, inequality (4) is not fulfilled, which confirms the validity of neglecting induced emission in the photon balance.

Process 2 is the collision relaxation of O₂ molecules in the b ¹Σ_g⁺, V' = 0 state to the singlet level of the a ¹Δ_g state with the rate constant $k_{b \rightarrow a}^{\text{O}_2} \approx 4.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [13]. One can expect that the rate of this process will exceed the rate of process 3

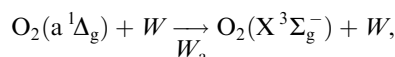


by more than an order of magnitude, the rate constant of the latter being $k_{a \rightarrow X}^{\text{O}_2} \approx 1.7 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ [12, 15].

Processes

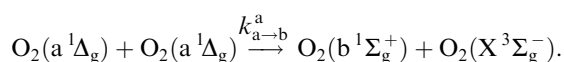


and



which are not indicated in Fig. 1, describe the loss of excited molecules due to their diffusion to the boiler walls followed by heterogeneous relaxation. The rates of these processes can be estimated from the empirical relation presented above. Under normal conditions the rate $W_{b,a}$ and the rate $1/\tau_b$ of the radiative decay of the state b ¹Σ_g⁺ are of the same order of magnitude ($\sim 10^{-2} \text{ s}^{-1}$). The rate of the spontaneous decay of the a ¹Δ_g singlet state is even smaller. Taking into account the smallness of $1/\tau_b$ and $W_{b,a}$, we can expect that the influence of these processes on the generation efficiency of O₂(a ¹Δ_g) will be quite insignificant and, therefore, they can be neglected.

The population N_b of the b ¹Σ_g⁺, V' = 0 state is substantially determined, apart from processes considered above, by process 4



The rate constant of this process was estimated as $k_{a \rightarrow b}^a \approx 2 \pm 0.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [14].

Based on the analysis of the scheme of processes presented in Fig. 1, we can write the system of equations describing the population kinetics of the X, b, and a states in the form

$$\frac{dN_b}{dt} = \rho \bar{\sigma} c N_X - k_{b \rightarrow a}^{\text{O}_2} N N_b + k_{a \rightarrow b}^a N_a^2, \quad (5)$$

$$\frac{dN_a}{dt} = k_{b \rightarrow a}^{\text{O}_2} N N_b - k_{a \rightarrow X}^{\text{O}_2} N N_a - 2k_{a \rightarrow b}^a N_a^2, \quad (6)$$

where

$$N = N_X + N_a + N_b. \quad (7)$$

Although the accumulation regime has no definite stationary state, the rates of changing of $\rho(t)$ and $N_i(t)$ become so small that the time derivatives in equations (2), (5), and (6) can be set equal to zero. As a result, we have a system of four algebraic equations for unknowns ρ , $X = N_X/N$, $Y = N_b/N$, and $Z = N_a/N$, which can be transformed to the fourth-degree equation with respect to Z :

$$Z^4 + AZ^3 - BZ^2 - CZ + D = 0, \quad (8)$$

where

$$A = \frac{\alpha(1 + 3\beta)}{2}; \quad B = \frac{\alpha[2\gamma - \alpha\beta(1 + \beta) + \delta]}{2};$$

$$C = \frac{\alpha^2[\gamma(1 + \beta) + \beta\delta]}{2}; \quad D = \frac{\alpha^2\gamma}{2}; \quad \alpha = \frac{k_{b \rightarrow a}^{\text{O}_2}}{k_{a \rightarrow b}^a};$$

$$\beta = \frac{k_{a \rightarrow X}^{\text{O}_2}}{k_{b \rightarrow a}^{\text{O}_2}}; \quad \gamma = \frac{P}{hvVN^2} \frac{1}{k_{b \rightarrow a}^{\text{O}_2}}; \quad \delta = 1 + \frac{3(1-r)}{\bar{\sigma}RN};$$

$N = \xi N_L$; N_L is the Loschmidt number; and $\xi \geq 1$.

Equation (8) contains both the initial parameters ($r = 0.999$, $R = 5$ cm, $\bar{\sigma} \approx 10^{-22} \text{ cm}^2$, $N_L = 2.68 \times 10^{19} \text{ cm}^{-3}$, $hv = 2.6 \times 10^{-19} \text{ J}$) and the variable parameter – the light flux power. In this case, the choice of the values of initial parameters is not optimised at all because it only illustrates the boiler efficiency. The numerical solution of Eqn (8) for the case $N = N_L$ (i.e. $\xi = 1$) showed that, for example, for $P = 3 \times 10^5$ W the relative concentrations of singlet oxygen produced in the boiler in the accumulation regime are $Z = N_a/N_L \approx 0.3$ and $Y = N_b/N_L = 0.11$.

As expected, the boiler efficiency is quite sensitive to the value of the reflectance r of the boiler walls, which directly determines the light field power loss. Thus, for example, for $r = 0.99$ and $P = 3 \times 10^5$ W, we obtain $Z = 0.16$ and $Y = 0.04$, i.e. in this case the boiler efficiency is less by half than that in the previous example. However, even in this case the optical boiler is more efficient than a high-frequency discharge. In addition, the operating pressure in the boiler (~ 1 atm) considerably exceeds the oxygen pressure in the discharge.

Note that the obtained relative concentrations correspond to the case of pure oxygen. At the same time oxygen can be 'contaminated' by the main components of the air mixture, namely, N₂, CO₂, and H₂O, which also efficiently quench the b ¹Σ_g⁺ state. According to [14], the strongest quencher among these components is water molecules which induce the b ¹Σ_g⁺ → a ¹Δ_g transition. The corresponding rate

constant is $k_{b \rightarrow a}^{\text{H}_2\text{O}} \approx 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, whereas the rate constant $k_{a \rightarrow X}^{\text{H}_2\text{O}}$ of quenching of the $^1\Delta_g$ state is much lower, being $\sim 10^{-18} \text{ cm}^3 \text{ s}^{-1}$. Another specific feature of water vapour is that the purification of oxygen from it is the most complicated, which is known from experiments. Even deep cryogenic freezing of gas (for example, at the gas pressure $p \approx 1 \text{ atm}$) does not allow the reduction of the partial pressure of the H_2O vapour below 0.05 Torr, which corresponds to the concentration $N_{\text{H}_2\text{O}} \approx 10^{15} \text{ cm}^{-3}$. In this connection it is appropriate to estimate the influence of H_2O molecules on the distribution of excited oxygen among the $b^1\Sigma_g^+$ and $a^1\Delta_g$ states. For this purpose, the relaxation term $k_{b \rightarrow a}^{\text{H}_2\text{O}} N_b N_{\text{H}_2\text{O}}$ was added to Eqns (5) and (6) with the corresponding signs (the term $k_{a \rightarrow X}^{\text{H}_2\text{O}} N_a N_{\text{H}_2\text{O}}$ was neglected due to its smallness). Taking into account that $N_{\text{H}_2\text{O}} \approx 10^{15} \text{ cm}^{-3}$, the numerical solution of the system of equations (2), (5)–(7) gave the following result. By the end of a 10^{-2} -s, 3×10^5 -W light pulse, the distribution of excited oxygen in the boiler volume is characterised by the relations $Y \approx 0.02$, $Z \approx 0.38$, and $X \approx 0.6$. By comparing this result with that obtained above for pure oxygen, we see that the oxygen excitation efficiency, determined by the total concentration $N_b + N_a$, is independent of the water vapour; however, its presence noticeably affects the distribution of O_2 molecules over excited states.

Thus, we have studied a simplified model of the interaction of radiation with O_2 molecules in a closed volume, which, of course, gives only approximate results. Nevertheless, these results show that the optical boiler proposed in the paper can be efficiently used to generate singlet oxygen. The simplest methods of increasing the boiler efficiency are the multiplexing of boilers, the broadening of the light field spectrum in the boiler volume and increasing of r . Depending on the field of applications of singlet oxygen, the optical boiler can operate in different regimes: pulsed, repetitively pulsed at pulse repetition rates up to a few tens of hertz, and cw regime with gas flow rates $\sim 10^3 \text{ cm s}^{-1}$. In addition, by varying the light flux power and pressure of oxygen in the boiler, the degree of excitation of O_2 molecules can be controlled.

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