

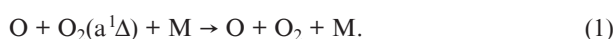
# Mechanism of singlet oxygen deactivation in an electric discharge oxygen–iodine laser

V.N. Azyazov, P.A. Mikheyev, A.A. Pershin, A.P. Torbin, M.C. Heaven

**Abstract.** We have determined the influence of the reaction of molecular singlet oxygen with a vibrationally excited ozone molecule  $O_2(a^1\Delta) + O_3(v) \rightarrow 2O_2 + O$  on the removal rate of  $O_2(a^1\Delta)$  in an electric-discharge-driven oxygen–iodine laser. This reaction has been shown to be a major channel of  $O_2(a^1\Delta)$  loss at the output of an electric-discharge singlet oxygen generator. In addition, it can also contribute significantly to the loss of  $O_2(a^1\Delta)$  in the discharge region of the generator.

**Keywords:** singlet oxygen, oxygen–iodine laser, deactivation, recombination, vibrationally excited ozone, discharge,  $O_2(a^1\Delta)$ ,  $O_3$ ,  $O(^3P)$ .

Small-signal gain of the active medium of an electric-discharge-driven oxygen–iodine laser (EOIL) [1] does not make it possible to effectively extract the energy stored in singlet oxygen  $O_2(a^1\Delta)$  [2]. To increase the gain, one should increase the concentration of both iodine atoms and  $O_2(a^1\Delta)$  molecules. Vasiljeva et al. found [3] that the rate of  $O_2(a^1\Delta)$  deactivation at the output of an electric-discharge singlet oxygen generator (ED SOG) increases with increasing concentrations of oxygen atoms [O], molecular oxygen [ $O_2$ ] and the buffer gas [M]. The rate of  $O_2(a^1\Delta)$  loss at the ED SOG output is satisfactorily explained by the phenomenological three-body deactivation mechanism [3]



Azyazov et al. [4–6] also observed an abnormally high rate of  $O_2(a^1\Delta)$  deactivation after laser photolysis of O– $O_2$ –Ar–He– $CO_2$  mixtures. In this case, the addition of Ar had no effect on the rate of  $O_2(a^1\Delta)$  deactivation, whereas the addition of He and  $CO_2$  even reduced it [6], which is in contradiction with mechanism (1). The rate of  $O_2(a^1\Delta)$  loss

after laser photolysis is well explained by the chemical process [5, 6]



where vibrationally excited ozone  $O_3(v)$  is produced during the three-body recombination [7]



Here,  $v = v_1 + v_2 + v_3$  is the total number of quanta at deformation ( $v_2 = 701 \text{ cm}^{-1}$ ), symmetrical ( $v_1 = 1103 \text{ cm}^{-1}$ ) and antisymmetrical ( $v_3 = 1042 \text{ cm}^{-1}$ ) stretching modes of ozone [7]. The authors of papers [7–10] also found that  $O_3(v)$  efficiently reacts with  $O_2(a^1\Delta)$ . Despite this, process (2) has not previously been used to explain the high rate of  $O_2(a^1\Delta)$  loss at the ED SOG output. The aim of this study is to determine the effect of process (2) on the dynamics of  $O_2(a^1\Delta)$  in an EOIL.

The kinetic scheme of the processes involving vibrationally excited ozone is given in [6]. The absence of the measured probabilities of excitation of vibrational modes of the  $O_3$  molecule in process (3) and of the rate constants of process (2) for specific sets of  $v_1$ ,  $v_2$  and  $v_3$  values complicates the modelling of vibrational kinetics of ozone. Azyazov and Heaven [5] showed that the simplified model of vibrational kinetics of ozone with a combined mode  $v$  adequately describes the experimental results obtained in Refs [4–6]. In process (3) an ozone molecule with  $v \geq 3$  is produced [5, 7]. In collisions with the particles of the medium, vibrational quanta are redistributed among the three modes. The ozone molecule  $O_3(v)$  is deactivated in the VT-process [7]



or removed in chemical reactions (2) and



Reactions (2) and (5) with  $v < 2$  are slow and have no significant effect on the kinetics of  $O_3(v)$  [5]. For  $v \geq 2$  Azyazov and Heaven [5] give the following values of the rate constants of reactions (2) and (5):  $k_2 = 4.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $k_5 = 1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

Quasi-stationary concentration of  $O_3(v \geq 2)$  can be obtained from the balance of its formation in process (3) and loss in processes (2), (4) and (5):

$$[O_3(v \geq 2)] = \frac{\sum_M k_3^M [O][O_2][M]}{k_2 [O_2(a)] + \sum_M k_4^M [M] + k_5 [O]}. \quad (6)$$

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Let us show that process (2) provides the same rates of  $O_2(a^1\Delta)$  loss as process (1) under the experimental conditions of paper [3], where the process of three-body deactivation was first proposed. To this end, we consider the ratio of the rates of these processes, taking into account (6):

$$Q_{2/1} = \frac{k_2[O_3(v \geq 2)][O_2(a)]}{\sum_M k_1^M[O][O_2(a)][M]} = \frac{k_2[O_2] \sum_M k_3^M[M]}{\sum_M k_1^M[M] \left( k_2[O_2(a)] + \sum_M k_4^M[M] + k_5[O] \right)}$$

Under the experimental conditions of paper [3] (Ar:O<sub>2</sub> = 99:1; mixture pressure, 100 Torr; concentration of singlet oxygen molecules,  $[O_2(a)] = 1.5 \times 10^{15} \text{ cm}^{-3}$  and  $[O] = 2 \times 10^{15} \text{ cm}^{-3}$ ; and mixture temperature,  $T = 300 \text{ K}$ ) at  $k_1^{Ar} = 0.62 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$  [3],  $k_1^{O_2} = 1 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$  [3],  $k_3^{O_2} = 6 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$  [3],  $k_3^{Ar} = 0.62 \times k_3^{O_2}$  [3],  $k_4^{O_2} = 3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  [7] and  $k_4^{Ar} = 5.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  [7], the ratio  $Q_{2/1}$  is close to unity, i.e., the rate of  $O_2(a^1\Delta)$  loss at the ED SOG output is equally provided by processes (1) and (2).

The rate of process (2) with (6) taken into account can be represented as:

$$R_2 = k_2[O_3(v \geq 2)][O_2(a)] = \frac{k_2[O_2(a)] \sum_M k_3^M[O][O_2][M]}{k_2[O_2(a)] + \sum_M k_4^M[M] + k_5[O]}$$

For typical conditions in a post-discharge zone of the ED SOG [1] ( $[He] = 9 \times 10^{17} \text{ cm}^{-3}$ ,  $[O_2] = 2.5 \times 10^{17} \text{ cm}^{-3}$ ,  $[O] = 5 \times 10^{15} \text{ cm}^{-3}$ ,  $[O_2(a)] = 3 \times 10^{16} \text{ cm}^{-3}$  and  $T = 550 \text{ K}$ ) the terms in the denominator satisfy the condition

$$k_2[O_2(a)] \gg \sum_M k_4^M[M] + k_5[O].$$

In this case,

$$R_2 \approx \sum_M k_3^M[O][O_2][M],$$

and the rate of process (2) is limited by the rate of  $O_3(v)$  production during three-body recombination (3). This was the reason why the authors of [3] considered the three-body process to be main mechanism of  $O_2(a^1\Delta)$  deactivation.

Reaction (2) can also make a significant contribution to the rate of  $O_2(a^1\Delta)$  loss in the discharge zone of the ED SOG. Consider the ratio of the rate of this reaction to the rate of the fastest process in the discharge zone – deactivation of  $O_2(a^1\Delta)$  by an electron impact:



Under the experimental conditions of paper [11], the ratio of the rates of processes (2) and (7),  $Q_{2/7}$ , is  $\sim 0.2$  in the case when O atoms are not removed from the system. In experiments with a reduced concentration of O atoms, the ratio is much smaller,  $Q_{2/7} = 0.03$ , due to addition of NO and coating of the chamber walls with mercury oxide. Consequently, process (2) also makes a significant contribution to the rate of  $O_2(a^1\Delta)$  loss in the discharge zone of the ED SOG in the case of excess O atoms. Braginsky et al. [11] produced a record concentration of  $O_2(a^1\Delta)$  in the ED SOG by removing excess oxygen atoms.

Thus, process (2) can ensure the observed rates of  $O_2(a^1\Delta)$  deactivation both in the post-discharge zone [3] and after laser photolysis [5]. Processes (2)–(5) should also be included in the kinetic scheme of the processes in the discharge zone of the ED SOG. The authors of [4–9] present experimental evidence to support a decisive role of process (2) in deactivation of singlet oxygen, whereas process (1) is phenomenological and cannot provide the rate of  $O_2(a^1\Delta)$  loss after laser photolysis [4, 5]. The rate of  $O_2(a^1\Delta)$  deactivation can be reduced by removing excess O atoms, for example, by adding NO into the mixture [1] or by coating the chamber walls with mercury oxide [11] and by adding  $O_3(v)$  quenchers, such as  $CO_2$ ,  $SF_6$ ,  $SiF_4$ , etc. to the mixture at the ED SOG output.

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