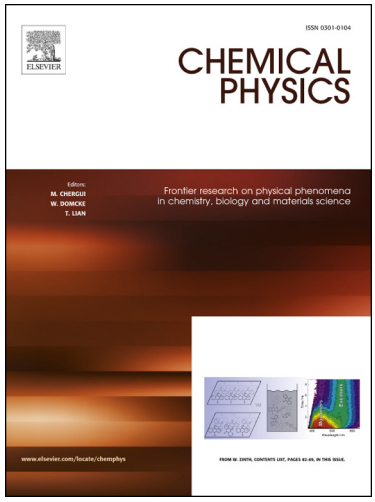


# Kinetics of Oxygen Species in an Electrically Driven Singlet Oxygen Generator

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# Kinetics of Oxygen Species in an Electrically Driven Singlet Oxygen Generator

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

*Abstract*— **The kinetics of oxygen species in the gaseous medium of a discharge singlet oxygen generator has been revisited. Vibrationally excited ozone $O_3(v)$ formed in $O+O_2$ recombination is thought to be a significant agent in the deactivation of singlet oxygen $O_2(a^1\Delta)$, oxygen atom removal and ozone formation. It is shown that the process $O_3(v\geq2) + O_2(a^1\Delta) \rightarrow 2O_2 + O$ is the main $O_2(a^1\Delta)$ deactivation channel in the post-discharge zone. If no measures are taken to decrease the oxygen atom concentration, the contribution of this process to the overall $O_2(a^1\Delta)$ removal is significant, even in the discharge zone. A simplified model for the kinetics of vibrationally excited ozone is proposed. Calculations based on this model yield results that are in good agreement with the experimental data.**

*Index Terms*— **discharge driven oxygen iodine laser, singlet oxygen, ozone, vibration, quenching, recombination, $O(^3P)$, $O_2(a^1\Delta)$, $O_3$.**

## I. Introduction

Gas phase processes involving the reactive oxygen species $O_2(a^1\Delta)$, $O(^3P)$ and $O_3$ have been studied extensively due to their importance in the terrestrial atmosphere [1-6], oxygen-containing plasmas [7-10], the oxygen-iodine laser [11-14] and combustion [15-16]. There has been a long standing interest in the possibility of developing a discharge driven oxygen iodine laser (DOIL), where $O_2(a^1\Delta)$ is produced via electric discharge [7-13]. In the DOIL devices investigated to-date [12], the low small-signal gain of the active medium has prevented the efficient extraction the energy stored in singlet oxygen $O_2(a^1\Delta)$ [17]. To increase the gain, the $O_2(a^1\Delta)$ concentration must be increased [8]. Vasiljeva *et al.* [18] found that the $O_2(a^1\Delta)$ quenching rate in the discharge afterglow increases with oxygen pressure much faster than predictions based on the two-body quenching due to the components of an oxygen containing plasma (O, $O_2$, $O_3$ etc.). They suggested that the faster deactivation of singlet oxygen at higher pressures was due to a three-body deactivation (3BD) process (reaction 1 in Table 1). With this assumption the rate of $O_2(a^1\Delta)$ deactivation increases with increasing concentrations of oxygen atoms [O], molecular oxygen [$O_2$] and the buffer gas [M]. To explain the singlet oxygen dynamics in the discharge afterglow in the $O_2$/Ar mixture, Vasiljeva *et al.* [18] proposed a rate constant for reaction (1) that was $k_1^{O2}=1\times10^{-32}$ cm$^6$/s for M=$O_2$ and $k_1^{Ar}=0.63\times10^{-32}$ cm$^6$/s for M=Ar.

The authors of Ref's [19, 20] attempted to measure the rate constant of reaction 1 using pulsed laser photolysis of $O_2/O_3$ mixtures at 248 nm to produce oxygen atoms and $O_2(a^1\Delta)$ molecules. They observed rapid quenching of $O_2(a^1\Delta)$ in $O(^3P)/O_2/O_3$ mixtures. It was found that the addition of Ar had no effect on the rate of $O_2(a^1\Delta)$ deactivation, whereas the addition of He and $CO_2$ decreased the quenching rate [19, 20], in contradiction with expectations based on the 3BD mechanism. Attempts to model the fast decay using the 3BD mechanism yielded a rate constant of $k_1^{O2}=(1.1\pm0.1)\times10^{-31}$ cm$^6$/s, which was inconsistent with the results of the flowing afterglow experiments.

As an alternative to the 3BD mechanism, the authors of Ref. [21] proposed that vibrationally-excited ozone ($O_3(v)$) formed in the recombination process (Table 1, reaction 2) is responsible for the fast $O_2(a^1\Delta)$ quenching via reaction 3 (2BD mechanism). $v = v_1+v_2+v_3$ is the total number of excited vibrational quanta for the ozone, where the labels indicate the symmetric stretch ($v_1$), bending ($v_2$) and asymmetric stretch ($v_3$) modes. The reaction set that is used here to model the singlet oxygen kinetics is presented in Table 1. It is well-known [22-25] that $O_3(v)$ forms in process 2. Although the rate constant for quenching of $O_2(a^1\Delta)$ by vibrationally cold $O_3$ is small ($4\times10^{-15}$ cm$^3$ s$^{-1}$), Kurylo *et al.* [26] found that the rate constant for quenching by $O_3$ that has one quantum of vibrational energy is faster by a factor of 38±20. Rawlins *et al.* [27] reported an estimated rate constant for quenching of $O_2(a^1\Delta)$ by ozone that has two or more quanta of the stretch modes to be in the range $10^{-11}$-$10^{-10}$ cm$^3$ s$^{-1}$. Recently [4, 19-21] additional experimental evidence for the critical role of vibrationally excited ozone in the quenching of $O_2(a^1\Delta)$ in $O(^3P)/O_2/O_3$ systems was reported.

There are two pathways that determine the fate of $O_3(v)$ formed by recombination process 2. Stabilization of $O_3(v)$ is achieved by process 4. Process 3 results in the dissociation of $O_3(v)$ and regeneration of oxygen atoms, $O(^3P)$. Two odd oxygen species, $O_3(v)$ and $O(^3P)$, are removed by reaction 5. Processes involving vibrationally-excited ozone may have a significant impact on the oxygen species kinetics in a DOIL. The objectives of the present study were to examine the influence of processes with $O_3(v)$ on the rates of $O_2(a^1\Delta)$ quenching, $O(^3P)$ removal and $O_3$ formation under conditions relevant to DOIL systems.

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