A pared-down gas-phase kinetics for the chemical oxygen-iodine laser medium

S.Yu. Pichugin [a,*], M.C. Heaven [b]

[a] P.N. Lebedev Physical Institute of RAS, Samara Branch, Samara 443011, Russia
[b] Department of Chemistry, Emory University, Atlanta, GA 30322, USA
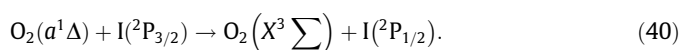
ABSTRACT

Kinetic data obtained in the last decade has resulted in revisions of some mechanisms of excitation and deactivation of excited states in the chemical oxygen-iodine laser (COIL) medium. This review considers new kinetic data and presents analyses of the mechanisms of pumping and quenching of electronically and vibrationally excited states in the oxygen-iodine laser media. An effective three-level model of I_2 molecule excitation and relaxation has been developed. The calculated effective rate constants for deactivation of $I_2(X, 11 \leqslant \upsilon \leqslant 24)$ by O_2, N_2, He and CO_2 are presented. A simplified kinetic package for the COIL active medium is recommended. This model consists of a 30-reaction set with 14 species. The results of calculations utilizing simplified model are in good agreement with the experimental data.

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1. Introduction

The chemical oxygen-iodine laser (COIL) operates on the electronic $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ transition of iodine atom, inverted through energy transfer from singlet oxygen $O_2(a^1\Delta)$ to $I(^2P_{3/2})$ via the process:

$$O_2(a^1\Delta) + I(^2P_{3/2}) \rightarrow O_2\left(X^3\sum\right) + I(^2P_{1/2}). \qquad (40)$$

In the following text, $I(^2P_{3/2})$, $I(^2P_{1/2})$, $O_2(X^3\Sigma)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, $I_2(X^1\Sigma)$, $I_2(A'^3\Pi_{2u})$, $I_2(A^3\Pi_{1u})$, $I_2(B^3\Pi_0)$ are designated by I, I*, $O_2(X)$, $O_2(a)$, $O_2(b)$, $I_2(X)$, $I_2(A')$, $I_2(A)$ and $I_2(B)$, respectively. The reaction numbering used here is that of the standard kinetic package [1,2]. Progress in the development of COIL was achieved first of all due to the high yields of chemical singlet oxygen generators (SOG), where $O_2(a)$ is produced during chlorination of basic hydrogen peroxide solution. The yields of $O_2(a)$ in SOG output can exceed 60%. Along with oxygen molecules, the gas flow from chemical generators also contains H_2O, and Cl_2. $O_2(a)$ losses during transportation from SOG exit to mixing unit occur due to the processes:

$$O_2(a) + O_2(a) \rightarrow O_2(b, \upsilon) + O_2(X, \upsilon) \qquad (1)$$

$$O_2(a) + O_2(a) \rightarrow 2O_2(X, \upsilon) \qquad (3)$$
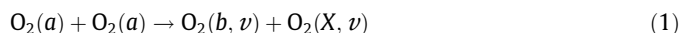
The products of reactions (1) and (3) are vibrationally-excited [3–7].

The active medium of a COIL is usually produced by injecting iodine vapor into a oxygen flow. Iodine molecules are dissociated in the presence of $O_2(a)$, and iodine atoms that are subsequently pumped by singlet oxygen to the $^2P_{1/2}$ state. The electronic energy of $O_2(a)$ is nearly resonant with I* (Fig. 1), and for the typical conditions of the COIL active medium the rates of EE energy exchange between these two states via process (40) and reverse process

$$O_2(X) + I^* \rightarrow O_2(a) + I \qquad (41)$$

are much higher than all others, such that a steady state ratio $N_{I^*}/N_I = K_{eq}N_a/N_X$ is established in $\leqslant 1$ μs. From the principle of detailed balance the equilibrium rate coefficient is $K_{eq} = K_{40}/K_{41} = 0.75\exp(402/T)$. N_{I^*}, N_I, N_a and N_X denote the concentrations of I*, I, $O_2(a)$ and $O_2(X)$, respectively. K_{40} and K_{41} are the rate constants of processes (40) and (41). The rate constant of process (41) was measured by different methods [8–14]. The rate constant K_{40} is related to K_{41} by the expression for K_{eq}. Fortunately $O_2(a)$ is resistant to deactivation by most collision partners. The main channels for the loss of electronic energy stored in singlet oxygen are through the removal of I* by collisions with H_2O, I_2, $O_2(a)$ etc. The rate constants of processes in the active medium of the COIL and their measurement methods were reviewed in [1,2,15] and [16].

The mechanism by which singlet oxygen dissociates iodine remains an important unsolved problem because of its complexity. It is well known that the I_2 dissociation process has initiation and chain stages, and that excited intermediate states of iodine are involved [17]. Deactivation of electronic energy in the active medium of COIL produces vibrationally excited O_2, H_2O, I_2 molecules [3–7,18–24]. Vibrationally excited O_2 and $I_2(\upsilon)$ can play an important role in the dissociation of molecular iodine [2,7,25].

* Corresponding author. Tel.: +7 8463340536; fax: +7 8463355600.
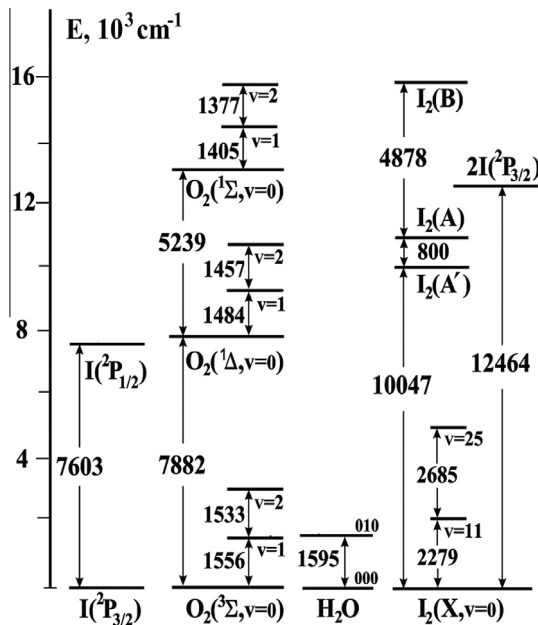E-mail addresses: theor@fian.smr.ru (S.Yu. Pichugin), mheaven@emory.edu (M.C. Heaven).

Fig. 1. The lower lying energy levels of O_2, I_2, H_2O and I.

Recently an I_2 dissociation model was developed in which the dominant intermediate is electronically excited iodine $I_2(A',A)$ [2,25]. The intermediates are populated by collisions of $I_2(X)$ with vibronically excited molecules $O_2(a, v = 1$ and/or 2) and by collisions of vibrationally excited iodine $I_2(X, 11 \leqslant v \leqslant 24)$ with $O_2(a)$.

The energy levels of I, O_2, I_2 and H_2O that most significantly involved in the kinetics of COIL active medium are exhibited in Fig. 1. Three electronic states of oxygen and at least four vibrational levels for each electronic state should be taken into account [26]. Energy of rotational excitation of species is much less than the energies of vibrational and electronic excitation and the I_2 dissociation energy, therefore, the rotational excitation makes a insignificant contribution to the COIL kinetics. About 50 vibrational levels of $I_2(X)$ are considered in calculations of the population distribution [27,28]. The reaction set then includes about 200 reactions and more than 70 species. This level of complexity makes computational modeling of the COIL active medium very challenging, especially when full three-dimensional fluid dynamics are included [29–34]. The primary goal of the present work was to reduce the number of reactions to a more digestible set. In this model the system of equations for populations of $I_2(X, v)$ levels with $v > 10$ is reduced to one equation for iodine molecules in vibrational levels $v = 11$–24 and a second equation for molecules with $v \geqslant 25$. The effective deactivation rate constants of $I_2(X, 11 \leqslant v \leqslant 24)$ and $I_2(X, v \geqslant 25)$ molecules taking into account the conditions of COIL medium are derived. We examine the ability of the simplified model to predict the dissociation rates observed in recent experimental investigations. The results of computer simulations utilizing simplified I_2 dissociation model were found to be in good agreement with the experimental data.

2. Transport of $O_2(a)$

Progress trend of COIL calls for the use of the high-pressure SOGs [35–38]. In the case of pulsed COILs, this will provide an increase in the specific energy extraction from the active medium volume [39]. For cw COILs with the supersonic flow of the active medium, an increase in the initial oxygen pressure leads to the increase in the Mach number by preserving the high density of $O_2(a)$

in the resonator and also simplifies a system for waste gas exhaust to the atmosphere [40].

The use of high-pressure SOG in COIL raises the serious problem of transporting singlet oxygen to a mixing unit [41] because of the rate of electronic energy loss in the processes (1) and (3) increases quadratically with $O_2(a)$ density. Energy-pooling process (1) was extensively studied [3,42–52] mostly due to $O_2(b)$ produced in this process. Two molecules of $O_2(a)$ are lost in process (3). Perram [1] recommends the rate constants of 2.7×10^{-17} cm^3 s^{-1} and 1.7×10^{-17} cm^3 s^{-1} for processes (1) and (3), respectively for $T = 300$ K. The quenching rate of $O_2(a)$ in the process

$$O_2(a) + M \rightarrow O_2(X, v) + M (M = O_2(X), N_2, He, H_2O, CO_2)$$
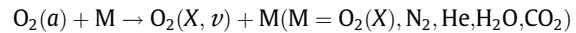
is much smaller [1,53–57] than that for process (1) and (40). Neglecting the $O_2(a)$ losses in this process and for $T = $ const the dependence of $O_2(a)$ yield $\eta_a(\tau) = N_a/N_{ox}$ on the transportation time τ is given by

$$\eta_a(\tau) = \frac{\eta_a(\tau = 0)}{1 + (K_1 + 2K_3)\eta_a(\tau = 0)N_{ox}\tau}$$

where $N_{ox} = N_a + N_X$ is the total oxygen concentration, $\eta_a(\tau = 0)$ is the $O_2(a)$ yield at $\tau = 0$. For $T = 300$ K the last relation can be rewritten as

$$\eta_a(\tau) = \frac{\eta_a(\tau = 0)}{1 + 1.96\eta_a(\tau = 0)P_{ox}\tau}$$

where P_{ox} is the O_2 partial pressure in Torr.

The obtained relation is correct if the gas temperature change lightly due to either high heat transmission to the wall or small value of the parameter $P_{ox}\tau$. Relaxation of stored in $O_2(a)$ electronic energy results in increase of gas temperature. The studies [3,46–48] indicated that the rate of $O_2(a)$ self-quenching increases with temperature. Heidner et al. [46] reported the temperature dependence of rate constant for process (1) to be $K_1 = 9.5 \times 10^{-28} T^{3.8} \exp(700/T)$. The influence of heat release on the transport of high-pressure singlet oxygen used in a supersonic COIL was analyzed in [41]. Recently Zagidullin et al. [58,59] remeasured the rate of $O_2(b)$ formation in the processes (1) and the overall rate of $O_2(a)$ self-quenching in processes (1) and (3) at $T \approx 330$ K. The rate constants obtained exceed by a factor of 1.5 the generally accepted values, given in the standard kinetic package [1,2].

The relaxation of $O_2(a)$ in the pooling reactions (1) and (3) occurs with a characteristic time $\tau_a = [(K_1 + K_3)N_a]^{-1} \approx 0.01 - 0.1$ s. Such a lifetime makes it possible to transport $O_2(a)$ over relatively large distances with insignificant losses. The electronically excited oxygen $O_2(b)$ formed in reaction (1) is quenched upon collisions with water molecules:

$$O_2(b) + H_2O \rightarrow O_2(a, v) + H_2O(v') \qquad (5)$$
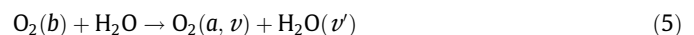
The steady-state concentration N_b of the electronically excited oxygen $O_2(b)$ in the gas flow is established during the time being $\tau_5 = (K_5 N_w)^{-1} \approx 10^{-5} - 10^{-4}$ s that is much smaller than of τ_a. The fraction of $O_2(b)$ in the total mass of oxygen $\eta_b = N_b/N_{ox}$ is insignificant and can be determined to a high degree of accuracy from the balance of the rates of its production in reaction (1) and its reduction in reaction (5): $\eta_b = K_1\eta_a^2/(K_5\eta_w) \approx 10^{-5} - 10^{-4}$, where $\eta_w = N_w/N_{ox}$, N_w is the water vapor concentration.

Rate constants of quenching of $O_2(b)$ have been measured by variety of colliders [54–57,60–77] and theirs values for $O_2(X)$ and buffer gasses He, Ar, N_2 are very small. In the conditions of COIL active medium $O_2(b)$ is predominantly quenched by H_2O and I_2. Recently the COIL operation with CO_2 buffer gas was demonstrated [78–80]. Although CO_2 is good quencher of $O_2(b)$ (6.1×10^{-13} cm^3 s^{-1}, Ref. [77]) it had very little influence on the I_2 dissociation