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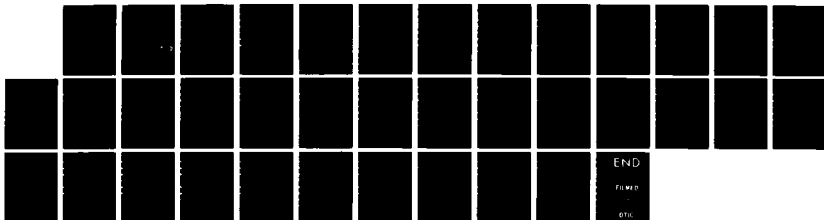
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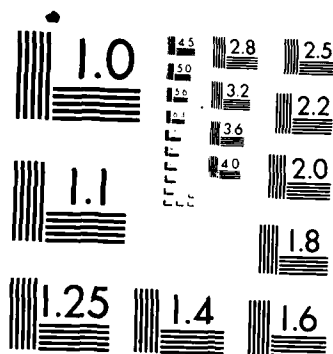
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Behavior of Singlet Oxygen in the Oxygen-Iodine Transfer Laser

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28 September 1985

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Prepared for
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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

into atoms. In the latter case, energy pooling between $O_2(^1\Delta)$ and I^* is the dominant process unless a strong I^* quencher (e.g., H_2O) is present. In the former case, the $O_2(^1\Delta)$ -driven chain reaction mechanism for I_2 dissociation is the dominant feature of the kinetics. A detailed description of each of these regimes is critical in understanding the oxygen-iodine laser.

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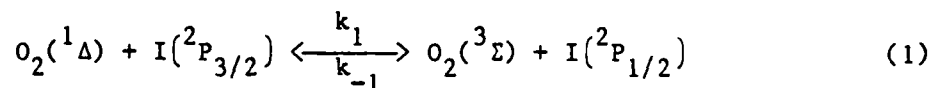
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I. INTRODUCTION

The chemical oxygen-iodine laser (COIL)¹⁻³ is based on transferring energy from a majority energy storage species [$O_2(^1\Delta)$] to a minority receptor species ($I^2P_{3/2}$):

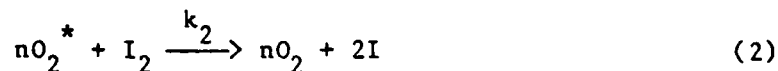


$$K_{EQ} = k_1/k_{-1} = 2.9 \text{ at } T = 295 \text{ K}$$

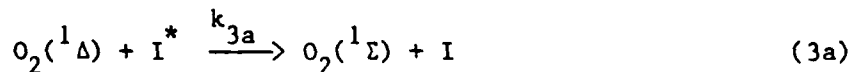
An energy level diagram for the low-lying electronic states of O_2 , I_2 , and I is shown in Fig. 1. Examination of the above electronic state equilibrium and the threshold criterion for the atomic iodine laser ($[I^*]/[I] > 0.5$) yields the conclusion that $[O_2(^1\Delta)]/[O_2(^3\Sigma)] > 0.17$ in order to sustain cw laser oscillation. While the yield of $O_2(^1\Delta)$ from the reaction of Cl_2 and basic hydrogen peroxide is extremely high, deactivation of $O_2(^1\Delta)$ to $O_2(^3\Sigma)$ quickly degrades the extractable energy from such a device.

Direct quenching of $O_2(^1\Delta)$ is extremely deleterious to laser performance; fortunately, most $O_2(^1\Delta)$ quenching processes are extremely inefficient. Quenching of I^* is important because Process (1) connects the $O_2(^1\Delta)$ energy storage reservoir with the I^* lasing medium. I^* quenching processes become significant loss mechanisms for $O_2(^1\Delta)$ at high ratios of $I^*/O_2(^1\Delta)$.

In the review to follow, particular attention will be paid to the mechanism by which O_2^* dissociates molecular I_2



and to the second-order energy pooling (k_{3a}) and electronic quenching (k_{3b} , k_{3c} , and k_{3d}) processes.



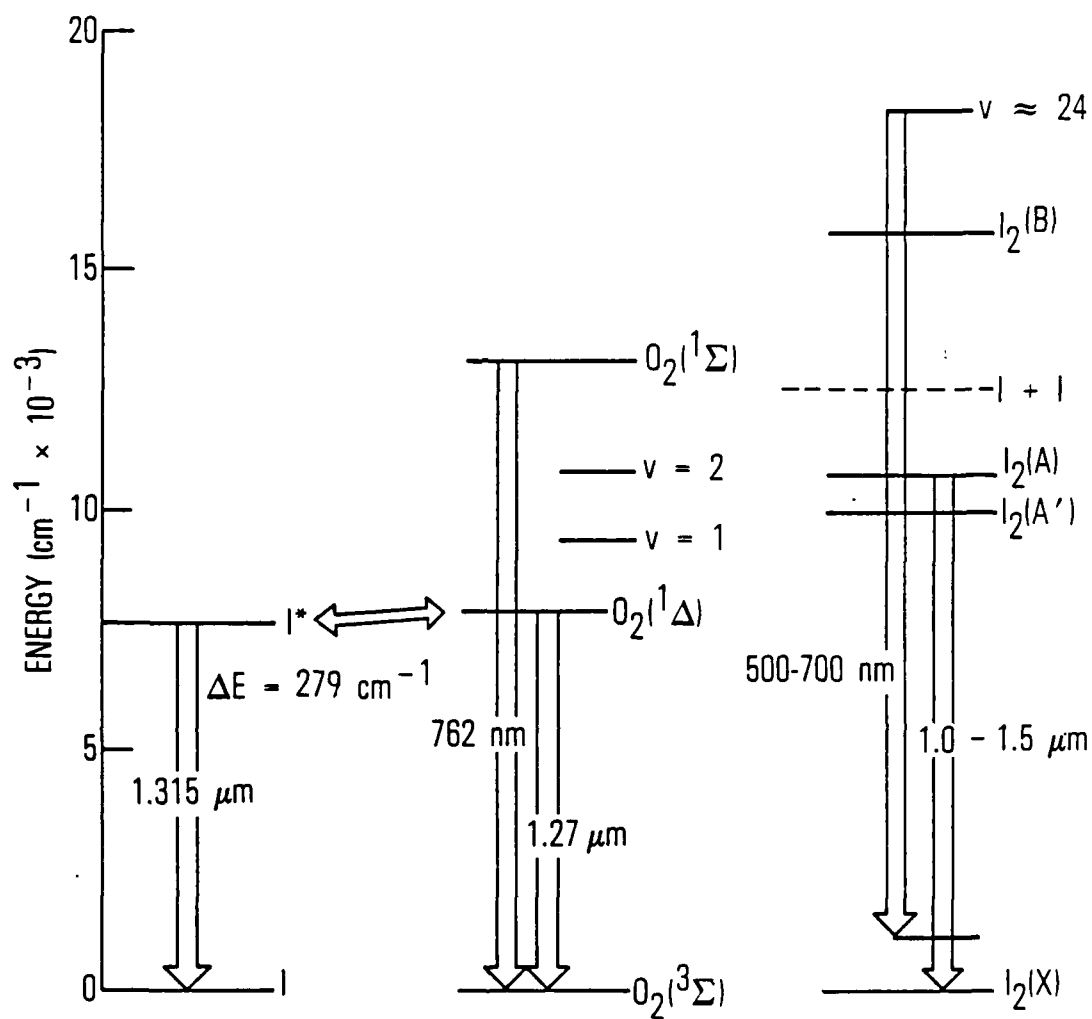


Fig. 1. Low-Lying Electronic Energy Levels and Observed Spectral Emissions for the O_2 and I_2 Molecules and the I Atom.



In the conventional COIL device, these processes are intrinsic loss processes for $\text{O}_2(^1\Delta)$ that must be tolerated. Finally, we will briefly examine the advantages of replacing I_2 by an alternate I-atom precursor that is premixable with $\text{O}_2(^1\Delta)$.

II. EXPERIMENTAL

The work reported from the Aerophysics Laboratory of The Aerospace Corporation has been performed on two different experimental systems. The kinetic flow tube apparatus (Fig. 2) has been described in great detail in Ref. 4. The excimer laser photolysis apparatus (Fig. 3) has been described in Ref. 5. In both cases, O_2^* is created by a microwave discharge in pure O_2 [$O_2(^1\Delta)/O_2(^3\Sigma) < 0.1$], and the $O(^3P)$ atoms are removed on a heated HgO surface just downstream of the discharge.

Although the apparatus in Fig. 3 is a flow system, the time histories of the important densities are monitored by time-resolved emission spectroscopy following the excimer laser photolysis pulse. In the apparatus of Fig. 2, steady-state emission intensities are monitored as a function of distance down the flow tube in order to extract kinetic information. In each case, the $[O_2(^1\Delta)]$ is calibrated absolutely by isothermal calorimetry, and the $[I^*]$ related to it by the ratio of the Einstein coefficients. Concentrations of $O_2(^1\Delta)$, $I_2(A^3\Pi_{1u})$, and $I_2(B^3\Pi_{0+})$ were also followed during some experiments. Two experimental details are worth emphasizing. First, the treatment of the walls in the flow tube apparatus were coated with a low melting halogenated wax (Halocarbon, Inc.) that was very inefficient at recombining I atoms. Secondly, the use of an extremely sensitive intrinsic Ge detector (ADC 403 HS) permitted the detection of $O_2(^1\Delta)$ and I^* in the flow tube with excellent S/N and I^* with good time response in the excimer photolysis apparatus.

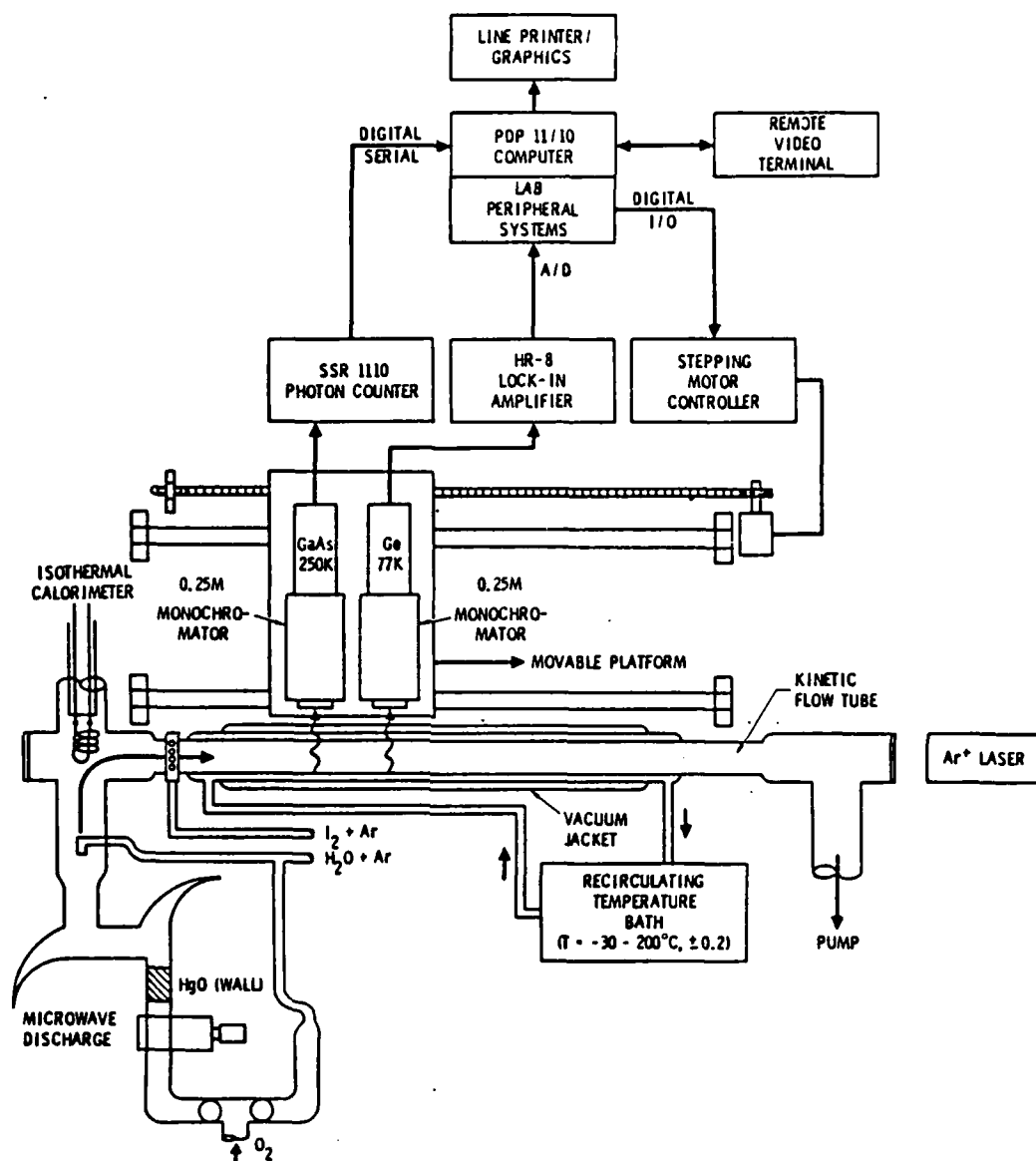


Fig. 2. Schematic Diagram of the Computer-Controlled Kinetic Flow Tube Apparatus.

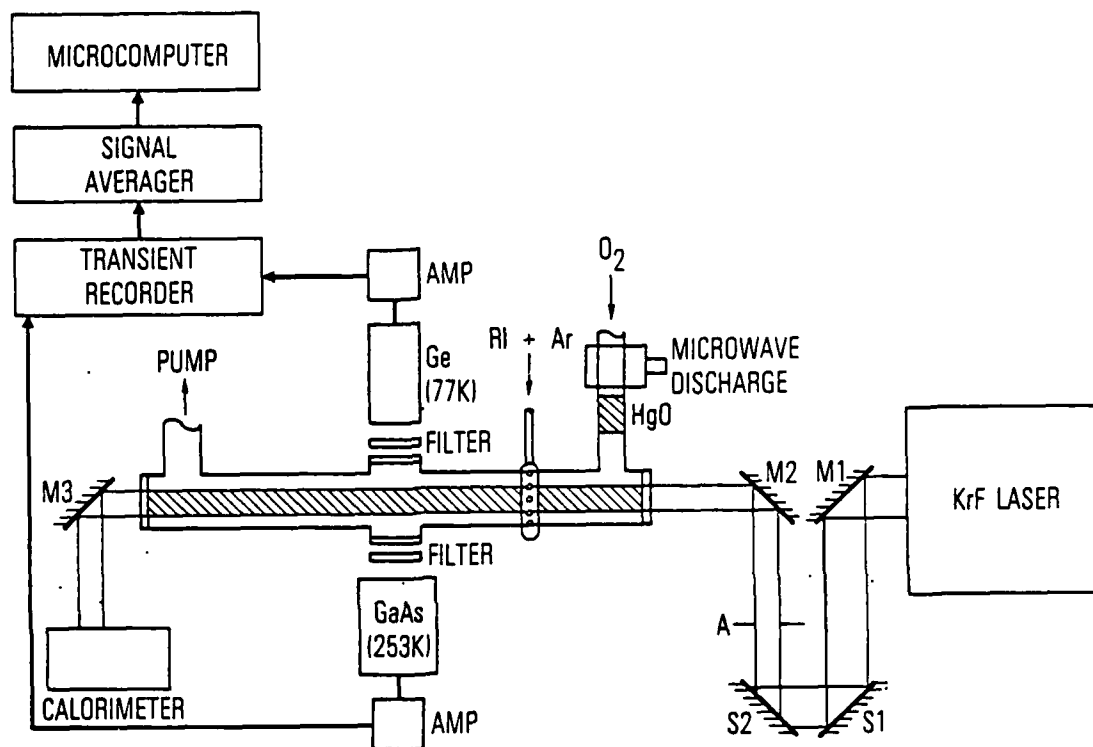
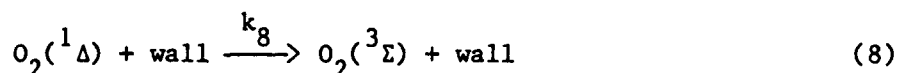
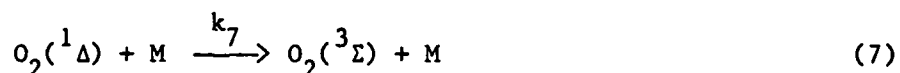
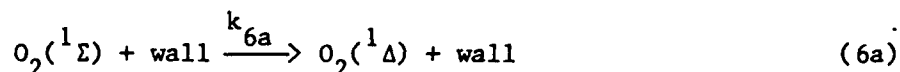
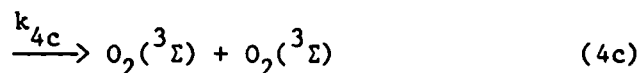
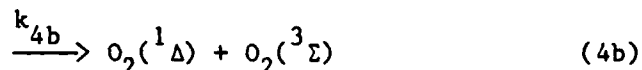
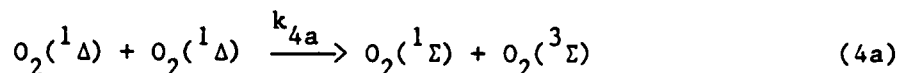


Fig. 3. Schematic Diagram of the Excimer Photolysis Flow Tube Apparatus.

III. RESULTS AND ANALYSIS

A. DECAY OF $O_2(^1\Delta)$ IN THE ABSENCE OF I_2 AND I

The decay of $O_2(^1\Delta)$ can be accurately described by a combined first- and second-order decay equation based on the following processes:



The solution can be written as follows:

$$[O_2(^1\Delta)]^{-1} = \{[O_2(^1\Delta)]_0^{-1} + \frac{A}{B}\} \exp(Bt) - \left(\frac{A}{B}\right) \quad (9)$$

$$\text{where } A = 2k_{4a} - \left\{ \frac{k_{4a}(k_{5a} + k_{6a})}{(k_5 + k_6)} \right\} + k_{4b} + 2k_{4c}$$

$$\text{and } B = k_8 + k_7^M[M].$$

Making the assumption that $O_2(^1\Sigma)$ is quenched predominantly to $O_2(^1\Delta)$ and that the two dominant quenchers from a COIL chemical generator are $O_2(^3\Sigma)$ and H_2O , we can write

$$A = k_{4a} + k_{4b} + 2k_{4c}$$

$$B = k_8 + k_7^{O_2} [O_2(^3\Sigma)] + k_7^{H_2O} [H_2O]$$

The necessary rate coefficient information for evaluating $O_2(^1\Delta)$ decays under these conditions is shown in Table 1. Because the rate coefficient k_4 is so small, it is extremely difficult to detect the second-order decay component in a pure O_2 or an $O_2 + H_2O$ system.

B. DECAY OF $O_2(^1\Delta)$ IN I and I^* ($[I_2] = 0$)

1. DECAY OF CURVES FOR $[O_2(^1\Delta)] \gg [O_2(^3\Sigma)]$

Under conditions that are approachable with a chemical generator for singlet oxygen, the relationship between $O_2(^1\Delta)$ and I^* can be written as follows⁴:

$$[I^*] = \frac{(2X) [I_2]_0}{(1 + X)} \quad (10)$$

where $X = K_{EQ} [^1\Delta] / [^3\Sigma] = [I^*] / [I]$. In this case, since $X \gg 1$, $[I^*] = 2[I_2]_0$, i.e., all the I atoms are in the excited state. Thus, $[I^*]$ can be treated as one of the constant quenchers in Eq. (7).

2. DECAY CURVES FOR $[O_2(^1\Delta)] = (0.1 - 1.0) [O_2(^3\Sigma)]$

In this important region for the chemical laser, analytic modeling is complicated, and numerical methods are to be preferred.

3. DECAY CURVES FOR $[O_2(^1\Delta)] < 0.1 [O_2(^3\Sigma)]$

In this regime where flow tube experiments employing microwave discharge production of O_2^* operate, Eq. (10) reduces to

$$[I^*] = \frac{2K_{EQ} [^1\Delta] [I_2]_0}{[O_2]_{tot} + 1.9[^1\Delta]} \sim C[^1\Delta] \quad (11)$$

Table 1. Rate Coefficient Data for $O_2(^1\Delta)$ Quenching
in Pure O_2 (T = 295 K)

Process	M	Rate Coefficient ($cm^3/molecule\text{-}sec$)	References
k_{4a}		$(2.0 \pm 0.5) \times 10^{-17}$	6
		$(2.0 \pm 0.6) \times 10^{-17}$	8
k_4		$< 5 \times 10^{-17}$	7
k_5	O_2	$(4.0 \pm 0.4) \times 10^{-17}$	9
		$(3.9 \pm 0.2) \times 10^{-17}$	10
	H_2O	$(5 \pm 1) \times 10^{-12}$	11
		4.7×10^{-12}	12
		$(6.7 \pm 0.5) \times 10^{-12}$	13
k_6	$\gamma^a =$	1×10^{-2} (pyrex)	6
		2×10^{-2} (pyrex)	8
		1×10^{-3} (Halocarbon)	8
k_7	O_2	$(1.6 \pm 0.05) \times 10^{-18}$	14
		$(1.5 \pm 0.05) \times 10^{-18}$	15
	H_2O	$(4 \pm 1) \times 10^{-18}$	11
k_8	$\gamma^a =$	2×10^{-5} (pyrex)	6
		1.2×10^{-5} (pyrex)	14
		3×10^{-5} (Halocarbon)	8

^a γ represents the wall recombination probability; $\gamma = (2Rk)/c$ in a cylindrical flow tube; c is the oxygen mean velocity; R is the tube radius; and k is the measured removal rate (sec^{-1}).

where $[I^*]$ is directly proportional to $O_2(^1\Delta)$. For this last case, we can write an $O_2(^1\Delta)$ decay equation analogous to Eq. (9) based on an analysis originally put forth by Derwent and Thrush¹⁶:

$$[O_2(^1\Delta)]^{-1} = \{[O_2(^1\Delta)]_0^{-1} + \frac{C}{D}\} \exp(Dt) - \frac{C}{D} \quad (12)$$

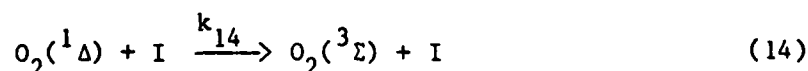
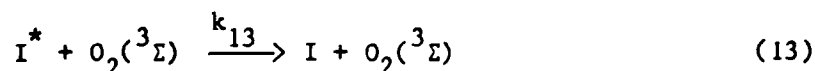
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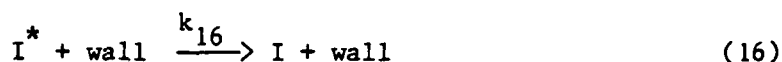
$$\begin{aligned} C &= A + \frac{k_1}{(k_{-1} + k_{13})} (k_{3a} + 2k_{3b} + k_{3c} + k_{3d}) \frac{[I]}{[{}^3\Sigma]} \\ &= A + K_{EQ}(k_{3a} + 2k_{3b} + k_{3c} + k_{3d}) \frac{[I]}{[{}^3\Sigma]} \end{aligned}$$

and

$$\begin{aligned} D &= B + \left\{ k_{14} + \frac{k_{13}k_1 + k_1(k_{15}^M [M] + k_{16} + k_{17})/[{}^3\Sigma]}{(k_{-1} + k_{13})} \right\} [I] \\ D &= B + \{ k_{14} + K_{EQ}(k_{13} + (k_{15}^M [M] + k_{16} + k_{17})/[{}^3\Sigma]) \} [I] \\ &= B + \{ k_{eff} + K_{EQ}(k_{15}^M [M] + k_{16} + k_{17})/[{}^3\Sigma] \} [I] \\ k_{eff} &= k_{14} + K_{EQ}k_{13} \end{aligned}$$

The terms A and B were defined in Eq. (9). The term k_{eff} was introduced by Derwent and Thrush¹⁶ and has been used subsequently by other authors⁸ in order to analyze their data. The additional processes introduced above are defined as follows:





We will show that $k_{-1} \gg k_{13}$ allowing K_{EQ} to replace the term $k_1/(k_{-1} + k_{13})$ in the definitions of C and D above. Figure 4, taken from Ref. 17, shows that using H_2O as an I^* quencher that one observes qualitatively a regime where first- and second-order components are both significant $[(H_2O) = 0]$. Upon the addition of H_2O , one begins to see single exponential decays. As noted in Ref. 17, the derived value of $k_{15}^{H_2O} = 1.7 \times 10^{-12} \text{ cm}^3/\text{molecule-sec}$ is in good agreement with literature values (Table 2).

As is the typical case for combined first- and second-order decays, an unambiguous deconvolution is very difficult without exceedingly precise data. This system is no exception to that rule. Derwent and Thrush¹⁶ concluded that the second-order component of the $O_2(^1\Delta)$ decay in the presence of I^* was not observable, however, our studies are not consistent with that conclusion.

In Fig. 5a, we see an $O_2(^1\Delta)$ decay curve versus time taken in our kinetic flow tube. A two parameter nonlinear least squares fit to these data is superimposed. In Fig. 5b, the data are plotted as though they represent a pure second-order decay. The first-order wall decay (measured without I atoms) is exceedingly small and, clearly, the incremental first-order decay component in the presence of I and I^* is small as well. It should be noted that the relative $[O_2(^1\Delta)]$ must be determined by obtaining a difference spectrum since $I_2(A^3\Pi_{lu} \rightarrow X^1\Sigma)$ emission overlaps the $O_2(a^1\Delta \rightarrow X^3\Sigma)$ emission band. Analysis of the C and D coefficients in Eq. (12) as a function of $[I]/[^3\Sigma]$ gives the plot in Fig. 6. From it, we estimate that $k_{3a} + 2k_{3b} + k_{3c} + k_{3d} = 2.1 \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$. The rate coefficient k_{3a} has been measured to be $\sim 1 \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$ (Table 2). Upon addition of I_2 , we find that the increase in the first-order decay coefficient, i.e. (D-B), is not statistically significant. Using the value $(D-B) < 0.13 \text{ sec}^{-1}$ gives the following inequality:

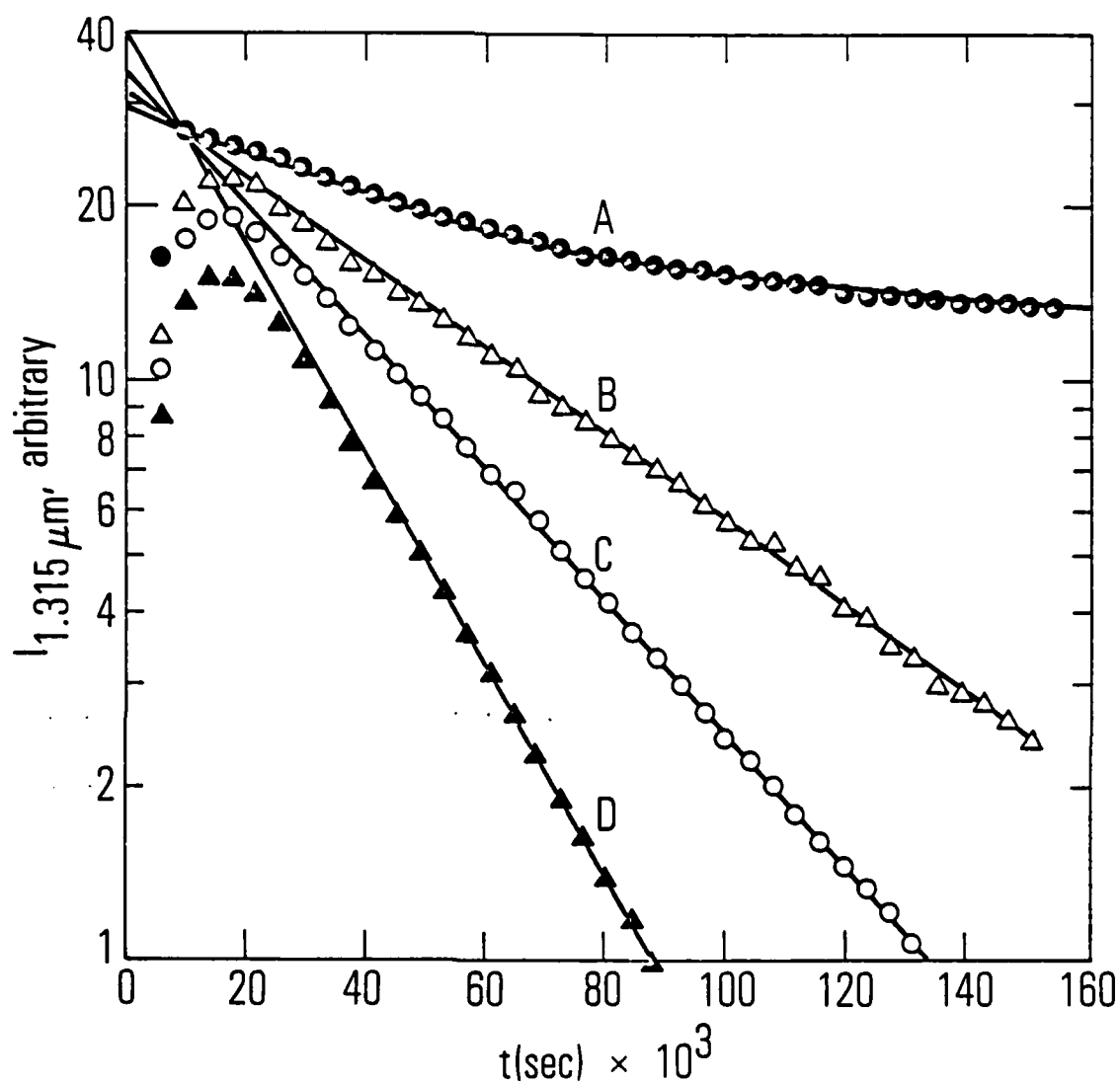


Fig. 4. I^* Decay Profiles as a Function of $[H_2O]$. (These profiles mimic $[O_2(^1\Delta)]$ decays.) Experimental conditions: $P = 3.15$ Torr, $[^1\Delta]_0 = 6.5 \times 10^{15}$, $[^3\Sigma]_0 = 7.4 \times 10^{16}$, $[I_2]_0 = 7.1 \times 10^{13}$ molecules/cm³. Curves A - D: $[H_2O] = 0, 1.0 \times 10^{15}, 2.1 \times 10^{15}$, and 4.1×10^{15} /cm³ ($[Ar] = \text{balance}$).

Table 2. Rate Coefficient Data for $O_2(^1\Delta)$ Behavior in the Presence of I^* and I

Process	M	Rate Coefficient ($cm^3/molecule\text{-}sec$)	References
k_{-1}		$(2.7 \pm 0.3) \times 10^{-11}$	18
(k_1)		$(7.8 \pm 0.8) \times 10^{-11}$	a
k_{3a}		2.7×10^{-14} (1.3×10^3)	6,16 ^b
		8×10^{-14} (4×10^3)	8 ^b
		1.1×10^{-13} (5.5×10^3)	19 ^{b,c}
		8.4×10^{-14} (4.2×10^3)	19 ^{b,c}
k_3		2.1×10^{-13}	This Work
k_{eff}^d		1.3×10^{-13}	6
		3×10^{-14}	8
		$< 1 \times 10^{-15}$	This Work
k_{13}		4.6×10^{-14}	6
		1×10^{-14}	8
		$< 3.5 \times 10^{-16}$	This Work
		$(0.9 \pm 4) \times 10^{-12}$	18
k_{14}		1.3×10^{-13}	6
		3×10^{-14}	8
		$< 1 \times 10^{-15}$	This Work
k_{15}	H_2O	$(2.5 \pm 0.5) \times 10^{-12}$	20
	.	$(2.1 \pm 0.3) \times 10^{-12}$	21
		1.7×10^{-12}	17
	$I(^2P_{3/2})$	$< 1.7 \times 10^{-13}$	This Work
		$< 1.6 \times 10^{-14}$	22

Table 2. Rate Coefficient Data for $O_2(^1\Delta)$ Behavior in the Presence of I^* and I (Continued)

Process	M	Rate Coefficient ($cm^3/molecule\text{-}sec$)	References
k_{16}		$< 30 \text{ sec}^{-1e}$	This Work
k_{17}		$< 30 \text{ sec}^{-1}$ 7.8 sec^{-1}	This Work 23

^aThe forward rate coefficient, k_1 , is determined by the reverse rate coefficient and the equilibrium constant, K_{EQ} .

^bThe values in parentheses are the measured ratios of k_{3a}/k_{3b} .

^cThe quoted values were obtained in Ref. 19 by alternate methods for calculating the I atoms in the system.

^dThe term k_{eff} is determined in the text as a combination of rate coefficients.

^eThe diffusion rate to the wall in this system is calculated to be 40 s^{-1} from the diffusion equation for a long cylinder and using a diffusion coefficient of $0.1 \text{ cm}^2/s$.

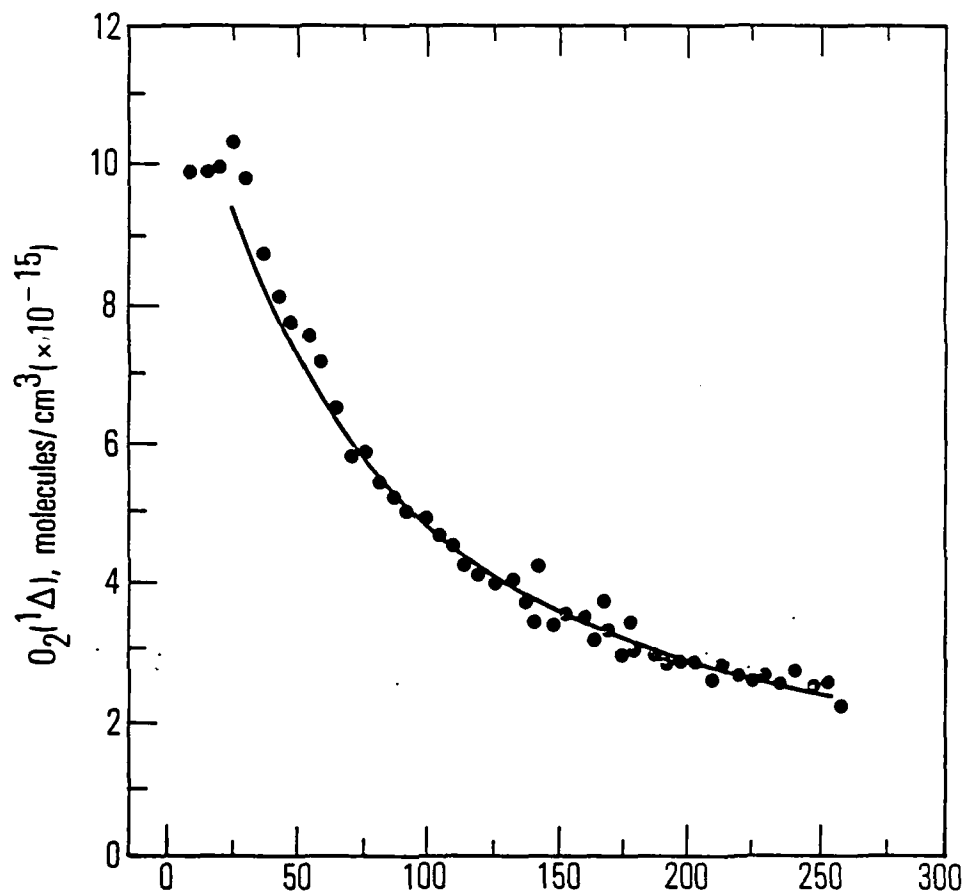


Fig. 5a. Decay of $O_2(^1\Delta)$ at High I^* Density. $[^1\Delta]_0 = 1.0 \times 10^{16}$ and $[I_2]_0 = 1.98 \times 10^{13}/\text{cm}^3$. Solid line is a fit to Eq. (12).

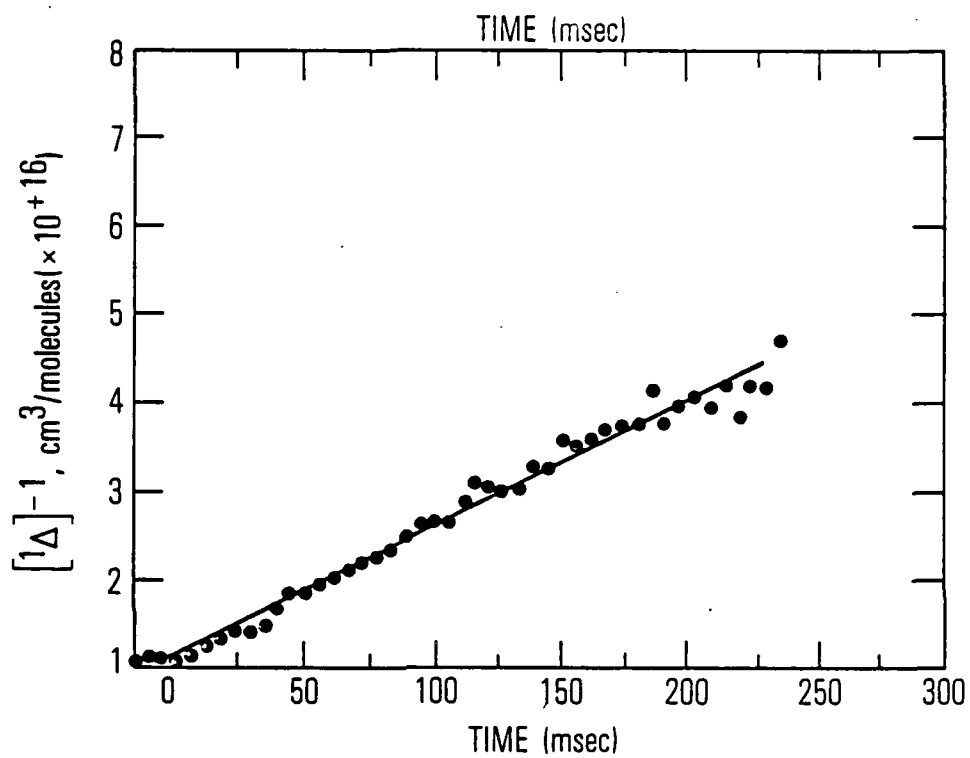


Fig. 5b. Data of Fig. 5a Plotted as a Pure Second-Order Decay Process.

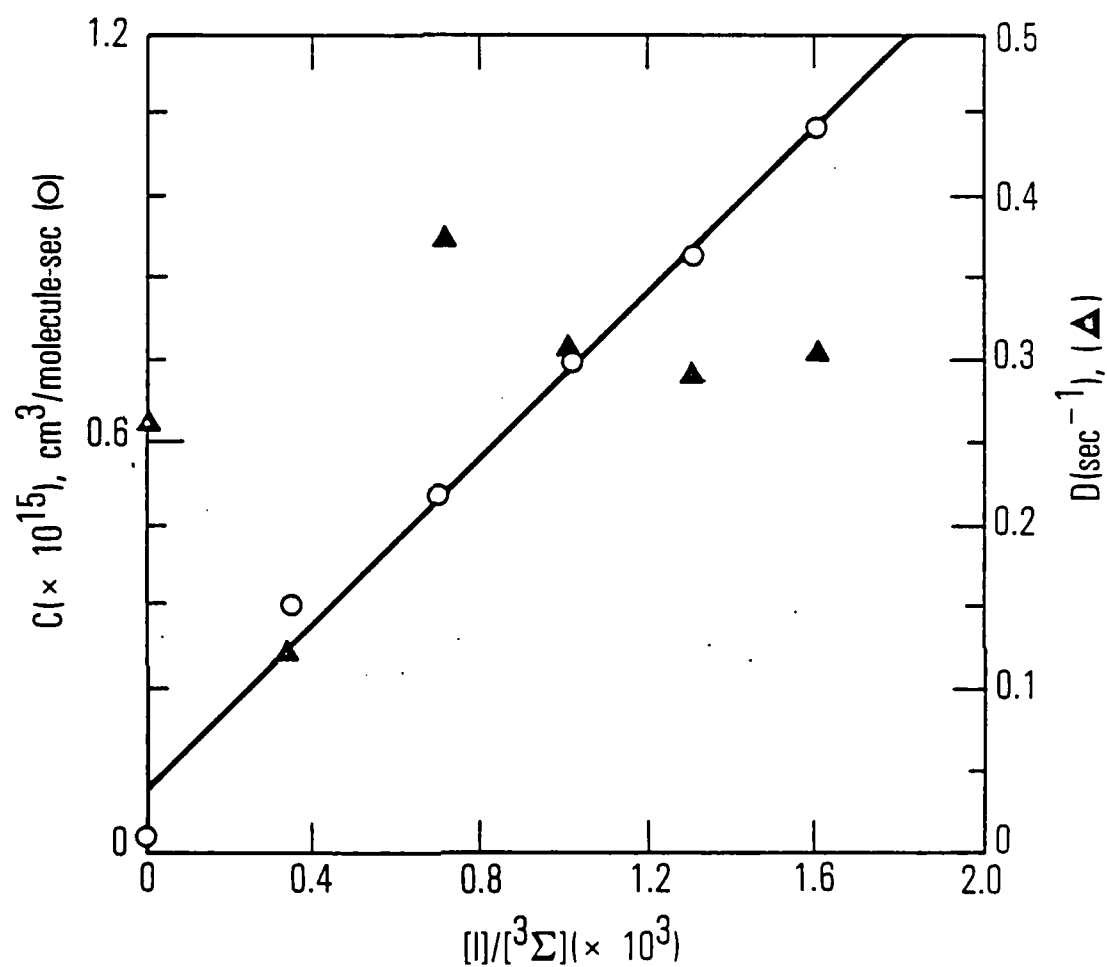


Fig. 6. Plot of the First-Order (D) and Second-Order (C) Decay Coefficients as a Function of $[I]/[{}^3\Sigma]$ [see Eq. (12)].

$$k_{14} + K_{EQ} \{k_{13} + (k_{15} M [M] + k_{16} + k_{17}) / [{}^3\Sigma]\} < 1 \times 10^{-15} \text{ cm}^3/\text{sec}$$

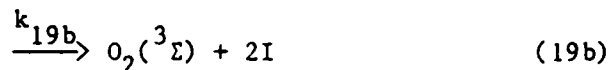
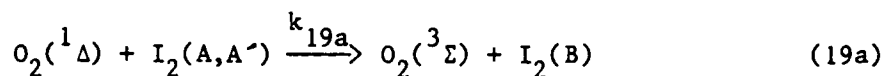
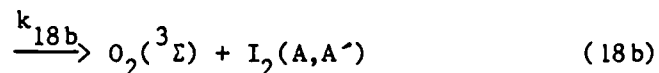
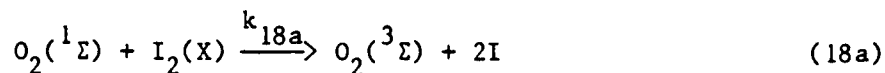
Using this inequality, we can derive the upper bounds for a number of first-order quenching processes that might be occurring in the COIL system. These rate coefficients are $k_{14} < 1 \times 10^{-15}$, $k_{13} < 3.3 \times 10^{-16}$ ($\ll k_{-1}$), and $k_{15}^I < 1.7 \times 10^{-13} \text{ cm}^3/\text{molecule-sec}$. The rates $k_{16} < 30 \text{ sec}^{-1}$ and $k_{17} < 30 \text{ sec}^{-1}$ are determined as well. These upper bounds are considerably lower than those proposed by Derwent and Thrush¹⁶ and are somewhat lower than those reported by Fisk and Hays.⁸ The limit imposed upon k_{17} is a factor of four larger than the accepted spontaneous emission rate from I^* ($A_{EIN} = 7.8 \text{ sec}^{-1}$).²³

These results are offered as an example of the difficulty in deconvolving first- and second-order decays in a regime where their magnitudes are comparable. Although our results seem quite different from those of Fisk and Hays,⁸ it should be realized that they represent a difference in rate increase of 0.13 sec^{-1} in one experiment and perhaps 2 sec^{-1} in the other. Neither experiment should be considered to be definitive in determining these small changes in such a complex system. Clearly, the second-order component of the decay plays a significant role based on independent evidence regarding the formation of $O_2({}^1\Sigma)$. On the basis of our own work, we believe that most of the I-atom catalyzed first-order decay processes for $O_2({}^1\Delta)$ can be ignored. The exceptions are the quenching processes for I^* . The results of this study are compared to previous work in Table 2.

C. DECAY OF $O_2({}^1\Delta)$ IN I , I^* , and I_2

The stored energy in O_2^* is known to be capable of dissociating I_2 . The efficiency of this dissociation process is thus a primary consideration for the design of a COIL device. Examination of the energy level diagram in Fig. 1 shows that two quanta of $O_2({}^1\Delta)$ energy are required in order to break the I_2 bond (35.1 kcal/mol).

One of the original suggestions made by Ogryzlo and coworkers²⁴ and endorsed by the extensive work of Derwent and Thrush^{25,26} was that I_2 was both excited and dissociated by $O_2({}^1\Sigma)$:

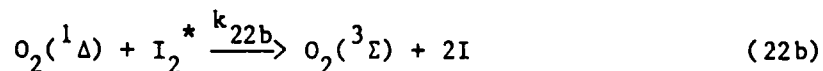
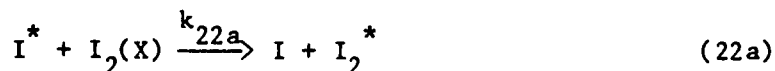
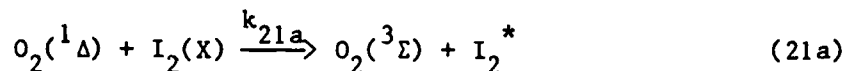


The $\text{O}_2(^1\Sigma)$ is formed by Processes (3a) and (4). Although the details of the kinetic model that describes this mechanism are complex, the efficiency of the process in terms of $\text{O}_2(^1\Delta)$ storage molecules consumed can be written down by inspection relative to an efficiency of 1.0 for the consumption of 2 $\text{O}_2(^1\Delta)$ molecules per I_2 dissociated:

$$E = \frac{k_{18a}[\text{I}_2]}{(k_{18}[\text{I}_2] + k_5^M[\text{M}] + k_6)} \quad (20)$$

If I_2 is the chief loss mechanism for $\text{O}_2(^1\Sigma)$, then the dissociation efficiency is given by $E = k_{18a}/k_{18}$, which has been measured to be < 0.2 .²⁷ If there are other loss mechanisms for $\text{O}_2(^1\Sigma)$, the efficiency is lower still.

Although this mechanism may be operative in the COIL system, recent experiments^{17,27} have shown that k_{18a} is too slow to account for the phenomenological dissociation rates of I_2 in O_2^* . A sequential excitation model⁴ for I_2 dissociation can be proposed that is kinetically identical:



Either or both of the above sequences are kinetically acceptable, however, we prefer sequence (22) as it invokes collisions of the intermediate I_2^* with a majority flow species [$O_2(^1\Delta)$] rather than a minority one (I^*). Either high vibrational levels of $I_2(X)$ or the electronically metastable $I_2(A, A')$ states have been examined as candidates for the intermediate state in Processes (21) and (22). At present, there is qualitative support for all of the suggested intermediate states. Further quantitative work must be done. Assuming that Process (22) is responsible for the bulk of the I_2 dissociation, the efficiency of $O_2(^1\Delta)$ utilization is given by

$$E_{SQ} = \left\{ \frac{k_{22b}[^1\Delta]}{R_{I_2^*}} \right\} \left\{ \frac{k_{22a}[I_2]}{R_{I^*}} \right\} \quad (23)$$

where $R_{I_2^*}$ is the total rate of intermediate removal (sec^{-1}) and R_{I^*} is the total rate of I^* removal. Thus, the overall dissociation efficiency is the product of the I^* utilization efficiency in (22a) and the efficiency by which the I_2^* intermediate is used in (22b). It is interesting to note that COIL devices work well at $[O_2(^1\Delta)]/[I_2]$ ratios of approximately 100 and that k_{22a}/k_3 is approximately 300. We believe that $k_{22b}[^1\Delta]/R_{I_2^*}$ must be close to unity,⁴ although that may be an untenable assumption for a vibrationally excited $I_2(X)$ intermediate.

Removal of $O_2(^1\Delta)$ during the I_2 dissociation process is quite difficult to quantify experimentally. A seemingly trivial problem in flow tube methodology has rather serious consequences. It is difficult to mix small amounts of I_2 (MW 254) into a stream of O_2 (MW 32) in an efficient manner. A carrier gas (typically Ar) is saturated with I_2 (0.1 to 10% I_2 in Ar) and injected into the O_2 flow. We want to attain fast mixing and fast I_2 dissociation in order to decouple this $O_2(^1\Delta)$ loss from that caused by I and I^* (Section IIIB). In order to get fast mixing (i.e., on the timescale of the I_2 dissociation), one has to inject an Ar + I_2 mixture that represents roughly 5% of the O_2 molar flow rate. As shown schematically in Fig. 7, this Ar then

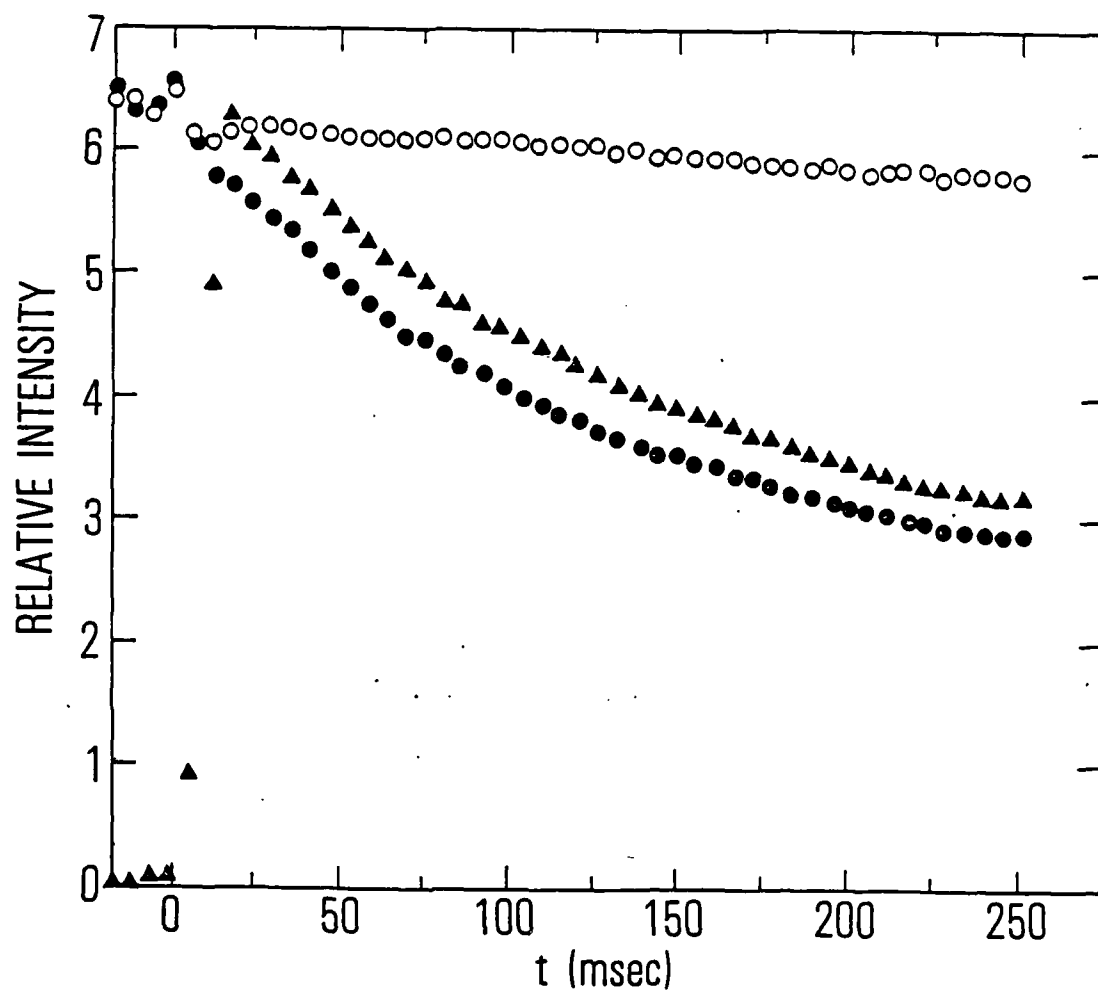


Fig. 7. Removal of $O_2(^1\Delta)$ During I_2 Dissociation. ($\circ$): dilution of $O_2(^1\Delta)$ by injected Ar. ($\bullet$) removal of $O_2(^1\Delta)$ by injected Ar + I_2 . (Δ): production of I^* during I_2 dissociation. Conditions: $[O_2(^1\Delta)]:[O_2(^3\Sigma)] = 5.2 \times 10^{15}: 7.7 \times 10^{16}$ molecules/cm³, $[I_2]_0 = 5.7 \times 10^{13}$ molecules/cm³ ($\bullet$, Δ).

dilutes the O_2^* by 5% at the mixing point. In our system, it is impossible to measure an $O_2(^1\Delta)$ decrease because of I_2 dissociation of $< 2\%$ in the presence of that dilution process. Table 3 is a matrix of percentage $[O_2(^1\Delta)]$ decrease as a function of initial $[^1\Delta]/[I_2]$ ratio and mean dissociation efficiency. The entries resulting in greater than 20% loss of $O_2(^1\Delta)$ are omitted. The weak area of this method involves measuring efficiencies for large $[^1\Delta]/[I_2]$ ratios. For ratios of 10^4 , we are tempted to assign a 2% $O_2(^1\Delta)$ decrease to an efficiency of 0.01, however, that efficiency is properly expressed as $[0.01 + 1.0 (-0.005)]$.

Our own data are convincing for $[^1\Delta]_0/[I_2]_0$ ratios of 100. It is shown that the dissociation efficiency is extremely high. We estimate that it is (0.75 ± 0.25) or that (3 ± 1) $O_2(^1\Delta)$ molecules are required to dissociate an I_2 . Our results depend critically on the fact that the Halocarbon wax surface of the flow tube inhibits I atom recombination (and perhaps even I^* relaxation). Thus, I_2 is not reformed on the walls by I atom recombination and redissociated by additional $O_2(^1\Delta)$. Results on $O_2(^1\Delta)$ loss in the I_2 dissociation regime clearly depend on wall and diffusional parameters of a particular experimental apparatus.

D. EXTENSION TO PHOTOINITIATED O_2^* - HI MIXTURES

The decay of $O_2(^1\Delta)$ in time-resolved kinetics experiments can be monitored by photodissociation of an I-atom precursor in the apparatus shown in Fig. 3. Although $O_2(^1\Delta)$ is difficult to monitor directly in such experiments, one can monitor $[I^*]$, which is proportional to it under the proper conditions [Eq. (11)]. The precursor chosen (HI) has an extremely small quenching coefficient for $O_2(^1\Delta)$. The results of these experiments are detailed in Ref. 5. In the present context, the effect is shown by increasing the density of the precursor (Fig. 8) in order to increase the initial I atom concentration produced by the laser. At low precursor densities, it has been shown that the coupled $I^* - O_2(^1\Delta)$ removal is dominated by a combination of axial diffusion, radial diffusion, and cell pumpout. As the initial $[I] + [I^*]$ density increases, the removal does accelerate. Also, the acceleration is entirely consistent with Process (3). Thus, independent confirmation is available that the first-order I-atom-related loss processes for $O_2(^1\Delta)$ are extremely small.

Table 3. Fractional Depletion of $O_2(^1\Delta)$ in the I_2 Dissociation Process: Mean Dissociation Efficiency, E , vs. $[^1\Delta]_0/[I_2]_0$

Mean Dissociation Efficiency (E)	Fractional Depletion for the Following Values of $[O_2(^1\Delta)]_0/[I_2]_0$			
	10	10^2	10^3	10^4
1	0.2	0.02	2×10^{-3}	2×10^{-4}
0.1	-	0.2	0.02	2×10^{-3}
0.01	-	-	0.2	0.02
0.001	-	-	-	0.2

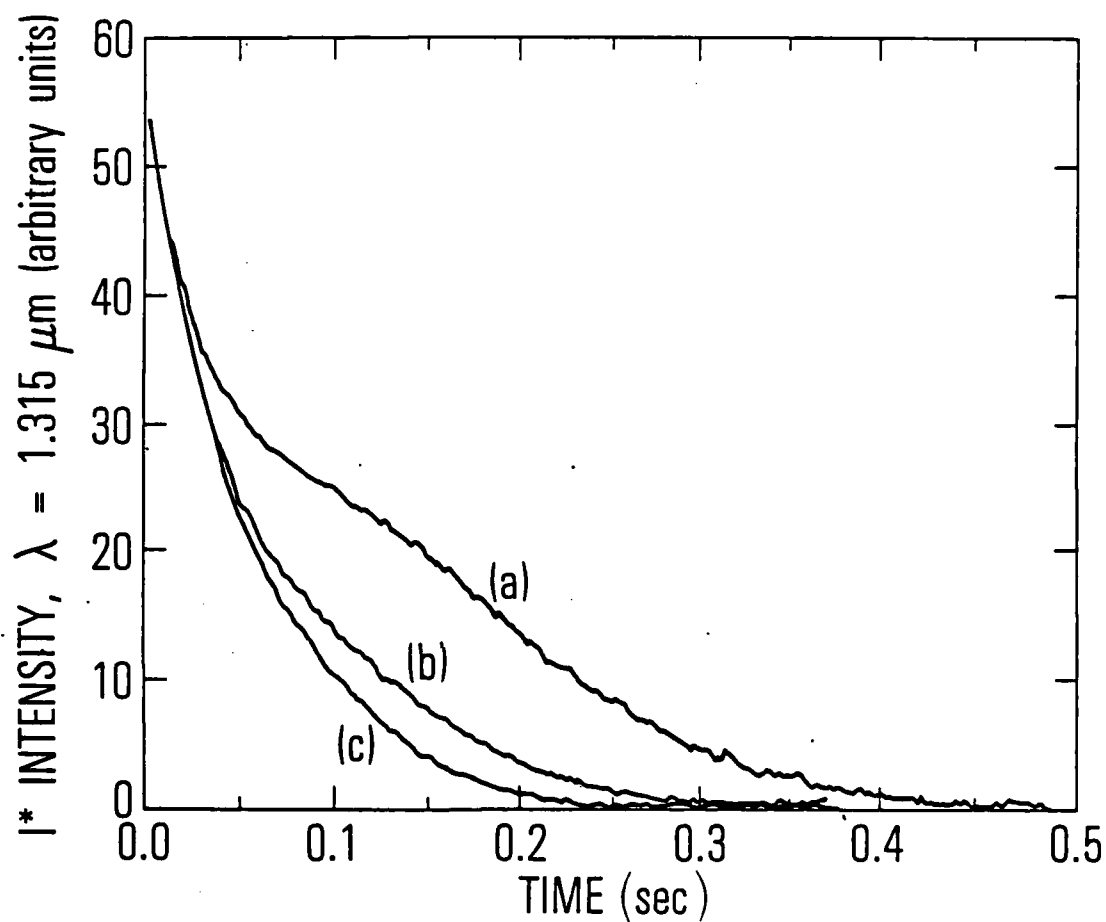


Fig. 8. Normalized I^* Decay Curves in O_2^* vs. $[\text{HI}]_0$. $[\Sigma] = 9.0 \times 10^{16}$, and $[^1\Delta] = 7.9 \times 10^{15}/\text{cm}^3$. Percentage photolysis of HI = 2.2%. Curves A-C: $[\text{HI}]_0 = 6.4 \times 10^{14}$, 2.5×10^{15} , and $4.4 \times 10^{15}/\text{cm}^3$.

IV. CONCLUSION

The kinetic processes that remove $O_2(^1\Delta)$ in a COIL system have been reviewed in this report. In the absence of I_2 , I^* , and I , the $O_2(^1\Delta)$ decays very slowly by energy pooling [second order Process (4)], gas phase quenching by H_2O and $O_2(^3\Sigma)$, and by wall quenching.

The removal of $O_2(^1\Delta)$ in the presence of I^* and I is described by introducing the energy pooling $O_1(^1\Delta)$ with I^* [second order Process (3)], and several first-order quenching processes for $O_2(^1\Delta)$ and I^* . In particular, we have considered the quenching of I^* by H_2O , $O_2(^3\Sigma)$, I atoms, and the walls. These processes have an increasingly important effect on draining the $O_2(^1\Delta)$ storage reservoir as the $I^*/O_2(^1\Delta)$ ratio increases.

The presence of I_2 causes $O_2(^1\Delta)$ removal by more complex processes. The $O_2(^1\Delta)$ energy can be used by several mechanisms to break the I_2 bond and to create free I atoms. The electronic equilibrium [Process (1)] occurs rapidly, so that the I^* density is determined by the $[^1\Delta]/[^3\Sigma]$ ratio and the total I atom density. The mechanism for I_2 dissociation by O_2^* is not completely defined, however, it is certainly represented by a class of processes that can be described as chain reactions with chain branching. These include Process (3a) followed by (18a), Process (21), and Process (22). All these mechanisms consume > 2 $O_2(^1\Delta)$ molecules per I_2 dissociated.

The use of $O_2(^1\Delta)$ to create the I atom laser medium can be avoided if an external power source is used to create free I atoms. A brief description has been given of the excimer laser photolysis of HI to perform that function and to create the possibility of a repetitively pulsed version of the COIL system.

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