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THE STANDARD CHEMICAL OXYGEN-IODINE LASER KINETICS PACKAGE

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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
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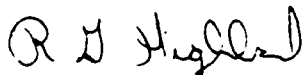
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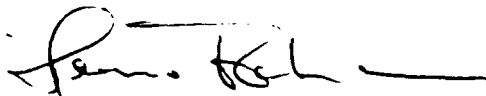
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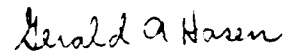


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27 April 1989

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PACKAGE

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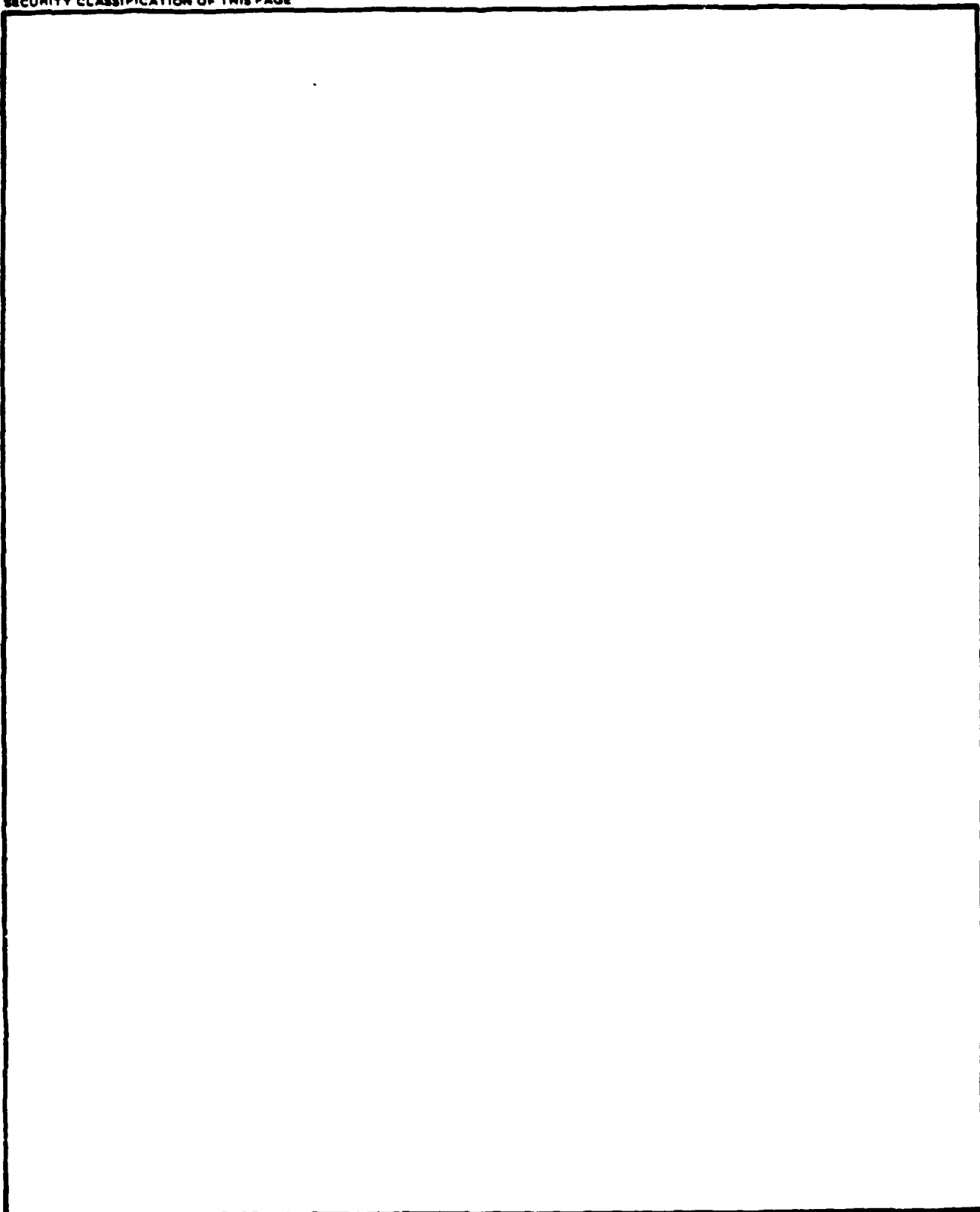
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PREFACE

This technical report presents the edited proceedings from the Air Force Weapons Laboratory Conference on Chemical Oxygen-Iodine Laser Kinetics held on 11 August 1987 at R&D Associates, 2301 Yale Blvd SE, Albuquerque, New Mexico. An expert panel was convened to review the data base and to recommend a standard package for the gas phase kinetics pertaining to chemical oxygen-iodine lasers. The members of this panel were:

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A complete documentation of this conference entitled "Proceedings of the 1987 Air Force Weapons Laboratory Conference on Chemical Oxygen-Iodine Laser Kinetics" was prepared by R&D Associates, the Aerospace Corporation, and the Air Force Weapons Laboratory and may be obtained from:

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1.0 INTRODUCTION

The Chemical Oxygen-Iodine Laser (COIL) is the shortest wavelength high energy chemical laser in existence today and has great potential for Air Force directed energy weapons applications. The Air Force Weapons Laboratory (AFWL), Kirtland Air Force Base, New Mexico, is vigorously pursuing the development of efficient, scalable COIL devices with high output power and excellent beam quality. While chemical oxygen-iodine lasers are in the early stages of large scale development, a 25 kW device is being built at AFWL and scaling to larger devices is currently under active investigation.

It has been long recognized that continuous-wave (CW) chemical lasers represent an extremely complex interaction between fluid mechanics, chemical kinetics, and optical physics. It is truly impossible to focus on one area without acknowledging its interdependence with the others. The chemical oxygen-iodine laser presents additional problems in that the energy storage medium, singlet oxygen, is generated by a liquid-gas phase reaction. The kinetics of chemical oxygen-iodine lasers can be divided into five categories: (1) the chemistry of singlet oxygen generators, (2) the chemistry of COIL in the presence of water aerosols, (3) transport of singlet oxygen in the absence of iodine, (4) the dissociation of molecular iodine by excited oxygen, and (5) the kinetics of iodine atoms and excited oxygen. Only the last three kinetics topics are covered in this review.

A large variety of research and engineering groups are involved in the development of COIL technology. A standardization of the chemical kinetics for COIL device modeling and data interpretation, gas phase kinetics studies, and power scaling studies is required to allow for optimal information exchange. A conference on chemical oxygen-iodine laser kinetics was held by R & D Associates for AFWL on 11 August 1987 and this report summarizes the proceedings of this meeting. Specifically, the AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is developed and reported.

Several reviews of the gas phase kinetics of COIL devices are available in the literature (Refs. 1--4). The previous AFWL standard COIL rate package was compiled by R.F. Shea (Ref. 5) in an informal document (16 November 1982) with addenda relating to optical broadening coefficients for iodine atoms

(15 November 1982) and iodine dissociation kinetics (12 November 1982). The current AFWL rate package is a revision of that document based on research in the intervening five years and on the deliberations of the current panel.

The purpose of the AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is to provide a baseline modeling condition to compare the predictions, analyses, and results of diverse research groups. It is not intended to stifle more novel and comprehensive modeling efforts. Indeed, the Air Force encourages continued consideration of the many, complex issues associated with modeling the performance of COIL devices. However, AFWL does request that such research efforts always be compared to the baseline model presented in this document.

An important philosophical aspect of this standard rate package is simplicity. The package was designed to include the important kinetic processes involved with small scale flow tube experiments as well as high power oxygen-iodine lasers, while at the same time being simple enough to allow for economic application and direct interpretation. The model includes only information that is directly supported by experimental evidence. This package addresses only the gas phase kinetics of COIL and specifically excludes any discussion of the fully coupled chemical kinetics, fluid mechanics and optical physics problems.

2.0 OVERVIEW OF THE CHEMICAL OXYGEN-IODINE LASER

The chemical oxygen-iodine laser, which operates on the hyperfine components of the $5^2P_{1/2} \rightarrow 5^2P_{3/2}$ transition in atomic iodine, is chemically pumped through energy transfer from the metastable energy carrier, $O_2(^1\Delta)$. The energy levels for molecular iodine and oxygen and atomic iodine are shown in Fig. 1. The singlet oxygen is produced by a two phase reaction of chlorine gas and liquid basic hydrogen peroxide (Ref. 6). Molecular iodine is injected into the primary oxygen flow and is dissociated to atomic iodine by way of a complicated, multistep reaction mechanism (Ref. 7). Once iodine atoms are produced, an equilibrium between excited iodine atoms and singlet oxygen is rapidly attained through the nearly resonant energy transfer reactions given by $I(^2P_{3/2}) + O_2(^1\Delta) \rightleftharpoons I(^2P_{1/2}) + O_2(^3\Sigma)$. A condition for zero gain at $T = 295$ K is achieved when the ratio of $O_2(^1\Delta)$ to total oxygen is approximately 0.17 (Ref. 8). Continuous-wave lasing action is achieved on a single hyperfine transition of the inhomogeneously broadened iodine atom at $1.315 \mu\text{m}$.

Subsonic and supersonic COIL devices have been demonstrated based on this reaction scheme. The performance of these lasers indicates great potential for scaling to higher powers. The description of the gas phase kinetics of these devices is incomplete, however.

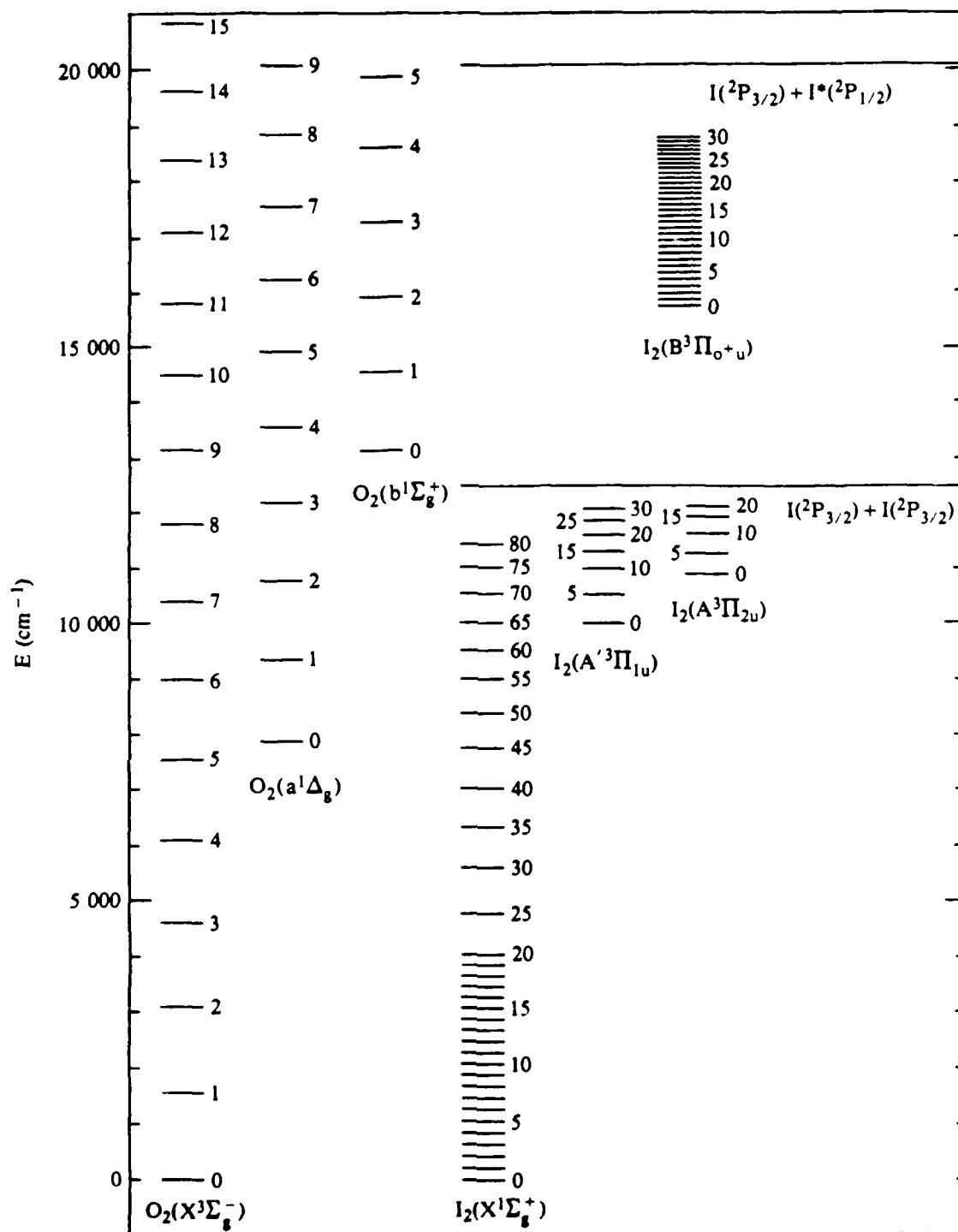


Figure 1. Energy level diagram for the oxygen-iodine system. Electronic and vibrational states for I_2 , O_2 , and I are shown on the same scale. This figure is reproduced from Ref. 20.

3.0 REVIEW OF THE KINETIC DATABASE

An overview of the chemistry involved with supersonic COIL devices is shown in Fig. 2. The generation of singlet oxygen is a separate topic and will be reviewed in a subsequent report. The following paragraphs will review the current understanding of: (1) the transport of oxygen to the iodine nozzle assembly, (2) the dissociation of molecular iodine by excited oxygen, and (3) the free iodine atom laser cavity kinetics. The chemistry and physics of water aerosols is an important aspect of COIL device modeling, but will not be discussed in this report.

3.1 SINGLET OXYGEN TRANSPORT

The gas phase kinetics of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ are quite well understood. These states are well isolated from the other electronic states of oxygen which have energies greater than 3 eV. The radiative lifetime of $O_2(^1\Delta)$ is 45 min (Ref. 9) and the energy pooling of $O_2(^1\Delta)$ to produce $O_2(^1\Sigma)$ is slow (Ref. 10) which allows for the transport of singlet oxygen to the iodine nozzle with low loss. Table 1 gives the recommended rate coefficients for the deactivation of singlet oxygen in the absence of iodine. The Tables 1--4 present the kinetic data base and give a single best value for each rate coefficient from the literature, rather than a weighted mean. All rate coefficients cited in this report are labeled according to the process number scheme listed in Tables 1--4. A confidence level of high (H), medium (M) or low (L) is suggested. In addition, an indication of the importance of the reaction to the complete mechanism is assigned for each process.

The crucial issues in the transport of singlet oxygen are the energy pooling rate, k_1 , and the total second order $O_2(^1\Delta)$ removal rate, $k_1 + k_2 + k_3$. Three absolute measurements of k_1 (Refs. 10, 11 & 12) and three measurements of the temperature dependence for $k_1(T)$ (Refs. 10 & 13) have been reported. The rate coefficient measured by H. V. Lilenfeld (Ref. 10) is preferred because the $O_2(^1\Delta)$ concentration is measured by an EPR technique. The agreement among all measurements is good.

Evaluating the second-order loss of $O_2(^1\Delta)$ is somewhat more difficult, but extremely important. The rate for total second order removal of $O_2(^1\Delta)$ is

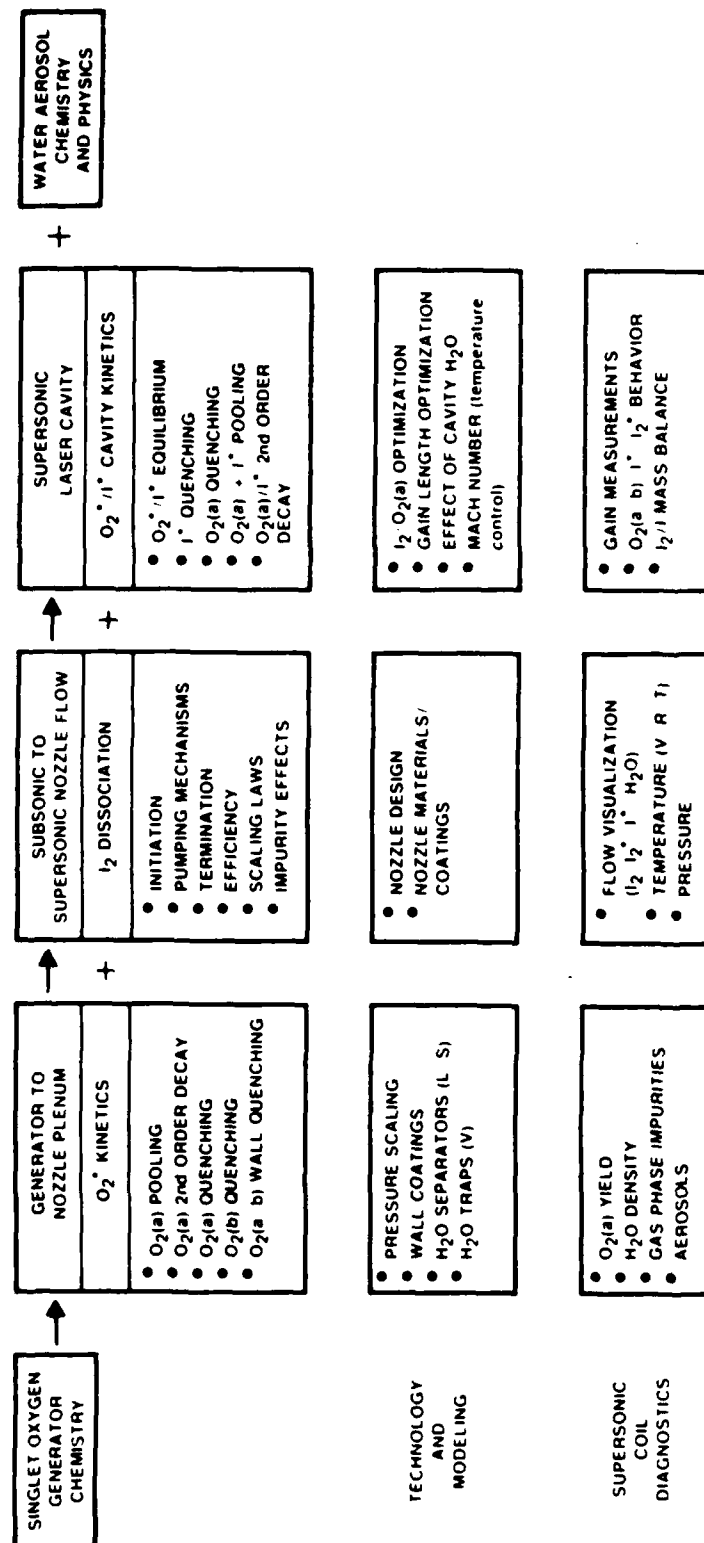


Figure 2. Overview of COIL chemistry modeling showing five distinct kinetics topics.

TABLE 1. O_2^* Kinetics: Generator to nozzle plenum.

Kinetic Process	Recommended Rate Coefficient ($cm^3/molecule-s$)	Confidence Level	Importance to Model	Reference
1. $O_2^{10} + O_2^{10} \rightarrow O_2^{15} + O_2^{35}$	$(2.7 \pm 0.5) \times 10^{-17}$	H	H	10
2. $O_2^{10} + O_2^{10} \rightarrow O_2^{10} + O_2^{35}$	0	L	H	10
3. $O_2^{10} + O_2^{10} \rightarrow O_2^{35} + O_2^{35}$	$(1.7 \pm 1 - .5) \times 10^{-17}$	L	H	10
4. $O_2^{15} + O_2^{35} \rightarrow O_2^{10} + O_2^{35}$	$(3.9 \pm 0.2) \times 10^{-17}$	H	L	16
5. $O_2^{15} + H_2O \rightarrow O_2^{10} + H_2O$	$(6.7 \pm 0.5) \times 10^{-12}$	H	H	17
6. $O_2^{15} + Cl_2 \rightarrow O_2^{10} + Cl_2$	$< 2 \times 10^{-15}$	H	L	18
7. $O_2^{15} + H_2O_2 \rightarrow O_2^{10} + H_2O_2$	3.3×10^{-13}	L	H	19
8. $O_2^{15} + He \rightarrow O_2^{10} + He$	1×10^{-17}	L	L	20
9. --	--	-	-	--
10. Reserved for model expansion	--	-	-	--
11. $O_2^{15} (+ wall) \rightarrow O_2^{10} (+ wall)$	$(\gamma = 10^{-2})$ Glass $(\gamma = 10^{-3})$ Halocar.	H	L	Numerous
12. --	--	-	-	--
13. Reserved for model expansion	--	-	-	--
14. $O_2^{10} + O_2^{35} \rightarrow O_2^{35} + O_2^{35}$	$(1.6 \pm 0.05) \times 10^{-10}$	H	H	21
15. $O_2^{10} + H_2O \rightarrow O_2^{35} + H_2O$	$(4 \pm 1) \times 10^{-10}$	H	H	20
16. $O_2^{10} + Cl_2 \rightarrow O_2^{35} + Cl_2$	$(6 \pm 3) \times 10^{-10}$	H	H	22
17. $O_2^{10} + H_2O_2 \rightarrow O_2^{35} + H_2O_2$	--	L	L	--
18. $O_2^{10} + He \rightarrow O_2^{35} + He$	$(8.0 \pm 2.6) \times 10^{-21}$	H	L	23
19. Reserved for model expansion	--	-	-	--
20. $O_2^{10} (+ wall) \rightarrow O_2^{35} (+ wall)$	$(\gamma = (2 \pm 1) \times 10^{-5})$ Glass	H	H	Numerous

TABLE 2. I_2 dissociation by O_2^*

Kinetic Process	Recommended Rate Coefficient ($cm^3/molecule-s$)	Confidence Level	Importance to Model	Reference
21. $I_2X + O_2I_5 \rightarrow I + I + O_2S$	$< 4 \times 10^{-12}$	H	H	24
22. $I_2X + O_2I_5 \rightarrow I_2X + O_2I_0$				
23. $I_2X + O_2I_5 \rightarrow I_2X + O_2S$	1.6×10^{-11} (a)	L	H	17
24. $I_2X + O_2I_5 \rightarrow I_2AIA_2 + O_2S$				
25. $I_2AIA_2 + O_2I_0 \rightarrow I + I + O_2S$	$> 1 \times 10^{-11}$	H	H	25
26. $I_2AIA_2 + O_2I_0 \rightarrow I_2B + O_2S$	--	-	-	--
27. $I_2A_1 \rightarrow I_2X + h\nu$	3.8×10^3 (s^{-1})	H	H	25
28. $I_2A_1 + M \rightarrow I + I + M$	--	L	H	--
29. $I_2A_2 + M \rightarrow I + I + M$	2.4×10^{-12} (SF_6) 5.5×10^{-11} (I_2) 2.8×10^{-14} (AF) 3.5×10^{-14} (N_2) 0.94×10^{-14} (H_2)	L	H	--
30. $I_2B \rightarrow I + I$	$(10^6 s^{-1})$	H	L	26
31. $I_2B \rightarrow I_2X + h\nu$	$(5 \times 10^3 s^{-1})$	H	L	26
32. $I_2X + O_2I_0 \rightarrow I_2^* + O_2S$	7×10^{-15}	L	H	27
33. $I_2X + I^* \rightarrow I_2^* + I$	$(3.8 \pm 0.3) \times 10^{-11}$ (b)	H	H	28
34. $I_2^* + O_2I_0 \rightarrow I + I + O_2S$	3×10^{-10}	L,M	H	27
35. $I_2^* + O_2S \rightarrow I_2X + O_2S$	5×10^{-11}	L,M	H	27
36. $I_2^* + H_2O \rightarrow I_2X + H_2O$	3×10^{-10}	L,M	H	27

(a) This rate coefficient is for all product channels other than (21), i.e. (22)-(24)

(b) The measured rate coefficient is for I^* disappearance. The rate of I_2^* production is assumed.

TABLE 3. Cavity kinetics (fully dissociated I₂).

Kinetic Process	Recommended Rate Coefficient (cm ³ /molecule-s)	Confidence Level	Importance to Model	Reference
37. I ² + He → I ² X + He	4 × 10 ⁻¹²	L	M	Assume same as Ar
38. I ² + Ar → I ² X + Ar	4 × 10 ⁻¹²	L,M	M	27
39. I ² (+ wall) → I ² X (+ wall)	(3 × 10 ³ s ⁻¹)	L,M	L,M	10
40. I + O ₂ I ₂ → I ² + O ₂ S	(7.8 ± 0.8) × 10 ⁻¹¹	H	H	10
41. I ² + O ₂ S → I + O ₂ I ₂	(2.7 ± 0.3) × 10 ⁻¹¹	H	H	29
42. I + O ₂ I ₂ → I + O ₂ S	< 1 × 10 ⁻¹⁵	M	L	8
43. I ² + O ₂ S → I + O ₂ S	< 3.5 × 10 ⁻¹⁶	M	L,M	8
44. I ² + O ₂ I ₂ → I + O ₂ I ₂	1.0 × 10 ⁻¹³	H	M	10, 13
45. I ² + O ₂ I ₂ → I + O ₂ I ₂	1.1 × 10 ⁻¹³	M	M	8
46. I ² + O ₂ I ₂ → I + O ₂ S	0	M	M	8
47. I ² + I → I + I	< 1.7 × 10 ⁻¹³	M	L	8
48. I ² + H ₂ O → I + H ₂ O	(2.1 ± 0.3) × 10 ⁻¹²	M	H	30
49. I ² + H ₂ O ₂ → I + H ₂ O ₂	(2.5 ± 1.5) × 10 ⁻¹¹	L	M,H	31, 32
50. I ² + He → I + He	< 5 × 10 ⁻¹⁶	L	L	33
51. Reserved for model expansion	--	-	-	--
52. I ² + wall → I + wall	γ < 10 ⁻³ (Halocarbon)	L	L	8
53. I ² → I + hv	7.8 sec ⁻¹	M	L	34

TABLE 4. Supplementary kinetics processes.

Kinetic Process	Recommended Rate Coefficient (cm ³ /molecule-s)	Confidence Level	Importance to Model	Reference
A. Chlorine Catalytic Cycle				
54. I ^o + Cl ₂	ICl + Cl	(5.5 ± 0.8) × 10 ⁻¹⁵	M	L
55. I ^o + Cl ₂	I + Cl ₂	< 8 × 10 ⁻¹⁵	M	L
56. I ^o + ICl	I ₂ X + Cl	1.5 × 10 ⁻¹¹	M	L
57. I ₂ X + Cl	ICl + I	2 × 10 ⁻¹⁰	L	L
58. ICl + Cl	Cl ₂ + I	(8 ± 1) × 10 ⁻¹²	M	L
B. I Atom Recombination				
59. I + I + I ₂ X	I ₂ X + I ₂ X	3.6 × 10 ⁻³⁰ (cm ⁶ /s ²)	M	L, M
60. I ^o + I + I ₂ X	I ₂ B + I ₂ X	<< 3.6 × 10 ⁻³⁰ (cm ⁶ /s ²)	L	L
61. I ^o (I) + Wall	1/2 I ₂ X	(γ = 2.5 × 10 ⁻⁴). (halocarbon) γ < 1 (metals)	M L	L M
				8, 11

$6 \pm 2 \times 10^{-17} \text{ cm}^3/\text{molecule-s}$ (Ref. 10). On comparison of this result with the measured value for k_1 , two interpretations of this rate can be made (Ref. 14); $\text{O}_2(^1\Delta)$ could pool to $\text{O}_2(^1\Sigma)$ followed by $\text{O}_2(^1\Sigma)$ quenching to ground state oxygen, $\text{O}_2(^3\Sigma)$. Such an interpretation requires $k_2 + k_3 = 0$. A more widely accepted view is that $\text{O}_2(^1\Sigma)$ is quenched to $\text{O}_2(^1\Delta)$ which requires $k_2 + 2k_3 = 3 \times 10^{-17} \text{ cm}^3/\text{molecule-s}$. No further deconvolution is possible. Note that one must be very careful not to mix these interpretations. Recently, M. B. Knickelbein and coworkers (Ref. 16) have confirmed the long standing supposition that $\text{O}_2(^1\Sigma)$ is quenched to $\text{O}_2(^1\Delta)$. This result is included in Table 1. Since k_3 is spin-allowed and k_2 is not, the assumption is made that k_3 and k_1 contribute all of the observed second order removal.

Numerous $\text{O}_2(^1\Delta)$ quenching studies have been conducted (Refs. 20--22, 37, 38, 39). The only relevant gas phase rate coefficient for $\text{O}_2(^1\Delta)$ that remains unmeasured is for quenching by H_2O_2 . The rate coefficient for this process would have to be very large to compete with the other, more abundant quenchers. It is more likely that species such as H_2O_2 and Cl_2 influence the walls and increase the heterogeneous quenching rates. Indeed, better heterogeneous quenching data for surfaces contaminated with basic hydrogen peroxide, HCl or other species is required. Some data on the wall deactivation of singlet oxygen has been reported (Ref. 40).

For the gas phase quenching of $\text{O}_2(^1\Sigma)$, all the relevant rate coefficients have been reliably measured (Refs. 15, 17, 20, 41) except for chlorine and hydrogen peroxide which have been qualitatively measured or estimated. Wall losses may or may not be important depending on the density of the quenchers and flow geometry. The $\text{O}_2(^1\Sigma)$ is in steady state, as given by the pooling reaction and quenching reactions.

The analytic solution for the total decay of $\text{O}_2(^1\Delta)$, assuming that $\text{O}_2(^1\Sigma)$ is in steady state, may be written:

$$[\text{O}_2(^1\Delta)]^{-1} = \{ ([\text{O}_2(^1\Delta)]_{t=0})^{-1} + A/B \} \exp(Bt) - A/B \quad (1)$$

where

$$A = k_1 + k_2 + 2 k_3$$

$$B = k_{20} + k_{14}[O_2(^3\Sigma)] + k_{15}[H_2O] + k_{16}[Cl_2] + k_{17}[H_2O_2] + k_{18}[He]$$

The traditional "chi-curve" analysis (Ref. 42) for the transport of singlet oxygen in COIL devices is based on this solution.

There is a general lack of temperature dependent quenching data for singlet oxygen. Given that all measured activation energies are small and that temperature rise in noncatalytic ducts should be small, the lack of $k(T)$ data is not a primary problem in this region.

3.2 IODINE DISSOCIATION

Despite the work done on the I_2 dissociation mechanism since the original papers of R. G. Derwent and B. A. Thrush (Refs. 12, 43, 44), much of the knowledge is empirical and descriptive at best. Originally, the dissociation mechanism was postulated to occur primarily through $O_2(^1\Sigma) + I_2$ (Ref. 12). However, the dissociation in COIL devices, where significant water concentrations severely reduce the steady-state singlet sigma oxygen concentrations, is too fast and efficient to be attributed solely to this mechanism (Refs. 17, 24). Multistep dissociation mechanisms involving $O_2(^1\Delta)$ were then investigated. S. J. Arnold originally postulated a sequence of two or more $O_2(^1\Delta)$ and $I_2(X)$ collisions as a source of atomic iodine (Ref. 45). Such a mechanism requires an intermediate I_2 state to store the energy between $O_2(^1\Delta)$ collisions. An energy level diagram for oxygen and iodine is shown in Fig. 1.

The spectroscopic studies by J. Tellinghuisen (Ref. 46) demonstrated that $I_2(A')$ is not energetically accessible from one $O_2(^1\Delta)$ collision. However, vibrationally excited ground state iodine, I_2^* , is produced in collisions with excited oxygen and excited iodine atoms (Refs. 7, 25, 47). The kinetics of I_2^* have been studied in flow tube reactors (Refs. 25, 27) and a model formulated for the dissociation of I_2 based on this vibrational intermediate (Ref. 27). A sample of the typical flow tube data is shown in Fig. 3.

All studies have shown that the rate of iodine dissociation accelerates as the dissociation proceeds. Evidence is strong that the first step in the sequential excitation and dissociation of I_2 is given by $I^* + I_2 \longrightarrow I + I_2^*$.

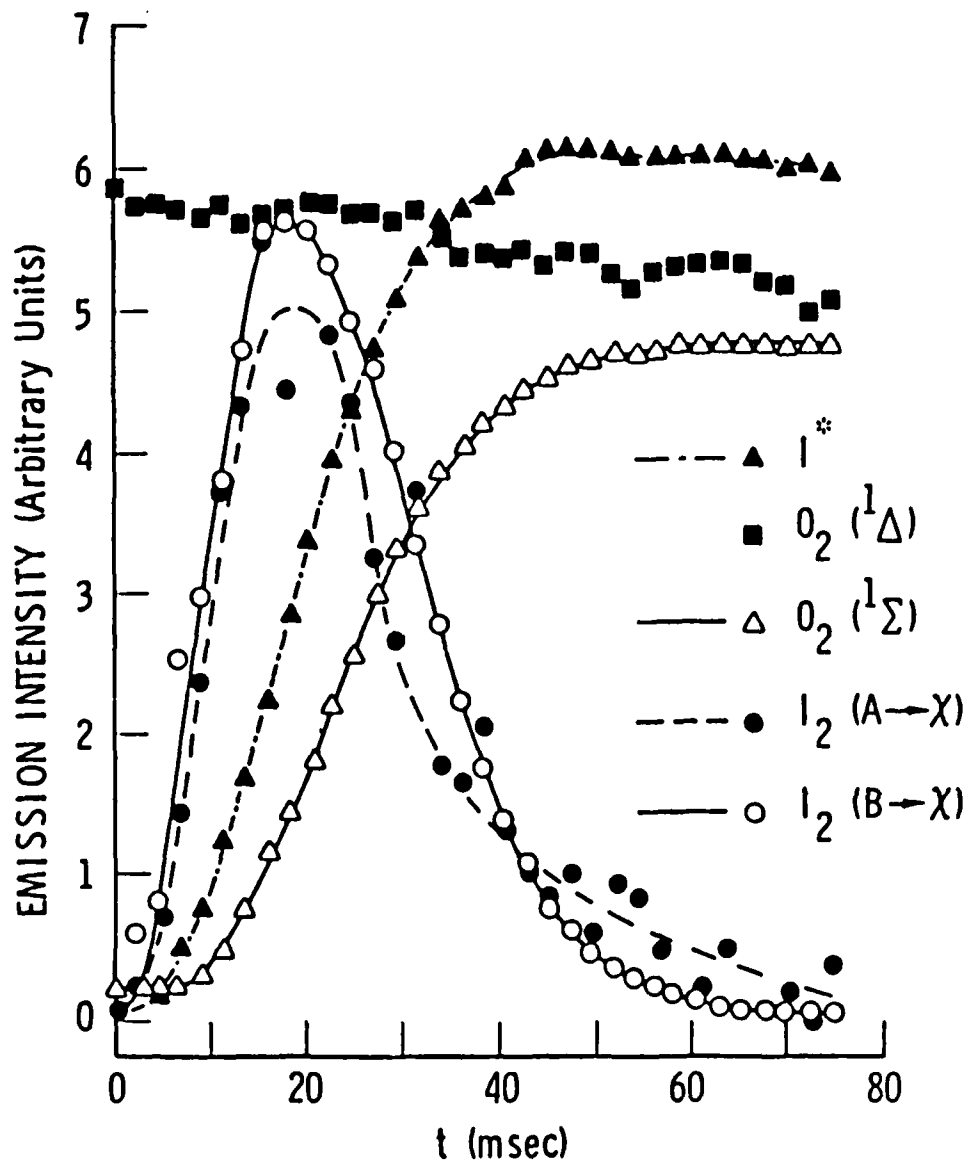


Figure 3. Time profiles of important species in the dissociation of molecular iodine by singlet oxygen under flow tube conditions. This figure is reproduced from Ref. 27.

The dissociation is then completed by $I_2^* + O_2(^1\Delta) \longrightarrow 2I + O_2(^3\Sigma)$. The excited iodine atoms, $I^* = I(^2P_{1/2})$, needed for process (32) are formed from process (40) and require an initiation step, probably given by process (21) or (32) of Table 2. Research groups (Refs. 7, 25, and 47), have observed high vibrational levels of I_2^* from I^* and $O_2(^1\Delta)$ collisions with I_2 directly or in a COIL environment. Recently, (Ref. 48) experimenters attempted a state-to-state model which competed $I_2(X)$ vibrational relaxation against its dissociation by $O_2(^1\Delta)$. This competition is reasonable because the first process must occur sequentially in a cascade down a substantial number of quantum levels while the latter can occur in a single step.

Recent work (Ref. 49) has emphasized the idea that excitation into the $I_2(A')$ state, and presumably into the more weakly bound $I_2(A)$ state to which it is collisionally coupled, creates a situation where iodine atoms are thermodynamically favored. In addition, the dissociation rates from all the vibrational levels of these electronic states are fast.

H. V. Lilenfeld (Ref. 25) has postulated from the observation of $I_2(A-X)$ emission scaling that dissociation of $I_2(A)$ can occur either through the expenditure of an $O_2(^1\Delta)$ or through a collision with the buffer gas. The later processes have substantial activation energies except for I_2 as the collision partner (Ref. 50). J. Tellinghuisen has postulated that the process $I_2(A') + I_2 \longrightarrow I_3 + I$ is responsible (Ref. 50). The rate coefficient for this process is so large that it could be much more important than process (25) in the COIL mixing zones.

In summary, the dissociation of molecular iodine in the presence of singlet oxygen is slowly initiated by process (32) followed by process (34) or by process (21) directly. Initially formed iodine atoms are rapidly excited from process (40) and the dissociation accelerates as process (33) begins to dominate the slower process (32).

The iodine dissociation mechanism as described in Table 2 is an empirical description of the way I_2 dissociates in flow tube studies where the reagents are essentially premixed and the excited state densities are low. The order of the dissociation process is known with modest accuracy. The mechanism is

not well known and inferred from the reaction order. The efficiency of this dissociation process is perhaps more uncertain than its rate. One of the most critical issues facing COIL modeling is the description of the number of $O_2(^1\Delta)$ required to dissociate an I_2 and where the residual energy is deposited in the flow.

3.3 LASER CAVITY KINETICS

The most important processes in the fully dissociated iodine regime are processes (40-41), the pump and inverse reactions. It should be noted that k_{41} has been measured while k_{40} has been calculated from the equilibrium constant. H. V. Lilenfeld has confirmed the value of the equilibrium constant, $k_{40}/k_{41} = 0.75 \exp(-403/T)$, by measuring all four species (Ref. 10). The data are not highly precise, however.

Three major processes can remove energy from the coupled I^* and $O_2(^1\Delta)$ system: (1) pooling, (2) water quenching, and (3) stimulated emission. A simple model for the extraction of lasing photons from this chemical system has been developed (Ref. 51).

The loss of energy from the highly coupled equilibrium states is measured by watching the decay of the $I^* - O_2(^1\Delta)$ system. One such loss is second order, namely the collisions between I^* and $O_2(^1\Delta)$. The energy pooling to form $O_2(^1\Sigma)$ is not the only product channel; quenching of either or both reactants is possible. As with the pure singlet oxygen pooling rate, the branching among product channels is not well described. The nonpooling contribution is arbitrarily assigned to process (45).

The quenching of $I(^2P_{1/2})$ has been studied for many years and most relevant removal rates are known (Refs. 30--33, 35, & 37). I^* quenching by water can have a substantial effect on device performance. The recommended value given for this rate coefficient in Table 3 was obtained in an experiment by A. J. Grimley and P. L. Houston (Ref. 30). The quenching rate for I^* by chlorine has been consistently overestimated, since the secondary products ICl and Cl atoms also quench I^* . The current recommended rate coefficient is

consistent with work of H. V. Lilenfeld (Ref. 25) who derived $k_{54} + k_{55} = 5.5 \pm 0.8 \times 10^{-15} \text{ cm}^3/\text{molecule-s}$. The rate coefficients for these chlorine reactions are sufficiently slow that they may be ignored in system modeling.

3.4 THE KINETIC DATA BASE

Although the current data base given in Tables 1--4 includes approximately 60 processes, many more reactions could be included. This is particularly true if individual vibrational states of iodine and oxygen were included. The current data base is not intended to be complete, but rather to provide the basis for a relatively simple standard rate package.

A numbering scheme for the reaction data base has been implied in Tables 1--4. This numbering scheme has been developed to segment the model into logical blocks that can be used in an identical manner by different modelers.

4.0 THE STANDARD CHEMICAL OXYGEN-IODINE LASER KINETICS PACKAGE

The current AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is given in Table 5. All rate coefficients are reported at $T = 295 \pm 5$ K.

The results of a detailed rate coefficient sensitivity analysis (Ref. 52) indicate that a reduced set of reactions adequately represents the essential features of COIL gas phase kinetics. Two reduced packages developed from this sensitivity analysis are presented in Tables 6--8. These reduced rate packages may be discussed with AFWL, and may prove useful for economical operation of test calculations on expensive codes incorporating mixing and optics. It should be noted that these smaller rate packages deviate from the data base in that the second order removal of $O_2(^1\Delta)$ is handled differently. In order to reduce the number of reactions, the deactivation of $O_2(^1\Sigma)$ is chosen so that the product is $O_2(^3\Sigma)$ and processes (2-3) are eliminated.

While no attempt to include temperature dependent rate coefficients was made in the current standard package, some experimental data for the more important temperature dependent rate coefficients is provided in Table 8.

TABLE 5. Standard AFWL rate package ($T = 295 \pm 5$ K).

Kinetic Process	Recommended Rate Coefficient ($\text{cm}^3/\text{molecule-s}$)
$\text{O}_2(^1\Delta) + \text{O}_2(^1\Delta) \rightarrow \text{O}_2(^1\Sigma) + \text{O}_2(^3\Sigma)$	2.7×10^{-17}
$\text{O}_2(^1\Delta) + \text{O}_2(^1\Delta) \rightarrow \text{O}_2(^1\Delta) + \text{O}_2(^3\Sigma)$	0
$\text{O}_2(^1\Delta) + \text{O}_2(^1\Delta) \rightarrow \text{O}_2(^3\Sigma) + \text{O}_2(^3\Sigma)$	1.7×10^{-17}
$\text{O}_2(^1\Sigma) + \text{O}_2(^3\Sigma) \rightarrow \text{O}_2(^1\Delta) + \text{O}_2(^3\Sigma)$	3.9×10^{-17}
$\text{O}_2(^1\Sigma) + \text{H}_2\text{O} \rightarrow \text{O}_2(^1\Delta) + \text{H}_2\text{C}$	6.7×10^{-12}
$\text{O}_2(^1\Sigma) + \text{Cl}_2 \rightarrow \text{O}_2(^1\Delta) + \text{Cl}_2$	2.0×10^{-15}
$\text{O}_2(^1\Sigma) + \text{H}_2\text{O}_2 \rightarrow \text{O}_2(^1\Delta) + \text{H}_2\text{O}_2$	3.3×10^{-13}
$\text{O}_2(^1\Sigma) + \text{He} \rightarrow \text{O}_2(^1\Delta) + \text{He}$	1.0×10^{-17}
$\text{O}_2(^1\Delta) + \text{O}_2(^3\Sigma) \rightarrow \text{O}_2(^3\Sigma) + \text{O}_2(^3\Sigma)$	1.6×10^{-18}
$\text{O}_2(^1\Delta) + \text{H}_2\text{O} \rightarrow \text{O}_2(^3\Sigma) + \text{H}_2\text{O}$	4.0×10^{-18}
$\text{O}_2(^1\Delta) + \text{Cl}_2 \rightarrow \text{O}_2(^3\Sigma) + \text{Cl}_2$	6.0×10^{-18}
$\text{O}_2(^1\Delta) + \text{H}_2\text{O}_2 \rightarrow \text{O}_2(^3\Sigma) + \text{H}_2\text{O}_2$	0
$\text{O}_2(^1\Delta) + \text{He} \rightarrow \text{O}_2(^3\Sigma) + \text{He}$	8.0×10^{-21}
$\text{I}_2(\text{X}) + \text{O}_2(^1\Sigma) \rightarrow \text{I} + \text{I} + \text{O}_2(^3\Sigma)$	4.0×10^{-12}
$\text{I}_2(\text{X}) + \text{O}_2(^1\Sigma) \rightarrow \text{I}_2(\text{X}) + \text{O}_2(^1\Delta)$	0
$\text{I}_2(\text{X}) + \text{O}_2(^1\Sigma) \rightarrow \text{I}_2(\text{X}) + \text{O}_2(^3\Sigma)$	0
$\text{I}_2(\text{X}) + \text{O}_2(^1\Sigma) \rightarrow \text{I}_2(\text{A,A}') + \text{O}_2(^3\Sigma)$	1.6×10^{-11}
$\text{I}_2(\text{A,A}') + \text{O}_2(^1\Delta) \rightarrow \text{I} + \text{I} + \text{O}_2(^3\Sigma)$	1.0×10^{-11}
$\text{I}_2(\text{A,A}') + \text{O}_2(^1\Delta) \rightarrow \text{I}_2(\text{B}) + \text{O}_2(^3\Sigma)$	8.0×10^{-11}
$\text{I}_2(\text{B}) \rightarrow \text{I}_2(\text{X}) + h\nu$	$6 \times 10^5 \text{ sec}^{-1}$
$\text{I}_2(\text{B}) \rightarrow \text{I} + \text{I}$	$6 \times 10^5 \text{ sec}^{-1}$
$\text{I}_2(\text{X}) + \text{O}_2(^1\Delta) \rightarrow \text{I}_2^\bullet + \text{O}_2(^3\Sigma)$	7.0×10^{-15}
$\text{I}_2(\text{X}) + \text{I}^\bullet \rightarrow \text{I}_2^\bullet + \text{I}$	3.8×10^{-11}
$\text{I}_2(\text{X}) + \text{I}^\bullet \rightarrow \text{I}_2(\text{X}) + \text{I}$	0
$\text{I}_2^\bullet + \text{O}_2(^1\Delta) \rightarrow \text{I} + \text{I} + \text{O}_2(^3\Sigma)$	3.0×10^{-10}
$\text{I}_2^\bullet + \text{O}_2(^3\Sigma) \rightarrow \text{I}_2(\text{X}) + \text{O}_2(^3\Sigma)$	5.0×10^{-11}
$\text{I}_2^\bullet + \text{H}_2\text{O} \rightarrow \text{I}_2(\text{X}) + \text{H}_2\text{O}$	3.0×10^{-10}
$\text{I}_2^\bullet + \text{He} \rightarrow \text{I}_2(\text{X}) + \text{He}$	4.0×10^{-12}
$\text{I}_2^\bullet \rightarrow \text{I}_2(\text{X})$	0
$\text{I}_2^\bullet + \text{I}^\bullet \rightarrow \text{I} + \text{I} + \text{I}$	0
$\text{I} + \text{O}_2(^1\Delta) \rightarrow \text{I}^\bullet + \text{O}_2(^3\Sigma)$	7.8×10^{-11}

TABLE 5. (Concluded).

$I^\bullet$	$+ O_2(^3\Sigma) \rightarrow I$	$+ O_2(^1\Delta)$	2.7×10^{-11}
I	$+ O_2(^1\Delta) \rightarrow I$	$+ O_2(^3\Sigma)$	1.0×10^{-15}
$I^\bullet$	$+ O_2(^3\Sigma) \rightarrow I$	$+ O_2(^3\Sigma)$	0
$I^\bullet$	$+ O_2(^1\Delta) \rightarrow I$	$+ O_2(^1\Sigma)$	1.1×10^{-13}
$I^\bullet$	$+ O_2(^1\Delta) \rightarrow I$	$+ O_2(^1\Delta)$	1.1×10^{-13}
$I^\bullet$	$+ O_2(^1\Delta) \rightarrow I$	$+ O_2(^3\Sigma)$	0
$I^\bullet$	$+ I \rightarrow I$	$+ I$	1.6×10^{-14}
$I^\bullet$	$+ H_2O \rightarrow I$	$+ H_2O$	2.0×10^{-12}
$I^\bullet$	$+ H_2O_2 \rightarrow I$	$+ H_2O_2$	2.5×10^{-11}

TABLE 6. Reduced AFWL rate package (Mod. 1)

Kinetic Process	Recommended Rate Coefficient (cm ³ /molecule-s)
$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$	2.7×10^{-17}
$O_2(^1\Sigma) + H_2O \rightarrow O_2(^3\Sigma) + H_2O$	$6.7 \times 10^{-12}^*$
$O_2(^1\Delta) + O_2(^3\Sigma) \rightarrow O_2(^3\Sigma) + O_2(^3\Sigma)$	1.6×10^{-18}
$O_2(^1\Delta) + H_2O \rightarrow O_2(^3\Sigma) + H_2O$	4.0×10^{-18}
$O_2(^1\Delta) + Cl_2 \rightarrow O_2(^3\Sigma) + Cl_2$	6.0×10^{-18}
$O_2(^1\Delta) + He \rightarrow O_2(^3\Sigma) + He$	8.0×10^{-21}
$I_2(X) + O_2(^1\Sigma) \rightarrow I + I + O_2(^3\Sigma)$	4.0×10^{-12}
$I_2(X) + O_2(^1\Sigma) \rightarrow I_2(X) + O_2(^1\Delta)$	1.6×10^{-11}
$I_2(X) + O_2(^1\Delta) \rightarrow I_2^* + O_2(^3\Sigma)$	7.0×10^{-15}
$I_2(X) + I^* \rightarrow I_2^* + I$	3.8×10^{-11}
$I_2^* + O_2(^1\Delta) \rightarrow I + I + O_2(^3\Sigma)$	3.0×10^{-10}
$I_2^* + O_2(^3\Sigma) \rightarrow I_2(X) + O_2(^3\Sigma)$	5.0×10^{-11}
$I_2^* + H_2O \rightarrow I_2(X) + H_2O$	3.0×10^{-10}
$I_2^* + He \rightarrow I_2(X) + He$	4.0×10^{-12}
$I + O_2(^1\Delta) \rightarrow I^* + O_2(^3\Sigma)$	7.8×10^{-11}
$I^* + O_2(^3\Sigma) \rightarrow I + O_2(^1\Delta)$	2.7×10^{-11}
$I + O_2(^1\Delta) \rightarrow I + O_2(^3\Sigma)$	1.0×10^{-15}
$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Sigma)$	1.1×10^{-13}
$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Delta)$	1.1×10^{-13}
$I^* + I \rightarrow I + I$	1.6×10^{-14}
$I^* + H_2O \rightarrow I + H_2O$	2.0×10^{-12}

*In order to reduce the size of the model, Processes (2) and (3) of Table 5 have been eliminated. In order to correctly mimic the observed kinetics, the artificial assumption of quenching $O_2(^1\Sigma)$ to $O_2(^3\Sigma)$ by Process (2) above is introduced.

TABLE 7. Reduced AFWL rate package (Mod. 2)

Kinetic Process	Recommended Rate Coefficient (cm ³ /molecule-s)
$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$	2.7×10^{-17}
$O_2(^1\Sigma) + H_2O \rightarrow O_2(^3\Sigma) + H_2O$	$6.7 \times 10^{-12}^*$
$I_2(X) + O_2(^1\Sigma) \rightarrow I + I + O_2(^3\Sigma)$	4.0×10^{-12}
$I_2(X) + O_2(^1\Delta) \rightarrow I_2^* + O_2(^3\Sigma)$	7.0×10^{-15}
$I_2(X) + I^* \rightarrow I_2^* + I$	3.8×10^{-11}
$I_2^* + O_2(^1\Delta) \rightarrow I + I + O_2(^3\Sigma)$	3.0×10^{-10}
$I_2^* + H_2O \rightarrow I_2(X) + H_2O$	3.0×10^{-10}
$I + O_2(^1\Delta) \rightarrow I^* + O_2(^3\Sigma)$	7.8×10^{-11}
$I^* + O_2(^3\Sigma) \rightarrow I + O_2(^1\Delta)$	2.7×10^{-11}
$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Sigma)$	1.1×10^{-13}
$I^* + H_2O \rightarrow I + H_2O$	2.0×10^{-12}

*In order to reduce the size of the model, Processes (2) and (3) of Table 5 have been eliminated. In order to correctly mimic the observed kinetics, the artificial assumption of quenching $O_2(^1\Sigma)$ to $O_2(^3\Sigma)$ by Process (2) above is introduced.

TABLE 8. Reduced AFWL rate package (Mod. 2) available
temperature dependent rate data.

<u>Kinetic Process</u>	<u>Recommended Rate Coefficient (cm³/molecule-s)</u>
$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$ (Heidner et al [26]; Lilienfeld [9])	$9.5 \times 10^{-28} T^{3.8} \exp(700/T)$
$O_2(^1\Sigma) + H_2O \rightarrow O_2(^3\Sigma) + H_2O$ (no measurement reported)	6.7×10^{-12}
$I_2(X) + O_2(^1\Sigma) \rightarrow I + I + O_2(^3\Sigma)$ (no measurement reported)	4.0×10^{-12}
$I_2(X) + O_2(^1\Delta) \rightarrow I_2^* + O_2(^3\Sigma)$ (no measurement reported)	7.0×10^{-15}
$I_2(X) + I^* \rightarrow I_2^* + I$ (Deakin and Husain [35], normalized to Grimley and Houston [23])	$1.4 \times 10^{-13} \exp(1660/T)$
$I_2^* + O_2(^1\Delta) \rightarrow I + I + O_2(^3\Sigma)$ (no measurement reported)	3.0×10^{-10}
$I_2^* + H_2O \rightarrow I_2(X) + H_2O$ (no measurement reported)	3.0×10^{-10}
$I + O_2(^1\Delta) \rightarrow I^* + O_2(^3\Sigma)$ (calculated from 9 by microscopic reversibility)	$2.33 \times 10^{-8} T^{-1}$
$I^* + O_2(^3\Sigma) \rightarrow I + O_2(^1\Delta)$ (Deakin and Husain [35], normalized to Young and Houston [24])	$3.1 \times 10^{-8} T^{-1} \exp(-403/T)$
$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Sigma)$ (Heidner et al [26]; Lilienfeld [9])	$4.0 \times 10^{-24} T^{3.8} \exp(700/T)$
$I^* + H_2O \rightarrow I + H_2O$ (no measurement reported)	2.0×10^{-12}

5.0 CONCLUSIONS AND RECOMMENDATIONS

A standardized rate package for modeling the gas phase kinetics of chemical oxygen-iodine lasers has been developed to provide a basis for comparing the results of various research groups and to provide for optimal information exchange. By reviewing the kinetic data base, several prominent problem areas in fully understanding COIL kinetics have been identified.

Kinetics in the generator duct are fairly well understood. A more accurate rate for the total second order loss of $O_2(1\Delta)$, wall deactivation coefficients for $O_2(1\Delta)$, and the energy disposal in $O_2(1\Sigma)$ quenching are important areas for further study. The mechanism for the dissociation of molecular iodine by singlet oxygen is poorly understood. Areas of particular interest in this dissociation process include: (1) quantitative identification of intermediates, (2) the average number of $O_2(1\Delta)$ required to dissociate one iodine molecule, and (3) the temperature dependence of the dissociation rate and efficiency. The kinetics after complete iodine dissociation are fairly well characterized, but temperature dependent rate coefficients are needed. A test of the current rate package under supersonic COIL device conditions has not been completed. Such a program should be conducted with extensive diagnostics to characterize all the important chemical species, including excited molecular iodine states involved in dissociation.

AFWL encourages active discussion and investigation into the many complex issues associated with the modeling of chemical oxygen-iodine lasers. It is hoped that this AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package will serve as a good basis for future work in this area.

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