Energy Disposal in Electronically Excited Halogens and Oxygen

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Iodine Laser
Energy Transfer
Singlet Oxygen
Electronic State Quenching

Collisonal quenching of electronically excited iodine atoms by molecular oxygen has been investigated. The primary mechanism of the I*(2P(3/2)) deactivation is shown to be an electronic-to-electronic energy transfer process between the iodine and oxygen, creating electronically excited O2*(14E). In another experiment the total rate of deactivation of O2*(14E) by CO2 was found to be 5.0 x 10^13 cm^3 molecule^-1sec^-1.
Electronic-to-vibrational energy transfer from \( \text{I}^* (5 \ell_2^2 P_1/2) \) to \( \text{I}_2 (2S_x, y < 43) \) has been observed. Roughly 2% of the \( \text{I}^* \) deactivation result in \( \text{I}_2 (v=40) \) by argon, helium, and \( \text{I}_2 \) at room temperature are \((7.3 \pm 0.3) \times 10^{-6} \text{ sec}^{-1} \text{ torr}^{-1}\), \((1.0 \pm 0.2) \times 10^{-6} \text{ sec}^{-1} \text{ torr}^{-1}\), and \((1.8 \pm 0.4) \times 10^{-6} \text{ sec}^{-1} \text{ torr}^{-1}\), respectively. These results have important implications for the mechanism of \( \text{I}_2 \) dissociation in the chemical oxygen/iodine laser. A chain branching mechanism consisting of the steps \( \text{I}^* + \text{I}_2 \rightarrow \text{I} + \text{I}_2 (20x < 40) \), \( \text{I}_2 (20x < 40) + \text{O}_2 (1/2) \rightarrow 2\text{I} + \text{O}_2 \), and \( \text{O}_2 (1/2) + \text{I} + \text{O}_2 + \text{I}^* \) may be responsible for the dissociation.
A. Research Objectives

The chemical oxygen-iodine laser has been identified by AFWL as a favorable system for further development. However, the chemical dynamics of this laser are poorly understood. Inversion between the spin-orbit levels of iodine is thought to be produced by the following mechanism:

\[ \text{O}_2^{(1\Delta)} + \text{O}_2^{(1\Delta)} + \text{O}_2^{(1\Sigma)} + \text{O}_2^{(3\Sigma)} \]  \hspace{1cm} (1)  \\
\[ \text{O}_2^{(1\Sigma)} + \text{I}_2 \rightarrow \text{O}_2^{(3\Sigma)} + 2\text{I} \]  \hspace{1cm} (2)  \\
\[ \text{O}_2^{(1\Delta)} + \text{I} \rightarrow \text{O}_2^{(3\Sigma)} + \text{I}^* \]  \hspace{1cm} (3)  \\
\[ \text{I}^* + \text{O}_2^{(1\Delta)} + \text{I} + \text{O}_2^{(1\Sigma)} \]  \hspace{1cm} (4)

where \( \text{I}=\text{I}(^2\text{P}_3/2) \) and \( \text{I}^*=\text{I}(^2\text{P}_1/2) \). It has been our research objective during the past year to examine this mechanism in detail, to measure the relevant rate constants, and to determine the branching ratios for alternative steps in the kinetic scheme. Our efforts have focused primarily on steps (2) and (3) of the proposed mechanism. The status of our investigation is outlined below and in previously published papers (see Section C).
B. Status of the Research Effort (1981-1982)

1. The $I(2P_{1/2}) + O_2 = I(2P_{3/2}) + O_2(1\Delta)$ Equilibrium

The equilibrium between excited iodine atoms and oxygen has been examined by monitoring the time-dependent $I^*[\equiv I(2P_{1/2})]$ concentration following creation of this species by pulsed laser photolysis of iodine-containing precursors. A double exponential decay is observed which reflects a fast approach to equilibrium followed by a slower relaxation of the equilibrated mixture. Data obtained with the $I^*$ precursors HI and CH$_3$I show that the rate constant for the reaction $I^* + O_2 + I + O_2$ is insignificant compared to that for the reaction $I^* + O_2 + I + O_2(1\Delta)$. Data obtained from the precursors i-C$_3$F$_7$I, n-C$_3$F$_7$I, C$_2$H$_5$I, and CF$_3$I suggest that $O_2(1\Delta)$ is rapidly relaxed by the precursor itself, by the precursor radical, or by some product formed in a reaction between the precursor radical and oxygen. The rate constant for the process $I^* + O_2 + I + O_2(1\Delta)$ has been found to be $(8.8 \pm 0.9) \times 10^5$ sec$^{-1}$ torr$^{-1}$, while that for the process $I^* + O_2 + I + O_2$ is $(0.3 \pm 1.3) \times 10^5$ sec$^{-1}$ torr$^{-1}$.

2. Electronic-to-Vibrational Energy Transfer from $I^*(5\ 2P_{1/2})$ to $I_2(25<v<43)$

Electronic-to-vibrational energy transfer from $I^*(5\ 2P_{1/2})$ to $I_2(25<v<43)$ has been observed. $I^*$ was created by pulsed laser photolysis of either $I_2$/Ar mixtures at 475 nm or CF$_3$I/$I_2$/Ar mixtures at 266 nm, while the resulting vibrational distribution of $I_2$ was monitored by laser induced fluorescence on the $I_2(B+X)$
transition. The experimental results are consistent with an asymmetrically shaped nascent $I_2$ product distribution peaked near $v=40$ with half-maximum points at $v=41$ and $v=35$. Roughly 2\% of the $I^*$ deactivations result in $I_2(v=40)$. The rate constants for vibrational relaxation of $I_2(v=40)$ by argon, helium, and $I_2$ at room temperature are $(7.3 \pm 0.3) \times 10^5$ sec$^{-1}$ Torr$^{-1}$, $(1.0 \pm 0.2) \times 10^6$ sec$^{-1}$ Torr$^{-1}$, and $(1.8 \pm 0.4) \times 10^6$ sec$^{-1}$ Torr$^{-1}$, respectively. These results have important implications for the mechanism of $I_2$ dissociation in the chemical oxygen/iodine laser. A chain branching mechanism consisting of the steps $I^* + I_2 \rightarrow I + I_2(20<v<40)$, $I_2(20<v<40) + O_2(^1\Delta) + 2I + O_2$, and $O_2(^1\Delta) + I + O_2 + I^*$ may be responsible for the dissociation.

C. Complete List of Publications Supported by this Grant

The following publications resulted from work performed under support from this AFOSR grant. All of these publications have been sent to AFOSR with DD 1473 cover pages.


12. A. J. Grimley and P. L. Houston, "The Photochemistry of Nitrosyl Halides: The \( \text{X}_2 + \text{NOX} + \text{X}_2 + \text{NO\(v\)} \) Reaction (\( \text{X} = \text{Cl}, \text{Br} \))," *J. Chem. Phys.* **72**, 1471-1475 (1980).


15. R. G. Aviles, D. F. Muller, and P. L. Houston, "Quenching of Laser Excited \( \text{O}_2(\text{b}^1\Sigma^+) \) by \( \text{CO}_2, \text{H}_2\text{O}, \) and \( \text{I}_2 \)," *Appl. Phys. Lett.* **37**, 358-360 (1980).


D. Personnel

1. Paul L. Houston, Ph.D., 1973, Massachusetts Institute of Technology.
2. Zhen-nan Gu, Ph.D., 1964, Peking University.
5. G. E. Hall, Ph.D., University of Toronto.

E. Meeting Presentations