Recent data indicate that $O_2(^1\Delta_g)$ radiative lifetimes in various solvents are actually independent of the particular solvent and are equal to a value of approximately 4 s [3]. The suggestion is therefore that for solvents exhibiting high oxygen solubility, such as the Freons, sequential pressurization to levels approaching 100 atm from lesser values ought to span an important range, at the lower end of which emission due to $O_2(^1\Delta_g)$-solvent collisions is dominant, to the upper end where $O_2(^1\Delta_g)$-oxygen collisions control. At lower pressures, therefore, a quadratic dependence of emission intensity on pressure is expected, while at higher pressures transition to a cubic dependence should be observed.

Thus a series of runs was carried out in which the cylindrical observation section of a high pressure cell was filled with Freon-113 (1,1,2-trichlorotrifluoroethane) and the overlying volume was carefully pressurized with oxygen. The laser was positioned so that its beam axis coincided with that of the observation section of the cell. With the laser incident pulse energy fixed at 40 mJ, $O_2(^1\Delta_g)$ decay curves were obtained at time intervals of 1 h subsequent to pressurization. Corresponding decay times and amplitudes were obtained from each run. These times were observed to decrease steadily as oxygen diffused to the center of the cell, with an increase in the amplitude factor.

Equilibrium was attained after a period of 8 h. The dependence of the reciprocal equilibrium time constants on oxygen pressure was linear, with a slope consistent with the gas phase data and an intercept of 1.30 ms^{-1}, corresponding to a time constant of 770 μs, *i.e.* the deactivation time for $O_2(^1\Delta_g)$ infinitely dilute in the Freon-113 solvent. This value is substantially smaller than that obtained for this solvent under air-saturated conditions [4].

Dissolved oxygen levels were determined as a function of time from the sequential values of decay times obtained during the approach to equilibrium. Using a simplified model of the cell geometry, axial oxygen levels were calculated as a function of time from a one-dimensional diffusion equation. Comparison of results of these calculations with the experimental data yielded a diffusion coefficient $D = 5.8(-5)$ cm^2 s^{-1}.

The dependence of emission intensity on oxygen pressure exhibited a significant departure from a cubic dependence at the lowest pressures, indicating the dominance of $O_2(^1\Delta_g)$-solvent collisions in this region. However, the onset of the $O_2(^1\Delta_g)$-oxygen-collision-controlled regime occurs at lower values of pressure than would be predicted from lifetime calculations based on ref. 2.

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Laser kinetic studies of I($^2P_{1/2}$) and O$_2$($^1\Delta_g$)[†]

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Multiphoton ionization has been used to detect sensitively O$_2$($^1\Delta$), both in a microwave discharge and from the 266 nm photolysis of O$_3$. The spectra showed several vibrational levels for each of two Rydberg transitions in the 260 - 245 nm region as well as

a valence band near 340 nm. None of the $O_2(^1\Delta)$ states has previously been reported. Their assignment is currently in progress.

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_3I show that the rate constant for the reaction $I^* + O_2 \rightarrow I + O_2$ is insignificant compared with that for the reaction $I^* + O_2 \rightarrow I + O_2(^1\Delta)$. Data obtained from the precursors $i\text{-}C_3F_7I$, $n\text{-}C_3F_7I$, C_2H_5I and CF_3I 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 $I^* + O_2 \rightarrow I + O_2(^1\Delta)$ has been found to be $(8.8 \pm 0.9) \times 10^5$ s^{-1} Torr^{-1}, while that for the process $I^* + O_2 \rightarrow I + O_2$ is $(0.3 \pm 1.3) \times 10^5$ s^{-1} Torr^{-1}.

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_3I–I_2–Ar mixtures at 266 nm, while the resulting vibrational distribution of I_2 was monitored by laser-induced fluorescence on the $I_2(B \leftarrow X)$ transition. The experimental results are consistent with a nascent I_2 product distribution which is inverted, with a substantial fraction of the I_2 molecules formed in $v > 30$. 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 $(7.3 \pm 0.3) \times 10^5$ s^{-1} Torr^{-1}, $(1.0 \pm 0.2) \times 10^6$ s^{-1} Torr^{-1} and $(1.8 \pm 0.4) \times 10^6$ s^{-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 $I^* + I_2 \rightarrow I + I_2(20 < v < 40)$, $I_2(20 < v < 40) + O_2(^1\Delta) \rightarrow 2I + O_2$ and $O_2(^1\Delta) + I \rightarrow O_2 + I^*$ may be responsible for the dissociation.

Recent applications of singlet oxygen reactions in synthesis[†]

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The reactions of singlet oxygen with oxazoles have provided a novel method for protecting carboxyl groups which may then be regenerated in an activated form:
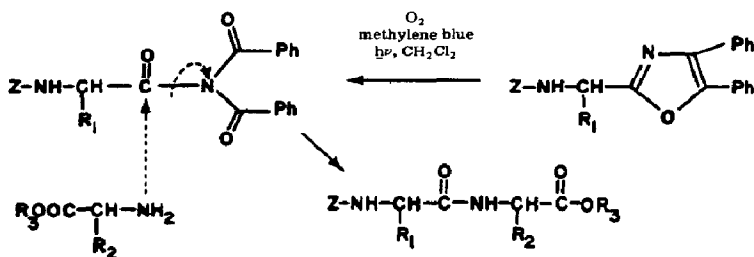
Recent use of this procedure in the synthesis of dipeptides is discussed.