

note that the levels of oxygen vary tremendously in these tissues, with very low levels being present in the ocular lens and very high levels in the retina.

Data on the spectral quality and quantities of radiant energy interacting with various ocular tissues, their oxygen content and enzymes and anti-oxidants present to scavenge or protect against photo-oxidative damage need to be collated in order to assess the potential hazard to these tissues relative to oxygen excited states and radicals. Such data are provided in our presentation. Besides this information chemopathological conditions have been observed in the ocular tissues (*i.e.* cataract, retinal degeneration) that have been ascribed to imbalances in the above-mentioned system. These are described and the potential that oxygen excited states and free radicals have an important role in the damages stated is discussed.

This talk introduces practical situations relating eye health to the handling of oxygen products induced by radiant energy and metabolism.

Optical determination of $O_2(^1\Delta_g)$ quenching rates and relative emission intensities in high pressure oxygen gas using pulsed laser excitation at $1.064 \mu\text{m}^\dagger$

J. G. PARKER

Applied Physics Laboratory, The Johns Hopkins University, Laurel, MD 20707 (U.S.A.)

Singlet molecular oxygen in the $v' = 1$ vibrational level of the $^1\Delta_g$ electronic state was generated in high pressure oxygen gas by means of pulsed laser radiation at a wavelength of $1.064 \mu\text{m}$. The resulting $O_2(^1\Delta_g)$ population was monitored optically, using a remotely positioned germanium photodiode in combination with appropriate filtering to record the subsequent IR emission. Pressures ranged from approximately 40 to 95 atm. Measurements were carried out both in the gas phase and also with the oxygen dissolved in a Freon solvent.

The observed time dependence of this IR emission in the gas phase is well described by an exponential function with an average time constant $p_0\tau = 0.0221 \text{ s atm}$. Runs were also made in which a sizable helium addition was used to investigate possible effects due to an increased vibrational quenching rate on the overall $O_2(^1\Delta_g)$ deactivation process. A slight increase in the time constant to the value 0.0250 s atm was found, comparing favorably with the value 0.0244 s atm obtained from earlier measurements on a similar mixture using a photoacoustic technique [1]. Lifetimes obtained by others using IR monitoring techniques, in which significantly different methods of $O_2(^1\Delta_g)$ generation were used, lie in the range from 0.0179 to 0.0259 s atm , encompassing the above values.

A series of runs was devoted to a determination of the dependence of emission intensity on oxygen pressure, with peak intensity being recorded as the pressure was increased sequentially from an initial value of 47.9 atm to a final value of 80.9 atm . A plot of the logarithm of the relative emission intensity I_R versus the logarithm of the pressure p_0 indicated that $I_R = Kp_0^3$. It is well known that the optical absorption at $1.064 \mu\text{m}$ leading to the formation of $O_2(^1\Delta_g)$ varies quadratically with pressure and the presence of the additional factor thus implies that the emission rate must depend linearly on p_0 in accord with experimental results obtained at lower pressure. The emission process at these pressures is therefore collisionally induced. Calculation, using the empirical dependence of radiative lifetime on gas pressure established by Badger *et al.* [2] at lower pressures, indicates that, in the pressure interval from 50 to 100 atm , this lifetime should range from 10 to 20 s .

[†]Abstract of a paper presented at the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4 - 7, 1984.

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 $770 \mu\text{s}$, 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 $D = 5.8(-5) \text{ cm}^2 \text{ s}^{-1}$.

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.

- 1 J. G. Parker, *J. Chem. Phys.*, 67 (1977) 5352 - 5361.
- 2 R. M. Badger, A. C. Wright and R. F. Whitlock, *J. Chem. Phys.*, 43 (1965) 4345 - 4350.
- 3 A. A. Krasnovsky, Jr., *Chem. Phys. Lett.*, 81 (1981) 443 - 445.
- 4 B. Stevens and K. L. Marsh, *J. Phys. Chem.*, 86 (1982) 4473 - 4476.

Laser kinetic studies of $I(^2P_{1/2})$ and $O_2(^1\Delta_g)$ †

G. E. HALL, W. MARINELLI, SIVARAM AREPALLI, A. T. YOUNG, P. L. HOUSTON and J. R. WIESENFELD

Department of Chemistry, Cornell University, Ithaca, NY 14853 (U.S.A.)

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

† Abstract of a paper presented at the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4 - 7, 1984.