Chemiluminescence Arising from Simultaneous Transitions in Pairs of Singlet Oxygen Molecules[1]

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Abstract: A complete spectroscopic comparison is made of the numerous chemiluminescence bands observed in the 20° aqueous solution reaction of hydrogen peroxide with hypochlorite ion, with gaseous molecular oxygen absorption bands at high pressure. Both single molecule and simultaneous transitions involving molecular pairs are observed, all involving the highly metastable singlet molecular oxygen states $^1\Delta_g$ and/or $^1\Sigma_g{}^+$. The visible chemiluminescence bands observed are simultaneous transitions; the red pair at 6334 and 7032 Å corresponding to the $(^1\Delta_g)(^1\Delta_g) \rightarrow (^3\Sigma_g{}^-)(^3\Sigma_g{}^-)$ transition and a green band at 4780 Å corresponding to the $(^1\Delta_g)(^1\Sigma_g{}^+) \rightarrow (^3\Sigma_g{}^-)(^3\Sigma_g{}^-)$ transition. These correlate spectroscopically with the high-pressure (150 atm) gaseous oxygen absorption bands. No emission was observed corresponding to the $(^1\Sigma_g{}^+)(^1\Sigma_g{}^+) \leftarrow (^3\Sigma_g{}^-)(^3\Sigma_g{}^-)$ absorption, but evidence for the production of this pair state is obtained from sensitized luminescence studies. An infrared chemiluminescence band centered on 7620 Å corresponding to the single molecule transition $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ for moleculai oxygen is shown to reveal rotational structure. Sensitized limunescence of organic fluorescent molecules present in the peroxide-hypochlorite reacting system is interpreted by means of a physical energy transfer from simultaneous transition singlet molecular oxygen pair states to the organic acceptor.

Oxygen molecules are among the most ubiquitous in nature and play a unique role in many photophysical, photochemical, and photobiological processes.[2] Yet in spite of the early observations on absorption spectroscopy of oxygen, interpreted in terms of its comparatively well understood excited electronic states, it is only in the last few years that the importance of these excited states has been recognized in the many systems in which oxygen participates as a physical or chemical agent. Especially have the lowest metastable singlet states of oxygen ($^1\Delta_g$ and $^1\Sigma_g{}^+$) appeared prominent in giving rise to visible region chemiluminescence phenomena.[3-8] As an immediate consequence of this demonstration, important new interpretations involving excited singlet oxygen have appeared, offering applications to photosensitized oxidations, reversible quenching of excited states of polyatomic molecules, and unique chemical reactions of the singlet oxygen species produced chemically.

Not only has the facile chemical production and the unusual metastability of the two singlet oxygen species resulted in this renascence of interest, but also attention has been focused as a consequence on oxygen molecule-pair interactions in their simultaneous transitions.

Simultaneous transitions as a one-photon two-molecule process were first invoked as an idea by Ellis and Kneser[9] in the interpretation of liquid oxygen absorption spectra in the visible and near-ultraviolet regions, based on a suggestion by Lewis[10] that an "$(O_2)_2$ species" could account for the paramagnetic behavior of liquid oxygen, although this latter problem is still not perfectly resolved. The observation of visible chemiluminescences in peroxide decompositions yielding molecular oxygen has similarly required invoking simultaneous transitions in pairs of excited singlet oxygen molecules as a corollary to the absorption process in condensed oxygen.

It is altogether surprising how slowly the recognition of the unusual chemiluminescences of molecular oxygen produced in the simple aqueous reaction

$$H_2O_2 + OCl^- \longrightarrow O_2^* + H_2O + Cl^- \qquad (1)$$

(where O_2^* represents $^1\Delta_g$ and $^1\Sigma_g{}^+$ oxygen) was established. In 1927 Mallet reported[11] a red chemiluminescence accompanying this reaction, but made no further observations on it except in a chemiluminescence sensitizing technique. In 1938, Groh duplicated[12] the simple observation (using alkaline Br_2 instead of hypochlorite), and in 1942 Groh and Kirrmann made an approximate measurement[13] of the prominent visible band associated with this chemiluminescence as occurring at 6320 Å. More importantly, these authors made the observation from thermochemical criteria that: "It is necessary to acknowledge that the emission results from an accumulation of energy of two reacting molecules, *e.g.*, by the collisions of two activated molecules of oxygen, which supposes a relatively long lifetime." Groh and Kirrmann also noted the correspondence of this red chemiluminescence emission with some astrophysical observations on atmospheric oxygen. These first observations did not come to a fruition worthy of the subject. Rediscoveries of these results were given in the qualitative observations by Gattow and

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[1] Work supported in part by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission, and the Florida State University; and in part by a contract between the Physics Branch, Office of Naval Research, and the Florida State University.

[2] (a) *Cf.* C. Reid, "Excited States in Chemistry and Biology," Butterworth and Co., Ltd., London, 1957, especially pp 98–106; (b) H. H. Seliger and W. D. McElroy, "Light: Physical and Biological Action," Academic Press, New York, N. Y., 1965.

[3] A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); **40**, 605 (1964).

[4] A. U. Khan and M. Kasha, *Nature*, **204**, 241 (1964).

[5] A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, **88**, 1574 (1966).

[6] S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

[7] R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc. London*, 117 (1964).

[8] J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, **4**, 963 (1965).

[9] J. W. Ellis and H. O. Kneser, *Z. Phys.*, **86**, 583 (1933).

[10] G. N. Lewis, *J. Amer. Chem. Soc.*, **46**, 2027 (1924).

[11] L. Mallet, *C. R. Acad. Sci., Paris*, **185**, 352 (1927).

[12] P. Groh, *Bull. Soc. Chim., Fr.*, **5**, 12 (1938).

[13] P. Groh and K. A. Kirrmann, *C. R. Acad. Sci., Paris*, **215**, 275 (1942).

Schneider[14] in 1954, and the quantitative observations of Seliger[15] in 1960, who reported a single emission band at 6348 Å with a half-band width of 170 Å, but gave no interpretation. Seliger's quantitative report focused new attention on the oxygen chemiluminescence phenomena.

Stauff and Schmidkunz[16] interpreted the "6348-Å band" as the direct emission corresponding to the liquid oxygen 6300-Å absorption band interpreted by Ellis and Kneser[9] as the double molecule 0,0 band for the $2(^1\Delta_g) \leftarrow 2(^3\Sigma_g^-)$ absorption. This possibly coincidental interpretation has been established subsequently by more rigorous spectroscopic investigation. However, other assignments of comparatively broad luminescences in reacting chemiluminescent systems made by Stauff and Schmidkunz[16] and by Stauff and Lohmann[17] on the basis of Ellis and Kneser absorption band positions must be regarded as mere coincidences on the basis of later work by the present authors and others.

Khan and Kasha discovered that the red chemiluminescence in the aqueous peroxide–hypochlorite reaction yields two principal bands[3] instead of the one previously noted, at 6334 Å (15788 cm^{-1}) and 7032 Å (14221 cm^{-1}), as well as two other faint bands in the near-infrared. The 1567-cm^{-1} spacing between these comparatively narrow (approximate half-band width of 100–125 Å; or 250 cm^{-1}) bands, compared with the ground state lowest vibrational spacing (1556 cm^{-1}) of molecular oxygen, confirmed that a molecular oxygen species was directly involved in the emission. The uncorrected spectrographic results showed surprisingly that the 0,0 and 0,1 bands were of comparable intensity. Seliger's determination[18] of the relative intensities of these two bands gave an integrated intensity ratio of 1/0.6 for the 0,0 *vs.* the 0,1 strong chemiluminescence bands, but other measurements (see below) yield ratios closer to 1/1. Seliger also observed an extremely weak band at 5780 Å (17,300 cm^{-1}). Khan and Kasha[3] considered two interpretations of the two main chemiluminescent bands, tentatively favoring the idea that the bands represented the oxygen $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition shifted by hydration, considering the Stauff and Schmidkunz comparison[16] with liquid oxygen double-molecule transitions as a possible coincidence.

However, in 1964 Arnold, Ogryzlo and Witzke,[6] pursuing research on molecular species in electrically discharged gaseous oxygen, noted that the red bands observed by Khan and Kasha were present although very weakly even in the gas-discharge spectrum. Moreover, the band envelopes and relative intensities (uncorrected) for the two bands (reported as 6340 and 7030 Å) were very similar to the bands determined by them for the peroxide–hypochlorite aqueous system. Equally significant was their observation of an extremely weak band at 7600 corresponding to the single-molecule $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ emission. Browne and Ogryzlo reported[7] more general spectroscopic observations at low resolution for the peroxide–hypochlorite reaction. The strong bands at 6340 and 7030 Å were definitely assigned as the $2(^1\Delta_g) \rightarrow 2(^3\Sigma_g^-)$ transition, with Seliger's weak 5800-Å band as a companion 1,0 band. Weak bands at 10,700 and 12,700 Å were identified as 1,0 and 0,0 bands of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition. Weak bands in the region 7600–8700 Å were assigned to the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ single molecule transition of O_2.

The unusual and unexpected appearance of a double-molecule simultaneous transition of molecular oxygen (at one atmosphere) in aqueous chemiluminescence spectra requires a complete spectroscopic investigation. In the following section a complete correlation is made of chemiluminescence spectra for the peroxide–hypochlorite aqueous system with high-pressure gaseous oxygen absorption spectra in the corresponding regions.

Correlation of Oxygen Chemiluminescence Spectra for Aqueous Solutions with Absorption Spectra of Gaseous Oxygen at High Pressure

In polyatomic molecular luminescence studies the correlation of the lowest absorption band for each multiplicity change with the corresponding luminescences (normally two) is the established method for testing authenticity of the luminescences in one-photon, one-molecule excitations. The molecular oxygen spectroscopy case is more complex phenomenologically for two reasons. First, the absence of radiationless transitions[19] would permit any excited state of a diatomic molecule to exhibit an intrinsic luminescence spectrum, and, second, the absence of intramolecular vibrational relaxation mechanisms in diatomics[20] makes metastable states of diatomics exceedingly susceptible to intermolecular perturbations.

For molecular oxygen, several luminescences are observed in chemiluminescence experiments in aqueous peroxide oxidation. Not only is emission observable from single-molecule oxygen metastable excited states (*i.e.*, $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$) but also from O_2–O_2 molecular pair excited states (*e.g.*, $[^1\Delta_g][^1\Delta_g] \rightarrow [^3\Sigma_g^-][^3\Sigma_g^-]$) as *simultaneous transitions*, arising from one-photon, two-molecule nonresonance interactions. (We use the *wave function convention* $[^1\Delta_g][^1\Delta_g]$ to describe simultaneous transition *states*, and the *energy convention* $[^1\Delta_g + {}^1\Delta_g]$ in reference to transition *frequencies.*)

For *luminescence* observations on O_2–O_2 pairs, low pressures such as 1 atm suffice (the "solution" chemiluminescences arise from metastable singlet oxygen molecules trapped in gas bubbles). All of the chemiluminescences observed involve pairs of metastable $^1\Delta_g$ and/or $^1\Sigma_g^+$ molecules in binary collisions. Owing to the extreme metastability of these two lowest singlet states of molecular oxygen, pair interaction leading to simultaneous emission of one photon can occur even at very low partial pressures of the metastable species.

For *absorption* observations on O_2–O_2 pairs, effectively a rare ternary event is required for a simultaneous transition to occur: a photon must interact with an O_2–O_2 collision pair undergoing electron exchange interaction. Thus, high gas pressure (here 140–150 atm) in 6.5-cm optical cells must be used to find simultaneous transitions in the molecular gas. It is understandable then why the spectrum of liquid (or solid)

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[14] G. Gattow and A. Schneider, *Naturwissenschaften*, **41**, 116 (1954).

[15] H. H. Seliger, *Anal. Biochem.*, **1**, 60 (1960).

[16] J. Stauff and H. Schmidkunz, *Z. Phys. Chem.* (Frankfurt am Main), **35**, 295 (1962).

[17] J. Stauff and F. Lohmann, *ibid.*, **40**, 123 (1964).

[18] H. H. Seliger, *J. Chem. Phys.*, **40**, 3133 (1964).

[19] B. R. Henry and M. Kasha, *Ann. Rev. Phys. Chem.*, **19**, 161 (1968).

[20] P. J. Gardner and M. Kasha, *J. Chem. Phys.*, **50**, 1543 (1969).

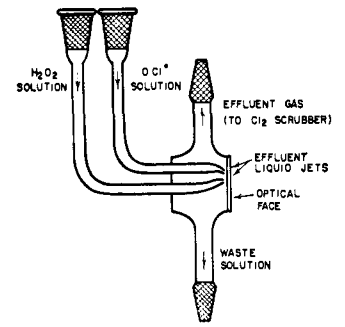

Figure 1. Continuous flow liquid–liquid mixing cell for spectral study of peroxide–hypochlorite chemiluminescence.

oxygen would exhibit simultaneous optical absorption transitions which could correlate with chemiluminescence simultaneous transitions for low-pressure systems.

In this section we shall present the full correlation of all the presently observed oxygen solution chemiluminescence spectra with the high-pressure gaseous absorption spectra.

Experimental Section

Reports in the literature indicated that a red chemiluminescence could be observed by mixing alkaline aqueous hydrogen peroxide with sodium hypochlorite or hypobromite. Initially the mixing apparatus for two liquid stream shown in Figure 1 was developed. The reagent grade hydrogen peroxide (10–30%) was kept chilled to 0°, and introduced into a separatory funnel above the apparatus just before use. Commercial hypochlorite bleach solution as well as reagent grade dilute sodium hypochlorite was similarly disposed. Constant slow flow of the two solutions produced a bright red-orange glow on the optical face, disposed within the cone of vision of the spectrograph.

A Steinheil Universal GH spectrograph was used, with *f* 3.9 three-prism glass short-focus optics in a special infrared setting with a dispersion of 108 Å/mm at 7000 Å; the exposure times were 1–15 min at various slit settings using water-hypersensitized Kodak I-N infrared spectrographic plates. Neon discharge tube lines were used for calibration.

For high resolution studies and for the observation of very weak bands, an apparatus involving gaseous chlorine proved more convenient and efficient for very long observation periods. This specially designed Hirtian apparatus[21] is illustrated in Figure 2. The surface of the fritted filter glowed brilliantly as the flow of gaseous Cl_2 into alkaline 10–30% chilled aqueous H_2O_2 was optimized. The Steinheil GH three-prism glass spectrograph with *f* 10 long-focus optics was used, yielding a dispersion of 41 Å/mm at 7000 Å.

For extremely weak band emissions ultra-high-speed Polaroid film (Type 410, ASA 10000) was used with the Steinheil GH three-prism spectrograph with *f*3.9 glass optics with visible setting.

Absorption spectra of gaseous oxygen at high pressure were determined with a Cary Model 15 spectrophotometer, using enhanced optical density recording with 0.1 absorbance unit full scale. An Aminco high-pressure quartz optics absorption cell was used with an optical path of 6.5 cm. Purified tank oxygen at 140–150 atm at 20° was used.

Discussion of Spectral Observations

Red Chemiluminescence Bands. The $2[^1\Delta_g] \rightarrow 2[^3\Sigma_g^-]$ Transition. The spectrum for the prominent red chemiluminescence bands (Figure 3c) with prominent peaks at 6334 Å (15,788 cm^{-1}) and 7032 Å (14,221 cm^{-1}) was reported previously[3] for the hydrogen peroxide–aqueous hypochlorite reaction. The chemiluminescence is brilliant enough to be visible in strong daylight, and required exposure times of 1 sec or less under the best conditions. As indicated, the separation between these two main peaks is 1567 cm^{-1}, which should represent the ground state lowest vibrational spacing of molecular oxygen, which is known[22] to be 1556 cm^{-1}. In the experiments it is evident (see below) that the chemiluminescence is emitted from metastable excited oxygen molecules within the gas bubble. Comparison was then thought desirable with gas-phase visible region absorption of pure oxygen. Figure 4c shows the absorption spectrum of gaseous O_2 at 150.0 atm and 20° in a 6.5-cm optical path in the 5000–6300-Å region, corresponding to the red chemiluminescence region from 6100 to 7500 Å. The absorption envelope and wavelength correspond well to those reported by Salow and Steiner,[23] who accepted Ellis and Kneser's assignment[9] of this absorption as the simultaneous transition $2[^1\Delta_g] \leftarrow 2[^3\Sigma_g^-]$ for O_2 pairs. We shall discuss this interpretation in the next section. The comparison of the red chemiluminescence of Figure 3c and the corresponding absorption spectrum of Figure 4c shows a classical correlation of 0,0 bands and vibrational envelopes for luminescence and absorption. The 0,2 band for the $2[^1\Delta_g] \rightarrow 2[^3\Sigma_g^-]$ band appears very weakly at 7860 Å in Figure 3d.

The Franck–Condon envelopes for the $2[^1\Delta_g] \leftrightarrow 2[^3\Sigma_g^-]$ absorption and chemiluminescence are in good approximate correspondence; although the absorption contours are accurately given by the dual-beam spectrophotometer, the emission results require plate correction, so are approximate. Seliger's determination[18] yielded a value of 0.6 for the integrated ratio for the 0,1/0,0 solution chemiluminescence bands. Whitlow and Findlay[24] measured 0.93 ± 0.1 for the 6340/7030 Å or 0,0/0,1 band ratio for the electrical discharge gaseous oxygen luminescence. The lack of agreement of these intensity ratios is puzzling; since our absorption data (Figure 4c) were obtained from a dual beam spectrophotometer (1 atm air path blank), any source of error connected with luminescence measurements would be absent. We obtain as integrated areas for 0,0/1,0/2,0 bands (Figure 4c) the values 1.00/1.21/0.09; however, the small optical densities involve an error of *ca.* 10% in these values. It is clear, however, that in the $2[^1\Delta_g] \leftrightarrow 2[^3\Sigma_g^-]$ transition, the 1,0 or 0,1 band is of

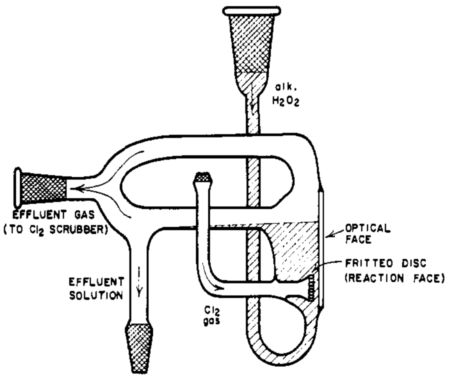

Figure 2. Hirtian apparatus: continuous mixing gas–liquid cell for spectral study of peroxide–hypochlorite chemiluminescence.

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[21] A. Hirt, *Vieux Carré*, New Orleans, La.

[22] G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[23] H. Salow and W. Steiner, *Nature*, **134**, 463 (1934); *Z. Phys.*, **99**, 137 (1936).

[24] S. H. Whitlow and F. D. Findlay, *Can. J. Chem.*, **45**, 2087 (1967).

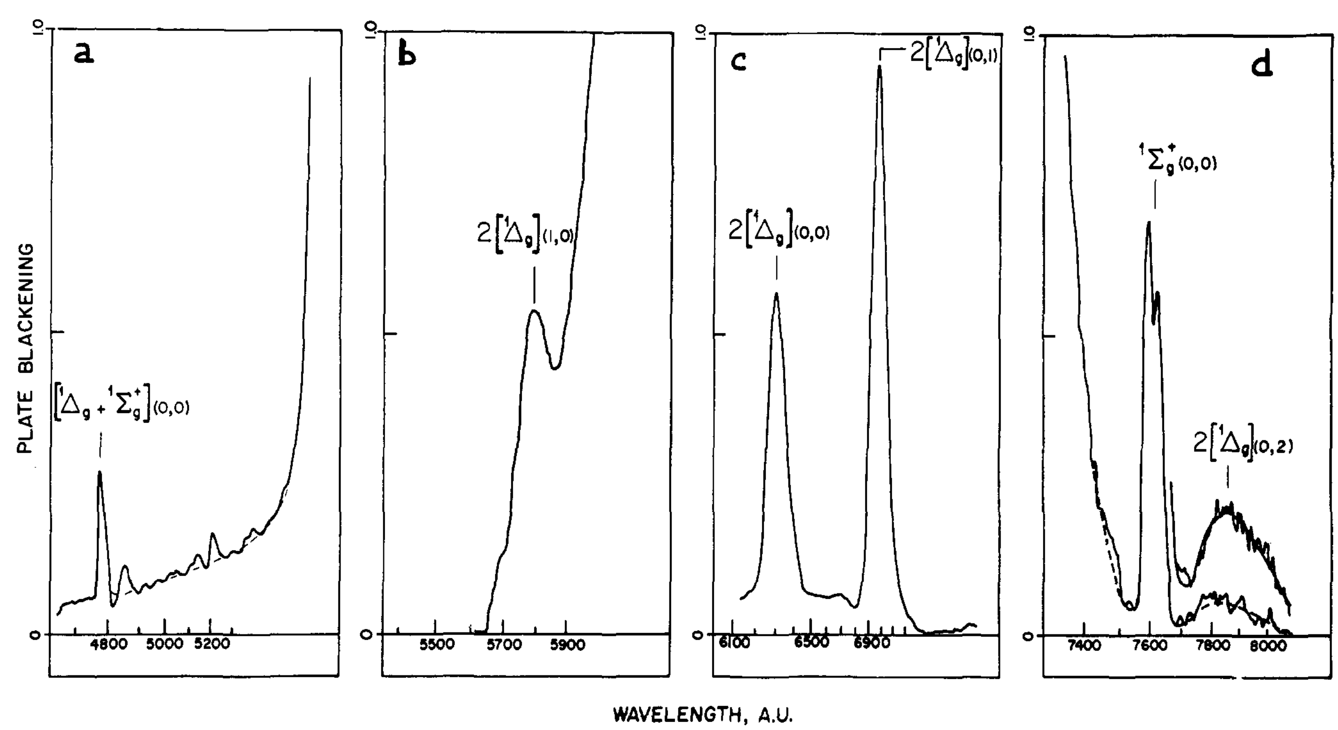

Figure 3. Chemiluminescence bands for the aqueous reaction at 20° of hydrogen peroxide with hypochlorite. Bands labeled according to upper electronic state by energy convention, with vibronic components.

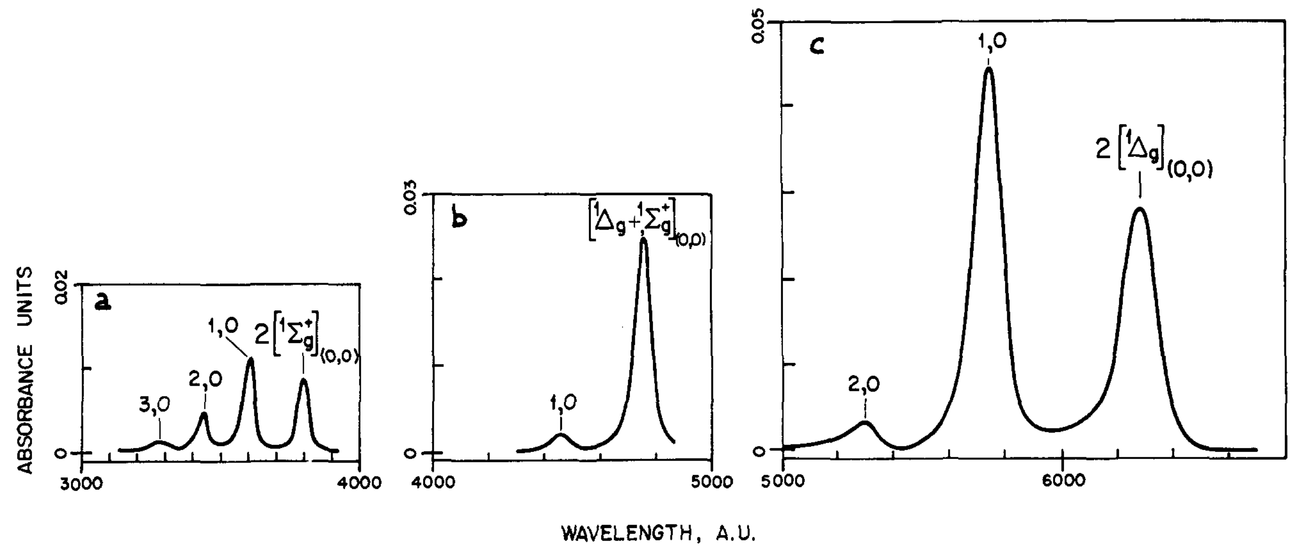

Figure 4. Enhanced optical density absorption spectra of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

comparable intensity to the 0,0 band; a comment on this Franck-Condon anomaly of the simultaneous transition compared with the single-molecule Franck-Condon intensities will be made in the next section.

The 6334- and 7032-Å chemiluminescence bands for the $2[^1\Delta_g] \rightarrow 2[^3\Sigma_g^-]$ transition, in spite of their being effectively gas-phase emissions, proved to be not further resolvable. Using medium focus glass optics at $f/10$ in the Steinheil spectrograph, a setting which revealed[4] rotational structure in the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ solution chemiluminescence bands at 7600 Å, failed to reveal any further detail in the 6334- and 7032-Å bands. This lack of further structure has been confirmed by other workers.[24,25]

The vibrationally excited band 1,0 for the $2[^1\Delta_g] \rightarrow 2[^3\Sigma_g^-]$ reported by Seliger[18] at 5780 Å and assigned by Browne and Ogryzlo[7] is shown in Figure 3b. This appears as an extremely weak shoulder on the high-frequency side of the intense 0,0 band at 6334 Å.

An additional weak but persistent band was found on all plates at about 6700 Å, but is not assigned. It cannot correspond to the 6900-Å 1,0 hot band for $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ reported by Whitlow and Findlay,[24] since their resolved structure clearly shows it to be on the high-frequency side of the 7032-Å band; sighting along

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(25) L. W. Bader and E. A. Ogryzlo, *Discuss. Faraday Soc.*, No. 37, 46 (1964).

this side of the 7032-Å band in our figure is a very slight convexity corresponding to this 1,0 band.

Green Chemiluminescence Bands. The $[^1\Sigma_g{}^+ + {}^1\Delta_g] \rightarrow 2[^3\Sigma_g{}^-]$ Transition. The spectrum for a green chemiluminescence was determined by searching under spectroscopic conditions of extreme sensitivity in the region of the 4770-Å band of gaseous molecular oxygen identified by Salow and Steiner[23] as the 0,0 band of the Ellis and Kneser[9] $[^1\Sigma_g{}^+ + {}^1\Delta_g] \leftarrow 2[^3\Sigma_g{}^-]$ oxygen pair transition. A very sharp green chemiluminescence band was found[5] (Figure 3a) for the Cl_2–alkaline hydrogen peroxide reaction at 4780 Å (20,920 cm^{-1}); only a single band was recorded, which must be the 0,0 band for the oxygen pair $[^1\Sigma_g{}^+ + {}^1\Delta_g] \rightarrow 2[^3\Sigma_g{}^-]$ emission. The corresponding absorption spectrum (Figure 4b) for gaseous molecular oxygen at 150.0 atm in a 6.5-cm optical path, at 20° indicates the close correspondence of the 0,0 bands in absorption and emission, and also that the 0,1 band is expected to be relatively weak, explaining our failure to observe it in the very feeble emission.

The Ultraviolet Bands. The $2[^1\Sigma_g{}^+] \leftarrow 2[^3\Sigma_g{}^-]$ Absorption. The absorption spectrum of gaseous oxygen at 150 atm, in a 6.5-cm optical path, at 20° in the region 3000–4000 Å was determined and is shown in Figure 4a. It is in agreement with the early work of Salow and Steiner,[23] who identified the four bands observed with the 0,0, . . . , 3,0 vibronic components of the $2[^1\Sigma_g{}^+ \leftarrow 2[^3\Sigma_g{}^-]$ oxygen pair transition of Ellis and Kneser.[9] An exhaustive search for chemiluminescence with the alkaline peroxide–Cl_2 reaction in the expected 4000–5000-Å region failed to reveal any bands. Dissolved and gaseous Cl_2 (liberated as a by-product in the exothermic reaction) absorption could possibly screen any feeble emission which would be present. Moreover, studies of the quenching of metastable $^1\Sigma_g{}^+$ oxygen by water[7] indicate that a very small fraction of the $^1\Sigma_g{}^+$ molecules would survive nucleation into bubbles from the water phase, so that emission for a $2[^1\Sigma_g{}^+]$ pair state would be even less likely than from the $[^1\Sigma_g{}^+ + {}^1\Delta_g]$ pair state, which we have found to be extremely weak. Nevertheless, luminescence sensitization experiments clearly indicate that even the $2[^1\Sigma_g{}^+]$ double molecule state has a finite probability of being excited in the peroxide–hypochlorite reactions, as discussed in the next section.[25a]

The Single Molecule $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ Infrared Chemiluminescence. The electrical discharge single-molecule infrared $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ luminescence in gaseous oxygen was first studied by Kaplan[26] at low resolution. We observed this emission as a very weak band in our first peroxide–hypochlorite chemiluminescence studies. The spectrum published by Browne and Ogryzlo[7] revealed weak bands of comparable intensity at 7619 and 7700 Å assigned as 0,0 and 1,1 bands of the $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ transition, and a much weaker band at 8645 Å as a 0,1 band. Using the same medium-resolution equipment described above for the red chemiluminescence bands, the infrared $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ chemiluminescence 0,0 band at 7620 Å (band center) was partially resolved (Figure 3d) into two *rotational* branches[4] even though the chemiluminescence was generated from an aqueous reaction of alkaline peroxide with chlorine.

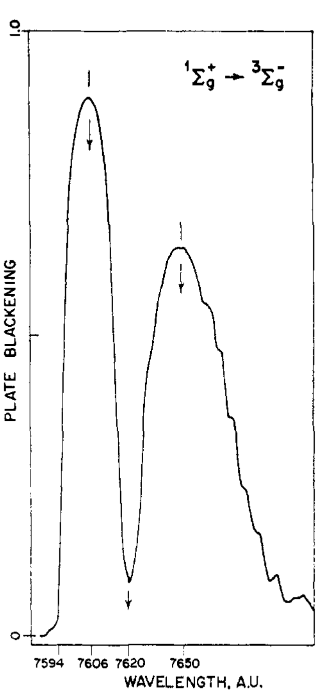

Figure 5. Gas-phase luminescence of molecular oxygen at room temperature in electrical discharge indicating rotational resolution.

The high resolution rotationally resolved spectrum obtained by Branscomb[27] for the $^1\Sigma_g{}^+ \rightarrow {}^1\Sigma_g{}^-$ emission produced in electrodeless discharge in gaseous oxygen reveals a missing Q branch near 7621 Å as expected for the $^1\Sigma$–$^3\Sigma$ band of a diatomic. A Q-branch gap appeared clearly near 7620 Å in the solution chemiluminescence spectrum at medium resolution (Figure 3d). A spectrum of the gas-discharge $^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_g{}^-$ luminescence of O_2 at similar medium resolution is presented in Figure 5. This observation confirmed the qualitative interpretation that the observed chemiluminescence in the aqueous hydrogen peroxide–hypochlorite reaction comes from metastable oxygen molecules which survive as excited molecules upon nucleation into gas bubbles.

A comparison of the absorption envelope for the first vibrational band of the 7620-Å $^1\Sigma_g{}^+ \leftarrow {}^3\Sigma_g{}^-$ transition (Figure 7) and the corresponding emission envelope for the 0,0 band at 7620 Å of the same transition (Figure 3d) reveals identical contours, as is expected for rotational envelopes.

Mechanism of Singlet Oxygen Formation, Simultaneous Transition in Molecular Oxygen Pairs, and Singlet Oxygen Sensitization of Chemiluminescence

Metastable Molecular Oxygen Singlet States, $^1\Delta_g$ and $^1\Sigma_g{}^+$. In molecular oxygen, starting with a single configuration molecular orbital wave function in zeroth order, configurational splitting as a result of electron repulsion leads to three distinct molecular states.

$$[(K)(K)(\sigma_g)^2(\sigma_u)^2(\sigma_g)^2(\pi_u)^4](\pi_g)^1(\pi_g)^1 \equiv {}^1\Sigma_g{}^+ + {}^1\Delta_g + {}^3\Sigma_g{}^- \quad (2)$$

The highest multiplicity state of a given configuration lying lowest leads to a triplet ground state for the even-electron molecule O_2. The ground state of O_2 is thus

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[25a] Note Added in Proof. E. W. Gray and E. A. Ogryzlo, *Chem. Phys. Lett.*, **3**, 658 (1969), have now found gas discharge bands at 3800 and 4000 A corresponding to the O_2-pair uv transition.

[26] J. Kaplan, *Nature*, **159**, 673 (1947); *Phys. Rev.*, **71**, 274 (1947).

[27] L. Branscomb, *ibid.*, **86**, 258 (1952).

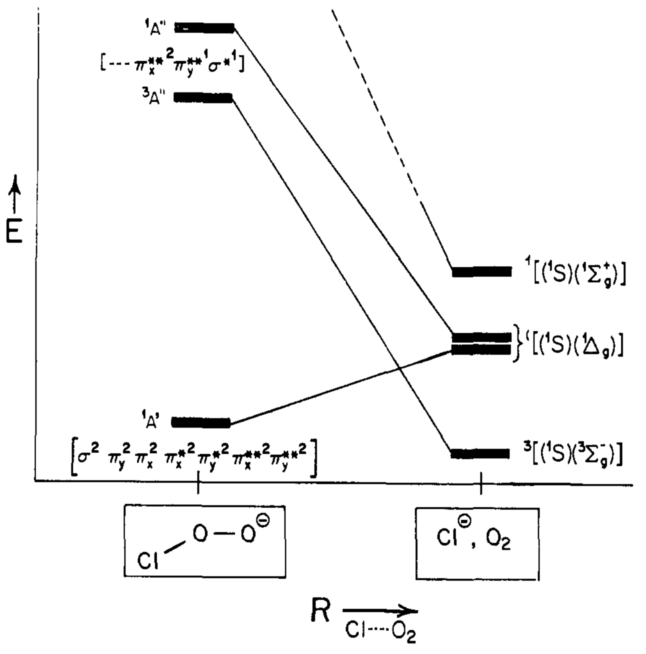

Figure 6. Mechanism of singlet oxygen formation in peroxide oxidation. Spin-state correlation diagram for chloroperoxy ion and its products.

${}^3\Sigma_g{}^-$, with ${}^1\Delta_g$ observed[22] at 7882.4 cm^{-1} (0.9772 eV, 22.544 kcal) and ${}^1\Sigma_g{}^+$ at 13,120.9 cm^{-1} (1.6266 eV, 37.527 kcal) above the ground state, respectively.

The optical transitions ${}^1\Sigma_g{}^+ \leftrightarrow {}^3\Sigma_g{}^-$ and ${}^1\Delta_g \leftrightarrow {}^3\Sigma_g{}^-$ are strictly electric dipole forbidden. The transition ${}^1\Sigma_g{}^+ \leftrightarrow {}^3\Sigma_g{}^-$ represents a spin-forbidden, symmetry-forbidden magnetic dipole transition, with an intrinsic mean radiative lifetime of 7 sec.[28] The transition ${}^1\Delta_g \leftrightarrow {}^3\Sigma_g{}^-$ is a spin-forbidden, symmetry-forbidden, orbitally forbidden magnetic dipole transition with an intrinsic mean radiative lifetime of 45 min.[29] Both of these transitions are pressure sensitive, and acquire electric dipole character through intermolecular perturbation.

The electronic structure and spectra of molecular oxygen have been studied in exhaustive detail.[22,30,31] The *electronic mechanism of chemical production* of singlet molecular oxygen from hydrogen peroxide poses a special problem. It might appear since the three lowest states, ${}^3\Sigma_g{}^-$, ${}^1\Delta_g$, and ${}^1\Sigma_g{}^+$, all arise from the same molecular orbital configuration, that a quantum mechanical analysis based on MO theory could not directly assist in deciding that singlet oxygen should be uniquely evolved by the peroxide–hypohalite reaction (eq 1). The spectroscopic evidence is definite that both ${}^1\Delta_g$ and ${}^1\Sigma_g{}^+$ molecular oxygen are produced, and chemical reactivity studies[32] with singlet oxygen show that the yields of product may exceed 70% and approach unity. The kinetic mechanism of the alkaline-peroxide hypohalite reaction was studied by Cahill and Taube,[33] who used isotopic labeling to prove that the O–O bond of the peroxide did not undergo fission, and that the rate-determining intermediate in the reaction was the chloroperoxy ion OOCl$^-$. It is clear that ionic fission of this species to yield chloride ion must *perforce leave an oxygen molecule with all electrons paired, i.e.*, ${}^1\Delta_g$ oxygen, as deduced from the spin-state correlation diagram (Figure 6). It appears that the reaction

$$ {}^1\Delta_g + {}^1\Delta_g \longrightarrow {}^1\Sigma_g{}^+ + {}^3\Sigma_g{}^- \qquad (3) $$

may account for the presence of ${}^1\Sigma_g{}^+$ in the peroxide system in small amounts, the ratio $[{}^1\Sigma_g{}^+]/[{}^1\Delta_g]$ being[34] less than 10^{-6}.

Simultaneous Transition in Molecular Oxygen Pairs. A spectroscopic summary of the optical absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 20° and 150 atm (6.5-cm cell) is given in Figure 7. In *energy* labeling are designated the vibronic components of the three *simultaneous transitions for molecular oxygen pairs* in the near-uv and visible regions. In the infrared are the vibronic components of the *single molecule* O$_2$ *transitions.*

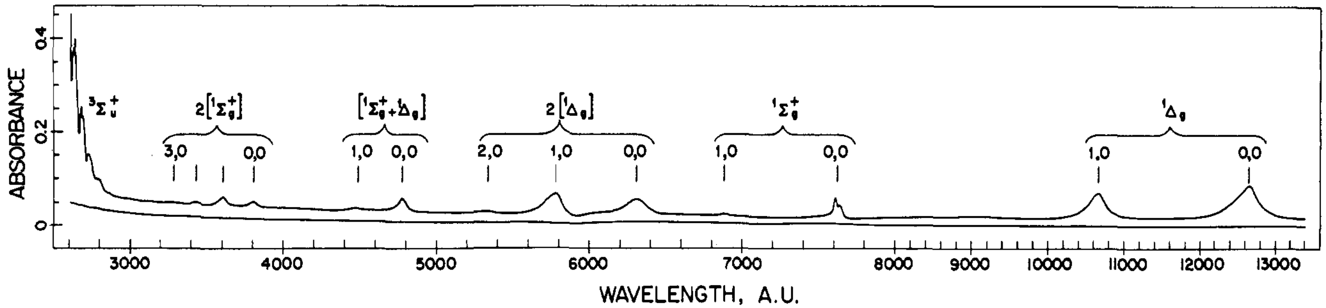

Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

In Figure 8 is given an energy level diagram (wave function labeling) for molecular oxygen using experimental data for the vibronic levels observed by us in absorption at high pressure (~150 atm) in gaseous O$_2$, and in solution chemiluminescence studies. It is striking to note the richness of electronic and vibronic states of molecular oxygen in the near-uv, visible, and near-ir regions.

The possibility of *simultaneous transition* from pairs of metastable singlet molecular oxygen molecules offers a mechanism of "quantum doubling" in the sense that the electron spin coupling collision of two excited molecules can lead to the emission of one photon of additive excitation energy. We may describe the simultaneous transition as a *transition for a pair of atomic or molecular species to an (algebraically) additive composite excited state.*

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[31] J. Slater, "Quantum Theory of Molecules and Solids. I. Electronic Structure of Molecules," McGraw-Hill Book Co., New York, N. Y., 1963, *cf.* Appendix 11, p 294 ff.

[32] (a) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879, 3880 (1964); (b) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

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Experiments on simultaneous transitions in oxygen molecules clearly show that these one-photon two-molecule processes are collisionally induced. The transitions have low oscillator strength and spectrally appear to correspond almost exactly to the sum of the energy of the states of the colliding partners. Robinson,[35] Rettschnick and Hoytink,[36] and Krishna[37] have treated this problem theoretically, and have successfully explained a number of the qualitative aspects for transitions in oxygen pairs. They have shown that forbidden transitions in the single molecules can acquire enhanced transition probability in the complex by borrowing intensity from an allowed (uv) transition under the influence of intermolecular interactions.

We may describe the *intermolecular* enhancement[35–37] of the highly forbidden transitions of molecular oxygen in simple terms involving combined multiplicities for molecular oxygen pair states. The spin-forbidden transition ${}^1\Delta_g \leftrightarrow {}^3\Sigma_g^-$ becomes spin-allowed for the simultaneous transition

$$ {}^1[({}^1\Delta_g)({}^1\Delta_g)] \longleftrightarrow {}^{1,3,5}[({}^3\Sigma_g^-)({}^3\Sigma_g^-)] \qquad (4) $$

The superscript prefix denotes the combined multiplicities for the molecular pairs; in the molecular pair, a singlet–singlet component exists. The Schumann–Runge pair state ${}^{1,3,5}[({}^3\Sigma_u^-)({}^3\Sigma_u^-)]$ could provide the perturbation intensity source. Similarly, the spin-forbidden single molecule transition ${}^1\Delta_g \leftrightarrow {}^3\Sigma_g^-$ may become spin-allowed in the collision pair involving a second normal oxygen molecule

$$ {}^3[({}^1\Delta_g)({}^3\Sigma_g^-)] \longleftrightarrow {}^{1,3,5}[({}^3\Sigma_g^-)({}^3\Sigma_g^-)] \qquad (5) $$

in which a triplet–triplet component now appears. Thus, as the spectra of Figure 7 emphasize, both the simultaneous transitions and the forbidden single-molecule transitions appear with comparable intensity, and all become pressure- or collision-dependent electric dipole transitions. The intrinsic lifetimes of the metastable singlet states of molecular oxygen may become shortened many orders of magnitude by O_2–O_2 collisions, as well as by the influence of other intermolecular collisions. It is characteristic of *vibrationally deficient*[20] molecules to be unusually collision-sensitive, owing to the absence of intramolecular relaxation mechanisms.

The Franck–Condon envelopes observed for the simultaneous transitions in molecular oxygen pairs in some cases differ widely from those of the single molecule transitions. For example, the relative intensities of the (0,0), (1,0), and (2,0) vibronic components in the $({}^1\Delta_g)\,({}^1\Delta_g) \leftarrow ({}^3\Sigma_g^-)\,({}^3\Sigma_g^-)$ transition have ratios (integrated absorption) of 1/1.21/0.1, respectively, whereas both experimental and theoretical values[38] for the single-molecule Franck–Condon factors of the corresponding vibronic components in the ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition have ratios of 1/0.013/0.000, respectively. Similar behavior is shown also in the vibronic intensities of the $({}^1\Sigma_g^+)({}^1\Sigma_g^+) \leftarrow ({}^3\Sigma_g^-)({}^3\Sigma_g^-)$ transition. Such a change of vibronic intensities could come from O_2 distortion due to strong interaction between the two molecules, but for the weakly interacting O_2–O_2 pairs this is not applicable.

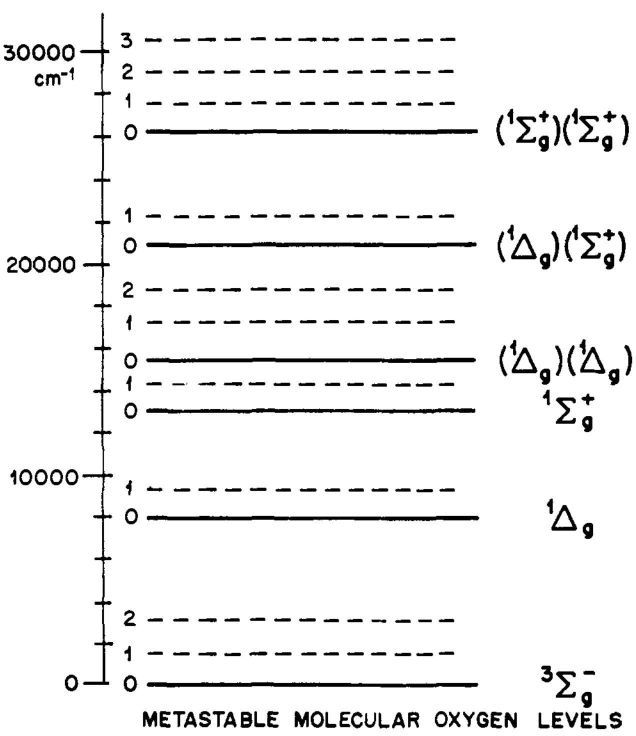

Figure 8. Complete experimental energy level diagram of molecular oxygen up to the near-uv, showing vibronic components observed for single molecule states and simultaneous transition molecular pair states.

Moreover, in the mixed simultaneous transition $({}^1\Sigma_g^+)({}^1\Delta_g) \leftarrow ({}^3\Sigma_g^-)({}^3\Sigma_g^-)$ the vibronic components (0,0) and (1,0) have ratios of about 1/0.06, respectively, which resemble those of the single molecule transitions. The Franck–Condon envelopes for the simultaneous transitions indicate that the Born–Oppenheimer separation of the nuclear and electronic wave functions may not be valid. A detailed investigation of the vibronic coupling is needed. Dianov-Klokov has suggested loss of center of symmetry with vibrational excitation in one member of the molecular pair as a qualitative explanation.[39]

Singlet Oxygen Sensitization of Chemiluminescence. Chemiluminescence is a widely occurring phenomenon which can arise by a variety of mechanisms. The case described by Mallet[11] is of particular interest since it involves observation of organic molecule luminescence in the peroxide–hypochlorite aqueous reaction system. Further studies of this type were described by Kurtz, who studied especially violanthrone luminescence sensitized by the peroxide reaction.[40] It is clear that in all of the cases studied the excitation energy of the metastable singlet oxygen separate molecules would be insufficient to sensitize the luminescence of the organic acceptor molecule. However, the simultaneous transition states of singlet molecular oxygen pairs would possess enough excitation energy to sensitize the luminescence of a suitable organic molecule.

Khan and Kasha[5] have proposed a physical theory of sensitized chemiluminescence for such cases, in which it is assumed that the singlet molecular oxygen produced in the peroxide reaction could transfer excitation energy from simultaneous transition pair states to the organic acceptor. In this mechanism it is assumed that a pene-

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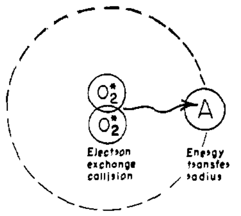

Figure 9. Mechanism of fluorescence sensitization by the O_2^*–O_2^* simultaneous transition pair state.

trating electron exchange collision of the metastable oxygen molecular pairs is required, but that the acceptor molecule may be at a considerable distance as an excitation acceptor (Figure 9), avoiding the usual unfavorable statistics on ternary processes. It is interesting to note that the efficiency of the sensitized "chemiluminescence" in the peroxide systems is much greater than the efficiency of direct oxygen (pair) chemiluminescence. Evidently, the energy transfer step successfully competes with quenching mechanisms for the metastable oxygen.

Ogryzlo and Pearson[41] have suggested an alternative mechanism involving effectively a two-step successive excitation of a very low-lying triplet of the organic acceptor, utilizing the energy of the $^1\Delta_g$ state. But the low energy of this molecular oxygen state (7882.4 cm^{-1}, 0.9772 eV) makes this mechanism unacceptable, since there are almost no organic molecules with such low-lying triplet states. It is possible that the Ogryzlo and Pearson "disproportionation pooling" mechanism would fit the rare cases of molecules with lowest singlet–triplet transitions below 7800 cm^{-1}. Recently Wilson[42] reported a study of rubrene luminescence excited by energy transfer from singlet oxygen. Her studies do not permit an absolute distinction between (a) the two-step excitation of the lowest singlet excited state of the acceptor (rubrene) with the lowest triplet excited state as an intermediate, and (b) the near-triple collision between the acceptor and a "dimol" $[^1O_2]_2$. The latter description conforms to the proposal made by Khan and Kasha[5] as elaborated above.

The study of excitation energy transfer for organic molecules to and from singlet molecular oxygen, or the various simultaneous transition pair states, deserves much additional study. The detailed theoretical mechanisms[43] proposed for such processes may become refined only when the physical criteria become more clearly delineated. A complete spectroscopic study of the resonance conditions for efficient energy transfer in the singlet oxygen molecular and pair states is needed, with a complete correlation with the full electronic energy manifold of the interacting organic molecule.

Summary

Singlet molecular oxygen, once neglected as of mere astrophysical interest, is now being found to be a possibly ubiquitous intermediate in physical, chemical, and biological processes involving molecular oxygen. The many methods now available for its generation and detection allow extensive studies to be made in systems in which it was previously assumed normal ground state oxygen ($^3\Sigma_g^-$) was involved. The extreme metastability of the singlet species ($^1\Delta_g$ and $^1\Sigma_g^+$) and their unique reactivity at normal temperatures make them species of exceptional chemical interest. It is well established now that these excited states of oxygen participate in ordinary chemical steps involving molecular oxygen.

In excitation phenomena, involving photo- and radiation-induced processes, it could also be expected that the metastable singlet molecular oxygen states would be especially prominent. It is now established that in the reversible quenching of excited states of molecules by normal oxygen, and in chemiluminescences accompanying the evolution of molecular oxygen, physical energy transfer steps involve singlet molecular oxygen either as single molecules or as molecular-pair states. These processes are of great importance in photochemistry and photobiology, and their applicability to radiation events should be investigated.

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