Translated from *Uspekhi Khimii*, 50, 406 - 428 (1981) U.D.C. 546.21:541.515

Singlet Oxygen: Methods of Preparation and Detection

N.V.Shinkarenko and V.B.Aleskovskii

An historical account of the discovery of singlet oxygen is given, its physicochemical properties are discussed, and existing methods of preparation and detection are reviewed. 171 references.

CONTENTS

I.	Introduction	220
II.	Methods of preparation of singlet oxygen	222
III.	Methods of detection of singlet oxygen	228

I. INTRODUCTION

15 years ago singlet oxygen was either unknown to most chemists or treated as a spectroscopic state of theoretical interest in the physics of the upper atmosphere. In recent years, however, singlet oxygen has come to the notice of a wide range of researchers. It was shown to have a high reactivity towards many organic compounds, to play an important role in the chemistry of atmospheric pollution, to be involved in the degradation of organic materials by light and oxygen, to take part in the life processes of plants and animals, to behave as a carcinogen, etc.

The first papers dealing specifically with singlet oxygen appeared in the mid-1960's, and by the year 1970 the number of such publications was over 100. According to Kasha and Khan[1] all our views on the participation of molecular oxygen in various chemical and biological systems must now be reconsidered from the standpoint of our new understanding of singlet molecular oxygen. In the Soviet literature very little has been published so far on singlet molecular oxygen. In 1965 Arbuzov referred to singlet oxygen in a review[2] of the oxidation of organic compounds, and a more recent review[3] mentions the quenching of singlet oxygen in the context of the resistance to photo-oxidation of organic compounds. The foreign literature contains a number of reviews dealing with various aspects of the singlet molecular oxygen problem[1,4-15]. In the present review we shall discuss the nature of singlet oxygen and the methods by which it can be prepared and detected.

In Fig.1 the ground state of the oxygen molecule is shown as an energy level diagram[13,16], illustrating the formation of molecular orbitals (MO) following the close approach of two oxygen atoms. Each oxygen atom has eight electrons. Four of these remain in $\sigma(1s)$ and $\sigma^*(1s)$ orbitals, while the next four move into $\sigma(2s)$ and $\sigma^*(2s)$ orbitals. The next six electrons move into three bonding MO: $\sigma(2p_x)$, $\pi(2p_y)$, and $\pi(2p_z)$. The last pair of electrons can be accommodated either on one of the π^* orbitals (if the electrons have opposite spins) or on two MO [$\pi^*(2p_y)$ and $\pi^*(2p_z)$] if the spins are parallel. The latter variant is energetically preferred, because of the large repulsion energy between two electrons in the same orbital: the two electrons are further apart when in different orbitals, and their mutual repulsion is less marked. This preferred electronic configuration is illustrated in Fig.1.

This state of the oxygen molecule is known as the triplet sigma-state ($^3\Sigma$). The higher-energy configuration, in which the last two electrons are located in the same $\pi^*(2p_y)$ orbital, is shown in Fig.2. It corresponds to the lower excited state of the oxygen molecule, which is a singlet state because the electrons are paired. This state of the oxygen molecule is denoted as $^1\Delta$ and lies 22.5 kcal mole^{-1} above the $^3\Sigma$ ground state (Table 1). This energy level was obtained by emission spectroscopy[17], the $^1\Delta \rightarrow {}^3\Sigma$ transition corresponding to a wavelength of 1269 nm (0.9772 eV). The next excited state of the oxygen molecule is 37.5 kcal mole^{-1} above the ground state[17] and has the electronic configuration shown in Fig.3: it is denoted by the symbol $^1\Sigma$. It differs from the $^3\Sigma$ state in that the last two electrons in the π^* orbitals have antiparallel spins in the $^1\Sigma$ state. In terms of group theory and of the theory of symmetry properties these three states of the oxygen molecules can be described as $^3\Sigma_g^-$, $^1\Delta g$, and $^1\Sigma_g^+$ respectively. Some of the characteristics of these three states are listed in Table 1.

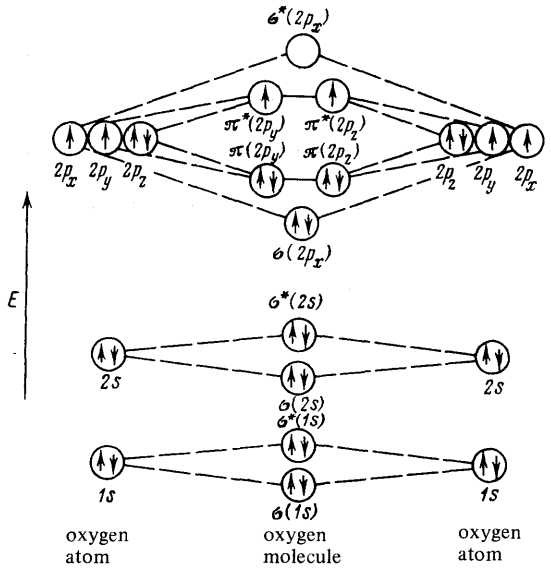


Figure 1. Normal (or triplet) $O_2(^3\Sigma_g^-)$.

The photochemical reactions of organic compounds with molecular oxygen were studied in detail in the first half of the present century. Some of these reactions are of the utmost importance in biological terms. For example, it was shown that some endoperoxides can regenerate an oxygen molecule when heated. Thus red rubrene gives a colourless peroxide when exposed to light in the air, but on being heated it becomes red again and begins to fluoresce[18]. The formal

analogy between this type of reaction and the reversible absorption of oxygen by hemoglobin is evident.

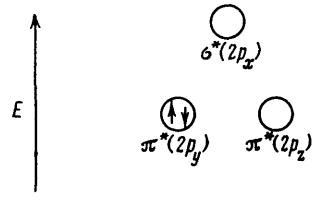


Figure 2. Singlet $O_2(^1\Delta_g)$.

Table 1. Lowest electronic states of an oxygen molecule, and their properties[1].

Electronic state	Life time, s		Relative energy, kcal mole^{-1}	Position of the 0.0 band, λ, nm	Equilibrium internuclear distance, A
	vacuum	solution			
$^1\Sigma_g^+$	7	10^{-11}	37.51	762.14	1.227
$^1\Delta_g$	2700	10^{-6}	22.53	1268.7	1.216
$^3\Sigma_g^-$	∞	∞	0	—	1.207

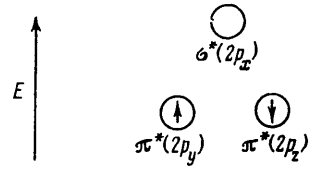


Figure 3. Singlet $O_2(^1\Sigma_g^+)$.

The classical work of Kautsky[19] in the 1930's demonstrated that photo-excitation of a sensitiser in the presence of oxygen can cause oxidation of an organic molecule physically removed from the sensitiser. He concluded that the light energy absorbed by the sensitiser (dye) is transferred to the oxygen (by fluorescence quenching of the dye) which is thus converted from its ground triplet state into one of the excited singlet states ($^1\Delta$ or $^1\Sigma$). The singlet oxygen then attacks the organic molecule, giving the oxidation product[19]. Thus Kautsky's mechanism can be summarised as

$$\begin{aligned} S &\xrightarrow{h\nu} {}^1S \\ {}^1S &\rightarrow {}^3S \\ {}^3S + {}^3O_2 &\rightarrow S + {}^1O_2 \\ {}^1O_2 + A &\rightarrow AO_2 \ . \end{aligned} \qquad (1)$$

Direct energy transfer from the sensitising dye to the organic molecule can be excluded, because the absorption bands of many organic molecules lie at wavelengths shorter than those of the dyes used as sensitisers, and therefore the energy of the excited dye molecules is insufficient to raise these acceptors into their excited states[14].

In the 1940's Terenin generalised Kautsky's model by pointing out that the total electron spin is conserved in this process. He described the energy transfer process as follows[20,21,106]:

$$S[\uparrow][\uparrow] + O_2[\downarrow][\downarrow] \rightarrow \tilde{S}[\uparrow\downarrow][\ ] + {}^1O_2[\uparrow\downarrow][\ ]$$

where the symbol ~ denotes an excess of vibrational energy.

However, Kautsky's mechanism was not accepted by most of the leading foreign workers, and for many years singlet oxygen remained of interest only to astrophysicists and to specialist gas kineticists. However, the situation changed in 1960 when Seliger[22] discovered a red luminescent emission on mixing H_2O_2 and HClO. The spectrum of this radiation, which had been first reported by Mallet 33 years previously[23], was found to consist of a narrow band at 634 nm.

Khan and Kasha[24,25] confirmed Seliger's results and observed an additional band at 703 nm. The separation of these two bands (1567 cm^{-1}) agrees within experimental error with the vibrational frequency of molecular oxygen in the ground state (1580 cm^{-1}); furthermore, the O–O bond in the hydrogen peroxide molecule was shown to remain undisturbed by the reaction

$$H_2O_2 + HClO \rightarrow O_2 + HCl + H_2O \ . \qquad (2)$$

On these grounds the authors ascribed[24,25] this radiation to an excited state of molecular oxygen. Though this assignment was later shown[26] to be only partly correct (see below), Khan and Kasha had correctly associated the luminescence with metastable, excited, singlet oxygen. Following this assignment, Kautsky's hypothesis was more widely accepted.

The same two bands were observed[26] in the radiation from a stream of gaseous oxygen exposed to an electric discharge. The chemiluminescence of the H_2O_2–HClO system was re-examined, and in addition to the bands at 634 and 703 nm a new, weak band was discovered at 762 nm, corresponding to the transition $O_2(^1\Sigma) \rightarrow O_2(^3\Sigma)$, as well as a stong band at 1270 nm, corresponding to the transition $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$.[27] Obviously, the bands at 634 and 703 nm must have the same origin whether the luminescence is produced in solution or in a gas discharge.

It has been suggested[10,26] that the bands at 634 and 703 nm are produced by a dimer consisting of two excited $O_2(^1\Delta)$ molecules, which are deactivated simultaneously and emit a single quantum of energy:

$$2O_2(^1\Delta) \rightarrow 2O_2(^3\Sigma) + h\nu \ . \qquad (3)$$

This transition produces radiation at 634 nm if both molecules of the product are in the vibrational ground state: if one of the product molecules is in the first vibrational level the radiation will be at 703 nm.

The hypothesis of simultaneous electronic transitions was not novel. The absorption bands at 634 and 580 nm in liquid oxygen, which are responsible for its blue colour, had previously been assigned to double transitions of the same type, in which the absorption of one photon causes the simultaneous transfer into excited states of two electrons in two different molecules[28,29]:

$$2O_2(^3\Sigma) + h\nu \rightleftarrows 2O_2(^1\Delta)$$

Thus, the hypothesis put foward by Arnold and coworkers[26] is consistent with earlier reports. The band at 634 nm is convenient for monitoring the concentration of $O_2(^1\Delta)$ singlet oxygen, because its intensity is proportional to the square of the concentration of $O_2(^1\Delta)$ (thus confirming the validity of the hypothesis). In addition to the double transition (3), the following transitions have also been proposed[10,26]:

$$2O_2(^1\Sigma) \rightarrow 2O_2(^3\Sigma) + h\nu_{381\,nm} + h\nu_{381\,nm}$$

$$2O_2(^1\Delta^1\Sigma) \rightarrow 2O_2(^3\Sigma) + h\nu_{478\,nm} \qquad (4)$$

All these dimers are assumed to be simple collisional complexes.

Thus singlet oxygen was rediscovered in the reaction between H_2O_2 and HClO and in a stream of oxygen exposed to an electric discharge. It was later found[30] that the oxidation products of organic molecules exposed to the H_2O_2–NaOCl system are identical to those obtained by the sensitised oxidation of the same acceptors. Excited oxygen molecules generated in a discharge upstream from the organic solution have been shown[31] to react with various substituted anthracenes and alkenes to give oxidation products identical to those of the sensitised photo-oxidation of the same acceptors. These comparisons led to the conclusion that singlet oxygen is the reactive intermediate in sensitised photo-oxidation reactions, as originally suggested by Kautsky.

In a later variant of Kautsky's experiment the sensitiser and the oxygen acceptor were placed on opposite sides of a stearic acid film[32,33]. In spite of the 500 Å separation between the sensitiser molecules and the acceptor, sensitised photo-oxidation took place as a result of diffusion of the singlet oxygen molecules through the film.

Thus Kautsky's mechanism is now universally accepted. On the other hand, up to the mid-1960's the Terenin–Schenck mechanism (called the Schenck mechanism in the foreign literature) was more widely used. Terenin[20,34] and (later) Schenk[35] proposed the following scheme for dye-sensitised photo-oxidation reactions

$$S \xrightarrow{h\nu} {}^1S$$
$${}^1S \rightarrow {}^3S$$
$${}^3S + {}^3O_2 \rightarrow [S \ldots O_2]$$
$$[S \ldots O_2] + A \rightarrow S + AO_2$$

where the metastable $[S...O_2]$ complex is the reactive intermediate which transfers oxygen to the acceptor A.

Following the demonstration[30,31] that singlet oxygen is the active intermediate in many sensitised photo-oxidations, interest in the Terenin–Schenck mechanism began to wane, but there was still no proof that a long-lived complex (as postulated in that mechanism) was not formed as a precursor of the free, singlet molecular oxygen. This important problem has been finally resolved by comparing the effectiveness of oxygen quenching of the fluorescence of pyrene excimers under low- and high-intensity irradiation respectively (using light from a nitrogen laser[36]). Under high irradiation intensity each oxygen molecule can produce 200 excited pyrene excimers, the fluorescence quenching being comparable (~91%) with the quenching observed at very much lower irradiation intensities (93%). In order to explain this effect we have to assume that each O_2 molecule has sufficient mobility to quench ~100–200 pyrene molecules, and therefore that the life time of the pyrene–oxygen complex is less than 2×10^{-10} s. These experiments exclude the possibility of complex formation between an excited pyrene molecule and oxygen, and they also exclude the existence of any excited formation (including oxygen) having a life time greater than 2×10^{-10} s.

A theoretical study of the energies of different states of the $(S...O_2)$ complex has shown[14,37] that though the $({}^3S + {}^3O_2)$ complex corresponds to a weak minimum ($\leq$300 cm^{-1}) this state has a very short life time ($<10^{-10}$ s due to its fast relaxation into lower-lying dissociative states of the complex: $[S...O_2({}^1\Delta)]$ and $[S...O_2({}^1\Sigma)]$, giving $O_2({}^1\Delta)$ or $O_2({}^1\Sigma)$. Obviously, the oxide complex is too short-lived to act as an intermediate responsible for oxygen transfer in sensitised photo-oxidation reactions. Additional evidence against the existence of oxide complexes was provided by measurements[38] of the decomposition kinetics of the endoperoxide of diphenylfuran, aimed at explaining whether oxygen transfer to other oxygen acceptors A occurs by the direct bimolecular reaction

$$DPFO_2 + A \rightarrow AO_2 + DPF$$

or with the participation of a singlet oxygen molecule

$$DPFO_2 \rightarrow DPF + {}^1O_2$$
$${}^1O_2 + A \rightarrow AO_2.$$

In these equations $DPFO_2$ is a molecule of diphenylfuran endoperoxide, A is an oxygen acceptor molecule (tetramethylethylene, cyclohexa-1,3-diene, or rubrene), and DPF is a molecule of diphenylfuran. The results convincingly favour the second mechanism (i.e. the singlet oxygen mechanism).

II. METHODS OF PREPARATION OF SINGLET OXYGEN

Singlet oxygen can be prepared by physical or by chemical methods. The physical methods of preparative value include photo-sensitisation and radio-frequency discharge. Among the chemical methods the most important are the decomposition of hydrogen peroxide by hypochlorite or hypobromite and the decomposition of some ozonides.

1. Formation of Singlet Oxygen in Photo-processes

a) Photo-sensitisation

Photo-sensitised oxidation occurs by the following scheme[39]:

$${}^1S_0 + h\nu \xrightarrow{k_1} {}^1S_1 \text{ (absorption)}$$
$${}^1S_1 \xrightarrow{k_2} {}^1S_0 + h\nu' \text{ (fluorescence)}$$
$${}^1S_1 \xrightarrow{k_3} {}^1S_0 \text{ (internal conversion)}$$
$$\left.\begin{aligned} {}^1S_1 &\xrightarrow{k_4} {}^3S_1 \\ {}^3S_1 &\xrightarrow{k_5} {}^1S_0 \end{aligned}\right\} \text{ (intercombination conversion)}$$
$$\left.\begin{aligned} {}^1S_1 + {}^3O_2 &\xrightarrow{k_6} {}^1S_0 + {}^1O_2 \\ {}^3S_1 + {}^3O_2 &\xrightarrow{k_7} {}^1S_0 + {}^1O_2 \end{aligned}\right\} \text{ (energy transfer; formation of singlet oxygen)}$$
$${}^1O_2 \xrightarrow{k_8} {}^3O_2 \text{ (deactivation of singlet oxygen)}$$
$${}^1O_2 + {}^1A_0 \xrightarrow{k_9} {}^1(AO_2)_0 \text{ (formation of product)}$$

In these equations ${}^1S_0$, ${}^1S_1$, and ${}^3S_1$ are the singlet ground state, the singlet excited state, and the triplet excited state of the sensitiser S, ${}^1A_0$ and ${}^1(AO_2)_0$ are the singlet ground states of the organic molecule A and of the product AO_2, and ${}^3O_2$ and ${}^1O_2$ are the triplet state and the singlet excited state of oxygen ($^3\Sigma$; $^1\Sigma$, and (or) $^1\Delta$ respectively).

One of the most important conclusions from studies of dye-sensitised photo-oxidation reactions is that singlet oxygen molecules can be obtained by energy transfer from the sensitiser molecules in excited triplet or singlet states[6–9]. The mechanism of the energy transfer process is assumed to involve intermediate formation of a contact pair between the sensitiser and the oxygen molecule[14,39,40] (Fig.4). Since the ground state of the organic molecule is singlet, and that of the oxygen is a triplet $^3\Sigma$ state, the ground state of the contact pair (or weak complex) $S...O_2$ must be triplet[40]. Excitation of S or of O_2 produces a series of excited states of the complex: some possibilities are illustrated in Fig.4. In addition to these states of the complex we have to consider states involving charge transfer (CT), formed by the transfer of an electron from S to O_2. For example, for the benzene–O_2 complex the charge transfer complex lies approximately

100 kcal mole^{-1} above the ground state[41]. The next lower excited state of the contact pair is the *F*-state[1,3,5], which can transfer oxygen[4] and from which transitions into the three repulsive states $^3G_0$, $^1X_1$, and $^1X_2$ can be expected. These transitions give oxygen in the ground triplet state and in two singlet states ($^1\Delta$ and $^1\Sigma$) respectively.

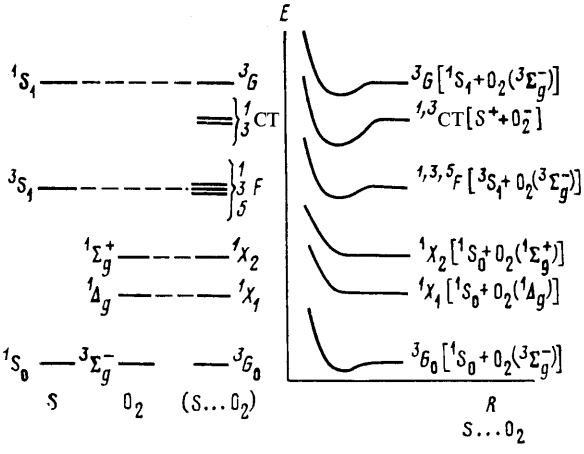


Figure 4. Energy level diagram and potential energy curves for the sensitiser, the oxygen, and the sensitiser–oxygen pair.

Quenching of triplet states by oxygen. Various mechanisms have been proposed to explain the oxygen quenching of molecules in the triplet state[19,42,43]. An analysis[14] of the energy level diagram (Fig.4) was based on the following processes for the quenching of molecules in the triplet state:

$$\begin{aligned}&(a)\ {}^1({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^1\Sigma)\\&(b)\ {}^1({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^1\Delta)\\&(c)\ {}^3({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^3\Sigma)\end{aligned}\qquad(5)$$

The first two mechanisms were first suggested by Kautsky [see Ref.(1)], the third implies an enhancement of the intercombination transition in the S molecule resulting from interaction with the paramagnetic oxygen molecule. Although in principle this process can be assisted by the inhomogeneous magnetic field of the paramagnetic oxygen molecule[43], the effect has been shown[44] to be negligibly small. Furthermore, a study of the quenching of molecules in the triplet state by paramagnetic ions has shown[45] that the quenching efficiency is not correlated to the magnetic moment of the paramagnetic ions.

Another mechanism, proposed by Weiss[42], assumes electron transfer to the oxygen. In most cases this mechanism is excluded by energy considerations (see Fig.4), though it is quite probable in the case of molecules with a very low ionisation potential (amines) in a polar solvent[14].

Direct interaction between a triplet organic molecule and an oxygen molecule in the ground state is another possible quenching mechanism; however, it has been shown experimentally that even in the case of molecules undergoing photooxygenation this reaction is not involved in the quenching of the triplet molecules[14].

Calculations[46] for the aromatic hydrocarbon–oxygen contact pair, with an intermolecular distance of ~4 Å, clearly show that the transfer of energy to triplet oxygen, leading to the formation of $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ (see Eqns.5*a* and 5*b*), should be far more effective (100–1000-fold) than quenching in the ground state without energy transfer (Eqn.5*c*). This is because the process involving the conversion of the smallest amount of electronic energy into vibrational energy will be the predominant one: on the other hand, intercombination transitions always involve the conversion of the largest amount of electronic excitation energy into vibrational energy.

The following unimolecular rate constants have been calculated[40] for the quenching of a molecule in the triplet state having an energy $E_T = 60$ kcal mole^{-1}:

$$\begin{aligned}&{}^1F\rightarrow {}^1X_2\ (10^{12}\ s^{-1};\ \text{energy transfer to } O_2({}^1\Sigma))\\&{}^1F\rightarrow {}^1X_1\ (10^{11}\ s^{-1};\ \text{energy transfer to } O_2({}^1\Delta))\\&{}^3F\rightarrow {}^3G_0\ (10^9\ s^{-1};\ \text{enhanced intercombination conversion}).\end{aligned}$$

The quenching of molecules in the triplet state by oxygen has been studied in the vapour[47–50], the liquid[51–54], and the solid phase[32,55–59]. Evidence that energy transfer to the oxygen is the basic mechanism of the oxygen quenching of triplet molecules has been obtained also by ESR: the quantum yield of the formation of singlet oxygen, which is proportional to the number of triplet molecules of naphthalene produced, was shown[60] by this technique to be ~1.

Since $^1O_2(^1\Sigma)$ has an excitation energy of 37.7 kcal mole^{-1} it can be produced by using sensitisers in which the energy of the triplet excited level is 37.7 kcal mole^{-1}, whereas $^1O_2(^1\Delta)$ can be obtained by energy transfer from any sensitiser of energy >22.6 kcal mole^{-1}. The ratio $O_2(^1\Sigma)/O_2(^1\Delta)$ has been studied[40] as a function of the triplet state energy of the sensitiser. It was found that the quenching of molecules with a high triplet state energy ($E_T > 50$ kcal) produces ~10 times more $O_2(^1\Sigma)$ than $O_2(^1\Delta)$. This is because a smaller amount of electronic energy is converted into vibrational energy by the creation of a $^1\Sigma$ (as compared to a $^1\Delta$) state. In the case of molecules having a triplet state energy <37 kcal only $^1\Delta$ molecules can be formed. For intermediate values of the triplet state energy of the sensitiser molecule ($50 > E_T > 37$ kcal) the ratio $O_2(^1\Sigma)/O_2(^1\Delta)$ falls smoothly to zero (Fig.5).[14]

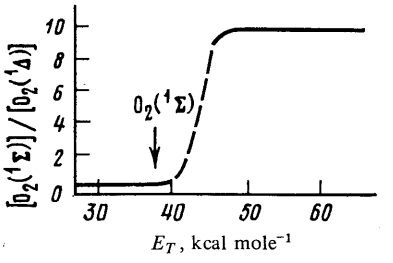


Figure 5. $O_2(^1\Sigma)/O_2(^1\Delta)$ ratio against the triplet state energy of the sensitiser.

Gollnick and coworkers[39] studied the triplet states of various types of sensitiser (dyes, aromatic hydrocarbons, carbonyl compounds). Electronic excitation of aromatic hydrocarbons and dyes give $^3(\pi,\pi^*)$ triplets, whereas carbonyl compounds (except naphthyl phenyl ketones[61] and fluorenone[62]) give $^3(n,\pi^*)$ triplets. As Table 2 shows, the triplet state energies of the sensitisers examined in that work[39] cover the range 30–85 kcal mole^{-1}.

Quenching of singlet states by oxygen (fluorescence quenching). It has long been recognised that oxygen can effectively quench the fluorescence of many organic molecules[63–68], but the mechanism of this effect was not understood. By applying theoretical calculations to the energy level diagram of the sensitiser–oxygen contact pair (Fig. 4) Kearns[14] concluded that relaxation of the excited organic molecule into a state with charge transfer (CT), i.e.

$$^1S_1 + {}^3O_2 \rightarrow (S^+ + O_2^-)$$

is the main mechanism involved in the oxygen quenching of molecules in an excited singlet state, and that the probability of quenching directly to the ground state is very much lower.

Table 2. Lowest triplet state energies of various photosensitisers[39].

Sensitiser	E_T, kcal mole^{-1}	Sensitiser	E_T, kcal mole^{-1}
Azulene	38—31	Pyrene	48.7
Anthracene	42.0	Propiophenone	74.6
Acetophenone	73.6	Rhodamine B	43
Bengal Rose	39,5—42,2	Tetrachlorofluorescein	42.2—44.1
Benzaldehyde	72.0	Tetrachloro-eosin (phloxin)	39.5—42.2
Benzene	84.5	Tetracene	29.4
Benzophenone	68.5	Thioxanthone	65.5
1-Bromonaphthalene	59.0	Triphenylene	66.6
Biphenyl	65.7	Phenanthrene	62.2
Carbazole	70.1	Flavone	62.0
Xanthone	74.2	Fluorene	67.6
Methylene Blue	34	Fluorenone	53.3
Naphthalene	60.9	Fluorescein	45.2—48.1
1-Naphthyl phenyl ketone	57.5	Quinoline	62.0
2-Naphthyl phenyl ketone	59.6	Eosin	43.2—46.0
		Erythrosin	43.1—45.8

The importance of CT states is confirmed, for example, by the much higher (100-fold) effectiveness of NO in quenching the singlet states of hexafluoroacetone[69], since NO has a higher electron affinity than oxygen.

The oxygen quenching of the fluorescence of aromatic hydrocarbons is diffusion-controlled in solution as well as in the vapour phase[69–78].

Generation of singlet oxygen by sensitisers on a solid substrate. A new method of photo-oxygenation, described by Blossey and coworkers[79], relies on the generation of singlet oxygen by a photosensitiser supported on an insoluble polymeric substrate. The sensitiser Bengal Rose was bonded to chloromethylated polystyrene through its carboxyl and (or) phenolic groups. A suspension of sensitiser-coated polymer spheres in a suitable solvent (CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6, CS_2, etc.) containing the organic compound was irradiated in the presence of molecular oxygen. The photo-oxidised product was isolated simply by filtering off the sensitiser spheres and removing the solvent by evaporation. From these experiments the authors concluded[79] that free singlet oxygen is formed with high efficiency by energy transfer from the polymer–Bengal Rose system to the oxygen. The usual problems of photo-sensitised oxydation (solubility of the sensitiser, and its separation, bleaching, regeneration, etc.) are avoided by the use of a heterogeneous method of photo-oxygenation. The sensitiser bonded to the polymer can be re-used without significant loss of effectiveness. Other (related) sensitisers on a polymer substrate were also examined (eosin, fluorescein, chlorophyllin, and hematoporphyrin), but their quantum efficiency towards the singlet oxygenation process was found to be lower than that of Bengal Rose.

Ion-exchange resins, which form strongly bound complexes with ionic sensitisers, can also be used as the solid substrate[80]. Thus, the anionic dyes Bengal Rose and eosin have been introdued into the strongly basic Amberlite IRA-400 anion exchange resin, and the cationic dye Methylene Blue into the strongly acidic Amberlite IRC-200 cation exchange resin. The sensitisers supported on a resin, like those supported on a polymer, act as effective heterogeneous photo-oxidation catalysts.

Following Kautsky's experiments, Nielsson and Kearns[81] developed several heterogeneous sensitisers with an absorption bond. They found that silica gel covered with Bengal Rose or Methylene Blue, or alumina covered with pyrene, offer the same (albeit low) photo-sensitisation efficiency as the corresponding homogeneous systems.

Triphenylmethane dyes are reported[82] to be inactive as sensitisers in solution, but to become active when bound to polymers or used in a solid environment.

An interesting solid-phase, thin-film photochemical singlet oxygen generator has been described[83]. It consists of a water-cooled tube internally coated with a thin solid film of the sensitiser (Bengal Rose), irradiated with a tungsten lamp, and a flask coated with a film of solid rubrene, which acts as a trap for singlet oxygen. An opaque screen separates the tube from the flask so as to avoid self-photosensitised oxidation of the rubrene. The choice of rubrene as a trap was dictated by its high reactivity towards $^1O_2$ coupled with total inactivity towards $^3O_2$, and also by its low volatility. Passing a stream of dry air through the whole system at 3 mmHg for 24 h converted 65% of the rubrene into rubrene peroxide. The reaction was monitored spectroscopically (in benzene, at 494 and 530 nm). However, the reproducibility of the results obtained with singlet oxygen generated by this method is not high[83].

Photo-sensitised generation of singlet oxygen by near infra-red radiation. The generation of $^1O_2$ by irradiation with near infra-red light ($\lambda < 0.9$ μm) from a xenon lamp was first reported by Nathan and Adelman[84], who used the following sensitisers: 1,1′-diethyl-2,2′-tricarbocyanine iodide, xenocyanine, and 3,3′-diethyl-9,11,15,17-dineopentylene-thiapentacarbocyanine iodide. No singlet oxygen was obtained when other sensitisers were used. The reactions were carried out in dioxan and dichloroethane solutions, using 9,10-dimethylanthracene as the acceptor (which was converted into the 9,10-endoperoxide). The progress of the reaction was monitored by the intensity of the 9,10-dimethylanthracene absorption bands at 245 and 265 nm, which are not given by the endoperoxide.

b) Formation of singlet oxygen through charge transfer complexes

This mechanism for the formation of singlet oxygen was proposed after an investigation[85,86] of the reversible absorption of u.v. light (230–400 nm) by olefin–oxygen collision complexes.

Reversible absorption by olefins and aromatic hydrocarbons in the u.v. region, due to the presence of oxygen, has been observed repeatedly in the liquid and the gas phase[43,44,87–93], and was studied in detail in our laboratory[94,95] (see Ref. 95 for a detailed bibliography on this effect). This work led to the firm conclusion that any

compound able to act as an electron donor towards oxygen (aromatic and heterocyclic hydrocarbons, alkenes, and alkanes) can form a charge transfer complex (CTC) with oxygen in which the hydrocarbon acts as an electron donor and the oxygen as the acceptor. As a result, these hydrocarbons show additional absorption in the u.v. or visible region in the presence of oxygen, consisting of a very strong band in the shorter-wave region and much weaker (~100 times) bands in the longer-wave region. The stronger band is due to absorption with charge transfer (between the hydrocarbon and the oxygen), and the weaker bands to singlet–triplet absorption by the hydrocarbon induced by the oxygen (which is forbidden by the selection rules under normal conditions). The spectrum of the original hydrocarbon is shifted towards longer wavelengths by this additional absorption.

Collisions between hydrocarbon molecules (donor, D) and oxygen molecules (acceptor) produce weak complexes (contact pairs) which have a triplet character[86]:

$$^1D_0 + O_2(^3\Sigma) \rightleftarrows {}^3[D \ldots O_2(^3\Sigma)].$$

This complex can absorb light. The result is the transfer of an electron to the acceptor (oxygen) with formation of a charge-transfer complex which can be either in the triplet or in the singlet state, since both D^+ and O_2^- are in doublet states:

$$(a)\ {}^3[D \ldots O_2(^3\Sigma)] \xrightarrow{h\nu} {}^3[D^+ - O_2^-]$$

$$(b)\ {}^3[D \ldots O_2(^3\Sigma)] \xrightarrow{h\nu} {}^1[D^+ - O_2^-]. \qquad (6)$$

In reaction (6a) both the ground state and the CT state are triplet, which makes the transition allowed according to the spin conservation rule.

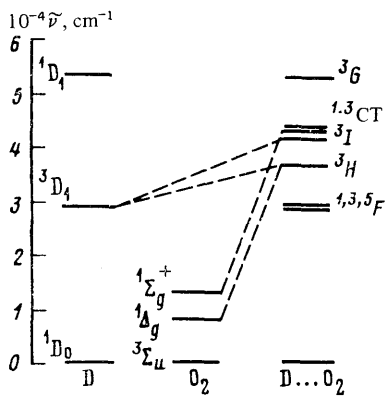


Figure 6. Energy level diagram for the donor, the oxygen, and their 1 : 1 contact pair.

The first excited singlet and triplet states of the donor and of the corresponding 1 : 1 pairs with oxygen in the ground state $O_2(^3\Sigma)$ are $^1D_1$, $^3D_1$, and ^3G, $^{1,3,5}F$ respectively (Fig. 6). The donor molecule in the first excited singlet state $^1D_1$ forms a CTC in the triplet state ^3G with oxygen in the ground state, whereas a donor molecule in the $^3D_1$ state can give quintet (^5F), triplet (^3F), and singlet (^1F) CTC states with oxygen in the ground state. If 1 : 1 pairs are formed between a triplet donor ($^3D_1$) and singlet oxygen in $^1\Delta$ or $^1\Sigma$ states, two additional states (denoted ^3H and ^3I) are created.

The CT state can interact with ^3G, obtaining its energy from the allowed transition between the ground and the singlet excited state of the donor. Similarly, ^3F can interact with ^{3}CT, thus borrowing energy from the CT transition and causing enhanced $S \rightarrow T$ absorption. It was shown[44] that the direct interaction between ^3F and ^3G states has a much weaker influence on the intensity of the $S \rightarrow T$ band than the interaction between the same states through a triplet state with charge transfer. Thus, the additional absorption observed consists of the allowed CT band, which borrows energy mainly from the allowed $^1D_0 \rightarrow {}^1D_1$ transition and also (to a much smaller extent) from the $S \rightarrow T$ band, which is strengthened by the ^{3}CT state. If this path for the internal conversion of energy from ^3G to ^3F through the ^{3}CT state is effective, the CTC in the ^3F state can produce a donor in the triplet state and molecular oxygen in the ground state:

$$^3[^3D_1 + O_2(^3\Sigma)] \rightarrow {}^3D_1 + O_2(^3\Sigma). \qquad (7)$$

An alternative mechanism includes the conversion of ^{3}CT into ^3I and ^3H states, which can then dissociate to give $^1O_2 + {}^3D_1$:

$$(a)\ {}^3CT \rightarrow {}^3I \rightarrow {}^3D_1 + O_2(^1\Sigma)$$

$$(b)\ {}^3CT \rightarrow {}^3H \rightarrow {}^3D_1 + O_2(^1\Delta). \qquad (8)$$

Reaction (7) gives singlet molecular oxygen by energy transfer from the triplet donor to the oxygen in the ground state (Kautsky's mechanism), whereas reaction (8) produces $^1O_2$ directly.

This mechanism for the formation of singlet oxygen is believed[86] to be very important in the chemistry of industrial atmospheric pollution.

c) *Direct optical excitation*

Liquid oxygen (and also gaseous oxygen at high pressure) has a series of bands in the u.v., visible, and i.r. region of the spectrum corresponding to various transitions (see above)[96,97]. The wavelength of the He–Ne laser (623.8 nm) corresponds almost exactly to the absorption band due to the $2O_2(^3\Sigma) \rightarrow 2O_2(^1\Delta)$ transition, and Evans[98] found that irradiation of a solution of 9,10-dimethylanthracene under a high oxygen pressure with light from a He–Ne laser causes photo-oxygenation of the anthracene (in the absence of a sensitiser). The quantum yield of the photo-oxidation was only 0.13, but it could be raised to ~0.6 by using a more reactive acceptor of singlet oxygen (1,3-diphenylisobenzofuran, DPBF). By using a range of different light sources Evans[98] established an approximate "action spectrum" for photo-oxidation by light of different wavelengths, and he showed that only light of wavelength corresponding to the known absorption bands of oxygen is active in promoting oxidation reactions. Though this method of generating singlet oxygen has little preparative value it is important in studies of the mechanism of various reactions involving singlet oxygen.

d) *Photolytic generation of singlet oxygen*

The photolysis of ozone is another method of producing $^1\Sigma$ and $^1\Delta$ oxygen in a gaseous system[99–104]:

$$O_3 + h\nu \rightarrow O_2[^1\Sigma \text{ or } {}^1\Delta) + O(^1D \text{ or } {}^3P).$$

From energy considerations we can establish the threshold

wavelengths for the direct production of $O_2(^1\Sigma)$ and $O_2(^1\Delta)$ by ozone photolysis. In principle the photolysis of ozone at $\lambda = 253.7$ nm can give either $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ plus an atom of oxygen in the excited ^1D state, but in practice only $O_2(^1\Delta)$ is obtained[100]. Formation of $O_2(^1\Sigma)$ takes place by the following side reaction, involving energy transfer from an excited oxygen atom to molecular oxygen in the ground state[99,101,102,105]:

$$O(^1D) + O_2(^3\Sigma) \rightarrow O(^3P) + O_2(^1\Sigma).$$

The following reactions (which also take place in the system),

$$O(^1D) + O_2(^3\Sigma) \rightarrow O_2(^1\Delta) + O(^3P)$$
$$O_3 + h\nu_{253.7\,nm} \rightarrow O_2(^1\Sigma) + O(^1D)$$

are only minor sources of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$.[100] It has been shown[14] that $O_2(^1\Sigma)$ can be obtained also by the photolysis of molecular oxygen from the reactions

$$O_2 + h\nu_{147\,nm} \rightarrow O(^1D) + O(^3P)$$
$$O(^1D) + O_2(^3\Sigma) \rightarrow O_2(^1\Sigma) + O(^3P).$$

2. Chemical Sources of Singlet Oxygen

a) Decomposition of hydrogen peroxide

The decomposition of hydrogen peroxide according to Eqn.(2) was used in the first definite demonstration of the participation of singlet oxygen in sensitised photo-oxidation reactions[30,107–109].

In the absence of organic compounds the resulting singlet oxygen is deactivated (with chemiluminescence) to triplet oxygen[107]. By comparing the chemiluminescence bands with the emission bands of gaseous oxygen in an electric discharge and with the absorption bands of liquid oxygen it was established that the decomposition of hydrogen peroxide gives a high yield of singlet oxygen molecules[24,25,107,108,110–112]. The chemiluminescence is produced by double molecular transitions [see Eqns.(3) and (4)] as well as by the single molecular transitions

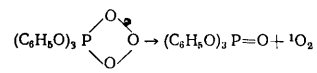
$$O_2(^1\Sigma) \rightarrow O_2(^3\Sigma) + h\nu_{760\,nm}$$
$$O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + h\nu_{1270\,nm}. \qquad (9)$$

Studies of chemiluminescence[24,25,107,110] have yielded some other interesting results. Firstly, this work showed that the strongest band in the chemiluminescence spectrum (703.2 nm) results from a cooperative transition involving a pair of $O_2(^1\Delta)$ molecules, which is explained by the generation of large amounts of excited singlet oxygen during the decomposition of H_2O_2. Secondly, in solutions the chemiluminescence band at 760 nm [for the $O_2(^1\Sigma) \rightarrow O_2(^3\Sigma)$ transition] has a rotational fine structure which suggests that the radiation is from singlet oxygen molecules in gas bubbles[108] rather than from dissolved oxygen. Though the rotational structure has not been resolved in the other bands it is assumed that the whole of the radiation comes from oxygen molecules in the gas phase, because the life time of singlet oxygen in solution is very much shorter than in the gas phase (see Table 1).

The yield of singlet oxygen during the decomposition of hydrogen peroxide is very sensitive to the nature of the solvent[113]. In methanol the yield is 70%, and high yields are obtained also in ethanol and in a methanol–t-butanol mixture. In other solvents miscible with water the yield is usually <10%.[113] This effect is not understood at present. Since photo-sensitised oxygenation is not sensitive to the solvent it follows that the nature of the solvent can influence the formation of singlet oxygen but not its reactions[7].

b) Decomposition of ozonides

One of the most convenient methods of chemical generation of singlet oxygen is the decomposition of the adduct of triphenyl phosphite with ozone, which can be prepared at −70 °C. When heated to −35 °C this compound gives singlet molecular oxygen by the reaction[114–118]:



The proof of the formation of singlet oxygen by the decomposition of this adduct rests on the observation that various oxygen acceptors can be oxidised by it to give the same products as the recognised reactions of singlet oxygen with the same acceptors. Wasserman and coworkers[119] showed by ESR spectroscopy that the decomposition of this ozonide produces $O_2(^1\Delta)$, which could be detected in the gas phase after being evolved from the solution. However, the possibility of complicating side reactions was later pointed out[120]. Tetramethylethylene (TME) was found to react with triphenylphosphiteozone at −60 °C, i.e. below the temperature at which the rate of decomposition of the adduct is sufficient to produce free oxygen in substantial amounts. Furthermore, by comparing the reactions of this adduct with TME and with 2,5-dimethylfuran (another effective acceptor of singlet oxygen) we note that TME is the more effective acceptor towards this adduct whereas in the sensitised oxidation reactions the opposite is true.

This work[120] led to the conclusion that direct transfer of O_2 from triphenylphosphiteozone (by an alternative mechanism) must be possible. The mechanism yields the same products as the reaction with free singlet oxygen, but it has a different selectivity towards various organic compounds. The study was extended to other alkenes[121], and direct transfer of O_2 from the adduct to the acceptor was again observed. In this sense the ozonides are very similar to the molecular oxides of Terenin and Schenck's mechanism[14,20,34,35].

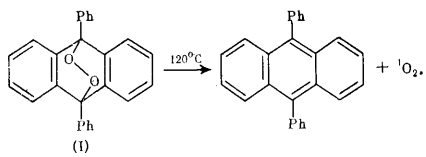
The ozonides of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane[122] and 1-phospha-2,8,9-trioxa-adamantane[123] have also been used as sources of singlet oxygen, which they generate at somewhat higher (and more convenient) temperatures.

c) Decomposition of endoperoxides

Various aromatic hydrocarbons (especially linear polyacenes) undergo sensitised photo-oxidation reactions in the presence of oxygen to give endoperoxides which dissociate on heating, regenerating the initial hydrocarbon and free molecular oxygen[9,124]. Theoretical considerations suggest that the oxygen generated by the dissociation of endoperoxides can be in an excited singlet state[125].

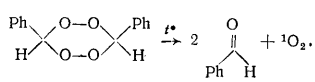
Wasserman and Scheffer[126] showed that the decomposition of 9,10-diphenylanthracene peroxide (I) in the presence of suitable acceptors of singlet oxygen can be used to promote

typical singlet oxygen reactions:



(I)

Similarly, singlet oxygen can be generated[127] by heating 3,6-diphenyl-1,2,4,5-tetroxan (II):



d) Decomposition of the O_2^- ion

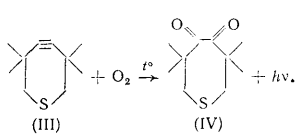
The peroxide ion O_2^- is a potential source of singlet oxygen, since by losing an electron of the appropriate spin it can give either molecular oxygen in the ground state or singlet excited oxygen[14]:

$$^2O_2^- \rightarrow {}^{1,3}O_2 + e^-$$

Evidence of sensitised fluorescence has been detected[128] by adding various fluorescent dyes to a saturated solution of potassium peroxide in dimethylsulphoxide. This was interpreted[128] as evidence for the formation of singlet oxygen in this system, but other chemiluminescence mechanisms cannot be excluded, and doubts were later expressed[129] on this conclusion.

e) Thermal preparation of singlet oxygen

Turro and coworkers[130] reported that the seven-membered alkyne compound 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (III) when heated (~90 °C) in the dark in the presence of atmospheric oxygen yields the dione (IV) with chemiluminescence [Eqn.(10)]:



(III) (IV) (10)

The same product is obtained by the reaction between the compound (III) and singlet oxygen. Since atmospheric oxygen is triplet, intercombination conversion must be taking place at some stage during reaction (10). The authors conclude[130] that a reactive intermediate (probably an ionic acetylene–oxygen adduct) is formed during the reaction. They suggest that the triple bond in this adduct increases the probability of finding both the electrons from the electron pair of the oxygen molecule on the same oxygen atom, and hence it increases the probability of forming singlet oxygen by the pairing of these electrons.

Free singlet oxygen is generated by the decomposition of the acetylene–oxygen intermediate complex. In this way the starting compound is regenerated, and therefore the process can be classified as a catalytic thermal generation of singlet oxygen from triplet oxygen. This process could be very important in biological systems.

f) Other chemical sources of singlet oxygen

Peroxyacetyl nitrate (PAN), a component of smog, is easily decomposed in the presence of bases[14]:

$$CH_3\overset{O}{\overset{\|}{C}}OONO_2 + 2OH^- \rightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + H_2O + NO_2^- + O_2.$$

Steer and coworkers[131] studied this reaction, and detected a weak radiation at 1270 nm during the decomposition of PAN which they assigned to the $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$ transition. They ascribed the high reactivity of PAN in chemical and biological systems to its ability to generate singlet oxygen.

Some other compounds also could be of interest for the generation of singlet oxygen. They include the monomeric adducts of oxygen with various transition metals[132–135], and also clathrate oxygen compounds[136]. It has been reported[137] that even in oxyhemoglobin singlet oxygen is formed in the light by a reaction photosensitised by heme:

$$Hem—{}^3O_2 \overset{h\nu}{\rightleftarrows} {}^1Hem^*—{}^3O_2 \rightarrow Hem + {}^1O_2.$$

Although heme does not fluoresce, and hence cannot sensitise the formation of $^1O_2$ in the normal way, its physical proximity to an oxygen atom in the oxyhemoglobin molecule appears to compensate for the short life time of the excited state[137].

3. Electrical Discharge

In this physical method of generating singlet oxygen, discovered by Noxon[138] and developed by various workers[12,111,139,140], an electrodeless microwave or radio-frequency discharge in a stream of oxygen in a discharge tube produces ~10% of $O_2(^1\Delta)$. A mass spectroscopic study of this reaction[142] has shown that the $O_2(^1\Delta)$ continues to exist beyond the discharge region. A small amount of $O_2(^1\Sigma)$ is also produced in the discharge[143], but it rapidly relaxes to $O_2(^1\Delta)$. Oxygen atoms are also formed in the electric discharge, but they can be removed by placing a film of mercuric oxide between the discharge and the observation point[144].

Ozone is another component formed in the discharge. It can react with $O_2(^1\Sigma)$ according to the equation[145]

$$O_2(^1\Sigma) + O_3 \rightarrow O_2 + O_2 + O.$$

The oxygen atoms produced by this reaction can react with a further molecule of ozone:

$$O + O_3 \rightarrow 2O_2.$$

In the absence of ozone and other gases the de-activation of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ occurs mainly through collisions with the walls of the flow system[140].

4. Incandescent Lamps as Sources of Singlet Oxygen

Khan has shown[146] that electronically excited molecular oxygen can be generated by an ordinary tungsten filament lamp. He found that the radiation from a tungsten filament lamp consists of a series of distinct peaks on a continuous background, and he noted that these peaks correspond to emission bands which had been previously assigned to simultaneous transitions of oxygen pairs. It is assumed that excited oxygen molecules are formed on the tungsten surface, and are then emitted from this surface[147].

Spectroscopic observations[146] have led to the suggestion[14] that the weak luminescence at 520–620 nm which accompanies the chemisorption of oxygen on clean tungsten surfaces[148] may also be due to radiation from excited oxygen molecules.

A relationship between the weak luminescence observed[149] at 600–800 nm during the adsorption of oxygen molecules on various solid oxide surfaces and the formation of singlet oxygen molecules is also possible.

III. METHODS OF DETECTION OF SINGLET OXYGEN

1. Gas-phase Methods

Various methods of detecting singlet oxygen in the gas phase are discussed in recent reviews[1,12,14].

a) Paramagnetic resonance

Oxygen in the $^1\Delta$ state is paramagnetic by virtue of its orbital angular momentum, and several workers[60,119,150–152] have observed and analysed the paramagnetic resonance spectrum of $O_2(^1\Delta)$ in a discharge. In particular, signals corresponding to transitions with $\Delta M = 1$ have been observed for states with a full angular momentum $J = 2$ in addition to the normal signals for the triplet ground state of oxygen. In this way it was shown that the concentration of $O_2(^1\Delta)$ is 10% of the total concentration of oxygen in the discharge. The same method has been used to demonstrate the formation of $O_2(^1\Delta)$ in the gaseous decomposition products of the triphenyl phosphite–ozone adduct[119], and the formation of $O_2(^1\Delta)$ by energy transfer from sensitisers in the triplet state[60,152].

The EPR method is specific for the $^1\Delta$ state of oxygen, because the $^1\Sigma$ state is diamagnetic.

b) Emission spectroscopy

Optical radiation from the $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ molecules can be detected in the gas phase[10,26,27,110,138,139,153–157]. Single molecular transitions occur at 1270 and 760 nm respectively [see Eqn.(9)]. At high oxygen pressures the cooperative (or bimolecular) radiation bands at 634 and 703 nm are easily observed [see Eqn.(3)], as well as the weaker bands at 381 and 478 nm [Eqn.(4)].

An important advantage of the emission spectroscopy method is its ability to detect both $O_2(^1\Sigma)$ and $O_2(^1\Delta)$ over a wide pressure range, whereas by the EPR method $O_2(^1\Delta)$ can be detected only at pressures of several Torr. The sensitivity of the method can be raised still further by using a reflective amplifier to detect the radiation[158].

c) Photo-ionisation

The ionisation potentials of singlet oxygen molecules in $^1\Delta$ and $^1\Sigma$ states are lower (by 1.0 and 1.6 eV respectively) than the ionisation potential of the $^3\Sigma$ ground state (12.5 eV).[159] The photo-ionisation method of detecting excited oxygen is based on this difference[160–163]. The method was used initially with monochromatic excitation[160–162], but later a large increase in sensitivity was obtained by using the resonance lines of the inert gases to ionise excited oxygen molecules[163]. For example, the krypton line at 1165 Å selectively ionises $O_2(^1\Sigma)$, whereas the argon resonance lines at 1067 and 1048 Å ionise both $O_2(^1\Delta)$ and $O_2(^1\Sigma)$, but not $O_2(^3\Sigma)$. The method has yielded valuable information on the rate constants of various reactions of singlet oxygen in the gas phase.

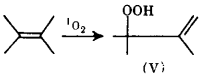
Though the photo-ionisation method is very sensitive, its applications are limited, because the method is not appropriate to systems containing organic molecules, oxides of nitrogen, or other compounds having an ionisation potential lower than 11 eV.

d) Calorimetry

The isothermal calorimetric method of detecting $O_2(^1\Delta)$ depends on the efficient deactivation of this species on a cobalt-coated platinum wire[10,110,111,164]. The heated wire is exposed to the gas stream, and the concentration of excited oxygen molecules can be calculated from the quantity of heat generated by the deactivation process. It has been shown[10,110] that a wire coated with cobalt can deactivate more than 95% of the $O_2(^1\Delta)$ present in the gas stream. The main disadvantage of this method is its lack of selectivity, since $O_2(^1\Sigma)$, atomic oxygen, and any other species in an excited state present in the gas can contribute to the heat evolution.

2. Methods of Detecting Singlet Oxygen in the Condensed Phase. Effect of the Solvent on the Life Time of Singlet Oxygen

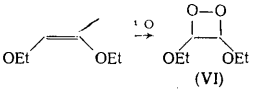
Since the life time of singlet oxygen in the condensed phase is approximately eight orders of magnitude [for $O_2(^1\Delta)$] and ten orders of magnitude [for $O_2(^1\Sigma)$] lower than in the gas phase (see Table 1), most of the methods used to detect singlet oxygen in the gas phase are inappropriate for solutions. Chemical methods are used for solutions, but they are not always reliable. Thus, the reaction of TME with singlet oxygen produces the rearranged allyl hydroperoxide (V):[6,7,30]



(V)

The formation of this hydroperoxide is usually taken as an indication of the presence of $^1O_2$.[85,128] However, there is evidence that this allyl hydroperoxide is formed also when TME reacts with oxygen in the ground state by a chain reaction mechanism including free-radical intermediates[120,165,166].

Singlet oxygen reacts with vinyl diethers to form dioxetanes (VI):[14]



(VI)

However, the same products can be obtained from "non-singlet" oxidation reactions[167], and additional experiments are needed to exclude other possible reactions. These involve adding one or two singlet oxygen fluorescence quenchers (for example, β-carotene, or a tertiary amine such as 1,4-diazobicyclo[2,2,2]octane), and also a typical inhibitor of free-radical auto-oxidation (a substituted phenol). The role of singlet oxygen can be inferred from a comparison of the two experiments.

Of all the reactions examined only the 1,4-cycloaddition to conjugated dienes can be used as an unambiguous test of the presence of singlet oxygen, since no other reagent appears to give the same product[165].

A new method of detecting singlet oxygen in solutions, based on measurements of the life time of singlet oxygen in solutions by infrared spectroscopy, was developed by Merkel

and coworkers[168,169]. These workers found that the life time of singlet oxygen is surprisingly very sensitive to the nature of the solvent. They generated[168,169] singlet oxygen ($\sim 5 \times 10^{-5}$ M) by energy transfer from Methylene Blue triplets excited by light pulses from a ruby laser. The singlet oxygen was then determined spectroscopically by its reaction with the coloured acceptor DPBF to give a colourless product. Measurements of the bleaching rate at two different acceptor concentrations gave the life time of the singlet oxygen and the rate constant of the reaction. When the concentration of DPBF was too low for this reaction to be the main deactivation path of the $O_2(^1\Delta)$ the life time of the singlet oxygen was calculated directly.

Table 3. Solvent dependence of the life time of $O_2(^1\Delta)$.[168,169]

Solvent	Water	Heavy water	Methanol	Ethanol	Cyclohexane	Benzene	Acetone	Chloroform	Hydrogen sulphide	Carbon tetrachloride
Life time of $O_2(^1\Delta)$, μs	2	20	7	12	17	24	26	60	200	700

Table 4. Solvent dependence of the life time of $O_2(^1\Delta)$.[171]

Solvent	n-Butanol	t-Butanol	Benzene methanol (4:1)	Bromobenzene/methanol (4:1)	Pyridine	Dioxan
Life time of $O_2(^1\Delta)$, μs	19±3	34±4	26±5	23±4	33±15	32±10

The results[168,169] revealed no correlation between the life time of the singlet oxygen and properties of the solvent such as the viscosity and dielectric constant. The same conclusion was reached independently in another investigation[170]. Merkel and coworkers[168,169] also found that the life time of singlet oxygen is 10 times higher in D_2O than in ordinary water (see Table 3).

More recently, measurements of life time by flash photolysis have been reported for other solvents (see Table 4).[171]

The deuterium isotope effect has been used[168,169] as a new method of detecting singlet oxygen in solutions. By monitoring the rate of bleaching of DPBF (10^{-5} M) in H_2O/CH_3OH (1:1) and D_2O/CD_3OD (1:1) mixtures under otherwise identical conditions they noted a ten-fold increase in the effectiveness of photo-oxidation in the deuterated solvent. Since the rate constant was unaffected by the deuteration, a ten-fold increase in the life time of singlet oxygen was inferred from these observations.

REFERENCES

1. M.Kasha and A.U.Khan, Annals New York Acad. Sci., 171, 5 (1970).
2. Yu.A.Arbuzov, Uspekhi Khim., 34, 1332 (1965) [Russ.Chem.Rev., No.8 (1965)].
3. V.Ya.Shlyapintokh and V.B.Ivanov, Uspekhi Khim., 45, 202 (1976)[Russ.Chem.Rev., No.2 (1975)].
4. K.Gollnick and G.O.Schenck, Pure Appl.Chem., 9, 507 (1964).
5. K.Gollnick and G.O.Schenck, Symposium "1-4 Cycloaddition Reactions" (J.Hamer, Editor), Academic Press, New York, 1967, p.255.
6. C.S.Foote, Science, 162, 963 (1968).
7. C.S.Foote, Acc.Chem.Res., 1, 104 (1968).
8. K.Gollnick, Adv.Chem.Ser., 77, 78 (1968).
9. K.Gollnick, Adv.Photochem., 6, 1 (1968).
10. S.J.Arnold, M.Kubo, and E.A.Ogryzlo, Adv.Chem. Ser., 77, 133 (1968).
11. T.Wilson and J.W.Hastings, Photophysiology, 5, 49 (1970).
12. R.P.Wayne, Adv.Photochem., 7, 311 (1969).
13. M.L.Kaplan, Chem.Technol., 621 (1971).
14. D.R.Kearns, Chem.Rev., 71, 395 (1971).
15. W.Adam, Chemiker-Zeitung, 99, 142 (1975).
16. G.Pimentel and R.Spratley, "How Quantum Mechanics Explains the Chemical Bond" (Translated into Russian), Izd.Mir, Moscow, 1973, p.115.
17. G.Herzberg, "Molecular Spectra and Molecular Structure. Vol.1. Spectra of Diatomic Molecules", Van Nostrand-Reinhold, New York, 1950, pp.217, 320.
18. C.Moureu, C.Dufraisse, and P.M.Dean, Compt. rend., 182, 1584 (1926).
19. H.Kautsky, Trans.Faraday Soc., 35, 216 (1939).
20. A.N.Terenin, Zhur.Fiz.Khim., 18, 1 (1944).
21. A.N.Terenin, Izv.Akad.Nauk SSSR, Ser.Fiz., 9, 305 (1945).
22. H.H.Seliger, Analyt.Biochem., 1, 60 (1960).
23. L.Mallet, Compt.rend., 185, 352 (1927).
24. A.U.Khan and M.Kasha, J.Chem.Phys., 39, 2105 (1963).
25. A.U.Khan and M.Kasha, J.Chem.Phys., 40, 605 (1964).
26. S.J.Arnold , E.A.Ogryzlo, and H.Witzke, J.Chem. Phys., 40, 1769 (1964).
27. R.J.Browne and E.A.Ogryzlo, Proc.Chem.Soc., 117 (1964).
28. J.W.Ellis and H.O.Kneser, Z.Physik, 86, 583 (1933).
29. V.I.Dianov-Klokov, Optika i Spektrosk., 6, 457 (1959).
30. C.S.Foote and S.Wexler, J.Amer.Chem.Soc., 86, 3879 (1964).
31. E.J.Corey and W.C.Taylor, J.Amer.Chem.Soc., 86, 3881 (1964).
32. B.Schnuriger and J.Bourdon, Photochem.Photobiol., 8, 361 (1968).
33. J.Bourdon and B.Schnuriger, Symposium "Physics and Chemistry of the Organic State. Vol.3" (D.Fox, M.M.Labes, and A.Weissberger, Editors), Interscience, New York, 1967, p.59.
34. A.N.Terenin, "Fotokhimiya Krasitelei i Rodstvennykh Organicheskikh Soedinenii" (Photochemistry of Dyes and Related Organic Compounds), Izd.Akad.Nauk SSSR, Moscow-Leningrad, 1947, Ch.7.
35. G.O.Schenck, Naturwiss., 35, 28 (1948).
36. I.B.Berlman, C.R.Goldschnidt, G.Stein, Y.Tomkiewiz, and A.Weinreb, Chem.Phys.Letters, 4, 338 (1969).
37. A.U.Khan and D.R.Kearns, J.Chem.Phys., 48, 3272 (1968).
38. A.M.Trozzolo and S.R.Fahrenholtz, Annals New York Acad.Sci., 171, 61 (1970).
39. K.Gollnick, T.Franken, G.Schade, and G.Dörhöfer, Annals New York Acad.Sci., 171, 89 (1970).
40. A.U.Khan and D.R.Kearns, Adv.Chem.Ser., 77, 143 (1968).

41. E.C.Lim and V.L.Kowalski, J.Chem.Phys., **36**, 1729 (1962).
42. J.Weiss, Trans.Faraday Soc., **35**, 48 (1939).
43. D.Evans, J.Chem.Soc., 1351, 3885 (1957).
44. H.Tsubomura and R.S.Mulliken, J.Amer.Chem.Soc., **82**, 5966 (1960).
45. G.Porter and M.R.Wright, Discuss.Faraday Soc., **27**, 18 (1959).
46. K.Kawaoka, A.U.Khan, and D.R.Kearns, J.Chem. Phys., **46**, 1842 (1967).
47. G.Porter and P.West, Proc.Roy.Soc., A, **279**, 302 (1964).
48. R.B.Cundall, G.B.Evans, and E.J.Land, J.Phys. Chem., **73**, 3982 (1969).
49. A.Gandini and K.O.Kutschke, Canad.J.Chem., **44**, 1720 (1966).
50. T.N.Rao, S.S.Collier, and J.G.Calvert, J.Amer. Chem.Soc., **91**, 1609 (1969).
51. S.Kusuhara and R.Hardwick, J.Chem.Phys., **41**, 2386 (1964).
52. G.Porter and M.W.Windsor, Proc.Roy.Soc., A, **245**, 238 (1958).
53. H.L.J.Backström and K.Sandros, Acta Chem.Scand., 12, 823 (1958).
54. E.J.Land, S.Sykes, and T.G.Truscott, Chem. Comm., 332 (1970).
55. B.Stevens and B.E.Algar, J.Phys.Chem., 72, 2582, 3468, 3794 (1968); **73**, 1711 (1969).
56. B.A.Baldwin and H.W.Offen, J.Phys.Chem., **49**, 2933 (1968).
57. S.Siegel and H.S.Judeikis, J.Phys.Chem., **48**, 1613 (1968).
58. G.Shaw, Trans.Faraday Soc., **63**, 2181 (1967).
59. G.Meyer, Bull.Soc.chim.France, 702 (1970).
60. D.R.Kearns, A.U.Khan, C.K.Duncan, and A.H.Maki, J.Amer.Chem.Soc., **91**, 1039 (1969).
61. G.S.Hammond and P.A.Leermakers, J.Amer.Chem. Soc., **84**, 207 (1962).
62. K.Yoshihara and D.R.Kearns, J.Chem.Phys., **45**, 1991 (1966).
63. P.Pringsheim, "Fluorescence and Phosphorescence", Interscience, New York, 1949.
64. T.Forster, "Fluorescenz organischer Verbindungen", Vandenhoeck and Ruprecht, Göttingen, 1951.
65. I.B.Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1965.
66. C.Reid, Quart.Rev.Chem.Soc., 205 (1958).
67. R.S.Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley, New York, 1970.
68. J.B.Birks, "Photophysics of Aromatic Molecules", Wiley–Interscience, New York, 1970.
69. W.R.Ware and S.K.Lee, J.Chem.Phys., **49**, 217 (1968).
70. W.R.Ware and P.T.Cunningham, J.Chem.Phys., 37, 583 (1962).
71. W.R.Ware, J.Phys.Chem., **66**, 455 (1962).
72. J.T.Dubois, J.Chem.Phys., **25**, 178 (1956).
73. B.Stevens, Trans.Faraday Soc., 51, 610 (1955).
74. H.Ishikawa and W.A.Noyes, Jr., J.Chem.Phys., **37**, 583 (1962).
75. A.Schmillen and R.Legler, in "Luminescence of Organic Compounds", Vol.3, Landolt-Börnstein (N.S), Springer Verlag, Berlin–Wilmersdorf, 1967.
76. E.K.C.Lee, M.W.Schmidt, R.G.Shortridge, and G.A.H.Haninger, Jr., J.Phys.Chem., 73, 1805 (1969).
77. C.S.Parmenter and J.D.Rau, J.Chem.Phys., 51, 2242 (1969).
78. A.Morikawa and R.T.Cvetanović, J.Chem.Phys., **52**, 3237 (1970).
79. E.C.Blossey, D.C.Neckers, A.L.Thayer, and A.P.Schaap, J.Amer.Chem.Soc., **95**, 5820 (1973).
80. J.R.Williams, G.Orton, and L.R.Unger, Tetrahedron Letters, 4603 (1973).
81. R.Nielsson and D.R.Kearns, Photochem.Photobiol., **19**, 181 (1974).
82. J.S.Bellin, Photochem.Photobiol., **8**, 383 (1968).
83. R.C.Petterson, S.M.Kalbag, and C.S.Irving, Annals New York Acad.Sci., **171**, 133 (1970).
84. R.A.Nathan and A.H.Adelman, Chem.Comm., 674 (1974).
85. J.W.Coomber and J.N.Pitts, Environ.Sci., Technol., 506 (1970).
86. J.W.Coomber, D.W.Hebert, W.A.Kummer, G.G.Marsh, and J.N.Pitts, Environ.Sci.Technol., 1141 (1970).
87. D.F.Evans, J.Chem.Soc., 2753 (1959).
88. D.F.Evans, J.Chem.Soc., 1735 (1960).
89. D.F.Evans, Proc.Roy.Soc., A, **255**, 55 (1960).
90. D.F.Evans, J.Chem.Soc., 1987 (1961).
91. H.Tsubomura, J.Amer.Chem.Soc., **82**, 40 (1960).
92. H.Tsubomura and R.P.Lang, J.Chem.Phys., **36**, 2155 (1962).
93. H.Ishida, H.Takahashi, H.Sato, and H.Tsubomura, J.Amer.Chem.Soc., **92**, 275 (1970).
94. N.V.Shinkarenko and V.B.Aleskovskii, Dep.VINITI No.2777-78 Dep.
95. N.V.Shinkarenko, Thesis, Leningrad, 1974.
96. L.Wallace and D.M.Hunter, J.Geophys.Res., **73**, 4813 (1968).
97. C.W.Cho, E.J.Allin, and H.L.Welsh, Canad.J.Phys., 41, 1991 (1963).
98. D.Evans, Chem.Comm., 367 (1969).
99. L.T.N.Jones and R.P.Waymer, J.Chem.Phys., 51, 317 (1969).
100. M.Gauthier and D.R.Snelling, Annals New York Acad.Sci., **171**, 220 (1970).
101. R.A.Young and G.Black, J.Chem.Phys., **47**, 2311 (1967).
102. T.P.J.Izod and R.P.Wayne, Proc.Roy.Soc., A, **308**, 81 (1968).
103. J.F.Noxon, J.Chem.Phys., **52**, 1852 (1970).
104. R.H.Kummler, M.H.Bortner, and T.Baurer, Environ. Sci.Technol., **3**, 248 (1968).
105. D.Biedenkapp and E.J.Blair, J.Chem.Phys., **52**, 6119 (1970).
106. A.Terenin, Acta Physicochim., **18**, 210 (1943).
107. A.U.Khan and M.Kasha, J.Chem.Phys., **39**, 2105 (1963); **40**, 605 (1964).
108. A.U.Khan and M.Kasha, Nature, **204**, 241 (1964).
109. E.McKeown and W.A.Waters, J.Chem.Soc.B, 1040 (1966).
110. S.J.Arnold, R.J.Browne, and E.A.Ogryzlo, Photochem.Photobiol., **4**, 963 (1965).
111. L.W.Bader and E.A.Ogryzlo, Discuss.Faraday Soc., **37**, 461 (1964).
112. E.W.Gray and E.A.Ogryzlo, Chem.Phys.Letters, **3**, 658 (1969).
113. C.S.Foote, S.Waxler, W.Ando, and R.Higgins, J.Amer.Chem.Soc., **90**, 975 (1968).
114. R.W.Murray and M.L.Kaplan, J.Amer.Chem.Soc., **90**, 537 (1968).
115. R.W.Murray and M.L.Kaplan, J.Amer.Chem.Soc., **91**, 5358 (1969).
116. R.W.Murray, J.W.-P.Lin, and M.L.Kaplan, Annals New York Acad.Sci., **171**, 121 (1970).

117. R.W.Murray and M.L.Kaplan, J.Amer.Chem.Soc., 90, 4161 (1968).
118. R.W.Murray, W.C.Lumma, and J.W.-P.Lin, J.Amer. Chem.Soc., 92, 3205 (1970).
119. E.Wasserman, R.W.Murray, M.L.Kaplan, and W.A.Yager, J.Amer.Chem.Soc., 90, 4160 (1968).
120. P.D.Bartlett and G.D.Mendenhall, J.Amer.Chem.Soc., 92, 210 (1970).
121. P.Schaap, 160-th National Meeting of the American Chemical Society, Chicago, 1970, Abstract ORG No.141.
122. M.E.Brannan, Chem.Comm., 956 (1970).
123. A.P.Schaap, A.L.Thayer, G.R.Faler, K.Goda, and T.Kimura, J.Amer.Chem.Soc., 96, 4025 (1974).
124. W.Bergmann and M.J.McLean, Chem.Rev., 28, 367 (1941).
125. D.R.Kearns and A.U.Khan, Photochem.Photobiol., 10, 193 (1969).
126. H.H.Wasserman and J.R.Scheffer, J.Amer.Chem. Soc., 89, 3073 (1967).
127. S.R.Abbott, S.Ness, and D.M.Hercules, J.Amer. Chem.Soc., 92, 1128 (1970).
128. A.U.Khan, Science, 168, 476 (1970).
129. R.Nielsson and D.R.Kearns, J.Phys.Chem., 78, 1681 (1974).
130. N.J.Turro, V.Ramamurthy, Kou-Chang Liu, A.Krebs, and R.Kemper, J.Amer.Chem.Soc., 98, 6758 (1976).
131. R.P.Steer, K.R.Darnall, and J.N.Pitts, Tetrahedron Letters, 3765 (1969).
132. J.P.Collman, Acc.Chem.Res., 1, 136 (1968).
133. L.Vaska, Science, 140, 809 (1963).
134. J.F.Drake and R.J.P.Williams, Nature, 182, 1084 (1958).
135. A.L.Crumbliss and F.Basolo, J.Amer.Chem.Soc., 92, 55 (1970).
136. D.F.Evans and R.E.Richards, J.Chem.Soc., 3295 (1952).
137. L.D.Possani, R.Banerjee, C.Balny, and P.Douzou, Nature, 226, 861 (1970).
138. J.F.Noxon, Canad.J.Phys., 39, 1110 (1961).
139. S.J.Arnold and E.A.Ogryzlo, Canad.J.Phys., 45, 2053 (1967).
140. K.Furukawa, E.Q.Gray, and E.A.Ogryzlo, Annals New York Acad.Sci., 171, 175 (1970).
141. R.P.Wayne, Adv.Photochem., 7, 400 (1969).
142. S.N.Foner and R.L.Hudson, J.Chem.Phys., 25, 601 (1956).
143. R.A.Young and G.T.Black, J.Chem.Phys., 44, 3741 (1966).
144. L.Elias, E.A.Ogryzlo, and H.I.Schiff, Canad.J. Chem., 37, 1680 (1959).
145. R.E.March, S.G.Furnival, and H.I.Schiff, Photochem.Photobiol., 4, 971 (1965).
146. A.U.Khan, Chem.Phys.Letters, 4, 567 (1970).
147. G.Mannella and P.Harteck, J.Chem.Phys., 34, 2177 (1961).
148. B.McCarroll, J.Chem.Phys., 50, 4758 (1969).
149. Yu.N.Rufov, A.A.Kadushin, and S.Z.Roginskii, Dokl.Akad.Nauk SSSR, 171, 905 (1966).
150. A.M.Falick, B.H.Mahan, and K.J.Meyer, J.Chem. Phys., 42, 1837 (1965).
151. A.M.Falick and B.H.Mahan, J.Chem.Phys., 47, 4778 (1967).
152. E.Wasserman, V.J.Kuck, W.M.Delevan, and W.A.Yager, J.Amer.Chem.Soc., 91, 1040 (1969).
153. S.J.Arnold, N.Finlanson, and E.A.Ogryzlo, J.Chem. Phys., 44, 2529 (1966).
154. S.H.Whitlow and F.D.Findlay, Canad.J.Chem., 45, 2087 (1967).
155. D.R.Snelling, Chem.Phys.Letters, 2, 346 (1968).
156. M.A.A.Clyne, B.A.Thrush, and R.P.Wayne, Nature, 199, 1057 (1963).
157. M.A.A.Clyne, B.A.Thrush, and R.P.Wayne, Photochem.Photobiol., 4, 957 (1965).
158. S.Ness and D.M.Hercules, Analyt.Chem., 41, 1467 (1969).
159. "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, 1953, p.2340.
160. R.B.Cairns and J.A.R.Samson, Phys.Rev., 139A, 1403 (1965).
161. R.J.McNeal and G.R.Cook, J.Chem.Phys., 45, 3469 (1966).
162. R.J.McNeal and G.R.Cook, J.Chem.Phys., 47, 5385 (1967).
163. I.D.Clark and R.P.Wayne, Molec.Phys., 18, 523 (1970).
164. G.J.Hoytink, Molec.Phys., 3, 67 (1960).
165. P.D.Bartlett, G.D.Mendenhall, and A.P.Schaap, Annals New York Acad.Sci., 171, 79 (1970).
166. J.A.Howard and K.U.Ingold, Canad.J.Chem., 45, 798 (1967).
167. A.P.Schaap and P.D.Bartlett, J.Amer.Chem.Sco., 92, 6055 (1970).
168. P.B.Merkel and D.R.Kearns, J.Amer.Chem.Soc., 94, 1029 (1972).
169. P.B.Merkel, R.Nielsson, and D.R.Kearns, J.Amer. Chem.Soc., 94, 1030 (1972).
170. C.S.Foote and R.W.Denny, J.Amer.Chem.Soc., 93, 5162, 5168 (1971).
171. R.H.Young, D.Brewer, and R.A.Keller, J.Amer. Chem.Soc., 95, 375 (1973).

Lensovet Leningrad Technological Institute