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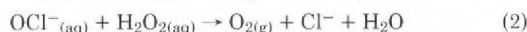
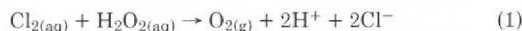
tested demonstrations

Singlet Oxygen in Aqueous Solution: A Lecture Demonstration

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Introduction

Lecture demonstrations involving chemiluminescence are useful for the purposes both of displaying chemical phenomena and of illustrating specific principles. Demonstrations are most effective if the lecturer relates (1) the observed phenomena to chemical concepts and principles. The red chemiluminescence due to singlet molecular oxygen can be observed when aqueous solutions of Cl_2 (or hypochlorite ion) and hydrogen peroxide are mixed



The red glow accompanying the OCl^- - H_2O_2 reaction was first reported by Mallet (2) in 1927. Kasha and co-workers (3) studied this reaction in some detail and have attributed the chemiluminescence to the simultaneous transition of two excited oxygen molecules [O_2 , ($^1\Delta_g$)] to the ground state in a two-molecule-one photon process



The red emission results (4) from excited gaseous O_2 which is trapped in bubbles that are formed in the reaction mixture.

The OCl^- - H_2O_2 oxidation-reduction reaction can be used as a lecture demonstration while discussion topics dealing with spectroscopy, chemical bonding, kinetics and mechanisms in introductory and upper-level college chemistry courses. In this paper we describe details of experimental designs which we have found effective for observing the production of singlet molecular oxygen in aqueous solution. Also, we present information which the teacher may find helpful in relating the observations to chemical concepts and principles. Our interest in the chemiluminescence of singlet molecular oxygen evolved from Kasha's presentation (5) at the Third Biennial Conference on Chemical Education.

Chemical Production of Singlet Oxygen

The red chemiluminescence may be readily observed on a small scale by using a hypodermic syringe to rapidly inject household bleach (5% NaOCl) into a beaker containing 30% H_2O_2 . Brighter emission may be observed by injecting chlorine gas dissolved in carbon tetrachloride into an alkaline solution

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¹ We thank Professor Robert Kuczkowski of the University of Michigan for calling our attention to this apparatus.

of hydrogen peroxide. In both cases, however, the emission is weak and is best observed in a darkened room.

Scaling up the demonstration for use in a large lecture hall requires more than simply increasing the size of the reaction (i.e., optical depth). Brabham and Kasha (6) point out that the intensity of the emission is highly sensitive to the rate of $\text{O}_2(^1\Delta_g)$ formation because: a) the emission is produced by a simultaneous transition in two excited O_2 molecules, so the intensity depends on the square of the singlet oxygen concentration; and b) the singlet oxygen is rapidly quenched in solution. For both reactions (1) and (2) the apparatus design and reaction conditions strongly influence the rate of singlet oxygen production. These considerations are discussed below.

It should be pointed out that other sources of singlet oxygen can be employed (7). The chlorine-peroxide reaction is probably the most convenient to use.

The Cl_2 - H_2O_2 Reaction

Bubbling Cl_2 into 30% H_2O_2 in a standard gas washing apparatus¹ results in the rapid evolution of O_2 accompanied by vigorous frothing. The rate of bubbling should be such that no frothing occurs in the region of injection; otherwise, the red glow will not be observed. This is probably due to the quenching of singlet oxygen by turbulence, thereby decreasing the rate of singlet oxygen production. The frothing effect can be minimized by using a gas washing apparatus (Kimble #31750) fitted with a glass frit covering the bottom. This allows the Cl_2 to enter at the bottom of the solution and effectively mix with the peroxide. The frothing occurs 1–2 cm above the glass frit and emission is observed from the region between the disc and the foam.

The intensity of emission is also enhanced by making the hydrogen peroxide solution alkaline. The reaction gradually causes the solution to become acidic (eqn. (1)) and, at $[\text{H}^+] > 1 \text{ M}$, the red glow is not observed. The intensity of emission is highest when the reaction conditions are alkaline. (Place 100 ml of 30% H_2O_2 and 25 ml of 6 M NaOH in the gas washing bottle; bubble Cl_2 at pressure sufficient to produce glow). The apparatus is shown in Figure 1.

CAUTION: The chlorine gas should be introduced in spurts (i.e., the cylinder valve should be turned on and off quickly). The temperature of the reaction system begins to rise due to the exothermicity of both the redox reaction and the neutralization reaction. In a matter of minutes, the catalytic decomposition of H_2O_2 becomes very vigorous and the entire mixture may boil over. After observing the glow 4–5 times it is best to quickly disconnect the gas washing bottle and empty its contents into a sink.

The OCl^- - H_2O_2 Reaction

Singlet oxygen chemiluminescence can be observed by injecting 3 ml of household bleach (5% NaOCl) from a syringe into 50 ml of 30% H_2O_2 solution. This small-scale procedure is not suitable for use in a large lecture hall. A special apparatus was designed to enable good viewing of the glow in a lecture hall that seats 350 students. The apparatus is shown

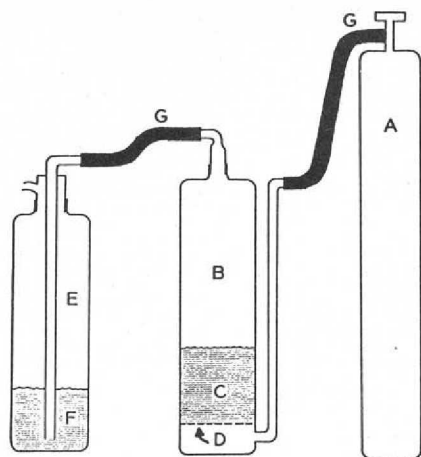


Figure 1. Apparatus used for $\text{Cl}_2\text{-H}_2\text{O}_2$ reaction. A, Lecture bottle of Cl_2 ; B, gas washing apparatus (Kimble #31750); C, alkaline 30% H_2O_2 ; D, glass frit; E, Cl_2 scrubber; F, 6 M KOH; G, rubber connecting hose.

in Figure 2. It consists of a 21 cm spiral coil of copper tubing (1 cm o.d.) which is placed at the bottom of a battery jar whose diameter is 24 cm. Small holes are drilled about 5 cm apart in the coil. The coil is covered with 30% H_2O_2 solution. The bleach is placed in another vessel (diameter $\sim 15\text{ cm} \times 21\text{ cm}$ high) made of Lucite and the two vessels are connected with copper tubing. In the apparatus shown in Figure 2 good visual observations can be made if 500 ml of 30% H_2O_2 are placed in the vessel containing copper tubing and 500 ml of household bleach placed in the other vessel. By applying air-pressure, the NaOCl solution can be forced rapidly through the holes in the copper tubing into the H_2O_2 solution. Frothing occurs sufficiently above the mixing zone and red emission can be observed readily.

It is noteworthy that injecting 30% H_2O_2 into household bleach does *not* produce emission. This is probably due to the large difference in concentration of the reactants (6) (30% H_2O_2 is $\sim 10\text{ M}$, 5% NaOCl is $\sim 0.7\text{ M}$). When the relatively dilute NaOCl solution is injected into peroxide, the oxidation-reduction reaction takes place near the point of injection. On the other hand, when peroxide is injected into household bleach, OCl^- is consumed near the point of injection and additional peroxide must diffuse into the rest of the solution before reaction can take place; thus, the rate of singlet oxygen production is slower. If the reactants are of comparable concentrations, the order of injection is no longer important and the red glow is observed either way.

The Halogen/ $\text{CCl}_4\text{-H}_2\text{O}_2$ Reaction

Red emission is observed when either Cl_2 or Br_2 is dissolved in CCl_4 and injected rapidly by means of a syringe into an alkaline H_2O_2 solution. The glow is intense and can be best observed in a darkened room. Hydrogen peroxide is not oxidized by molecular iodine.

Reaction Rates and Mechanisms

Table 1 summarizes the results of several qualitative experiments performed using a syringe to mix the reagents as described above. It should be emphasized that the intensity of emission obtained with Cl_2 in the gas washing apparatus was greatest at low hydrogen ion concentration ($\text{pH} > 9$) while at a pH of 0.5 or less there was no visible emission. Since the red emission appears to be related to the rate of singlet oxygen production (c.f., the mixing effects of the preceding section), it would seem reasonable that the pH of the reaction mixture may affect the red emission.

Connick (8) has studied the kinetics of the reactions in (1) and (2) and in (3) and (4) over a range of pH values. His results, when combined with the isotope labeling work of Cahill

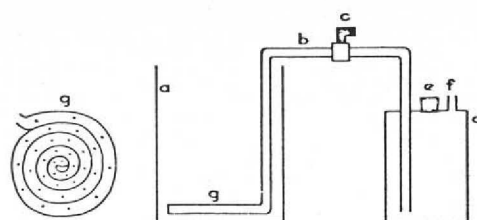


Figure 2. Apparatus used for H_2O_2 and OCl^- reaction. a, Battery jar; b, copper tubing; c, valve for controlling flow; d, pressurizable container (for bleach); e, filling port; f, hose connector; g, spiral of copper tubing with holes for mixing H_2O_2 and bleach.

Table 1. Summary of Experimental Procedures and Observations

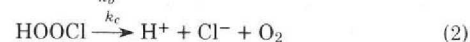
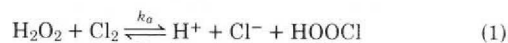
Reagent in Syringe	Reagent ^a in Beaker	Initial pH of H_2O_2 solution	Observation ^b
bleach	H_2O_2	3.6	moderate glow
bleach	H_2O_2	9.5	faint glow
bleach	H_2O_2	1.0	faint glow
H_2O_2	bleach	3.6	no glow
HOCl^c	H_2O_2	3.6	faint glow
HOCl^c	H_2O_2	9.6	bright glow
Cl_2 in CCl_4	H_2O_2	3.6	no glow
Cl_2 in CCl_4	H_2O_2	9.5	bright glow
Br_2 in CCl_4	H_2O_2	3.6	no glow
Br_2 in CCl_4	H_2O_2	9.5	moderate glow
I_2 in CCl_4	H_2O_2	3.6	no glow
I_2 in CCl_4	H_2O_2	9.5	no glow

^a Approximately 80 ml of 30% H_2O_2 was made acidic or basic by addition of about 5 ml 6 M HCl or 6 M NaOH.

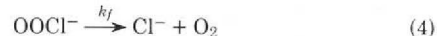
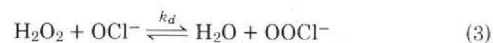
^b The intensity of the observed red emission was classified qualitatively as "faint," "moderate," or "bright".

^c Chloride-free HOCl prepared as in ref. (11).

and Taube (9), suggest that the mechanisms for the two reactions may be written as



and



According to Connick, the unimolecular decomposition (4) is very fast compared with the bimolecular process (3) and the values of the rate constants k_a and k_d , at 25°C , are

$$k_a = 1.8 \times 10^2 \text{ l moles}^{-1} \text{ sec}^{-1}$$

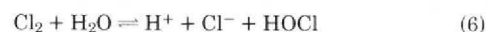
$$k_d = 2.8 \times 10^3 \text{ l moles}^{-1} \text{ sec}^{-1}$$

This order of magnitude difference in reaction rates suggests that the reaction in (3) and (4) should be more effective than the reaction in (1) and (2) for producing the red chemiluminescence.

Connick's kinetic results suggest that, in the region above 1 M hydrogen ion concentration, reaction (1) predominates; while, in the region of hydrogen ion concentration of 10^{-4} M or less, the Cl_2 is essentially all hydrolyzed to HOCl and the rapid equilibrium

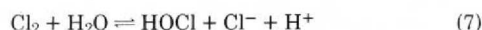


is followed by the reaction in (3) and (4). For reaction (5), $K_{aq} = 3 \times 10^{-8}$. In the pH region between these limits, the reaction scheme is probably very complex and Connick was unable to formulate a rate law. The ability to observe red emission in this pH region but not at pH below ~ 0.5 suggests that a possible mechanism at $\text{pH} = 1.4\text{--}4.0$ may be

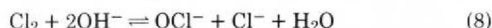


followed by (5) and (3) and (4). Eigen and Kustin (10) have measured the rate constant for the forward reaction (6) as 11.0 sec^{-1} . This rapid hydrolysis and disproportionation of Cl_2 followed by an order of magnitude faster reaction with H_2O_2 would provide a favorable competing mechanism with the direct reaction in (1) and (2) and explain the observation of red emission in this pH region.

The enhancement of emission at even lower $[\text{H}^+]$ for the Cl_2 reaction can be caused by two effects. The first is a concentration effect; the equilibrium constant for the reaction (7) is about 3×10^{-4}



On the other hand, in alkaline solution, the reaction is



for which K_{eq} is $\sim 9 \times 10^{16}$. The second effect is a possible enhancement of the rate of Cl_2 hydrolysis through direct reaction with OH^- (10). Both of the above would contribute to an increase in the rate of singlet oxygen production and hence an increase in observed intensity of red emission.

In view of the above considerations, it was interesting to examine the results of injecting solutions of Cl_2 , Br_2 , and I_2 in carbon tetrachloride into solutions containing hydrogen peroxide (Table 1). None of the reagents produces emission when injected into "neat" 30% H_2O_2 . Under this condition the redox is presumably slow compared to the rate of quenching. The halogen species are more soluble in CCl_4 than in water and the transfer to the aqueous phase is slow. In alkaline H_2O_2 , both Cl_2 and Br_2 produce red emission. It is also interesting to note that stability of the species XOH decreases in the order $\text{Cl} > \text{Br} > \text{I}$ (10) and this correlates with the observed ordering in the intensity of emission.

Molecular Spectroscopy and Bonding

Spectroscopic Considerations

A potential energy diagram for some of the lower lying states of molecular oxygen is shown in Figure 3. The lowest energy configuration is split by electron repulsion into three distinct states: $^1\Sigma_g^+$, $^1\Delta_g$, and $^3\Sigma_g^-$. The physical constants of these states are shown in Table 2. The term symbols used to designate diatomic molecular states are analogous to atomic term symbols with the electronic states designated Σ , π , Δ , ... similar to the S , P , D , ... notation for atoms; the left superscript indicates the multiplicity. The + or - right superscript in the case of sigma (Σ) states indicates whether the

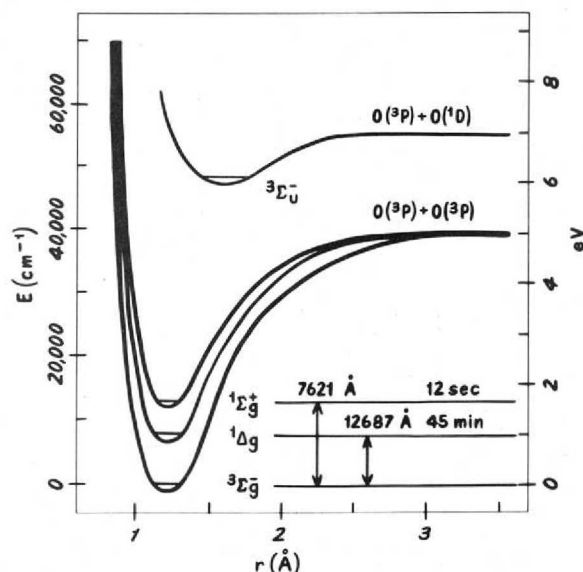


Figure 3. Potential energy diagram for some low lying states of O_2 (after Herzberg (13) and Khan and Kasha (3)).

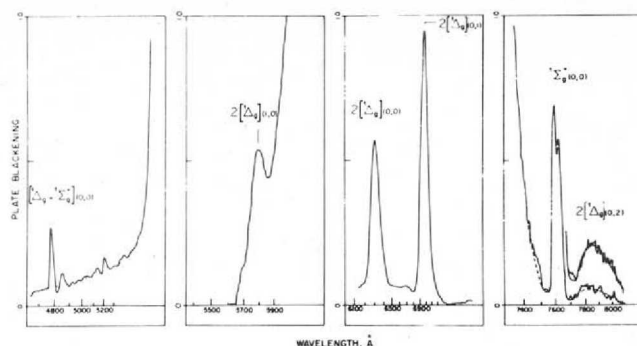
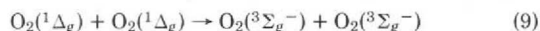


Figure 4. Chemiluminescence bands for the aqueous reaction at 20°C of hydrogen peroxide with hypochlorite. Bands labelled according to upper electronic state by energy convention, with vibrational components (after Khan and Kasha (3)).

electronic wavefunction remains the same or changes sign upon reflection through a plane passing through both nuclei. If the two nuclei in the molecule have the same charge, there is a center of symmetry and the electronic wavefunction may be even or odd with respect to inversion. This even or odd property is designated by a subscript g or u , respectively (from the German "gerade" or "ungerade").

On the basis of Hund's Rule, which holds for molecules as well as atoms, the ground state of O_2 is $^3\Sigma_g^-$. The transition between $^3\Sigma_g^-$ and $^3\Sigma_u^-$ states is allowed for electric dipole radiation and is readily observed as the Schuman-Runge band system (13) in the ultraviolet region of the spectrum. The electric dipole transitions between the triplet ground state and the $^1\Sigma_g^+$ and $^1\Delta_g$ states are forbidden on the basis of both spin and symmetry; in addition, the transition between the ground state and $^1\Delta_g$ is orbitally forbidden. The low transition probabilities are reflected in the long radiative lifetimes of the two states: 12 sec for $^1\Sigma_g^+$ and 45 min for $^1\Delta_g$ (14, 15). These lifetimes are in the limit of zero pressure and may be considerably modified by perturbations from surrounding gases. In fact, the transitions have been observed as the atmospheric oxygen bands ($^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^-$) at 7620 Å and the infrared atmospheric oxygen bands ($^1\Delta_g \leftrightarrow ^3\Sigma_g^-$) at $12,600 \text{ Å}$ (13).

The spectrum of the red chemiluminescence produced in the reactions in (1)–(4) has been studied by several researchers. Khan and Kasha (3) observed two prominent bands at 6334 Å and 7032 Å (Fig. 4) as well as weaker bands at 5780 Å and 7860 Å . They have assigned these bands to vibrational components of the double-molecule transition (two-molecule, one-photon)



Khan and Kasha also observed a band at 7620 Å which they assigned as the 0,0 band of the $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$ transition.

Simultaneous transitions of the type in eqn. (9) have also been observed (3) in the high pressure (150 atm) absorption

Table 2. Physical Constants of the Three Lowest Electronic States of Molecular Oxygen^a

State	Mean Lifetime (sec)	Equilibrium Inter-nuclear Distance (Angstroms)	Absorption Position (0,0 Band) ν (cm ⁻¹)	λ (Å)	E (kcal mole ⁻¹)
$^1\Sigma_g^+$	12 ^b	1.227	13,120.91 ^d	7,621.4	37.51
$^1\Delta_g$	2,700 ^c	1.216	7,882.39 ^e	12,687	22.53
$^3\Sigma_g^-$	—	1.207	—	—	—

^a Herzberg (13).

^b Wallace and Hunten (14).

^c Badger, Wright, and Whitlock (15).

^d Babcock and Herzberg (16).

^e Herzberg and Herzberg (17).

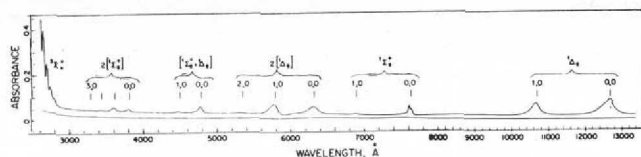
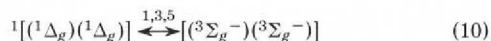


Figure 5. Complete absorption spectrum from 2600 Å to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5 cm cell at 20°C. Bands labeled according to upper electronic state by energy convention, with vibrational components (after Khan and Kasha (3)).

spectrum of oxygen (Fig. 5). The ordinarily spin-forbidden transition becomes allowed for the simultaneous transition because in the double-molecule $O_2(^3\Sigma_g^-)O_2(^3\Sigma_g^-)$ the coupling of the spins produces a singlet component. The transition may be represented as

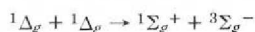


It is necessary to use high pressures to observe the absorption due to the very low probability of the three-body (two O_2 molecules and a photon) process required for absorption to occur. Emission, on the other hand, requires only a two body process and may be observed at atmospheric pressure, even with relatively low partial pressures of singlet oxygen. Note that the energy of the photon emitted or absorbed in the simultaneous transition (6300 Å) is double the energy for the single-molecule process (12,600 Å).

Bonding (Molecular Orbital Theory)

A molecular orbital analysis is useful in this case for elucidating the mechanism of singlet oxygen production in the peroxide-hypochlorite system. The chloroperoxy ion ($OOCl^-$) has been postulated (8) as an intermediate in the Cl_2 and OCl^- oxidation of H_2O_2 . The ground state of this ion is a singlet (1S) and ionic fission of the species to produce O_2 and Cl^- (1S) must leave the oxygen in a singlet state.

Khan and Kasha have used the spin-state correlation diagram (Fig. 6) to deduce that $^1\Delta_g$ is the only product of the fission of $OOCl^-$. Since the $^1\Delta_g$ state of O_2 is doubly degenerate (Fig. 7), it is necessary to go to even higher excited states of $OOCl^-$ to correlate with $^1\Sigma_g^+$. The spin-state correlation excludes the direct production of $O_2(^1\Sigma_g^+)$ in the breakdown of chloroperoxy ion. Since emission from this state is observed in the spectrum of the chemiluminescence (see above) the most likely mechanism of production is



The $^1\Sigma_g^+$ is present in very small amounts with the ratio $[^1\Sigma_g^+]/[^1\Delta_g]$ less than 10^{-6} .

Concluding Remarks

In this lecture demonstration an oxidation-reduction reaction is used to produce molecular oxygen in an excited state. The red chemiluminescence is readily observed, and it provides the lecturer with an interesting phenomenon which can be explained in depth to advanced students. The lecturer may choose to discuss the reaction conditions under which the red glow is observed as well as kinetics of the redox reaction, the spectroscopic properties of molecular oxygen and the molecular orbital model of bonding.

In an introductory college course the phenomenon can be displayed to show an unusual property of molecular oxygen. At Wisconsin, this demonstration is performed along with another demonstration that displays the paramagnetic properties of liquid oxygen. Both demonstrations are effective in displaying intrinsic properties of a very common and essential compound.

We wish to thank Professor Phillip R. Certain for his assistance with the molecular spectroscopy and bonding section of this paper. The financial support of the Graduate School Research Committee and the College of Letters and Science is gratefully acknowledged.

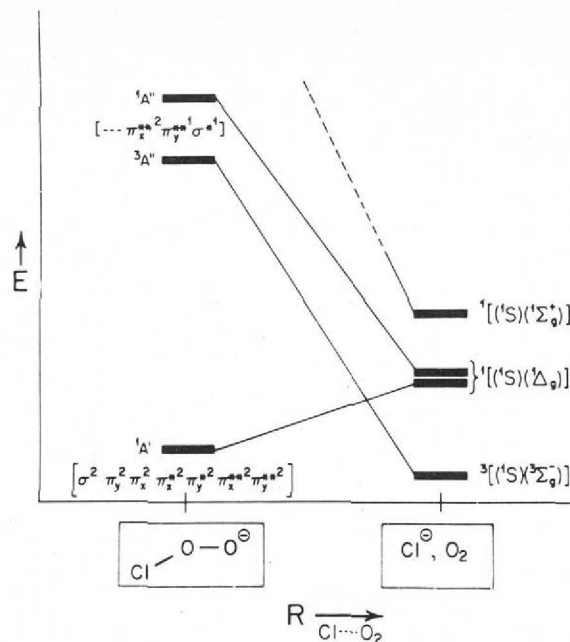


Figure 6. Spin-state correlation diagram for chloroperoxy ion $ClOO^-$ and its products, Cl^- and O_2 (after Khan and Kasha (3)).

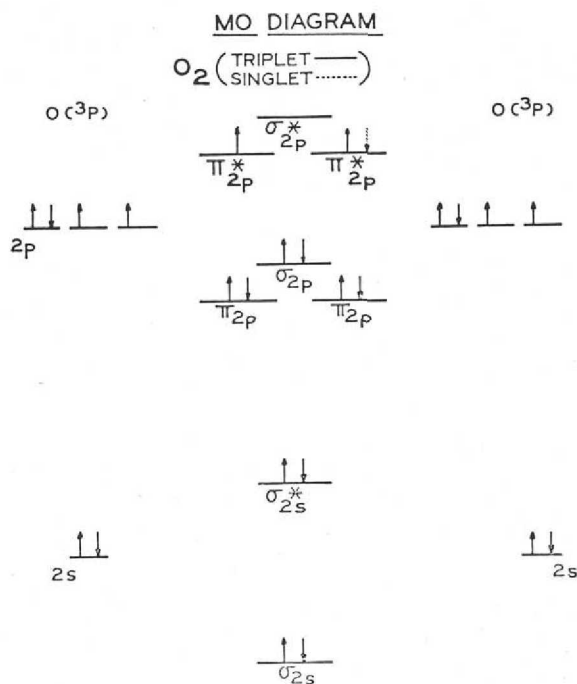


Figure 7. Molecular orbital energy level diagram for O_2 .

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