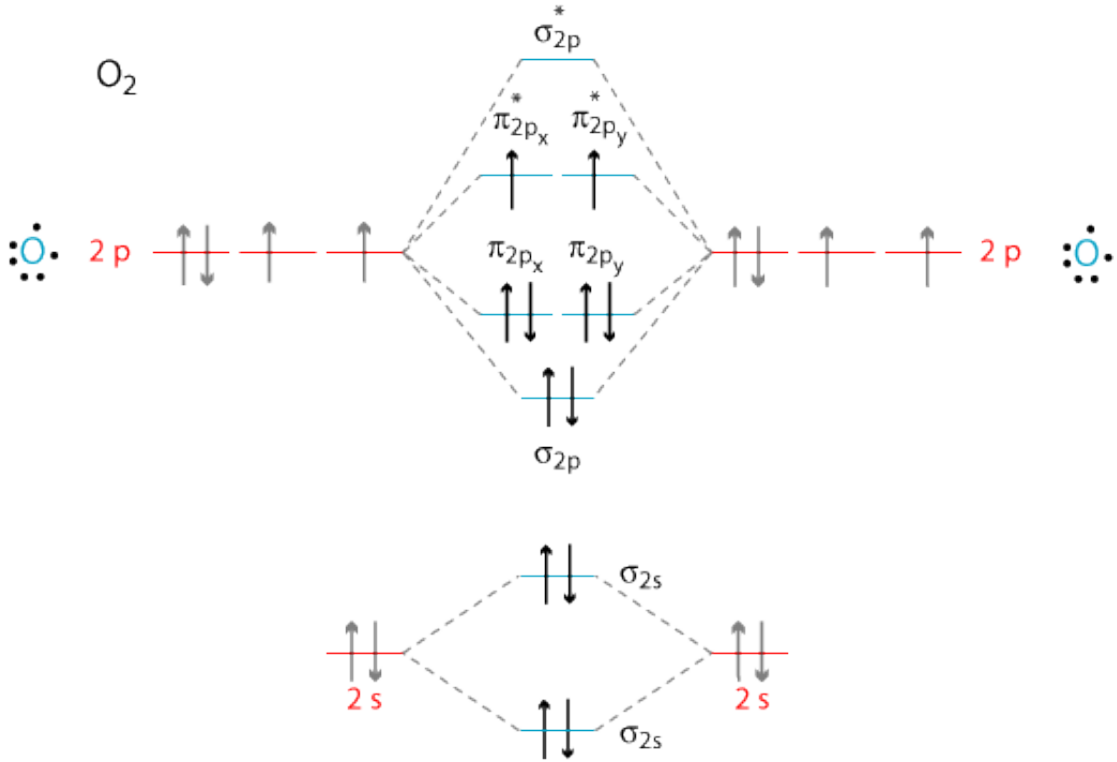
Oxygen Molecular Orbitals Electronic States and Application to Cancer Therapy ...and Appreciating Oxygen

Appreciating Oxygen

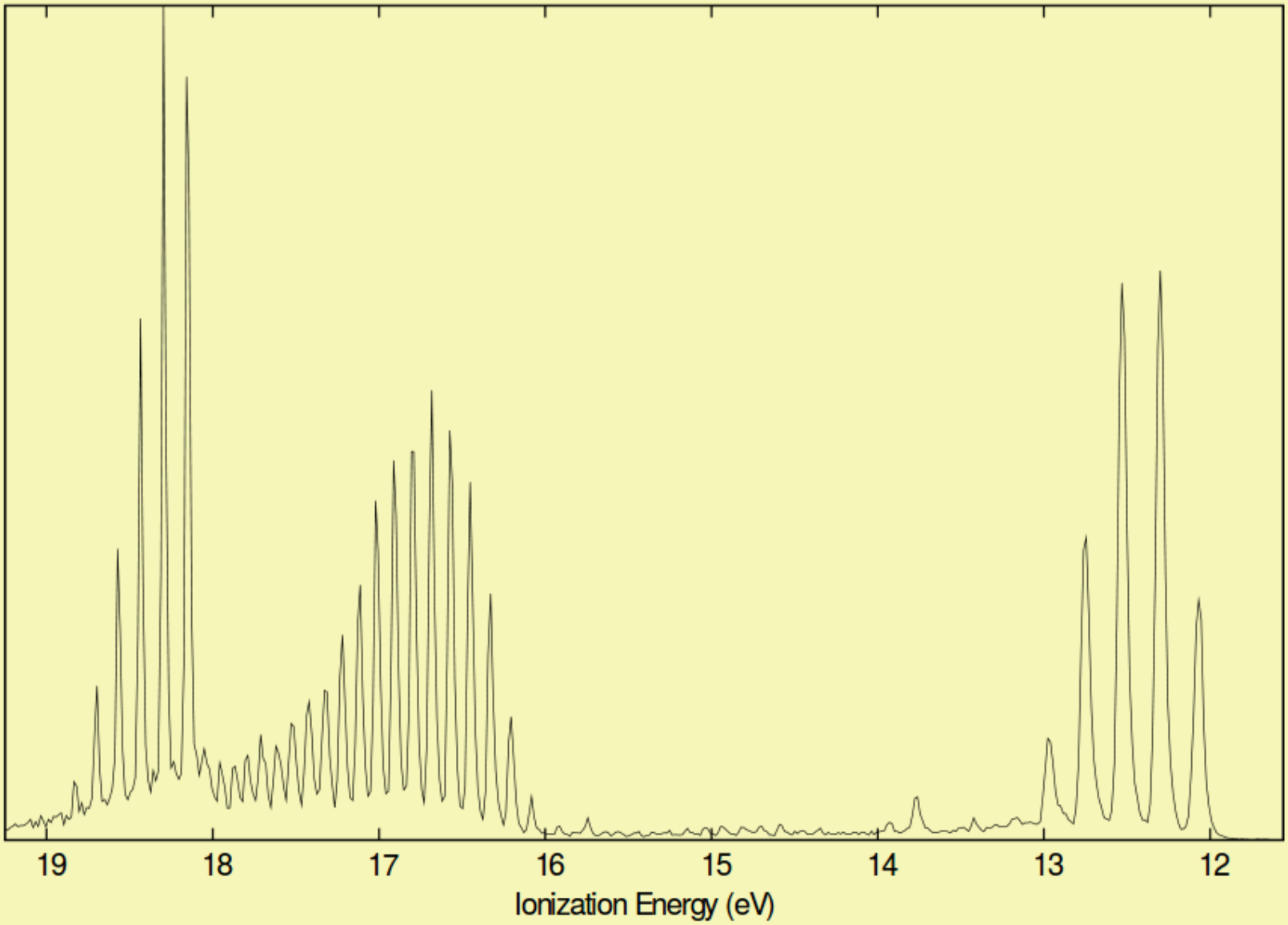
Hilton M. Weiss DOI: 10.1021/ed085p1218



Electron Configuration: $(\sigma_{2s})^2\ (\sigma_{2s}{}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p}{}^*)^2$

Bond Order $= \frac{1}{2}(2 - 2 + 2 + 4 - 2) = 2$ Double Bond

O_2 Photoelectron Spectrum



Oxygen Electronic States

Jean-Pierre Puttemans and Georges Jannes, DOI: 10.1021/ed081p639.1

- Interesting example of electron distribution over degenerate levels
- MO model predicts the existence of three forms of oxygen, three electronic states
- Explains paramagnetic character of the ground state, a triplet state
- Triplet state: $2S + 1 = 3$, 2e in π^* orbitals with parallel spins according to Hund's rule

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- $^1\Delta_g$ has outer electrons orbiting in the same sense and are paired in the same orbital
- The second excited state is $^1\Sigma_g^+$
- $^1\Sigma_g^+$ has the outer electrons orbiting in opposite directions and each π^* MO is singly occupied

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- The energy order is surprising and opposed to common sense
- One would expect the electronic repulsion to be lower if the electrons were to occupy different MOs
- The simple orbital description alone ignores electron correlation due to mutual repulsion between all electrons in the molecule
- All electrons in the molecule tend to synchronize their motion to keep apart as much as possible

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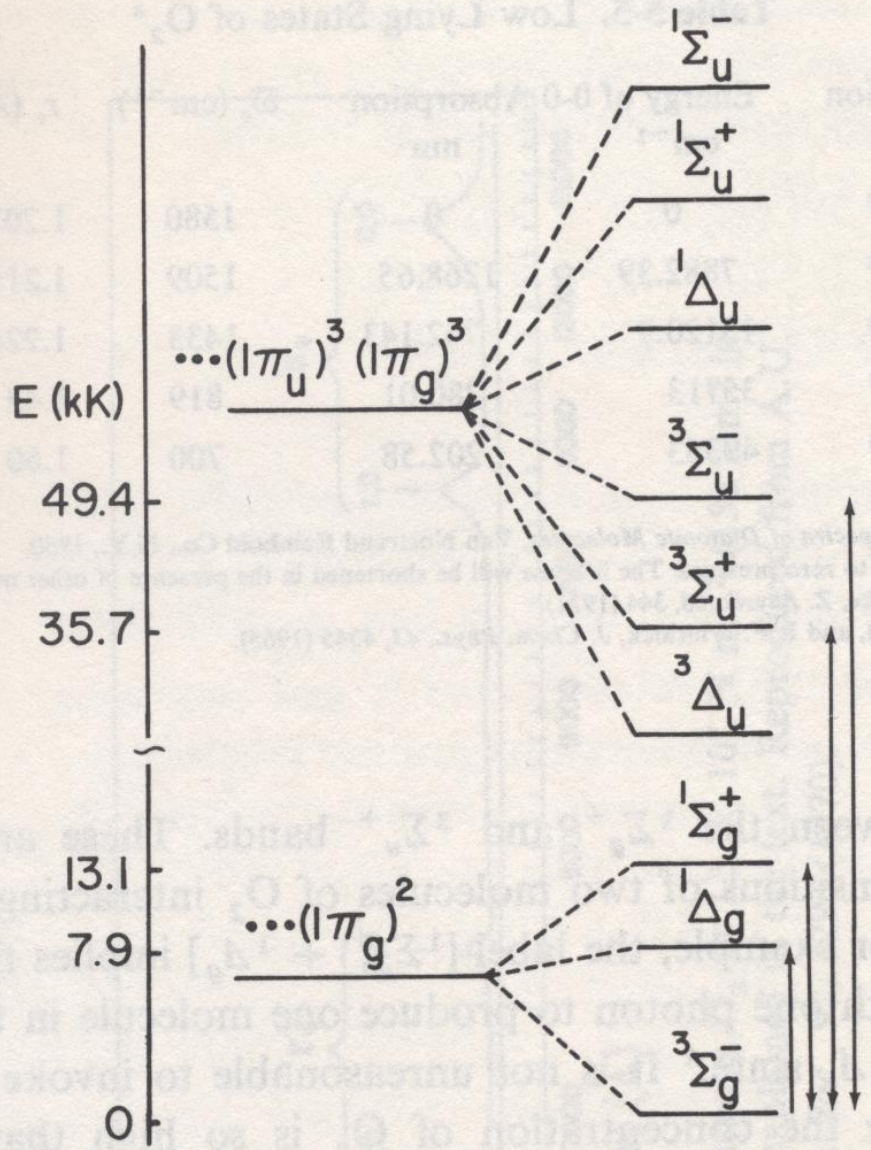

Fig. 5-16. State diagram of O_2 showing the lowest energy observed transitions.

O_2 Excited State Lifetimes

Table 5-5. Low Lying States of O_2[a]

State	Configuration	Energy of 0-0 Absorption cm^{-1}	Energy of 0-0 Absorption nm	$\bar{\omega}_e$ (cm^{-1})	r_e (Å)	Lifetime (s)[b]
$^3\Sigma_g^-$	$(\pi_u)^4(\pi_g)^2$	0	0	1580	1.2074	—
$^1\Delta_g$	$(\pi_u)^4(\pi_g)^2$	7882.39	1268.65	1509	1.2155	2700[c]
$^1\Sigma_g^+$	$(\pi_u)^4(\pi_g)^2$	13120.9	762.143	1433	1.2268	7.1[d]
$^3\Sigma_u^+$	$(\pi_u)^3(\pi_g)^3$	35713	280.01	819	1.42	—
$^3\Sigma_u^-$	$(\pi_u)^3(\pi_g)^3$	49363	202.58	700	1.60	—

[a] Data from G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand Reinhold Co., N.Y., 1950.
[b] Lifetimes are extrapolated to zero pressure. The lifetime will be shortened in the presence of other matter.
[c] W.H.J. Childs and R. Mecke, *Z. Physik*, *68*, 344 (1931).
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Photodynamic Therapy

The sensitization of cancer cells to light, DOI: 10.1021/ed076p592

- Photodynamic therapy (PDT) takes advantage of light, oxygen, and a drug (photosensitizer)
- The drug preferentially localizes in rapidly growing (malignant) cells
- Typical drugs for PDT are hematoporphyrin derivative, Hpd, and its active component, Photofrin II
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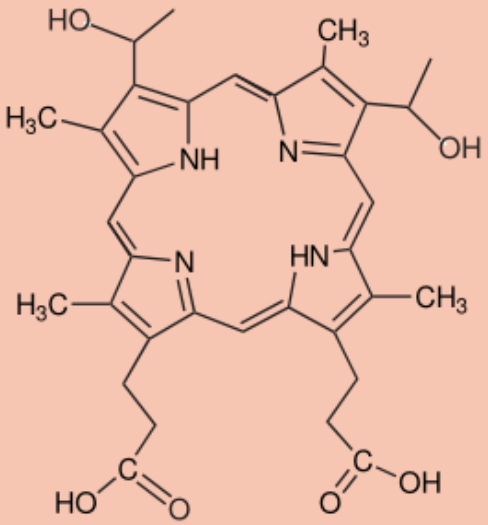

Figure 1. Hematoporphyrin

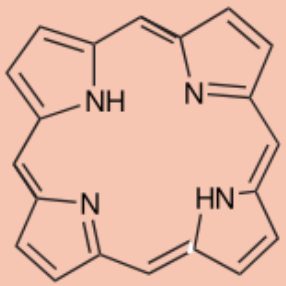

Figure 2. Porphyrin

- Hpd has photodynamic activity, it can augment or induce a toxic reaction when exposed to light

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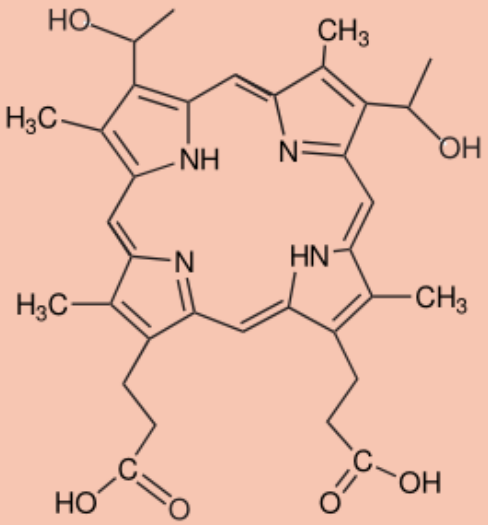

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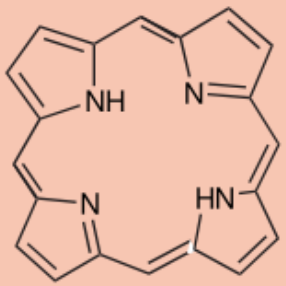

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- After the drug is administered, an incubation period is required
- During incubation, normal cells clear the drug but malignant cells accumulate it
- Incubation time ranges from minutes to hours, depending on the drug
- The target tissue is then irradiated using visible light (630 nm)
- In the presence of light the drug is activated to produce singlet oxygen; singlet oxygen reacts with biological molecules leading to cell death

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- The sensitizer absorbs a photon of energy and is promoted to its first electronically excited singlet state, S_1
- The energy of S_1 can be lost in a variety of ways, as shown in a Jablonski diagram
- It may fluoresce or transfer its energy to surrounding molecules
- If S_1 engages in electron transfer with a biological molecule, the photosensitizer will be bleached unproductively (Type I photoprocess)
- S_1 can also undergo intersystem crossing to an excited triplet state T_1; T_1 can then either phosphoresce, or react with triplet oxygen, $^3O_2$, to return to the ground state while making singlet oxygen ($^1\Delta_g$ state)

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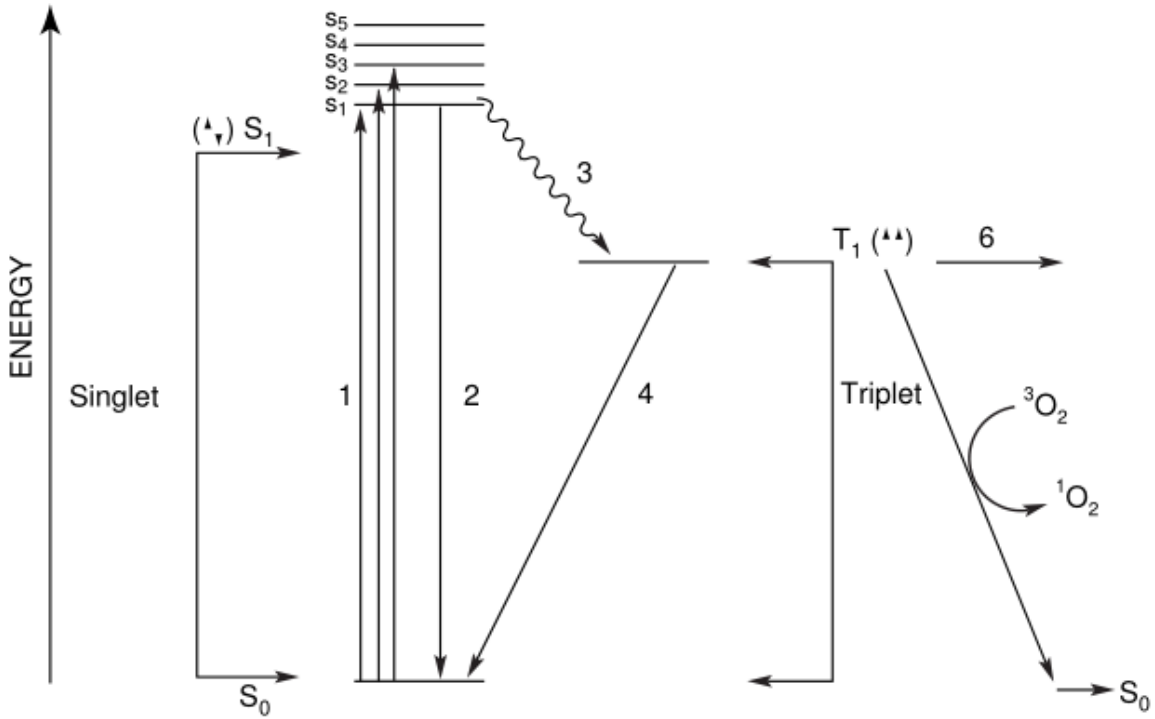


Figure 3. Modified Jablonski diagram for a typical photosensitizer showing: 1= Absorption of Light; 2= Fluorescence; 3= Intersystem Crossing; 4= Phosphorescence; 5= Production of Singlet Oxygen (Type II Photoprocess); 6= Hydrogen or Electron Transfer (Type I Photoprocess). A Jablonski diagram is a simplified representation of the electronic energy levels and radiative transitions of a molecule.

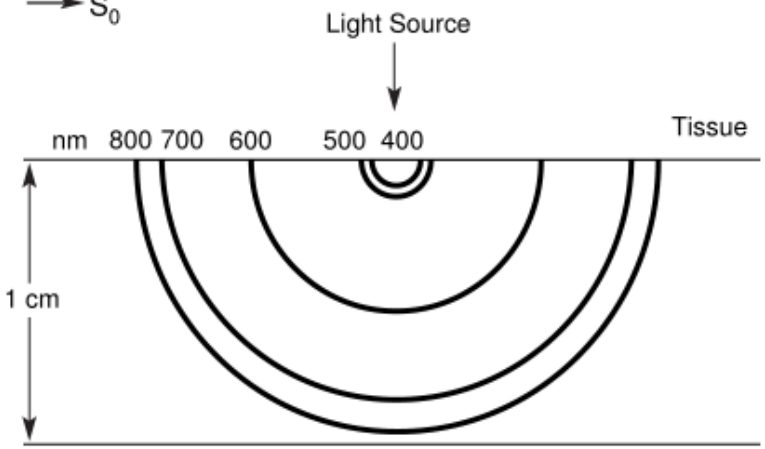
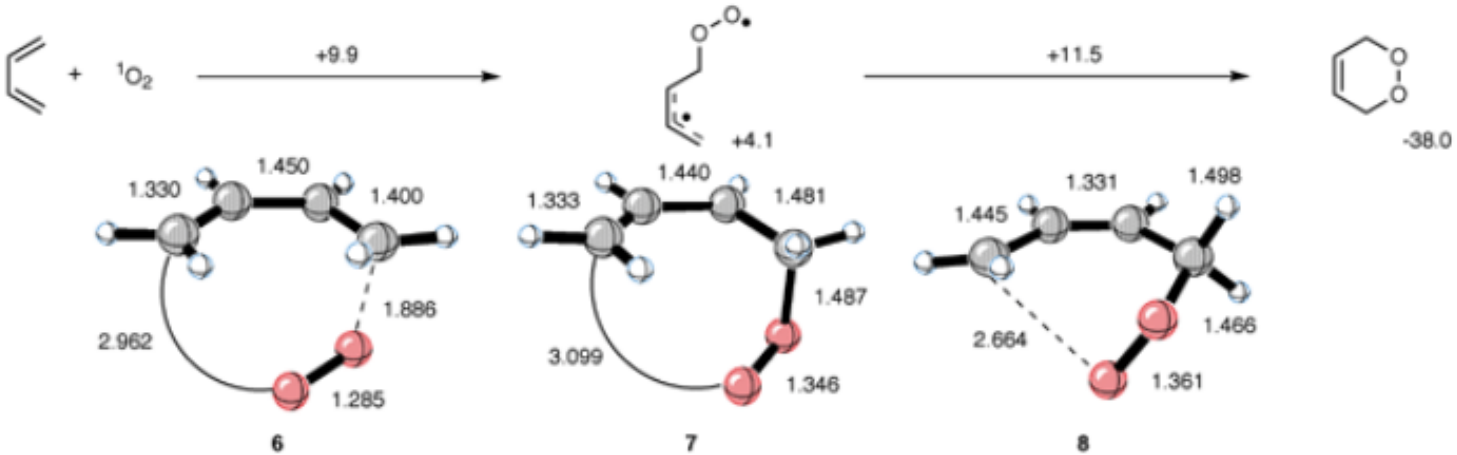


Figure 4. The relationship of the depth of penetration of light into a tumor and the wavelength of the light. Scattering and absorption are the predominant factors in limiting the penetration of light into the tumor. The depth of penetration doubles when the wavelength of light is increased from 550 to 630 nm (where Photofrin II is activated) and from 630 to 700 nm. Beyond 700 nm, the depth of penetration by light only increases another 10% by shifting into the infrared region (*1*, *2*).

Diels-Alder Reactions of Singlet Oxygen

Andrew G. Leach and K. N. Houk, DOI: 10.1039/B111251C



Scheme 3 CASSCF(10,8)/6-31G* optimised geometries and MCQDPT2 energetics for the Diels–Alder reaction between singlet oxygen and butadiene.[18] The energy for each species is given in kcal mol^{-1} relative to reactants.

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$$\Delta H^{\circ}_{rxn} = \text{products} - \text{reactants}$$

subtract sum of bonds broken
from sum of bonds formed
to find the enthalpic driving force

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- CO_2 (799 kJ/mol) and water (926 kJ/mol)
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Hilton M. Weiss DOI: 10.1021/ed085p1218

- The heat of combustion of any organic molecule can be calculated approximately by merely balancing the reaction and determining how many moles of oxygen are consumed
- For example, oxidation of methane uses two moles of O_2 per mole of CH_4 releasing ca. $2 \times 460 = 920$ kJ/mol *of methane*
- The experimental heat of combustion of methane is 890 kJ/mol
- Glucose combines with 6 O_2 for complete conversion to CO_2 and H_2O so $6 \times 460 = 2760$ kJ
- The experimental value is 2801 kJ/mol *of glucose*

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Table 1. Enthalpy Calculated from the Amount of Oxygen Used

Compound	Moles of O_2	$\Delta H°/(kJ\ mol^{-1})$		Error (%)
		Calc	Exp	
Methane	2.0	–920	–890	3.4
Octane	12.5	–5750	–5452	5.5
Methanol	1.5	–690	–726	5.0
Ethanol	3.0	–1380	–1367	1.0
Benzoic Acid	7.5	–3450	–3227	6.9
Sucrose	12.0	–5520	–5644	2.2
Thiophene	6.0	–2760	–2805	1.6

NOTE: The experimental data is from ref 2.

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- ATP bonds generated in glucose metabolism derive from oxidation of H atoms removed from the organic substrates
- Aerobic metabolism of a glucose molecule uses 6 O_2 and can generate 38 ATP bonds
- Anaerobic metabolism generates only 2 molecules of ATP per glucose molecule
- The small quantity of energy required for those two ATP bonds comes from rearranging the oxygen atoms of the carbohydrate molecule to generate products with improved bonding and no oxygen is consumed

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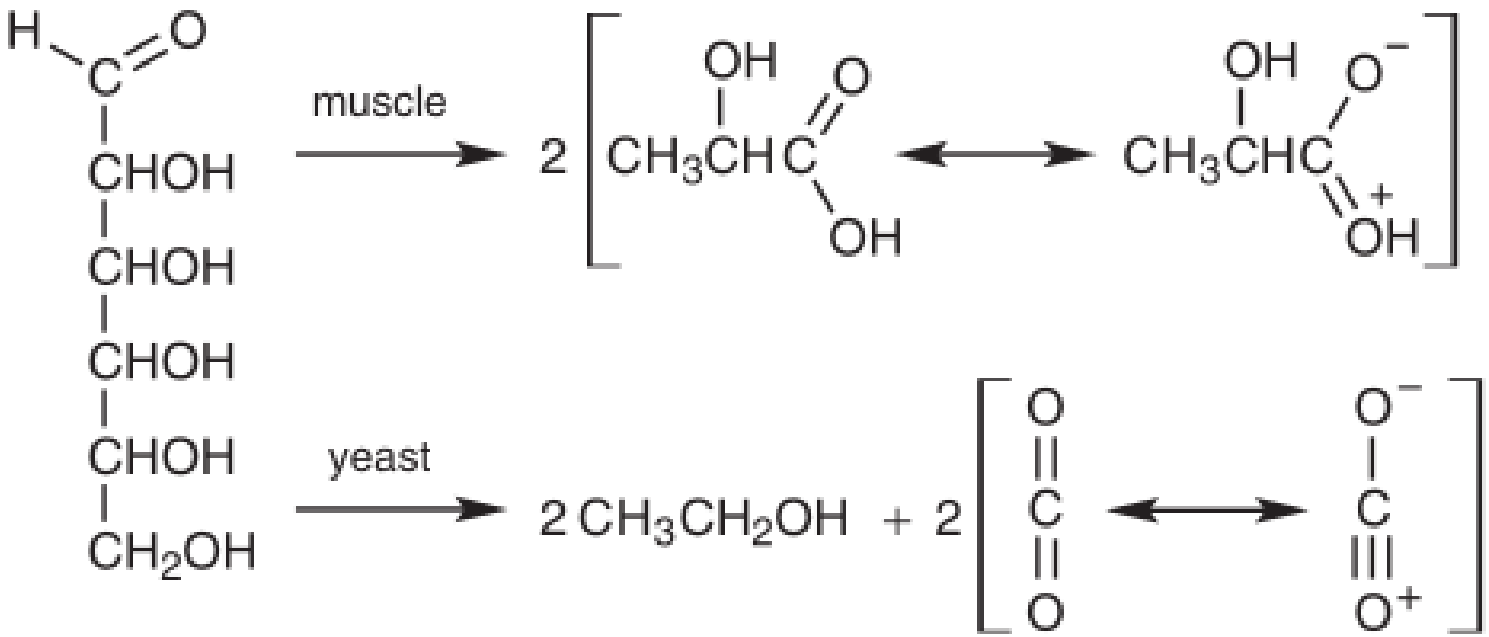

Scheme I. Balanced equations of the anaerobic metabolism of glucose.

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- Methane is abundant on many planets and moons far from the sun
- Free oxygen is found on none of them
- Oxygen atoms out there are all bound up with C, H, Si, metals, etc.
- While earthly "fuels" may result from the sun's energy, it is really the O_2 molecules generated during photosynthesis that trap the energy of the sun and facilitate life on earth

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