Planck's Black Body Radiation Law

$$PFD \approx \frac{\lambda^{-4}}{e^{\frac{hc}{\lambda kT}} - 1}$$

Relative Photon Flux Density (PFD)

6500 K—λ 550 nm
6000 K—λ 600 nm
5500 K—λ 655 nm
5000 K—λ 720 nm
4500 K—λ 800 nm
4000 K—λ 900 nm
3000 K—λ 1200 nm
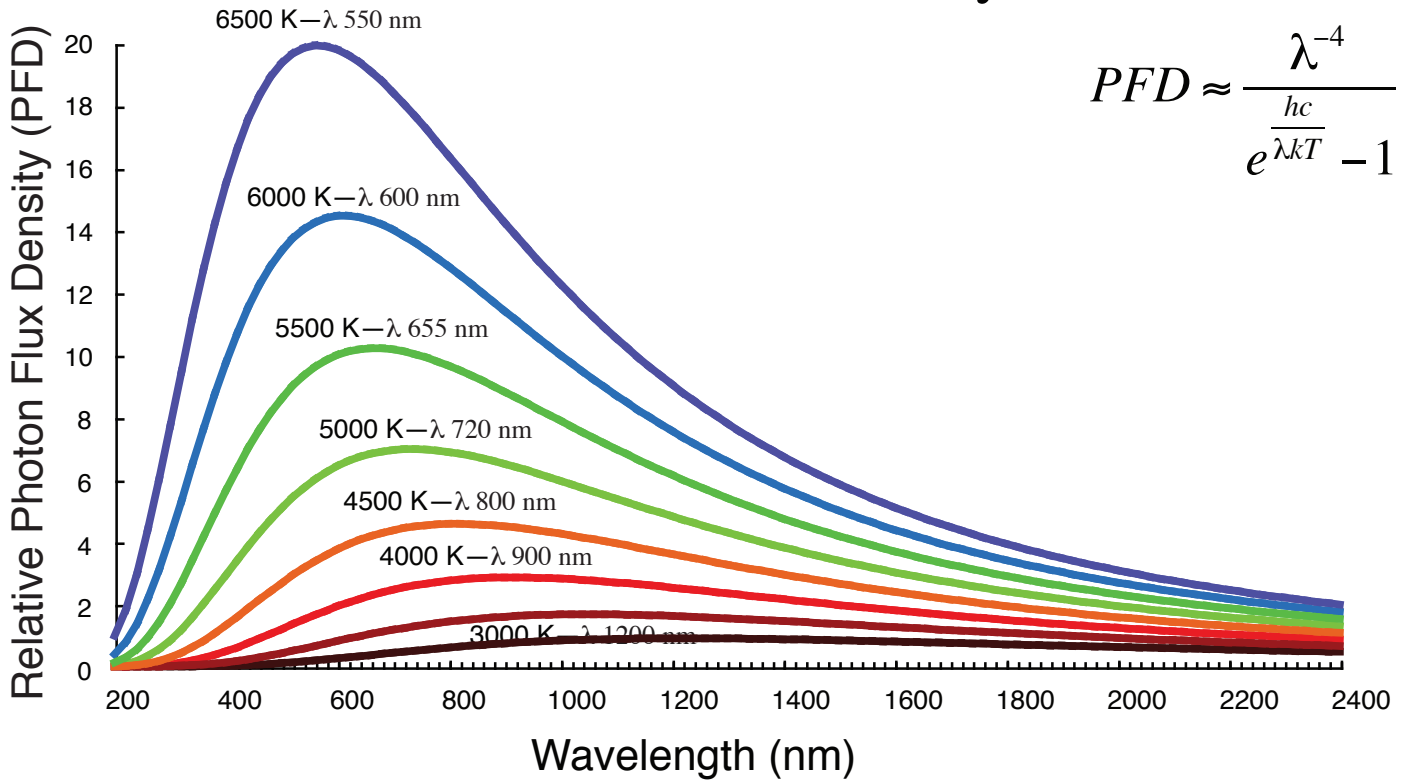
Wavelength (nm)

Solar Irradiance

Lower irradiance at sea level is due to Rayleigh scattering and atomic absorbance (Frauhoffer lines), and absorbance by atmospheric ozone (O_3 —UV wavelengths), and carbon dioxide and water vapor (CO_2 and H_2O —infrared wavelengths)
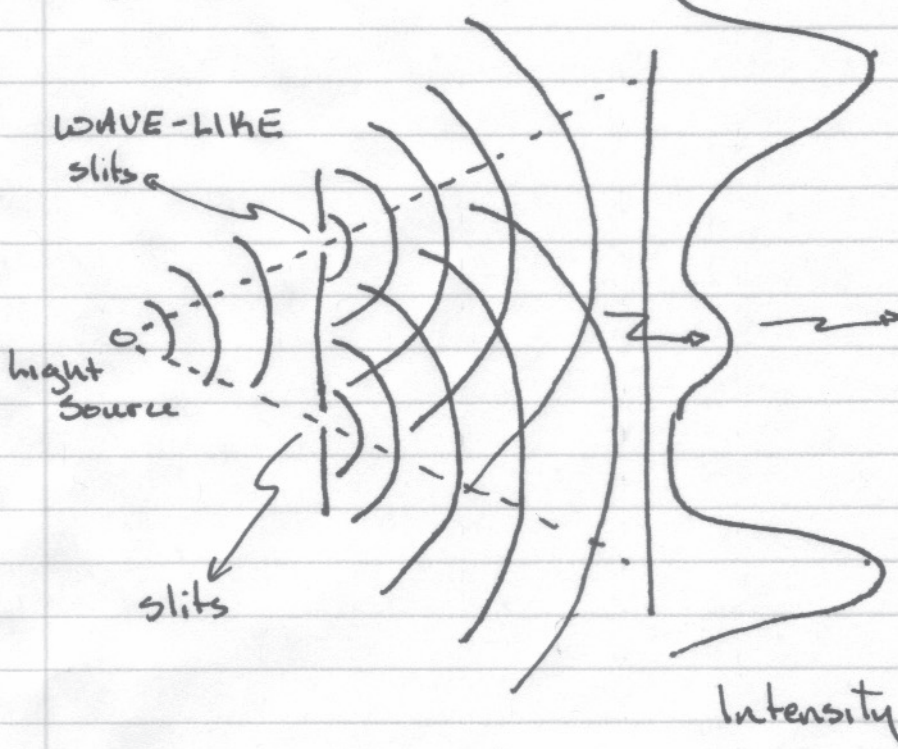
Irradiance (W m^{-2} nm^{-1})

Above Atmosphere

At Earth Surface (temperate latitudes)

Wavelength (nm)
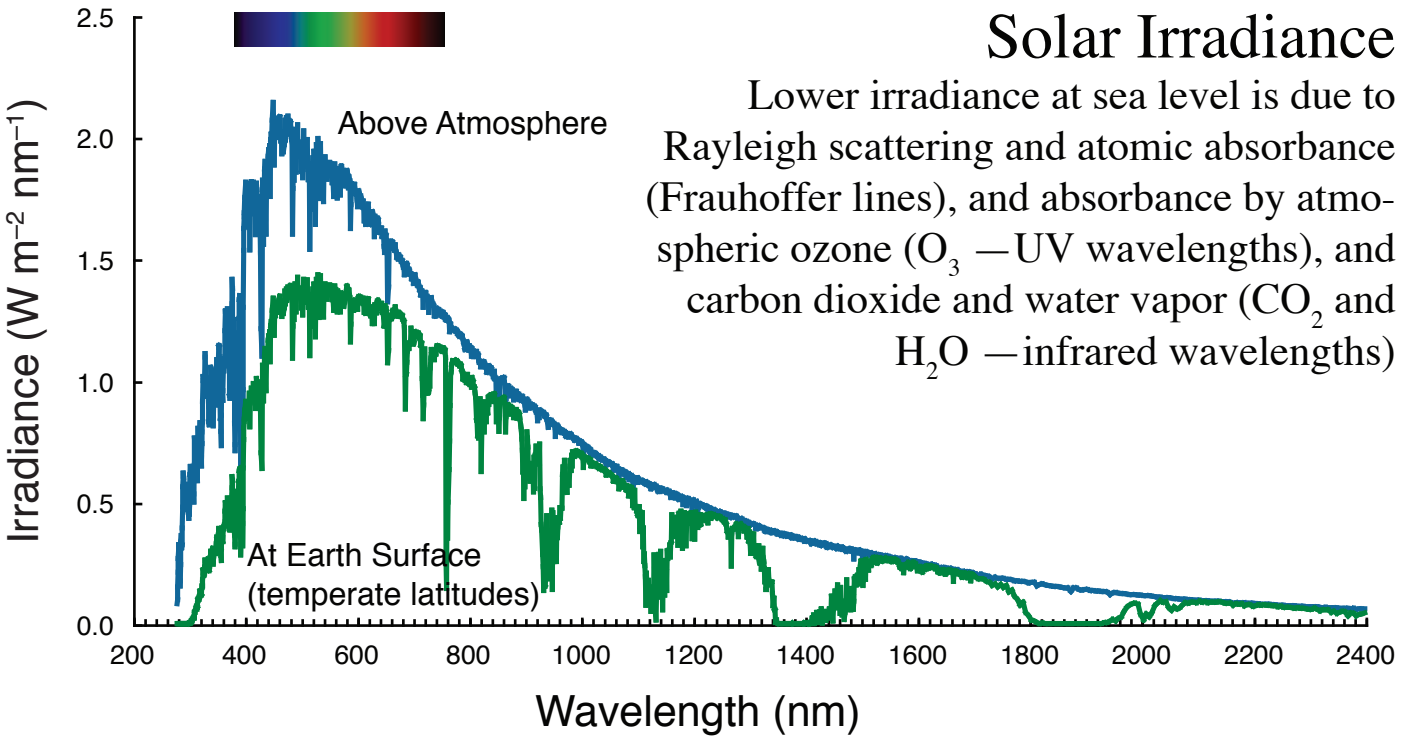
Lucida
Photosynthetica

LIGHT

Light has both wave-like & particle-like properties

WAVE-LIKE

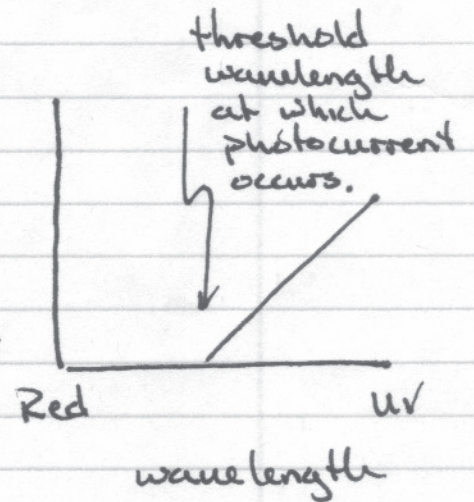slits

light source

slits

phenomena of interference which can be explained by the wave-like nature of light
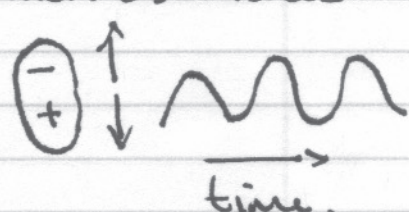
Intensity

(Fresnel experiment)

PARTICLE-LIKE

light

e^-

V
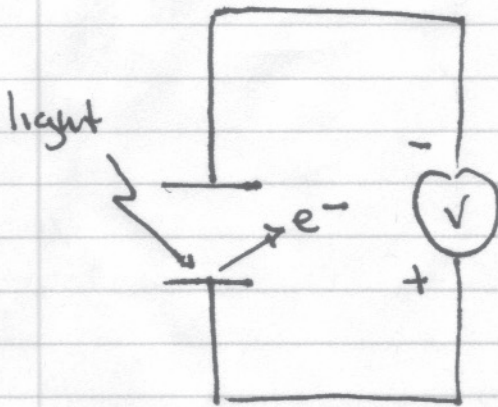
negative (anode) voltage for photocurrent

threshold wavelength at which photocurrent occurs.

Red   UV

wavelength

This is the photo-electric effect.

what is light?

First, consider a dipole $\boxed{\begin{smallmatrix}-\\+\end{smallmatrix}}$ which oscillates

at some frequency ν (nu): $\boxed{\begin{smallmatrix}-\\+\end{smallmatrix}}$ $\updownarrow$ ∿∿

time.

The motion of the dipole generates both a
magnetic and electric field, which then
propagate away from the dipole at some
velocity, v, which is independent of the frequency
ν (in cycles/sec).

In a vaccum, the velocity $v = \dfrac{1}{\sqrt{\varepsilon_0 \mu_0}} = c$ (the 'speed
of light')

$\underbrace{}$ dielectric
constant
for a
vacuum

$\underbrace{}$ magnetic
permeability

$(8.85 \times 10^{-12} \text{ F/m})$ $\quad 1.257$ henry/m.

In other materials

$v = \dfrac{c}{\sqrt{\varepsilon_R \mu_R}}$

$\underbrace{}$ relative
dielectric.

$\underbrace{}$ relative
magnetic
permeability.

$F = kg^{-1} m^{-2} A^2 s^4 \quad (m^{-1})$
$H = kg \, m^2 s^{-2} A^{-2} \quad (m^{-1})$
$s^4 s^{-2} \quad (s^2 m^{-2})$
sq root & invers. $m \, sec^{-1}$

3.335×10^{-6} sec/m
3×10^{6} m/sec.

For biological materials, $\mu_R \approx 1$, so: $v = \dfrac{c}{\sqrt{\varepsilon_R}}$

9.5 Maxwell's equations

Here we list the four Maxwell equations that are thought to apply in every situation and that define the properties of electric and magnetic fields:

$$\iint_S D_N \, dS = \iiint_V \rho_{\text{free}} \, dV,$$

$$\oint E_R \, dR = -\frac{d}{dt}\left[\iint_S B_N \, dS\right],$$

[9.10]

$$\iint_S B_N \, dS = 0,$$

$$\oint H_R \, dR = \iint_S \left[\tilde{J}_{\text{free}} + \frac{d\tilde{D}}{dt}\right]_N dS.$$

Note that in the second equation the flux of $\tilde{B}$ is taken over an open surface bounded by the path over which the emf is calculated. In the third equation the flux of $\tilde{B}$ is taken over a complete closed surface.

The relationship between the fields $\tilde{D}$ and $\tilde{E}$ is given by

$$\tilde{D} = \varepsilon_0 \tilde{E} + \tilde{P} \quad \text{or} \quad \tilde{D} = \varepsilon_R \varepsilon_0 \tilde{E},$$

[9.10]

where the first relation is universally true and the second holds for homogeneous dielectrics. Similarly, the relationship between $\tilde{H}$ and $\tilde{B}$ is given by

$$\tilde{B} = \mu_0(\tilde{H} + \tilde{M}) \quad \text{or} \quad \tilde{B} = \mu_R \mu_0 \tilde{H},$$

[9.11]

where again the first relation is universally true and the second holds for homogeneously permeable material.

In a region in which there is no free charge ($\rho_{\text{free}} = 0$) and which is non-conducting so that no free currents flow ($J_{\text{free}} = 0$), the equations in electric and magnetic fields show considerable similarities. It is easily shown that these equations combine to predict a self-propagating electromagnetic wave with a velocity v such that

$$v = \frac{1}{\sqrt{\varepsilon_R \varepsilon_0 \mu_R \mu_0}}.$$

[9.12]

or $v = 1/\sqrt{\varepsilon_0 \mu_0}$ in free space. These expressions predict the velocity of light or radio waves which are just examples of the general electromagnetic wave in different frequency ranges. The plane electromagnetic wave is such that the directions of oscillation of $\tilde{E}$ and $\tilde{B}$ are perpendicular to each other and to the direction of propagation. A rotation from the direction of $\tilde{E}$ to the direction of $\tilde{B}$ will advance a right-handed thread in the direction of propagation. Two independent modes are possible for a plane electromagnetic wave travelling in a given direction which have their electric and thus magnetic fields at right angles to each other.

It is beyond the scope of this book to develop the theory of electromagnetic waves but, having shown that an oscillating magnetic field will generate an oscillating electric field and that an oscillating electric field will generate an oscillating magnetic field, it can come as no surprise that together they form a self-propagating wave, even in a vacuum.

The equations for light velocity arise directly from Maxwell's equations, which are complex & include time-dependence.

The 'take-home message' is that the velocity of propagation depends upon how the electrical & magnetic fields interact with the medium through which they are propagating.
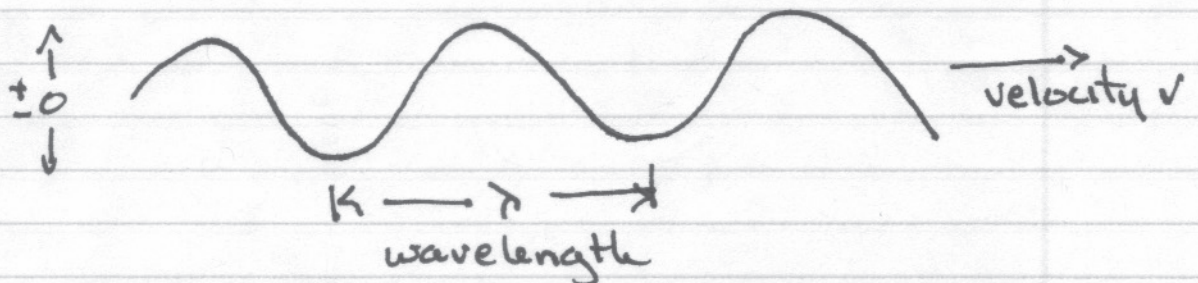
The effect can be striking:

% decrease compared to light velocity in vacuum.

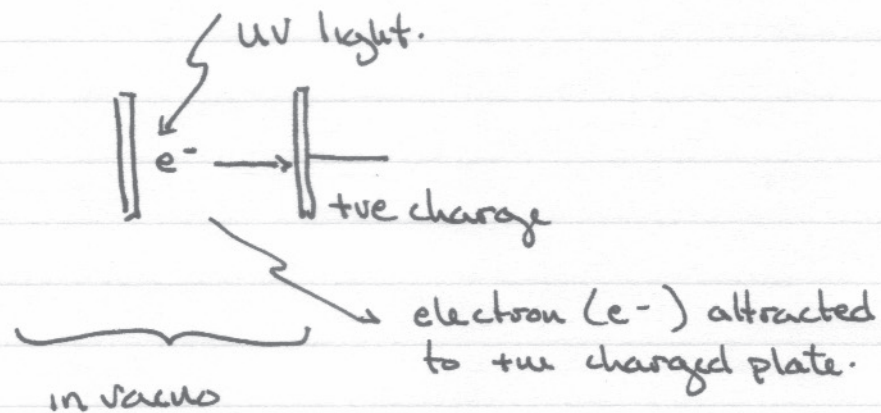|	
vacuum	0%
air	0.03%
water	25%
dense flint glass	40%

Note that the frequency (in cycles/sec) will remain constant, a property of the oscillating dipole.

The convention we are most familiar with is a 'wave' propagating through space:

wavelength

where frequency $\nu = \dfrac{\nu}{\lambda}$ $\dfrac{cm\ sec^{-1}}{cm\ cycle^{-1}} = \dfrac{cycles}{cm}$

Digression: Photoelectric Effect.

UV light.

e⁻ ⟶ +ve charge

electron (e⁻) attracted to +ve charged plate.

in vacuo

The e⁻ transfer results in current flow

Current flow is directly proportional to light intensity. This is the "first law of the photoelectric effect".

The second property is more complex.

cathode (+ve)

anode (-ve)

e⁻ $(\frac{1}{2}mv^2)$ ⟶

+ ‖ - Voltage bias. (eV)

the e⁻ is ejected with a kinetic energy $\frac{1}{2}mv^2$ which can be counteracted by the voltage bias

eV greater than $\frac{1}{2}mv^2$ will cause the e⁻ to turn back.
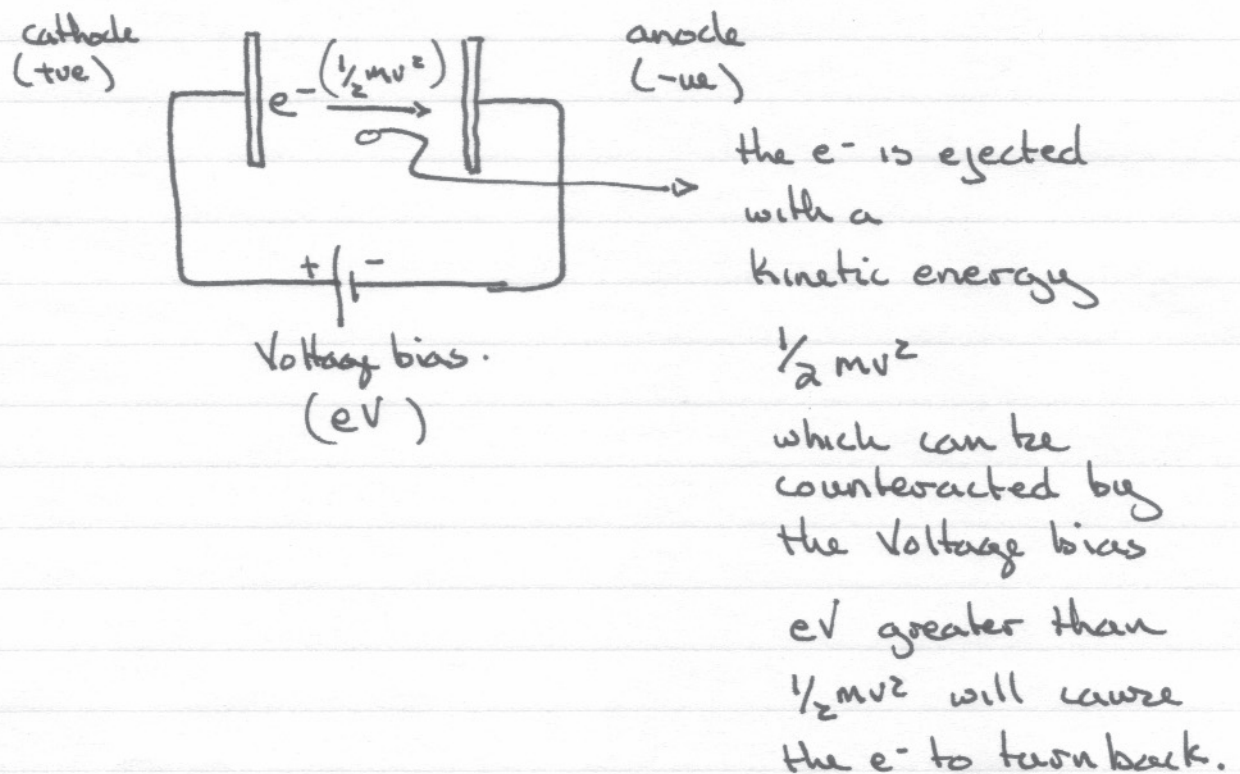
With this set-up, it is possible to measure the kinetic energy of the electron e^-

It was discovered (by Lenard in 1902) that the maximum electron kinetic energy is completely independent of the light intensity and instead depends upon the wavelength, or more accurately, the frequency:

$$\nu = \frac{c}{\lambda}$$

from which we obtain the graph:

$$\frac{mV_M^2}{2} = h(\nu - \nu_0)$$
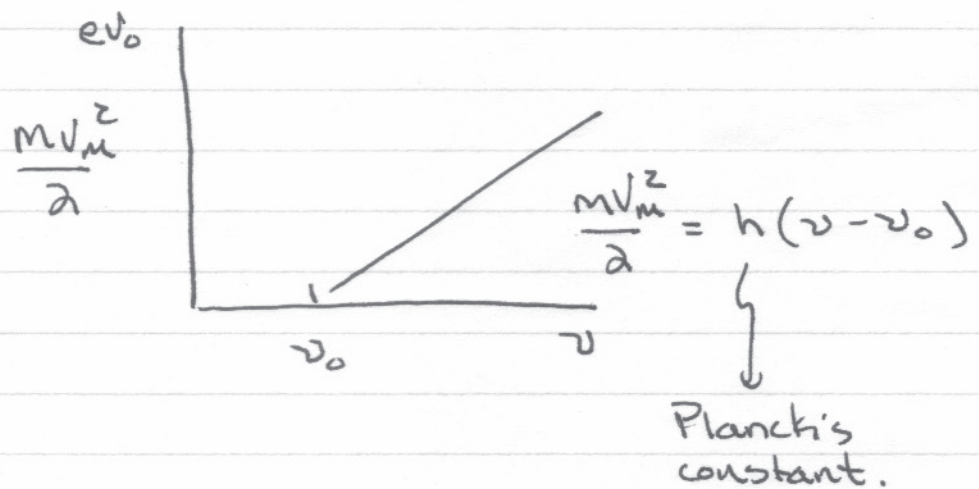
Planck's constant.

Einstein proposed the relation on theoretical grounds, based upon the idea of discrete energy quanta.
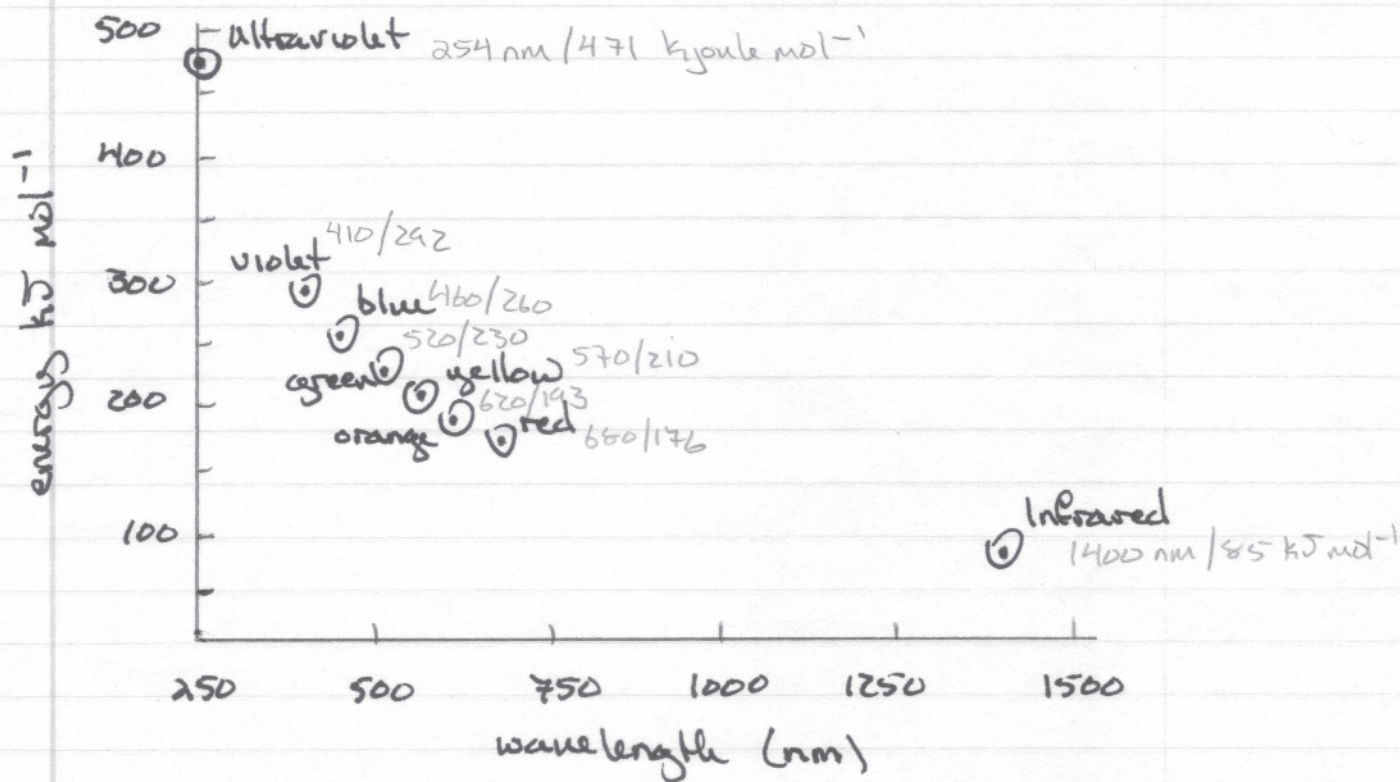
The energy of light (photons) is described by:

$$E_? = h\nu$$

, or, for a vacuum

$$E_? = h \frac{c}{\lambda_{vacuum}}$$

Planck's constant
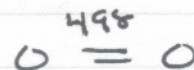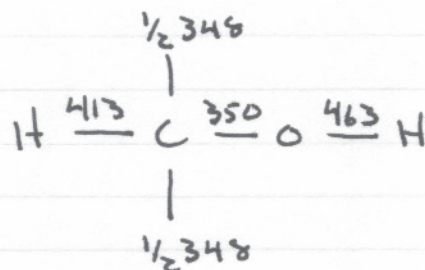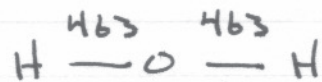
6.6×10^{-34} joule·sec

1.584×10^{-37} kcal·sec

By comparison, carbon - carbon bond energy 348 kJ mol⁻¹
oxygen - hydrogen ~ ~ 463 ~ ~

So photon energies are similar to bond energies.

$$H_2O + CO_2 \longrightarrow (CH_2O)_n + O_2$$

bond energies

$$H \overset{463}{\longrightarrow} O \overset{463}{\longrightarrow} H$$

$$H \overset{413}{\longrightarrow} \underset{\frac{1}{2}348}{\overset{\frac{1}{2}348}{C}} \overset{350}{\longrightarrow} O \overset{463}{\longrightarrow} H$$

$$O \overset{800}{=} C \overset{800}{=} O$$

$$O \overset{498}{=} O$$

reactants	products
2·463	413
2·800	348
	350
————	463
2526	498
kjoules mol^{-1}	————
	2072 kj mol^{-1}

Δ 454 kJ mol^{-1}
required to convert
reactants to products

Nobel 1991
page 246

Light is irradiated by hot objects (anything warmer than absolute zero, 0 °K)
Many lamps work on this basis, for example tungsten filament incandescent bulbs.

The sun, however, is our major light source.

The λ of emitted light is a function of the temperature: the hotter the object is, the shorter the wavelength

Wein's displacement law $\quad \lambda_{max} = \dfrac{3.6 \times 10^6 \; nm \cdot K}{T \, (°K)}$

describes the wavelength of maximal irradiation.

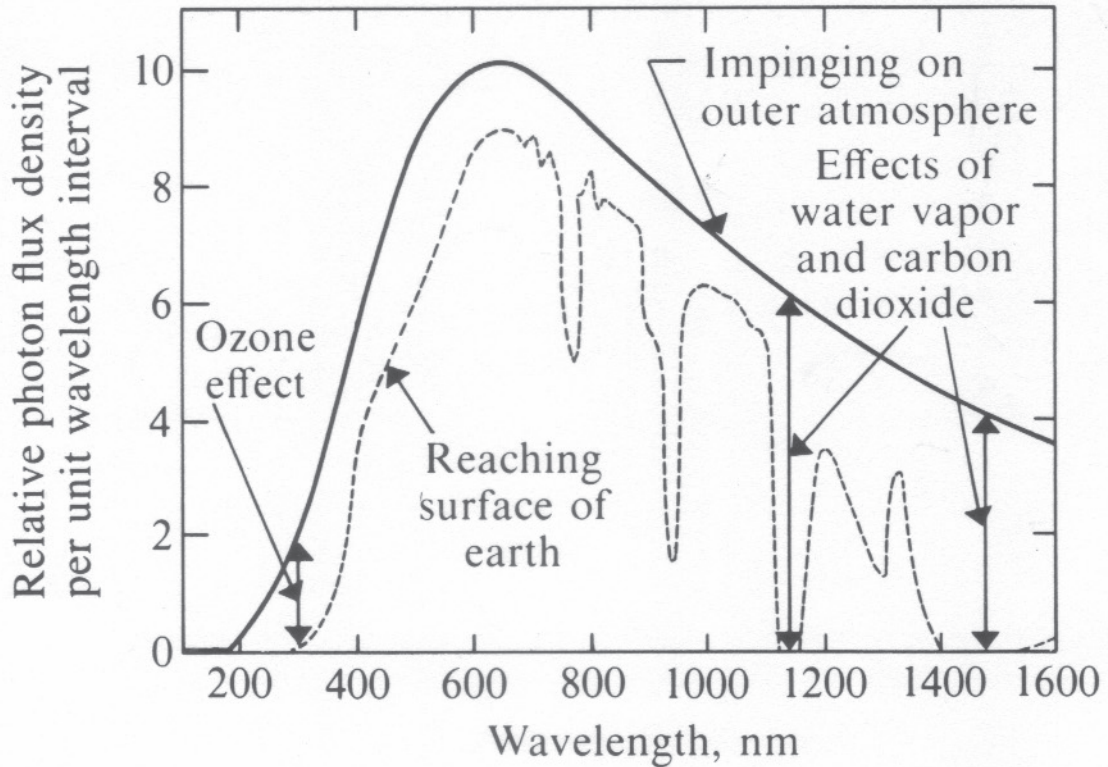|	°K	λ_{max}	
Sun	5800	620 nm	
tungsten bulb	2900	1240 nm	(that is, mostly heat)
for room temperature objects	298	12000 nm	

So, light sources (the sun) light energies are within the range of energies required for chemical bond re-arrangements.

In photosynthesis, it is necessary to trap and use the photonic energy.

Solar Irradiation

Figure 4.2

Wavelength distributions of the sun's photons incident on the earth's atmosphere and its surface. The curve for the solar irradiation on the atmosphere is an idealized one based on Planck's radiation distribution formula. The spectral distribution and the amount of solar irradiation reaching the earth's surface depend on clouds, other atmospheric conditions, altitude, and the sun's angle in the sky. The pattern indicated by the lower curve is appropriate at sea level on a clear day with the sun overhead (for further details see Bickford and Dunn, 1972; Gates, 1980; Monteith, 1973; and Seliger and McElroy, 1965).

Planck's radiation distribution formula describes the ideal photon flux density per wavelength interval:

$$\lambda^{-4} / (e^{(hc/\lambda kT)} - 1)$$

Wein's displacement law describes the wavelength of maximal irradiation as a function of temperature:

$$\lambda_{max} \bullet T = 3.6 \bullet 10^6 \quad nm \bullet K$$

Source: PS Nobel 1991. Physicochemical and Environmental Plant Physiology. Academic Press.

LIGHT ABSORPTION

The physical event of absorption must occur very rapidly, because a photon moves very quickly. When a light photon is absorbed by a molecule, its energy is transferred to an electron, which gains the energy of the photon

Typically, for a molecule, the ability to absorb a photon depends upon the discrete energy levels the electron may reside in. The discrete energy levels depend upon the available electron orbitals, and the vibrational sublevels of the nuclei of the molecule.
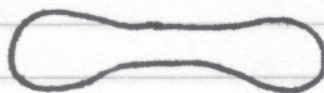
The properties of the discrete energy levels are not predicted by simple theory. For complex molecules like chlorophyll, light absorption causes a shift from a π orbital electron cloud:
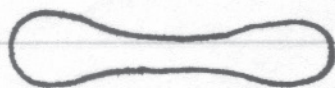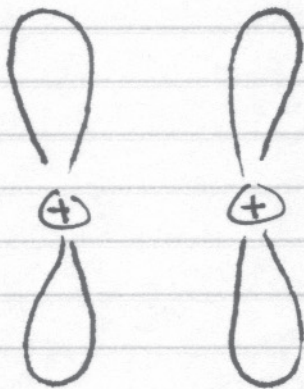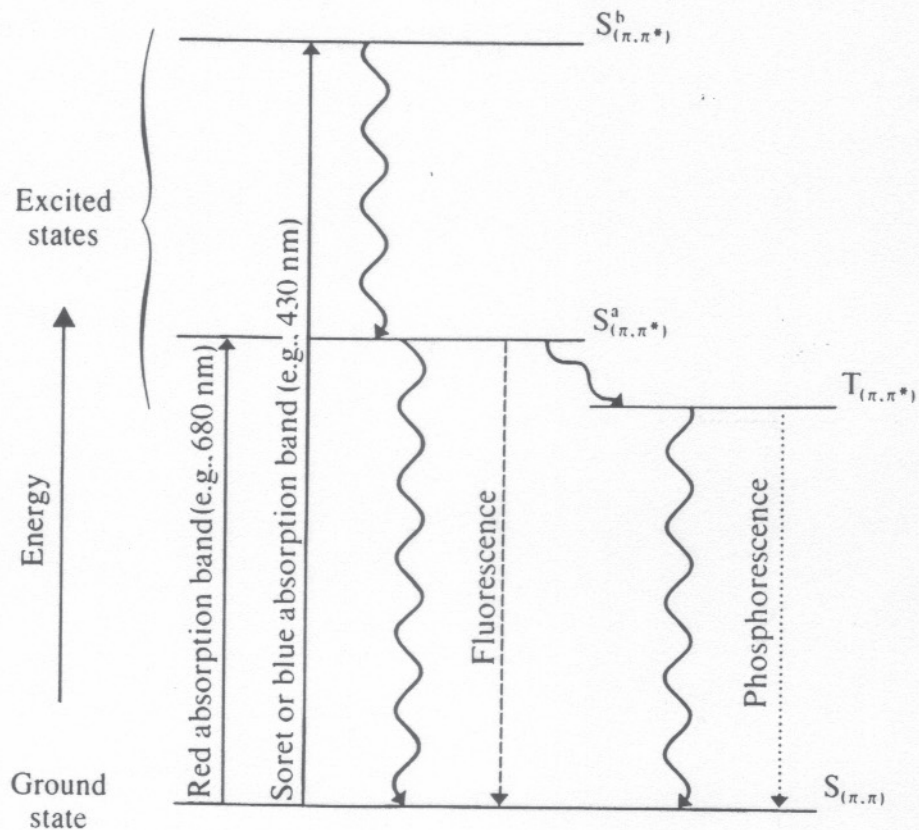
$\oplus$ $\oplus$ ← nucleus. π orbital (bonding)

to an "excited state" π^* orbital:

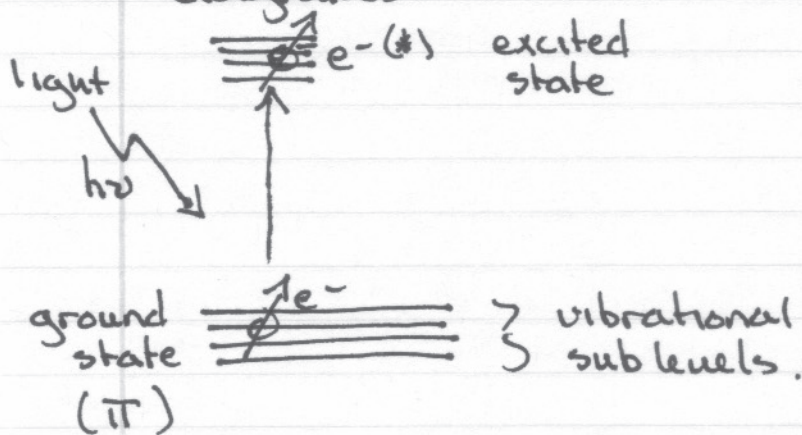$\oplus$ $\oplus$ π^* orbital (anti-bonding)

Figure 4.5

Energy level diagram indicating the principal electronic states and some of the transitions of chlorophyll. Straight vertical lines represent the absorption of light; wavy lines indicate radiationless transitions, for which the energy is eventually released as heat; broken lines indicate those de-excitations accompanied by radiation.
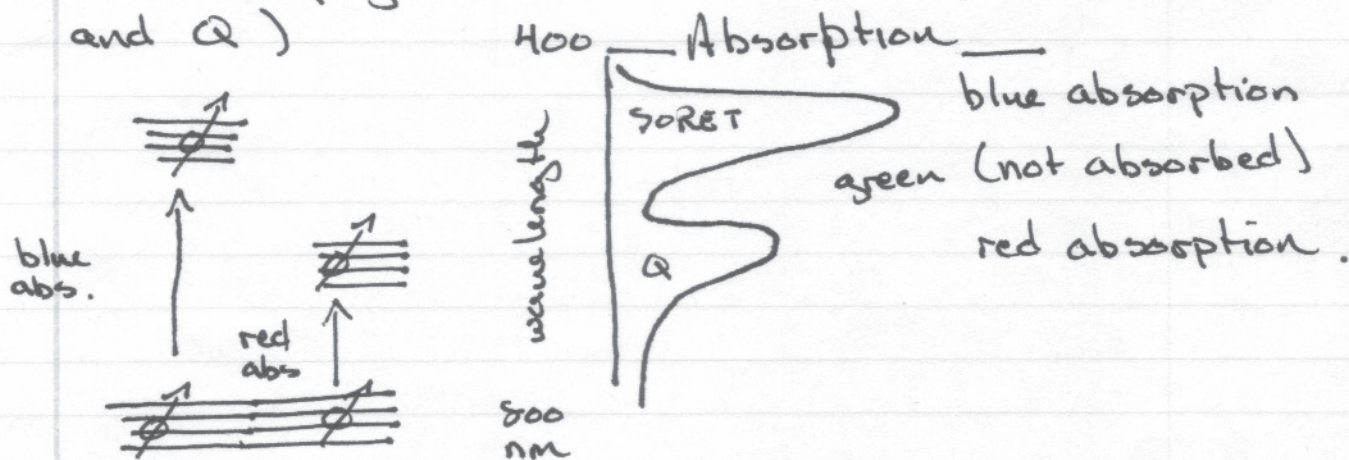

(a)   (b)
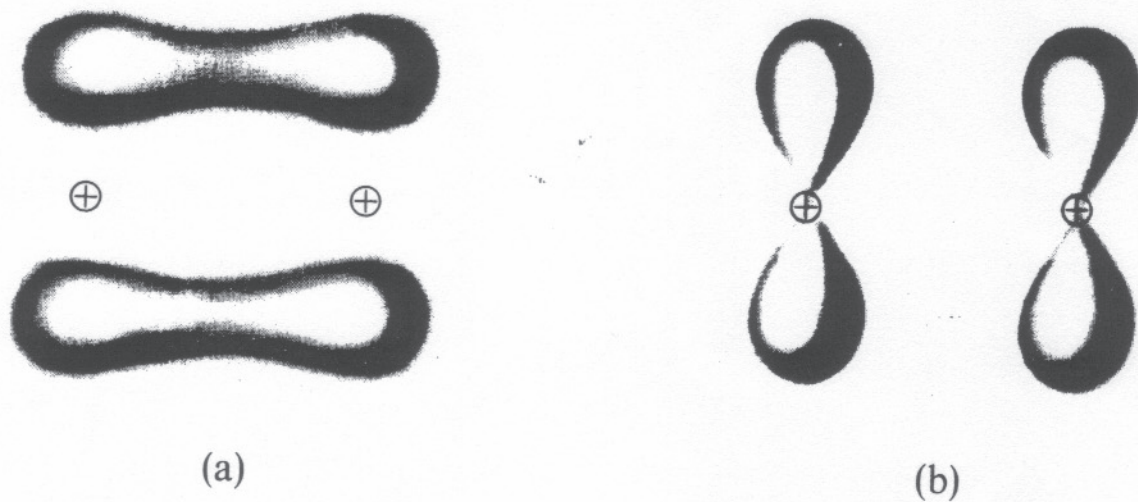
Figure 4.4

Typical π and π^* orbitals, indicating the spatial distribution about the nuclei ($\oplus$) where the greatest probability of finding the electrons occurs: (a) π orbital (bonding), and (b) π^* orbital (antibonding).

Nobel, Park S. (1991) Physicochemical and Environmental Plant Physiology. Acedemic Press.

Absorbtion is usually described by energy level diagrams:

light

hν

ground state
(π)

e⁻(*)   excited state

1 e⁻

} vibrational sublevels.

For chlorophyll, there are two excited states (Soret and Q)

blue abs.

red abs

400 — Absorption —

SORET

Q

800 nm

wavelength

blue absorption

green (not absorbed)

red absorption.

As a general rule of thumb, absorption depends upon the number of conjugated bonds in the molecule:

Double Bonds		λ_{max}	ϵ (extinction coefficient)
1	C–C=C–C	185 nm	10^4 l/mole·cm
2	C–C=C–C=C–C	217 nm	
3		286	
5		347	
7		400	
9		439	10^5 l/mole·cm
11/13		472/492	
15		510	

Number of Conjugated Bonds
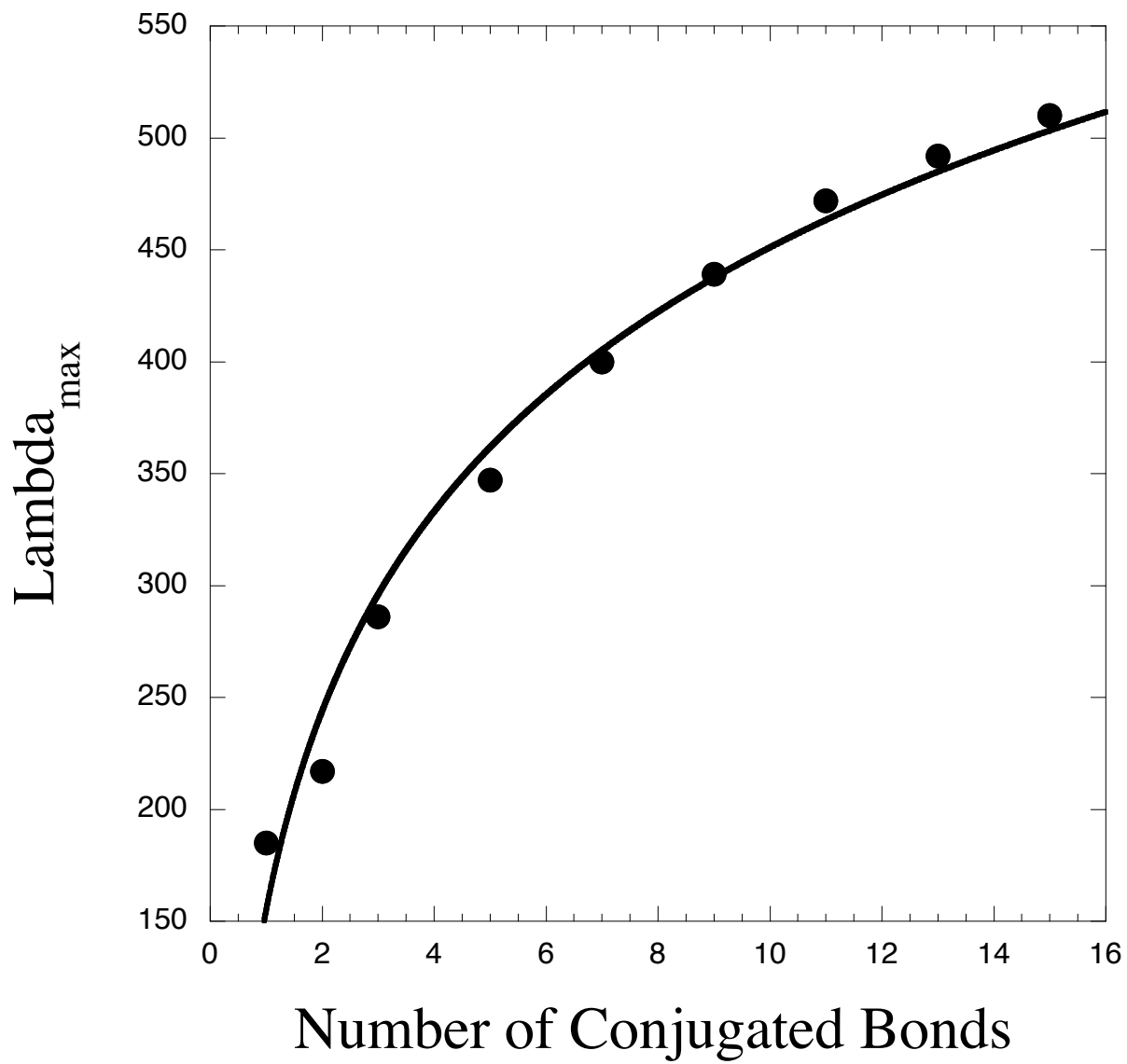
Absorption also depends upon the environment surrounding the molecule. The choice of solvent will affect A_{max} and the bandwidth of absorption.
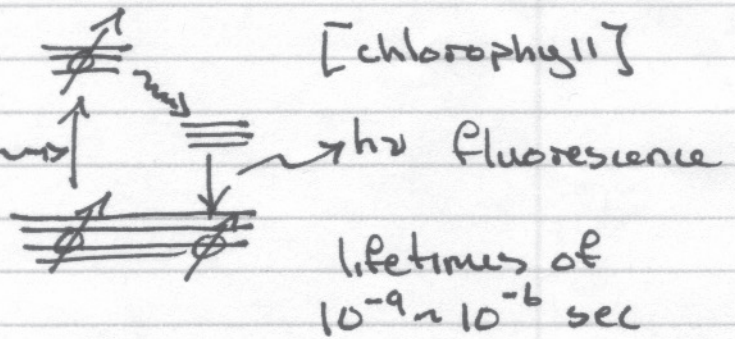
Temperature (at least room temperature versus very cold, e.g. liquid nitrogen) causes significant absorption band broadening.
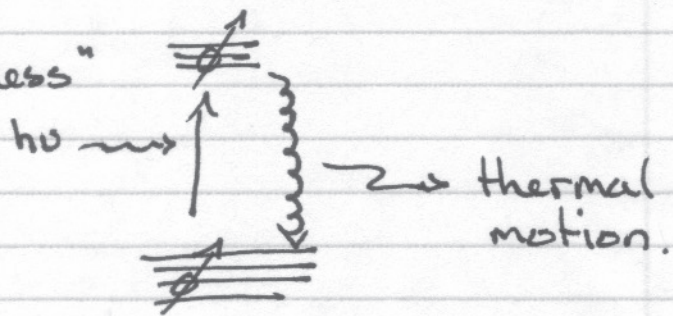
Once the photon is absorbed, what happens?

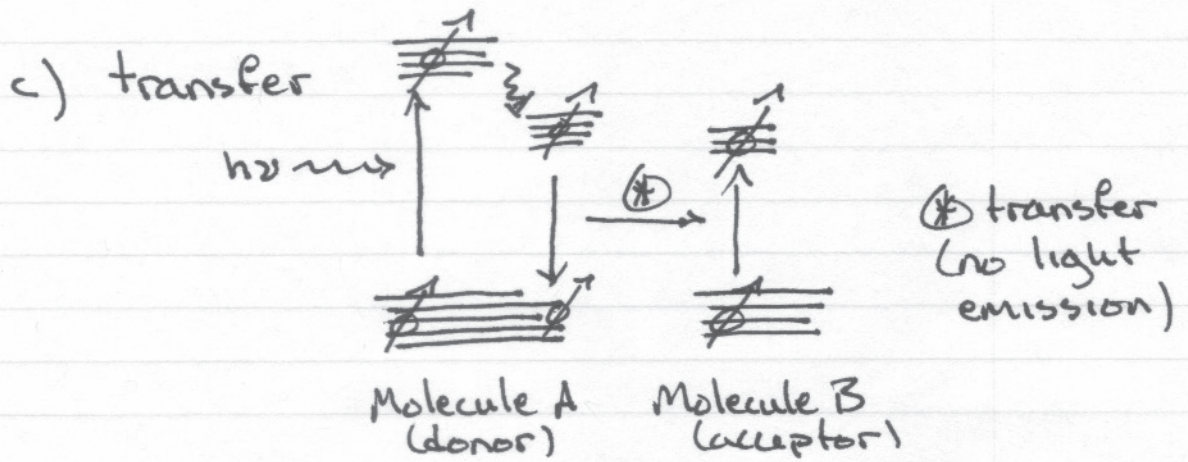Four Possibilities

PHOTON FATES

a) fluorescence

$h\nu \rightsquigarrow$

[chlorophyll]

$\rightarrow h\nu$ fluorescence

lifetimes of $10^{-9} \sim 10^{-6}$ sec

b) "radiationless"

$h\nu \rightsquigarrow$

$\rightsquigarrow$ thermal motion.

c) transfer

$h\nu \rightsquigarrow$

⊛ transfer
(no light
emission)

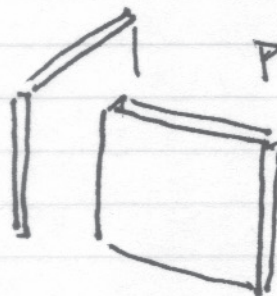Molecule A　　　Molecule B
(donor)　　　　　(acceptor)

Rate of transfer depends upon ① distance:

$$\frac{1}{d^6}$$

→ distance between donor and acceptor
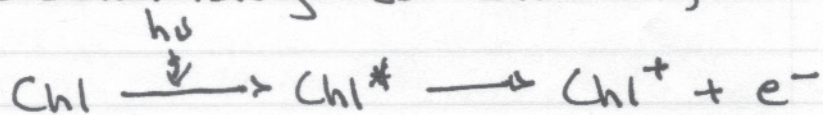
② the angle (cosine)

parallel : high rate of transfer

perpendicular:
low rate of transfer

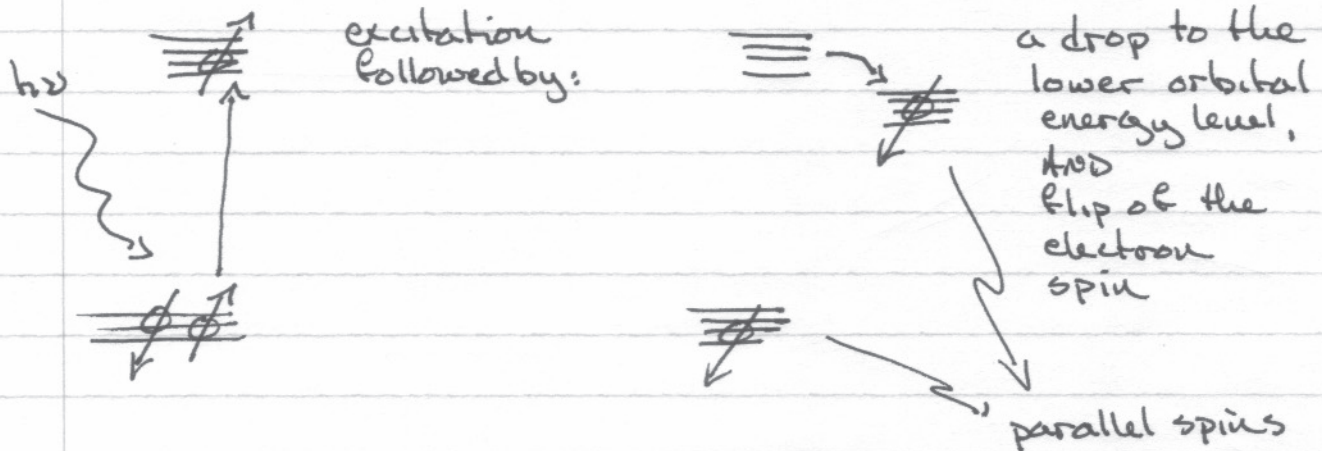③ And, overlap of emission & absorption energy levels

d) photochemistry (e⁻ donation)

$$Chl \xrightarrow{h\nu} Chl^* \longrightarrow Chl^+ + e^-$$

Transfer & photochemistry are crucial in photosynthesis.
Fluorescence & radiationless loss are useless.
Fluorescence is used to monitor photosynthetic efficiency

Chlorophyll triplet state (addendum)

Another fate of an absorption event is the relatively long-lived triplet state. For this, we need to consider 2 e^- of the π orbital:

excitation followed by:

a drop to the lower orbital energy level, AND flip of the electron spin

parallel spins

This is the triplet state.

Relaxation to the ground energy state is slow: msec to secs (much slower than relaxation/fluorescence) Thus it is called phosphorescence.

Chlorophyll triplets, Chl^T, can interact with oxygen:

$$O_2 \longrightarrow O_2^- \quad (\text{singlet } O_2)$$
$$(\text{highly oxidizing}).$$