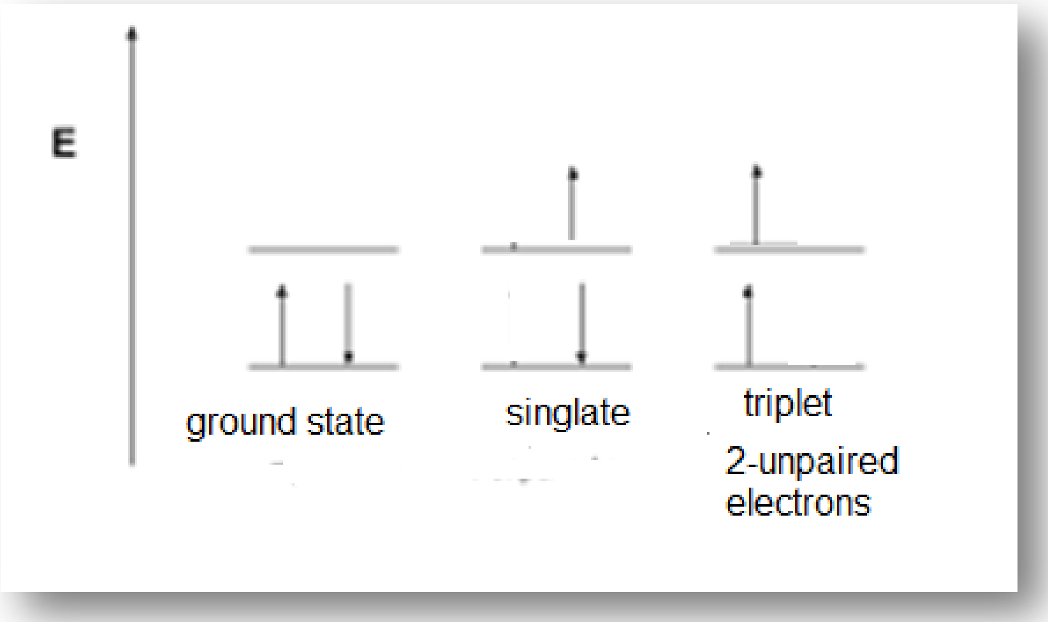
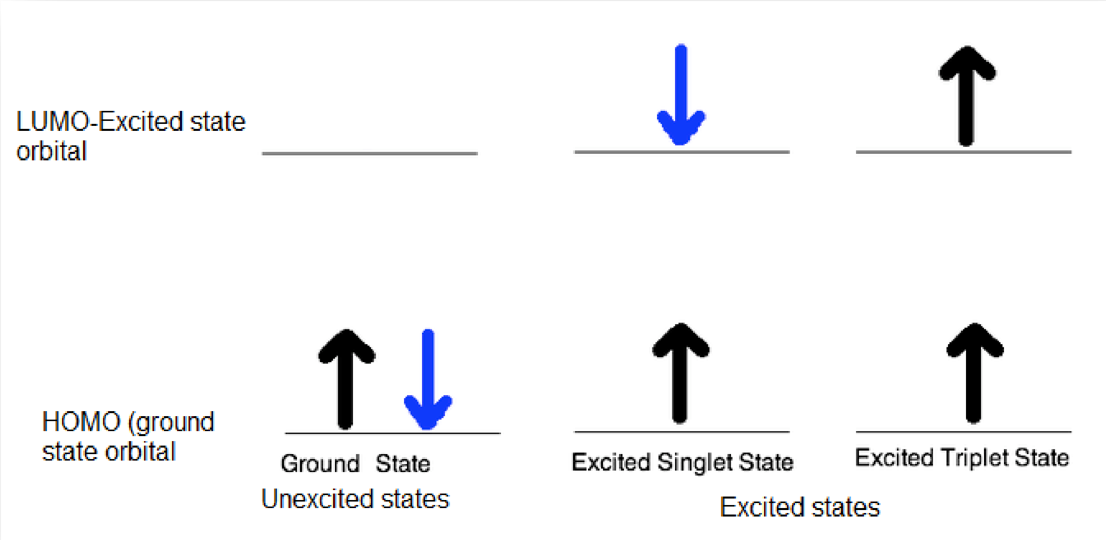
Singlet and tinplated excited states

When a matter absorbs light with a proper energy it would be excited to either Singlet or tinplated excited states. Electron in orbital has spin of +1/2 for up spin electron and s=-1/2 for down spin electron(, ms = −1/2, and +1/2).. In ground state spins are coupled (s=zero), but upon absorption of light, two possible routes would occur. Singlet or triplet depending on change or not spin of excited electron from HOMO into LUMO orbitals:





$S = 2\Sigma s + 1$

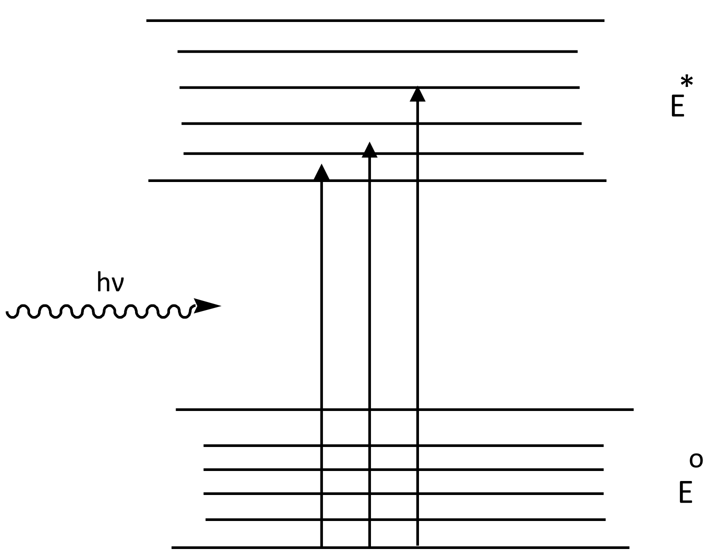
For singlet : $S=2(1/2-1/2)+1= 1$,

For triplet: $S=2(1/2+1/2)+1= 3$

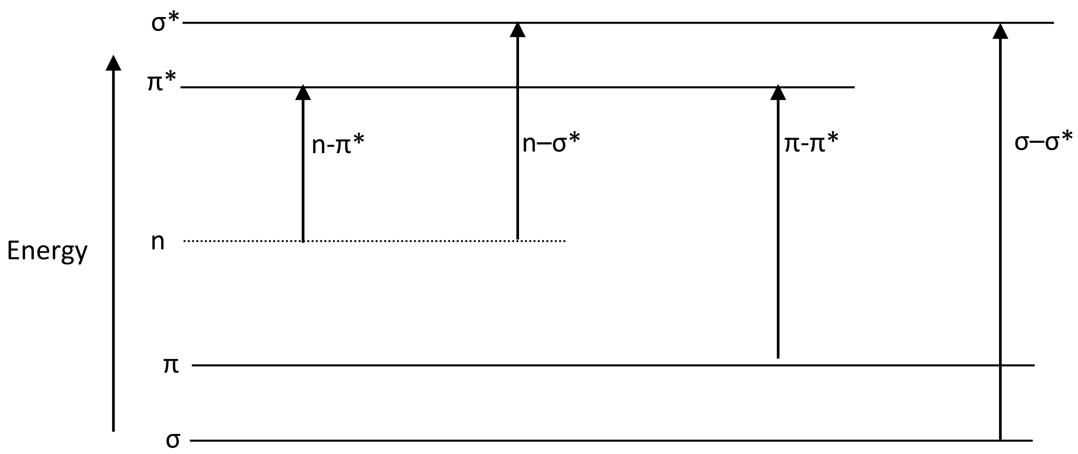
Generally, singlet state is more energetic than triplet state.

Absorption and emission of radiation

According to the concept of quantization of energy levels for each species only a particular energy with a characteristic wavelength (hν) can be absorbed or emitted by the chemical species. Absorption of radiation of photons with a sufficient energy, normally in the UV-visible region can lead to transitions between the ground state of the absorbing species (E_o) into the excited state (E^*) as shown below:



Generally, electronic transitions occur according to type of orbitals. Molecular orbitals based upon linear combination of atomic orbitals can be considered to give bonding and anti-bonding molecular orbitals (σ, σ* and π, π*). The possible electronic transitions are summarized in the following scheme



Generally, singlet excited states have a higher energy than triplet states and triplet states have longer lifetimes than singlet states due to spin inversion.

Photosynthesis

Photosynthesis is a process used by plants and other organisms to convert light energy into chemical energy that can later be released to fuel the organisms' activities (energy transformation). This chemical energy is stored in carbohydrate molecules, such as sugars, which are synthesized from carbon dioxide and water. In most cases, oxygen is also released as a waste product. Most plants, most algae, and cyanobacteria perform photosynthesis; such organisms are called photoautotrophs. Photosynthesis is largely responsible for producing and maintaining the oxygen content of the Earth's atmosphere, and supplies all of the organic compounds and most of the energy necessary for life on Earth.

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow{\text{Light}} \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$

Figure12 :Overall equation for the type of photosynthesis that occurs in plants

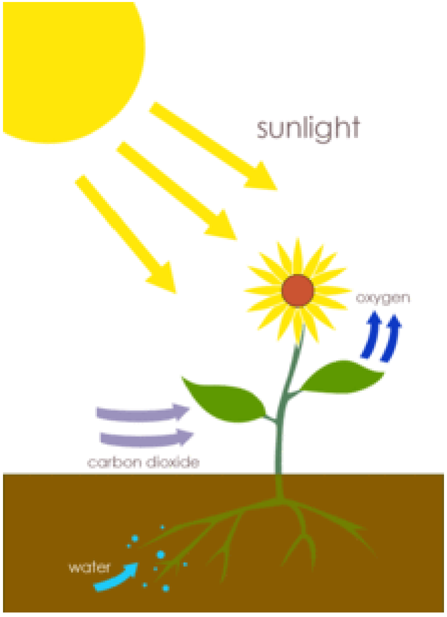


Figure 10: Schematic of photosynthesis in plants. The carbohydrates produced are stored in or used by the plant

Fluorescence and phosphorescence

When a molecule or atom in the ground state (S_0) absorbs light, one electron is excited to a higher orbital level. This electron maintains its spin according to the spin selection rule; other transitions would violate the law of conservation of angular momentum. The excitation to a higher singlet state can be from HOMO to LUMO or to a higher orbital, so that singlet excitation states S1, S2, S3… at different energies are possible .

Kasha's rule stipulates that higher singlet states would quickly relax by radiationless decay or internal conversion (IC) to S1. Thus, S1 is usually, but not always, the only relevant singlet excited state. This excited state S1 can further relax to S0 by IC, but also by an allowed radiative transition from S1 to S0 that emits a photon; this process is called fluorescence.

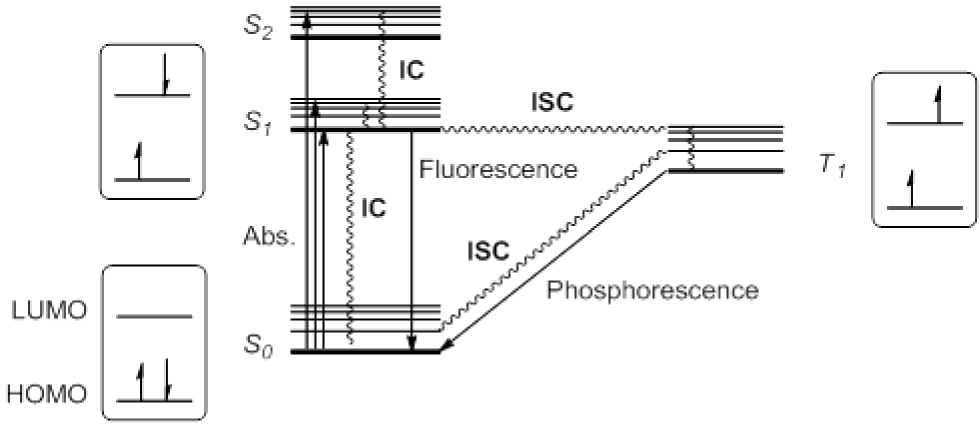


Figure 11: methods of loosing of photoexcitation energy

These excited species, either S1 or T1, have a half empty low-energy orbital, and are consequently more oxidizing than the ground state. But at the same time, they have an electron in a high energy orbital, and are thus more reducing. In general, excited species are prone to participate in electron transfer processes.

The quantum yield (Φ)

Quantum yield (Φ) is defined as the ratio of the number of molecule consumed or produced to the number of photons absorbed. Notably, quantum yield is independent of instrument settings and describes how efficiently a fluorophore converts by excitation light into fluorescence. Both absorbance and fluorescence emission (360 nm excitation) spectra are measured Quantum yield is calculated using the equation:

Φ= (number of formed or consumed molecules) /(number of absorbed photons), or

Φ= (number of formed or consumed moles)/(number of absorbed Ernestine),

Φ= (rate of chemical reaction)/(rate of light absorption), The value of Φ is normally ranged from (0upto 1) for normal photochemical reaction. However, in chain reaction and polymerization it reaches (10^6). Φ is useful in investigation rate of reaction and study mechanism of reaction. Generally, number of absorbed photon can be measured using physical and chemical actinometer.

Actinometry

Actinometer is a chemical system (chemical actinomete) or physical device (physical actinometer) which determines the number of photons in a beam integrally or per unit time. This name is commonly applied to devices used in the ultraviolet and visible wavelength ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer,

while bolometers, thermopiles, and photodiodes are physical devices giving a reading that can be correlated to the number of photons detected.

Potassium ferrioxalate is commonly used, as it is simple to use and sensitive over a wide range of relevant wavelengths (254 nm to 500 nm.

Example: Acetone vapor absorb 91.5% of the incident light (313 nm) in cell of volume of 59 mL with initial pressure of 7663 tor at 56.3 C and the intensity of incident light was 4.8×10^{-4} J/sec for 7 hours, find Φ for this process?

Solution:

Number of moles= PV/RT= (7663/760 x 0.05)/ 0.082 x 329.8= 4.85×10^{-5} moles,

Energy of Einstein= Nhc/λ,

$E= (6.02 \times 10^{23} \times 6.62 \times 10^{-34} \times 3 \times 10^{8})/ (313 \times 10^{-9})$

$E= 38.197 \times 10^{4}$ J/mol. (energy of one Einstein)

No. of Einstein= (absorbed energy x time in second)/(energy of one Einstein)

No. of Einstein= (48.1 x 10^{-4} x 0.915 x 7 x 3600)/ (38.197 x 10^{4}),

= 2.9 x 10^{-4} Einstein

Φ= (no of moles)/(no of Einstein),

Φ= (4.85 x10^{-5} moles)/(2.9 x 10^{-4} Einstein)

Φ= 0.17

How to loss photo-excitation energy

After a molecule absorbs light and it becomes photoexcited :

$A + h\nu \longrightarrow A^*$

Then it can loss its excitation energy via some routes:

1-chemical change,

2-physical change

1-According to the first route (chemical change), excited species is converted to another stable species via chemical reaction:

$A + h\nu \longrightarrow A^*$

$A^* \longrightarrow P$

In this case, activation energy for converting A to product is derived from energy of light.

2-Physical change

According to this route, excitation energy is lost via some physical changes:

a-photoprocesses,

b-thermal processes

a-photopysical changes: in this route excitation energy is lost as a radiation either fluorescence or phosphorescence.

$A + hv \longrightarrow A^*$

$A^* \longrightarrow A + hv^- \quad (hv > hv^-)$

If change occur with same spin then its fluorescence, if occurs between two cases then its phosphorescence..

$S_1^o \longrightarrow S_o^v + hv^-$ (fluorescence process)

$T_2^o \longrightarrow T_1^v + hv^-$ (fluorescence process)

$S_1^o \longrightarrow T_1^v + hv^-$ (phosphorescence)

$T_1^o \longrightarrow S_o^V + hv^-$ (phosphorescence)

b-Thermal processes:

In this route photoexcited species loss its excitation energy as a heat (not light) so that it is called thermal de-excitation processes and it occurs in two ways: if thermal process occurs between same spin then it is called (internal conversion, IC), if occurs between different spins then called (inter system crosses (ISC):

$A^* \longrightarrow A +$ heat

$S_1^o \longrightarrow S_o^v +$ heat (IC)

$T_2^o \longrightarrow T_1^v +$ heat (IC)

$S_1^o \longrightarrow T_1^v +$ heat (ISC)

$T_1^o \longrightarrow S_o^V +$ heat$^-$ (ISC)