Consequences of light absorption : Jablonski Diagram

Molecular Excitation:

When radiation of suitable energy is absorbed by the molecule, then an electronic excitation takes place.

Many molecules have **an even number of electrons** and thus in the ground state, all the electrons are spin paired. The quantity 2S+1, where S is the total electronic spin, is known as the **spin multiplicity** of a state. When the spins are paired ↑↓ the upward orientation(clockwise) of the electron spin is cancelled by the downward orientation (anticlockwise) so that total electronic spin S=0 . That makes **spin multiplicity of the state** 1.
$s_1=+1/2$; $s_2=-1/2$

so that $S=s_1+s_2=0$
Hence, 2S+1=1

the spin multiplicity of the molecule is 1(means that the **molecule is in the singlet ground state**.)
When by the absorption of a photon of a suitable energy hν , one of the paired electrons goes to a higher energy level (excited state), the spin orientation of the single electrons may be either parallel or anti-parallel.
• If spins are parallel, S=1 or 2S+1=3 i.e., the spin multiplicity is 3. This is expressed by saying that the molecule is in the triplet excited state.
• If the spins are anti-parallel, then S=0S=0 so that 2S+1=12S+1=1 which is the singlet excited state, as already discussed.
since the electron can jump to any of the higher electronic states depending upon the energy of the photon absorbed, we get a series of singlet **excited states**, Sn and a series of triplet excited state Tn where n=1,2,3…n=1,2,3… . Thus S_1,,S_2,,S_3,…,… etc are respectively known as first singlet excited states, second singlet excited states and so on. Similarly, in T_1,,T_2,,….., they are respectively known as first triplet excited state, second triplet excited state and so on.

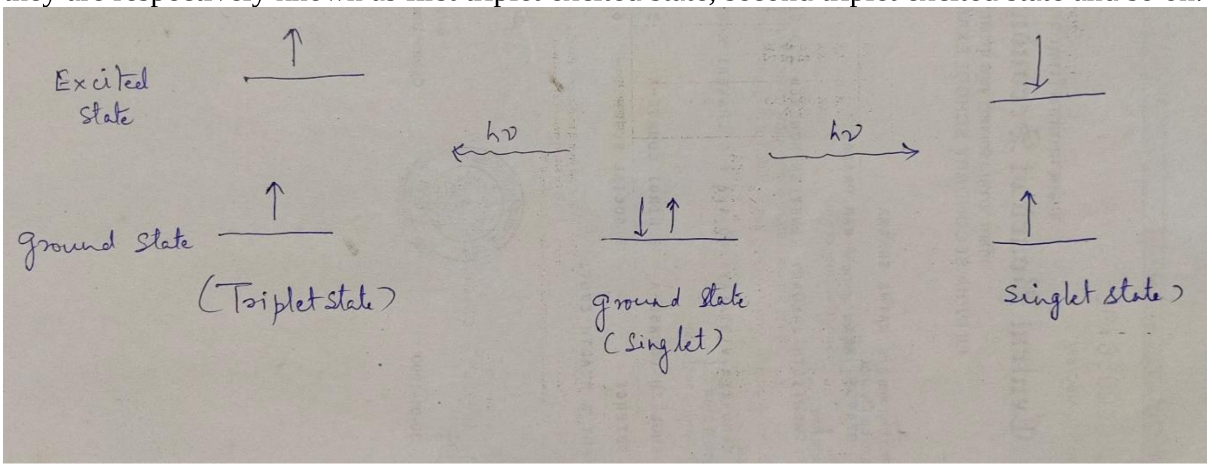
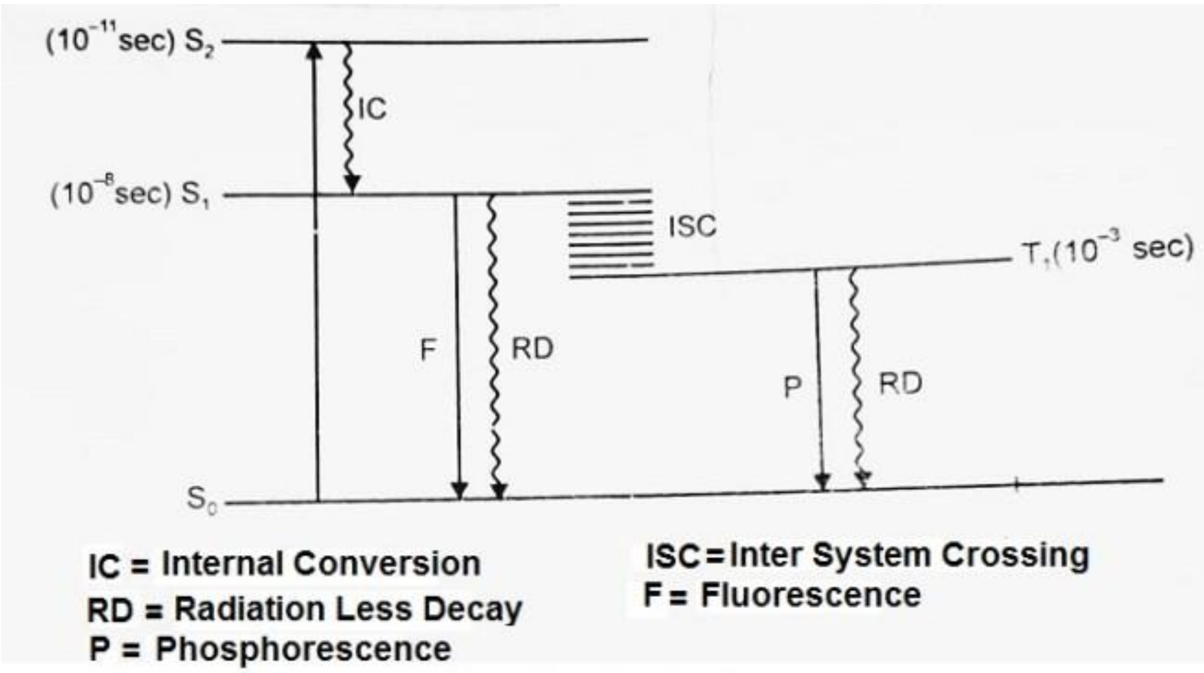


Fig. Spin orientation on absorption of photon of light

Jablosnki Diagram:

On absorption of photon of light , the electron of the absorbing molecule may jump from singlet ground state(S_0) to singlet excited state(S_1 , S_2 , S_3 , S_4 etc.) depending upon the energy of light absorbed. For each singlet state there is a corresponding triplet state (T_1, T_2, T_3 etc. respectively).



Jablonski Diagram

Singlet State:

Singlet states have all paired electrons in it. Molecules are diamagnetic. Absorption of light without spin inversion produces a singlet excited state.

S_0 = singlet ground state of the molecule

S_1 = First singlet excited state

S_2 = Second singlet excited state

. …….. S_n = n^{th} singlet excited state

Triplet State:

In triplet states all electrons are unpaired in it. Molecules are paramagnetic. . Singlet excited states may undergo spin inversion to produce triplet excited states.

T_1 = First triplet excited state

T_2= Second triplet excited state

.................**T_n= n^{th} triplet excited state**

Here, **n= 1, 2, 3, 4,......**

Radiative & Non-Radiative (Radiation less) Transitions:

The transitions take place between two molecular states with absorption or emission of the photon are called radiative Transitions.

The transitions that take place between two molecular states without emission of a photon are called non-radiative transitions.

Absorption:

The radiative transitions from a lower to a higher electronic state of a molecule take place by the adsorption of a photon. The energy of a photon is converted into the internal energy of a molecule. It is the fastest transition that takes place on the timescale order of **10^{-15}s.**

Adsorption of a photon promotes a molecule from S_0 to one of the vibrational levels of the singlet excited state **(S_1, S_2..).**

Non-Radiative (Radiation less) Transitions:

Internal Conversion (IC):

Radiationless transitions between higher energy states and lower energy states of the same spin multiplicity are called internal conversions. **$S_3 \rightarrow S_2$, $S_2 \rightarrow S_1$, $T_2 \rightarrow T_1$**, etc. are internal conversions that occur rapidly (**10^{-11} to 10^{-9} s).**

Fluorescence:

The radiative transition between two electronic states of the same spin multiplicity is fluorescence. The emission of light during the transition of singlet excited state $\mathbf{S_1}$ to the ground state is fluorescence.

Intersystem Crossing:

Transitions between the singlet state to lower triplet state or vice versa is called intersystem crossing. This is the non-radiative process that takes place between isoelectronic vibrational levels belonging to electronic states of different spin multiplicity. Example: $\mathbf{S_1}$ **to** $\mathbf{T_1}$

The intersystem crossing is slower than the internal conversion and has importance in photochemistry. It occurs on a timescale of $\mathbf{10^{-10}}$ **to** $\mathbf{10^{-6}}$ **s.**

Radiative transition

Fluorescence:

The radiative transition between two electronic states of the same spin multiplicity is fluorescence. The emission of light during the transition of singlet excited state $\mathbf{S_1}$ to the ground state is fluorescence. Time period is 10^{-9} sec. example: Some examples of fluorescence include LED lights, clothes that glow in "black light," which are light sources that contain UV light/blue, CaF_2, Uranium, Petroleum Chlorophyll.

Phosphorescence (or delayed fluorescence) :

Phosphorescence is the radiative transition from triplet state to ground state. The emission of light during the transition of $\mathbf{T_1}$ **to** $\mathbf{S_0}$ is phosphorescence. Time duration is greater than 10^{-3} sec or more. Examples: Zinc sulphide, alkaline - earth sulphides etc.