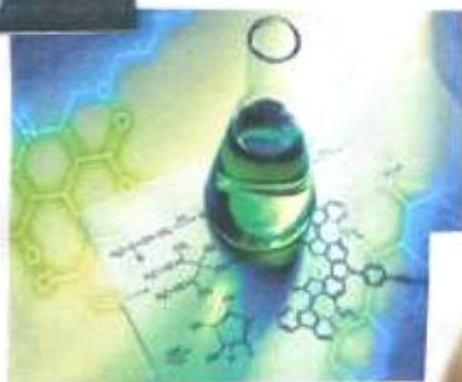


SRI SATHYA SAI COLLEGE  
FOR WOMEN  
BHOPAL

Session - 2022-2023

PHYSICAL CHEMISTRY

CCE-1



2.5 / 3.5  
13/11/22



Alexander Jablonski  
(1898-1980)

Submitted to  
Dr. Pooja Bhardwaj

Submitted by  
Nayan Sahu  
B.Sc. III year

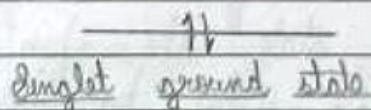


Q1) Explain Jablonski Diagram in detail

A1) Jablonski diagram is the depiction of various process during photochemical reaction.

- It is possible to interpret the initial processes in photochemical activation with the help of Jablonski diagram in terms or patterns of states.
- This diagram also help us to understand the phenomena of fluorescence and phosphorescence

Spin-multiplicity - If in any molecule  $S$  represents the total number of electrons spin in any electronic state then  $2S+1$  is known as the spin multiplicity of a state. When the spins are paired (11), the value of  $S=0$ .



$$s_1 = \frac{1}{2} \text{ (upward orientation of spin)}$$

$$s_2 = -\frac{1}{2} \text{ (downward orientation of spin)}$$

$$\text{So that } S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0$$

$$\text{Hence, } 2S+1 = 2 \times 0 + 1 = 1 \text{ (for ground state)}$$

- This indicates that the spin multiplicity of the molecule is 1. This state of affair is spoken as the singlet ground state of the molecule.



Parallel spin orientation

Antiparallel spin orientation

- When a molecule absorbs a photon (quantum) of a suitable energy  $h\nu$ , one of the paired electrons goes to higher state from a singlet ground state. Now in the excited state the spin orientation of these electrons may be either parallel ( $\uparrow\uparrow$ ) or antiparallel ( $\uparrow\downarrow$ )

If the spins are parallel then,

$$S = s_1 + s_2 = \left(\frac{+1}{2}\right) + \left(\frac{+1}{2}\right) = 1$$

so that  $2S + 1 = 2 \times 1 + 1 = 3$

- Thus the spin multiplicity of the molecule is three. This state of affairs is spoken as the **triplet excited state** of the molecule.

Further if the spins are antiparallel then,

$$S = s_1 + s_2 = \left(\frac{+1}{2}\right) + \left(\frac{-1}{2}\right) = 0$$

so that  $2S + 1$

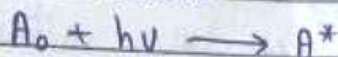
$$= 2 \times 0 + 1 = 1$$

- This shows that the spin multiplicity of the molecule is



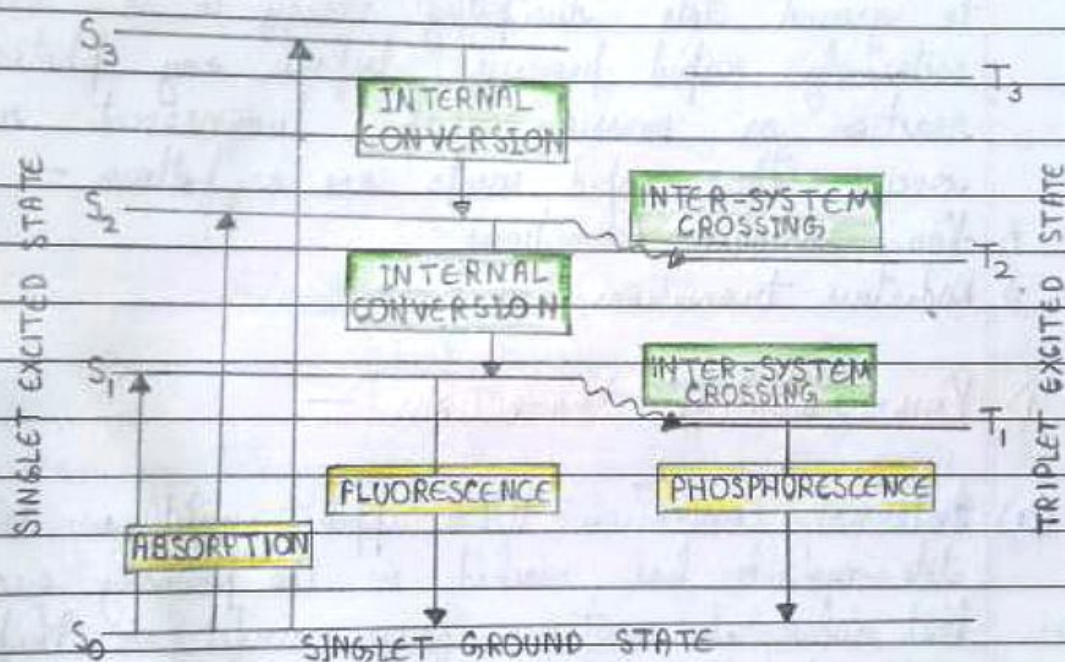
1, and the molecule is said to be in the singlet excited state.

The molecule whether in singlet or triplet state is said to be activated molecule.



where  $A_0$  stands for ground state

$A^*$  = excited state



Jablonski diagram depicting molecular energy levels

where  $S_0$  = singlet ground state

$S_n$  ( $n=1, 2, 3, \dots$ ) = singlet excited state

$T_n$  ( $n=1, 2, 3, \dots$ ) = triplet excited state

In most molecules the absorption of quantum leads to a transition from ground state ( $S_0$ ) to any of the singlet excited states  $S_1, S_2$  or  $S_3$  depending upon the energy of light photon absorbed. For each singlet excited state ( $S_1, S_2, S_3, \dots$ ), there must be a corresponding triplet



excited states ( $T_1, T_2, T_3 \dots$ )

- According to the application of quantum mechanics a singlet excited state will have higher energy than the corresponding triplet excited state
- The molecule which has been activated by the absorption of a quantum and is in any higher state (singlet excited state) ( $S_1, S_2$  or  $T_1, T_2$ ) immediately returns to ground state dissipating energy in a series of extremely rapid processes before any photochemical reaction or emission of luminescent radiation can occur. These rapid events are as follows -
  - 1) Non-radiative transitions
  - 2) Radiative transitions

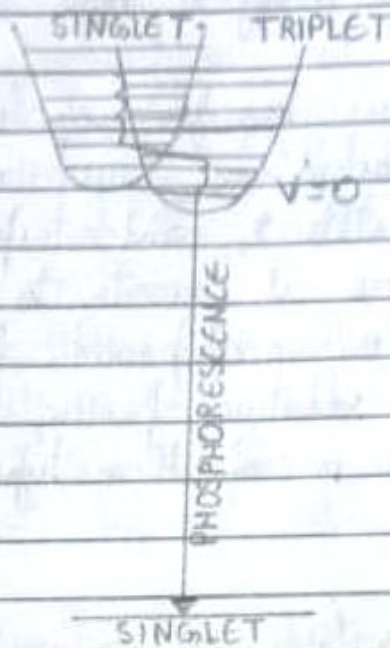
### 1) Non-radiative transitions: -

(a) **Internal conversion** - When upper singlet or triplet excited state molecule has reached in the primary quantum jump, but when it returns from singlet or triplet excited state it does not emit any radiation.

- This process of rapid radiationless transfer of energy is called internal conversion
- It has life time of  $10^{-11}$  seconds
- It occurs between the state of same multiplicity
- The energy of the molecule is dissipated in the form of heat by collision with another molecule

(b) **Intersystem crossing** - Non radiative transition between states of different multiplicities example from  $S_1$  to  $T_2$  or  $S_1$  to  $T_1$  is called intersystem crossing.

- It has life time of  $10^{-2}$  to  $10^{-6}$  seconds



### Intersystem crossing and phosphorescence

- Transition is taking place from singlet excited state to neighbouring excited triplet state
- These transition are induced by collisions
- Such transfer can only occur close to the cross over point of the two potential energy curves
- Once the molecule has reached to triplet state it cannot return to singlet excited state. It will then ultimately reach  $v=0$  state of the triplet state.

### 2) Radiative Transition: -

- If a molecule absorbs radiation of high energy, it reaches a high vibrational level after electronic excitation and is called an activated molecule. It then loses a part of its excess energy by intermolecular collisions.
- This part of excess energy is converted in the form of kinetic energy and appears as heat in the sample.



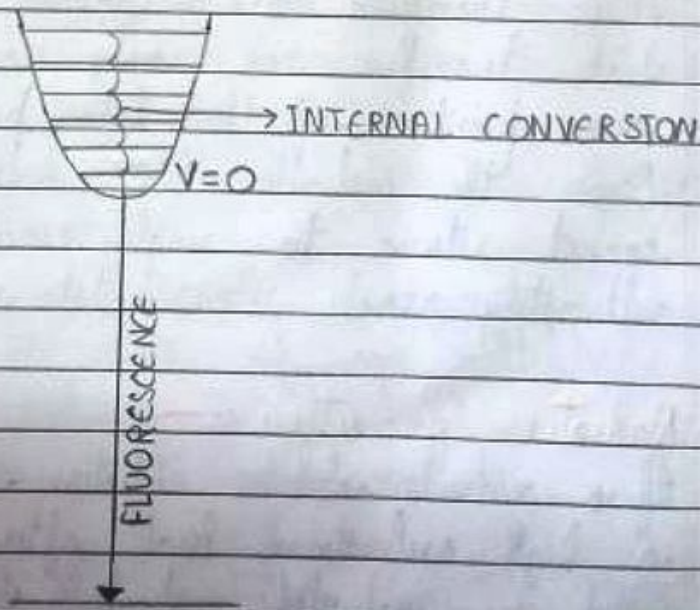
such transfer of energy is called radiationless transfer of energy.

- After radiationless transfer of energy, when activated molecule has reached a lower vibrational state  $v=0$ , singlet excited state  $S_1$ , and triplet excited state  $T_2$ , then from here it reverts to ground state  $S_0$ . Such transition is accompanied by emission of radiation and is called radiative process or transition.

• This transition is of three types: -

- (a) Fluorescence
- (b) Phosphorescence
- (c) Chemical reactions

(a) **Fluorescence** - When molecule reverts to the ground state  $S_0$  from first singlet excited state  $S_1$ , it may emit radiation. The radiation emitted in this process is called fluorescence spectrum.



Return of molecule from  $S_1$  or  $S_2$  to  $S_1$ , and then to ground state  $S_0$



- Fluorescence spectrum is normally of lower frequency than that of initial absorption, but under certain conditions it may be of higher frequency.
- The time between the initial absorption and return to ground state is of the order  $10^{-8}$  seconds.

(b) **Phosphorescence** - When the excited molecule returns from triplet excited state  $T_1$  to ground state  $S_0$ , the radiation is emitted. Actually this transition occurs when two excited states of different total spin have comparable energies.

- Although this transition is spectroscopically forbidden, it may take place, but much more slowly than an allowed electronic transition.
- Phosphorescent radiations are of shorter frequency than the absorbed or exciting radiation frequency.

(c) **Chemical Reaction** - The excited molecule may also lose its excess energy by performing chemical reaction.

- Time taken by a molecule to return from singlet excited state to ground state is very short ( $10^{-8}$  sec). Therefore, it gets no chance to undergo chemical reaction in this short period of excitation.
- On the other hand, a molecule in triplet excited state returns to ground state comparatively slowly. Thus this opens several opportunities for the excited molecules to collide with other molecules and react.
- Hence this molecule which takes part in a chemical reaction is one which is previously in triplet state.





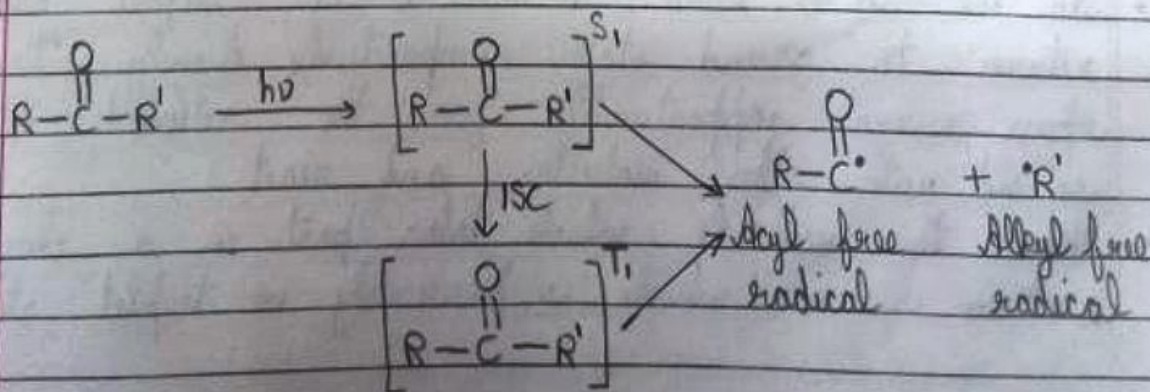
Q2) Explain photochemical reactions of organic compounds  
Norrish type I and II reactions

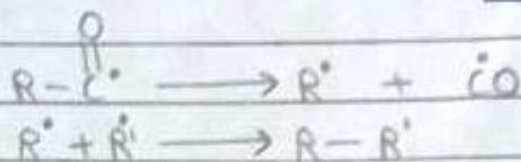
A2) It describes the photochemical reaction taking place with simple organic compounds like aldehydes and ketones.

- These reactions are named after the scientist Ronald George Wrayford Norrish. He was a British chemist and was awarded with Noble prize in the year 1967 for his work in chemistry.
- These types of reactions are further subdivided into Norrish type I reactions and Norrish type II reactions.

### Norrish Type I Reactions :-

- Norrish type I reactions describe the homolytic cleavage of aldehydes and ketones in presence of a photon ( $h\nu$ ).
- The cleavage results into the formation of two free radicals as intermediate species.
- The carbonyl group of aldehydes and ketones accepts a photon and is excited to a photochemical singlet state.
- This singlet state changes to triplet state, through the process of Inter System Crossing (ISC) mechanism.
- Both these singlet and triplet states on photochemical cleavage result into two free radical.

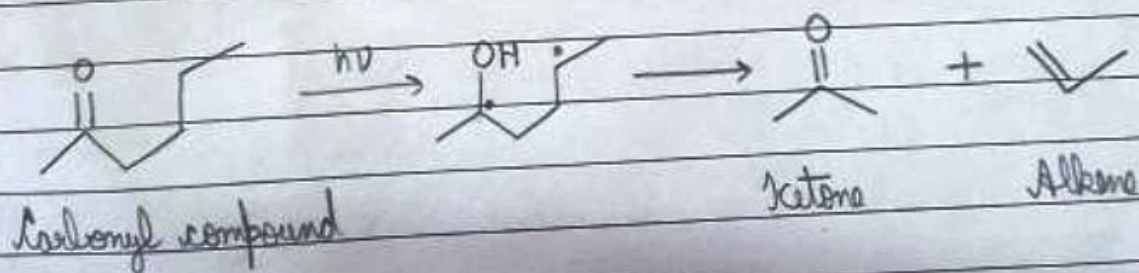




The synthetic utility of type I reactions are limited due to side reactions which leads to the formation of by-product which reduces the yield of main product.

### Norrish Type II Reactions:-

- Norrish type II reactions are a sort of intermolecular reactions and describes the cleavage of aldehyde and ketones.
- This type of Norrish reaction involves the removal of a  $\gamma$ -hydrogen atom ( $\gamma$ -CH) from the excited carbonyl compound.
- Forming, 1,4-Biradical as a photochemical product, which on decomposition yield enol and alkene.
- Enol state changes into carbonyl compound as a result of its tautomerism and isomerism process of enol.



SRI SATHYA SAI COLLEGE  
FOR WOMENS, BHOPAL

Chemistry Paper 1  
Assignment  
November 10, 22

Submitted to: Dr. POOJA. TIAM

Submitted by: Sushma Jain

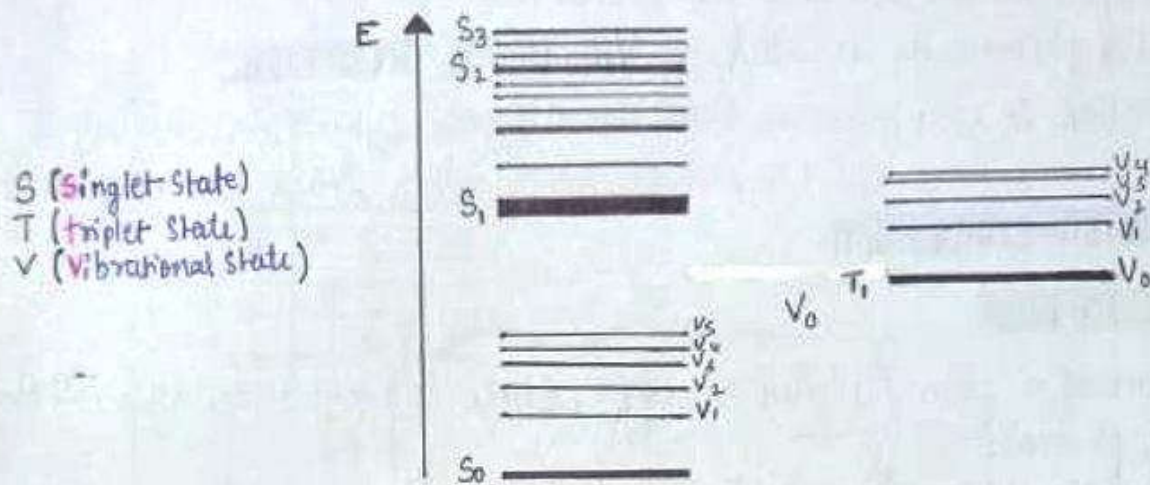
Class: B.Sc III<sup>rd</sup> yr.

3/35

03  
12/11/22

Q Explain Jablonski Diagram in detail.

- The Jablonski diagram represents the energy levels with a molecule where valence  $e^-$  can be excited.
- Is an energy diagram, arranged with energy on a vertical axis.



- Every Column usually represents a specific spin multiplicity for a particular species.
- Column contain electronic energy states (S, T)
- Within each electronic energy state are multiple vibronic energy states (V)
- As electronic energy states increase, the difference in energy becomes continually less.
- As the electronic energy levels get closer together, the overlap of vibronic energy levels increases.

### ABSORPTION OF LIGHT

- The absorbance of a photon of a particular energy by the molecules result in migration of  $e^-$  from lower energy state to higher energy state (excitation)
- This is indicated by a straight arrow pointing up.
- Only certain wavelength of lights (photon) are possible for absorbance that have energies that correspond to the energy difference between two different energy states of the particular molecules.

## VIBRATIONAL RELAXATION AND INTERNAL CONVERSION

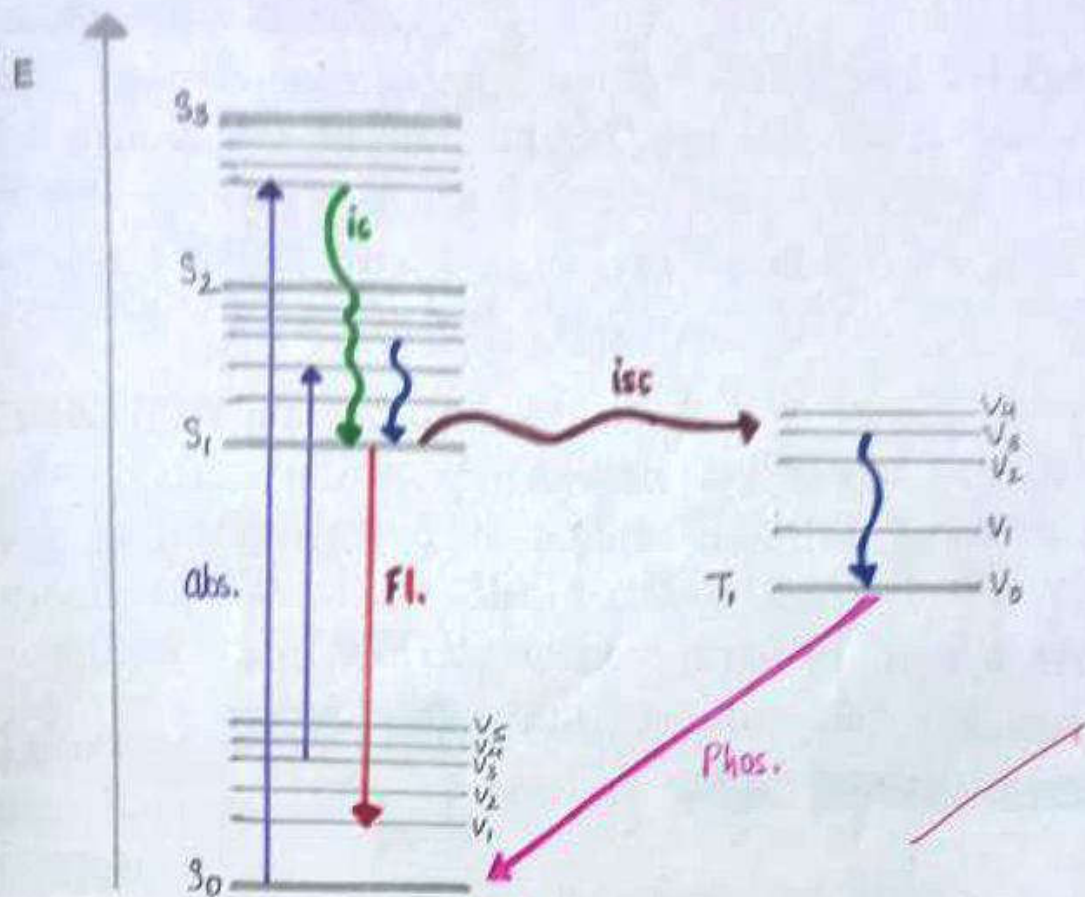
- Migration of  $e^-$  from higher energy states to lower energy state by losing their absorbed energy (relaxation)
- This is indicated as a curved arrow between vibrational levels.
- If relaxation occurs between vibrational levels in same electronic state, then this phenomenon is called as **Vibrational Relaxation**.
- If relaxation occurs between vibrational levels from one higher electronic state to another lower electronic state, then this phenomenon is called as **Internal Conversion**.

## FLUORESCENCE

- Migration of  $e^-$  from higher energy state to lower energy state by emitting photons.
- This is indicated as a straight line going down on the energy axis between electronic states.
- Fluorescence is a slow process  $10^{-9}$  to  $10^{-7}$  seconds. It is not a very likely path for relaxation.
- Fluorescence is most often observed between the first excited  $e^-$  state and the ground state.

## INTERSYSTEM CROSSING

- The electrons change spin multiplicity from an excited singlet state to an excited triplet state.
- This is indicated as a horizontal, curved arrow from one column to another. This is the slowest process.
- After crossing electron back to the ground electronic state via **Phosphorescence**, where a radiative transition from an excited triplet state to a singlet ground state occurs. This is also a very slow, forbidden transition.



Possible scenario with absorption (abs.), Internal Conversion (ic), Vibrational relaxation (Vr), Fluorescence (fl.), Intersystem Crossing (isc) and Phosphorescence (phos.) process shown.

Q Explain photochemical reaction of Organic Compounds Norrish type I and II reactions.

- Norrish reactions in organic chemistry describes the photochemical reaction taking place with simple organic compounds like ~~aldehydes and ketones~~.

These types of reaction are further subdivided into Norrish type I reactions and Norrish type II reaction. These reactions are named after the scientist **Ronald George Wreyford Norrish**.

He was a British chemist and was awarded with Noble prize in the year 1967 for his work in chemistry.

### NORRISH TYPE I REACTIONS:

The Homolytic cleavage of aldehydes and ketones in presence of a photon ( $h\nu$ ); this cleavage results into the formation of two free radicals as intermediate species. The carbonyl group of aldehydes and ketones accept a photon and is excited to a photochemical **Singlet state**. This, singlet state changes to **triplet state**, through the process of ~~intersystem crossing~~ **ISC**.

Both of these singlet and triplet state on photochemical cleavage result into two free radicals.

