

Overall Photochemical reactions consist of:

**a) Primary processes    b) Secondary processes**

**a) Primary processes:**

Light radiation ( $h\nu$ ) is absorbed by an atom or molecule giving rise to formation of an excited atom or molecule.



Absorbed energy give rise to the formation of excited molecule.

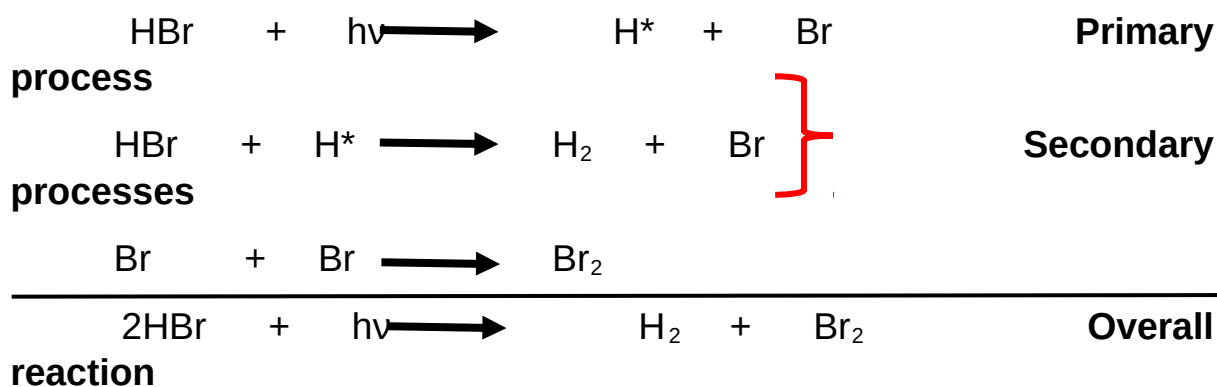
**b) Secondary processes:**

It is a thermal process in which the excited atoms produced in primary process are involved to form the products.

Sometimes the atoms initiate a series of chain reactions.



For example, the **decomposition of HBr** occurs as follows;



The primary process only obeys the law of photochemical equivalence strictly.

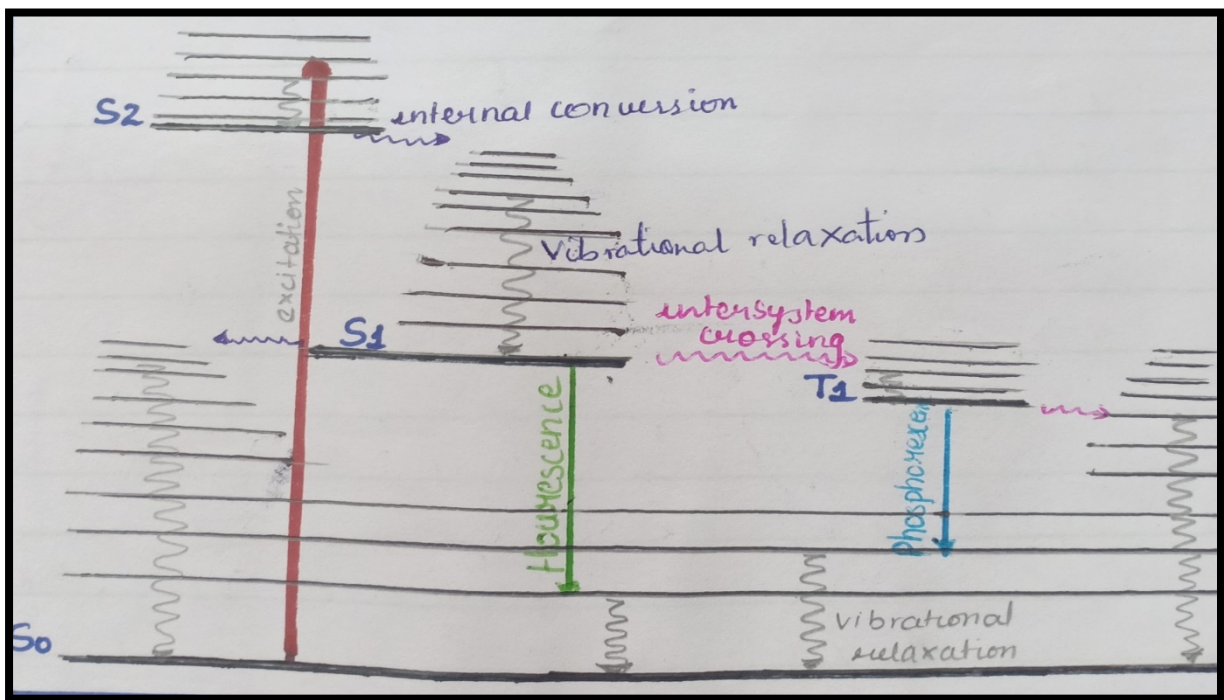
The Secondary process have no concern with the laws.

## JABLONSKI DIAGRAM

- ❑ It was named after Polished Physicist Alekskander Jablonski.

- ❑ Once a molecule has absorbed energy in the form of electromagnetic radiation, there are number of routes by which it can return to ground state. These processes are shown by Jablonski diagram.
- ❑ It illustrates the electronic states of molecule and transition between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity.
- ❑ Non-radiative transitions are indicated by squiggly arrows and Radiative transitions are indicated by straight arrows.
- ❑ Jablonski diagram is widely used in fluorescence spectroscopy to illustrate the excited state of a molecule and the radiative and non-radiative transitions that occurs between them.

### JABLONSKI'S DIAGRAM



#### ❖ **Singlet state:**

If a molecule have no unpaired electrons present ( $n=0$ ), then its multiplicity ( $n+1$ ) will be  $(0+1) = 1$ , i.e; 1 spin state. Such a state is called as Singlet state.

#### ❖ **Triplet state:**

If a molecule have two unpaired electrons present ( $n=2$ ), then its multiplicity ( $n+1$ ) will be  $(2+1) = 3$ , i.e; 3 spin state. Such a state is called as Triplet state.

### ❖ Radiative transitions:

It involves the absorption of a photon, if the transition occurs to a higher energy level (**ABSORPTION**) or the emission of photon for a transition to a lower level (**FUORESCENCE & PHOSPHORESCENCE**).

### ❖ Non-radiative transitions:

- They arise through several different mechanisms, all differently labelled in the diagram.

- These are transitions between energy levels of atoms or ions which are not associated with the emission of light.

They are as follows;

**VIBRATIONAL RELAXATION (VC),**

**INTERSYSTEM CROSSING (ISC) and**

**INTERNAL CONVERSION (IC)**

### Energy levels in Jablonski diagram:

- The energy levels of a molecule are shown by the horizontal lines, with energy along the vertical axis of the diagram.
- The thicker lines represent the lowest vibrational level of each electronic state, with the higher vibrational levels represented by thinner lines.
- The naming of the electronic state is based on the spin angular momentum configuration of the state. Singlet states are represented by an S and triplet state by T.
- $S_0$  is the Singlet ground state of the molecule.
- $S_1$  is the First excited singlet state of the molecule.
- $T_2$  is the first excited triplet state of the molecule.

## **PROCESSES OCCURRING AS SHOWN IN JABLONSKI DIAGRAM**

### **1. Absorption: (Type of Radiative transition)**

Absorption is a process in which a molecule is promoted from its ground state to a higher state by absorption of photon ( $h\nu$ ).

It is the fastest transition shown in the Jablonski diagram, occurring on a time scale of order  $10^{-15}$  second.

Absorption of a photon promotes the molecule from the  $S_0$  state to one of the vibrational levels of the singlet excited state. ( $S_0, S_1, \dots$ ).

## 2. Vibrational Relaxation: (Type of Non-radiative transition)

It is a non-radiative transition occurring to a lower vibrational level within same electronic state.

After a molecule has been promoted to an excited state by absorption and will eventually dissipate the energy that it has gained and return to the ground state.

It occurs on a rapid time scale of  $10^{-12}$  to  $10^{-10}$  seconds.

## 3. Internal Conversion: (Type of Non-radiative transition)

- It is a non-radiative transition between two electronic states of the same spin multiplicity i.e; from  $S_2$  to  $S_1$ .
- A molecule in a higher lying singlet electronic state undergo internal conversion to a lowest vibrational level of the electronic state.
- The rate of internal conversion is inversely proportional to the energy gap between the electronic states.
- It proceeds rapidly on a time scale of order  $10^{-11}$  to  $10^{-9}$  seconds.
- In contrast the energy gap between  $S_1$  and  $S_0$  is much wider and internal conversion between these two states occurs on a slower time scale and will be in competition with other transitions such as fluorescence and intersystem crossing.

## 4. Fluorescence: (Type of Radiative transition)

- It occurs between two electronic states of the same spin multiplicity.
- The emission of photons from  $S_1$  to  $S_0$ , radiative transition is known as Fluorescence which occurs on a time scale of  $10^{-10}$  to  $10^{-7}$  seconds.

## 5. Intersystem crossing: (Type of Non-radiative transition)

- It is a non-radiative transition between two isoenergetic vibrational levels belonging to electronic states of different multiplicity occurring from  $S_1$  to  $T_1$  state.
- It proceeds slowly on a time scale of order  $10^{-10}$  to  $10^{-6}$  seconds.
- After intersystem crossing, the molecule will immediately undergo vibrational relaxation to the ground vibrational level  $T_1$ .

## 6. Phosphorescence: (Type of Radiative transition)

- It occurs between two electronic states of different spin multiplicity.
- The emission of photons from  $T_1$  to  $S_0$  transition is known as Phosphorescence.
- It occurs on a much longer time scale than fluorescence, with typical time period of order  $10^{-6}$  to 10 seconds.

### TYPES OF TRANSITIONS SHOWN IN JABLONSKI DIAGRAM

Transition	Timescale	Type
Absorption	$10^{-15}$ s	Radiative (fastest transition)
Vibrational Relaxation	$10^{-12}$ – $10^{-10}$ s	Non-Radiative
Fluorescence	$10^{-10}$ – $10^{-7}$ s	Radiative
Internal Conversion	$10^{-11}$ – $10^{-9}$ s	Non-Radiative
Intersystem Crossing	$10^{-10}$ – $10^{-6}$ s	Non-Radiative
Phosphorescence	$10^{-6}$ – 10 s	Radiative (slowest transition)