Lecture - 1

Basic Concept of Photo Chemical Reaction of Inorganic Chemistry

M. Sc. Chemistry 4th Sem (402-I / U-IV)
Ph. D. Course Work -Section-II/U-II

Dr. Naresh Kumar

University Professor
Dept. of Chemistry
B. N. Mandal University, Madhepura

Photo Chemistry

Photo chemistry is the branch of chemistry which deals with the rate & mechanism of chemical reaction due to exposure of light (UV-100 – 400 nm, Visible - 400 – 750 nm or IR 750 – 2500 nm) which is called photo chemical reaction.

AB + hv (photon) = product

Role of light in photo chemical reaction.

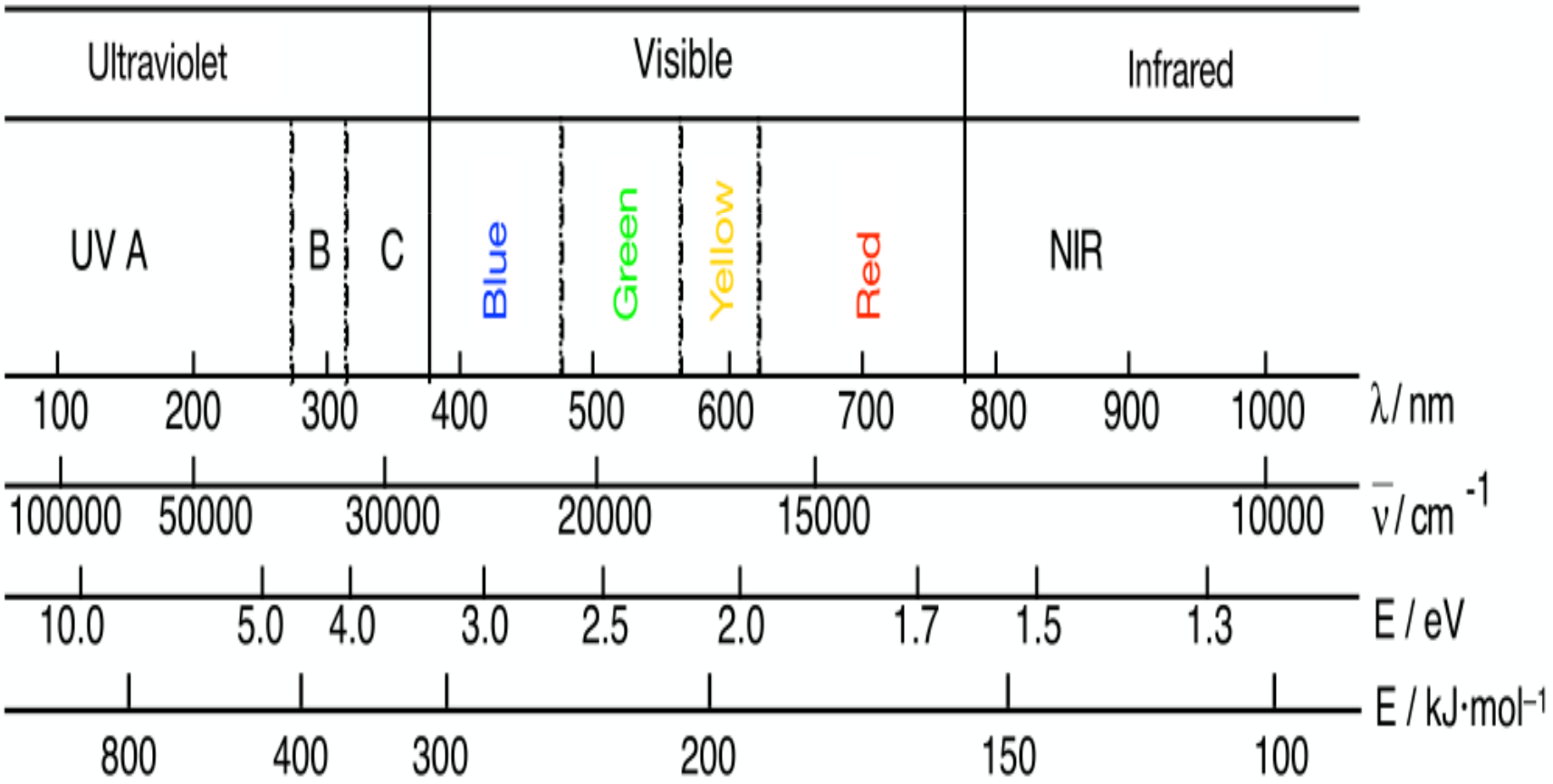
a. As reactant
b. As source of energy
c. To get excited state (activated state)
d. To supply breaking of bond

Photo= Light (UV visible, IR=Associated with energy) is source of energy,

= Smallest packet of light is as photon

= Energy (E=Nhc/ƛ) depending upon wave length.

= 1 Einstein



Chemical Reaction: Breaking of old bond & formation of new bond or charge transfer within or between molecules. It requires energy is called bond energy.

Bond	ΔH [kJ mol^{-1}]	λ [nm]	Bond	ΔH [kJ mol^{-1}]	λ [nm]
H–H	436	274	N–N	160	748
C–H	413	290	N=N	631	190
N–H	393	304	N≡N	941	127
P–H	297	403	N–O	201	595
C–C	347	345	N–P	297	403
C–O	358	334	O–H	464	258
C–N	305	392	O–S	265	451
C-Cl	397	301	O–Cl	269	445
C=C	607	197	O–O	204	586
C=O	805	149	C–F	552	216
O=O	498	240	C–S	259	461

Photochemical Reactions (PCR)

Reaction in which chemical reaction occurs on passing photo (hv) during this reaction energy required for their *activation* or deactivation is provided by an electromagnetic radiation like light.

Here,

Activation energies of the order of 100 kJ/mol and bond energies of the order 200-400 kJ/mol

Here,

absorption of photons that should individually carry an equivalent amount of energy as above data given in tables.

Fate of Incident light:

When incident light is passed through a substance then it may be absorbed, reflected or transmitted

i.e.

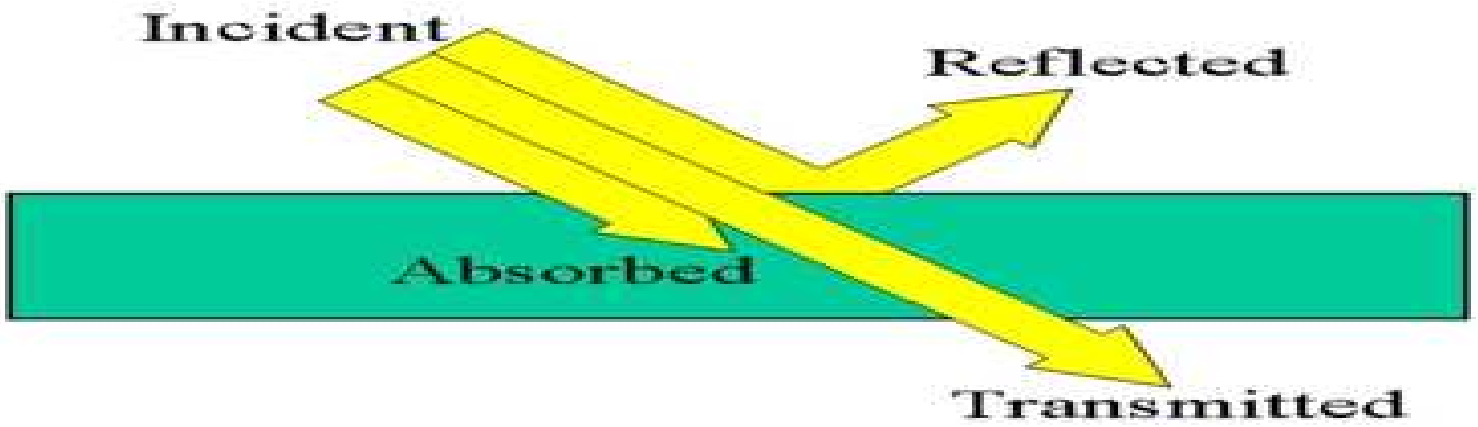
$$I=Ia+Ir+It$$

where I =Incident light

Ia = absorbed light (it is concerned with PC) having energy Nhc/ƛ depending upon wavelength of EMR.

Ir = reflected light (is very small)

It = transmitted light



Choice of absorbed light

a. Absorbed light have its own choice having energy depending upon the wavelength

b. It able to associate with chemicals & get excited state

c. It is guided by certain laws known as laws of photo chemistry

Laws of photochemistry (PC)

First law of PC/ Grotthuss-Draper law (1812-1842)

Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

Second law of PC/ Stark-Einstein law (1908-1913)

Also known as the "photo-equivalence law"

For each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction/ i.e. 1 molecule absorbs only one quanta i.e. 1:1 relationship b/w no. of quontas absorbed & no. of molecules reactive.

$E=Nhc/\lambda = 119620/\lambda$ kj/mole= 1 Einstein = 1 quanta

But law of Photo chemical equivalence is only valid in the case of primary process of PC reaction & it is expressed by quantum yield i.e.

Quantum yield (Ø) = no. of molecules reacting in given time/no. of Einstein absorbed in same time.

it may be Ø=1 normal reaction

Ø >1 high quantum yield

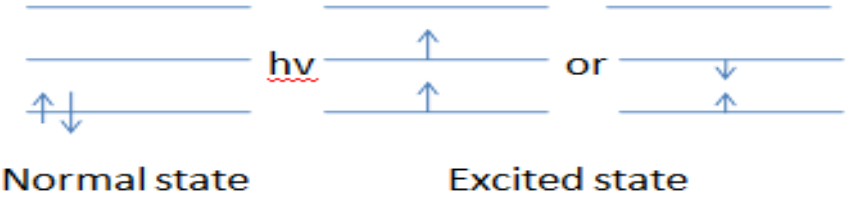
Ø<1 low quantum yield

Fate of absorbed light

Absorbed light undergoes change in photo physical process as well as photo chemical process i.e. there are changes in physical & chemical behavior of the molecules by absorption of one or more photons.

Photo Physical Process

It is the process in which by absorbing radiation electron is excited firstly & goes to higher energy level



But excited electron return to normal state either instantaneously is called fluorescence or after time lag is called phosphorescence.

But both fluorescence & phosphorescence is collectively known as luminescence & this process is called photo physical process.

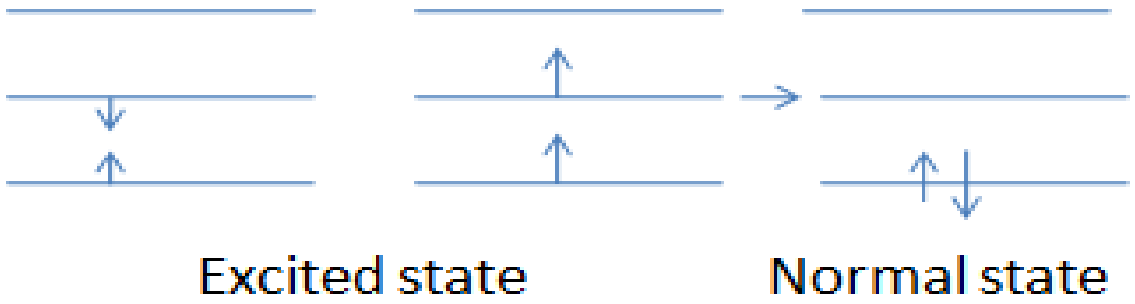


Photo Chemical Process

It is the process in which firstly by absorbing radiation electron get excited state (activated state) & goes to normal state to higher state of high spin multiplicity (2S+1) but excited electron returned to lower energy level with some chemical changes is called PC process

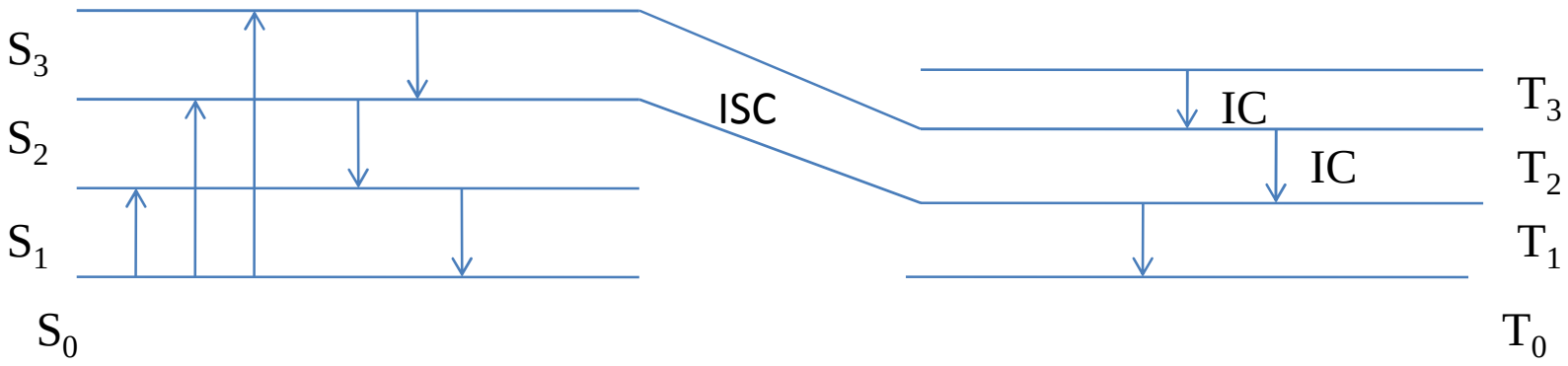
	Excited state	Normal state	Excited state
No. of UP e-	2	0	2
Spin multiplicity 2s+1	2*0/2+1 =1 singlet (S)	2*0/2+1 =1 singlet (S)	2*2/2+1 =3 triplet (T)

Excited state have been denoted by S_0, S_1, S_2, S_3 , T_0, T_1, T_2, T_3 etc depending upon value of spin multiplicity.

Types of Transition

Different types of transition of excited e- from high multiplicity to low multiplicity of energy level can be understand by a diagram known as jablonski diagram

Let us consider a molecule absorb light energy & get excited to higher energy level of spin multiplicity S_0, S_1, S_2, S_3 , T_0, T_1, T_2, T_3 etc & then return to lower energy level by two ways of transition.



Here, IC=internal conversion, ISC= inter system crossing

1. Non radiative transition: Transition of excited e- from higher to lower energy level involving no emission of radiation but emission of heat is called non radiative transition

(a) If transition Involves

Transition of excited e- from higher to lower but not to GS in same multiplicity.

$S_2 \rightarrow S_1$ or $T_2 \rightarrow T_1$

$S_3 \rightarrow S_1$ or $T_3 \rightarrow T_1$

(b) Internal Conversion (IC)

It involves energy loss in the form of heat & transition from higher to successive lower but not to GS in same multiplicity (transition allowed)

$S_3 \rightarrow S_2$ | $T_3 \rightarrow T_2$

$S_2 \rightarrow S_1$ | $T_2 \rightarrow T_1$

It takes only 10^{-11} Sec

(c) Inter System Crossing (ISC)

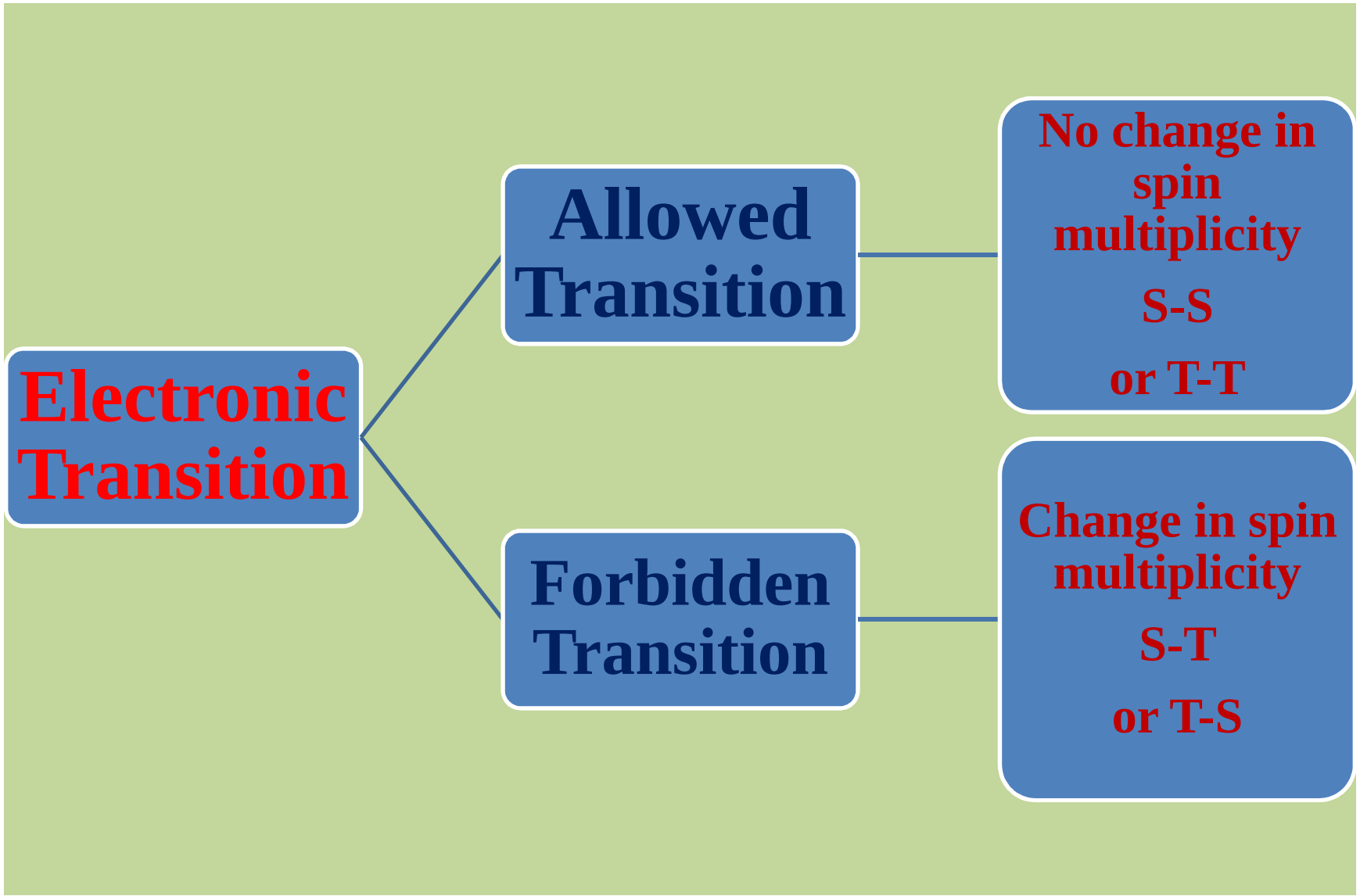
If transition of excited e- b/w two different multiplicity but not to GS (forbidden transition).

S_3 T_3

S_2 T_2

S_1 T_1

There are two types of electronic transition:
(a) Allowed Transition (b) Forbidden Transition



Radiative Transition

Transition of excited e- from higher to ground state with emission of radiation is called radiative transition

S_1 S_0 or T_1 T_0

(a) If transition occurs b/w same multiplicity S_1 S_0 or T_1 T_0 than it is called fluorescence. It occurs instantaneously in 10^{-8} sec. It is allowed transition. It is longer than absorbed light.

Example: chlorophyll, U-gas, Eosin etc

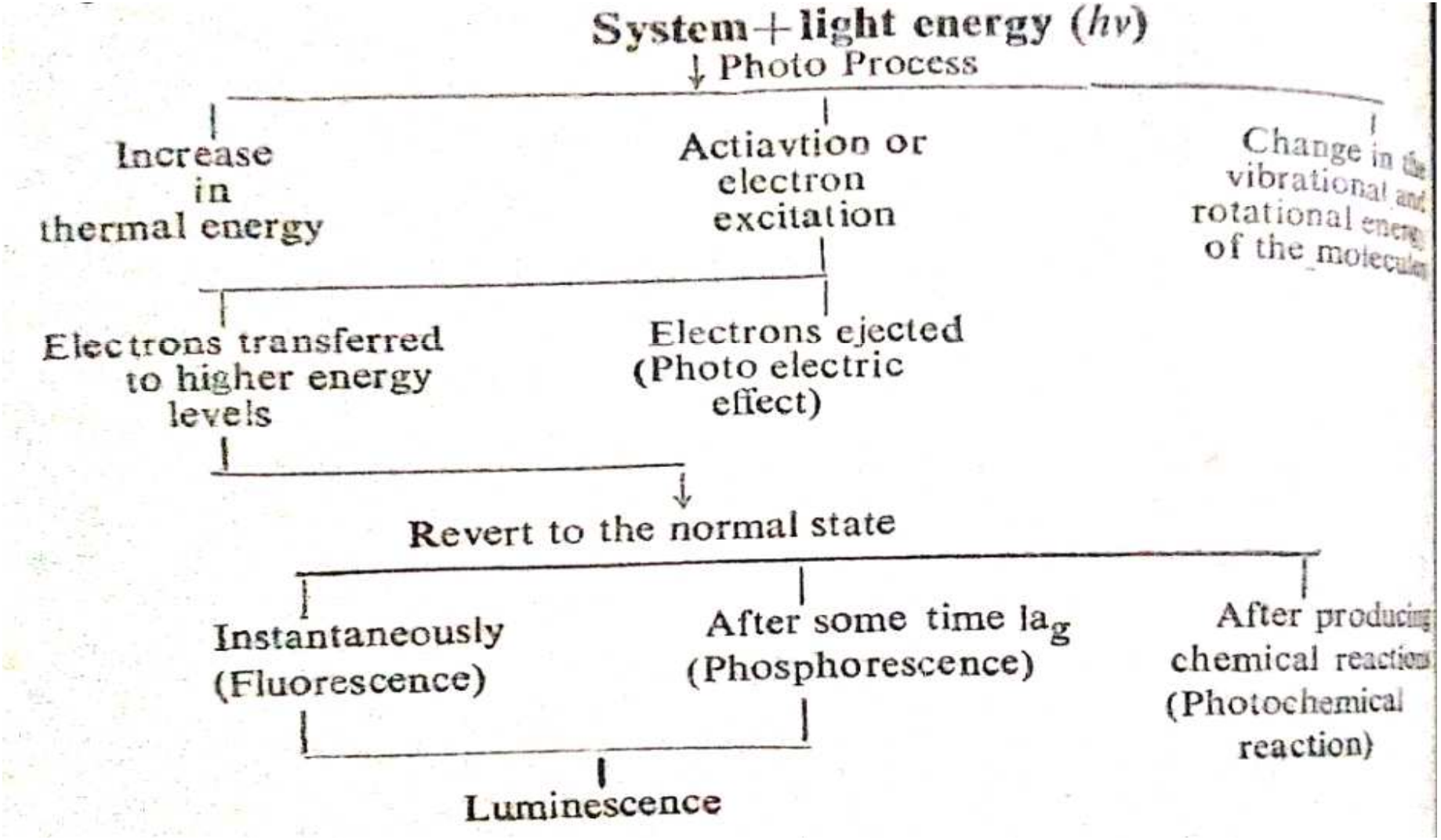
(b) If transition occurs for different multiplicity T_1 S_0 is called phosphorescence. If forbidden transition.

Example: organic dye, fungi, sulphide of alkali metal

Luminescence

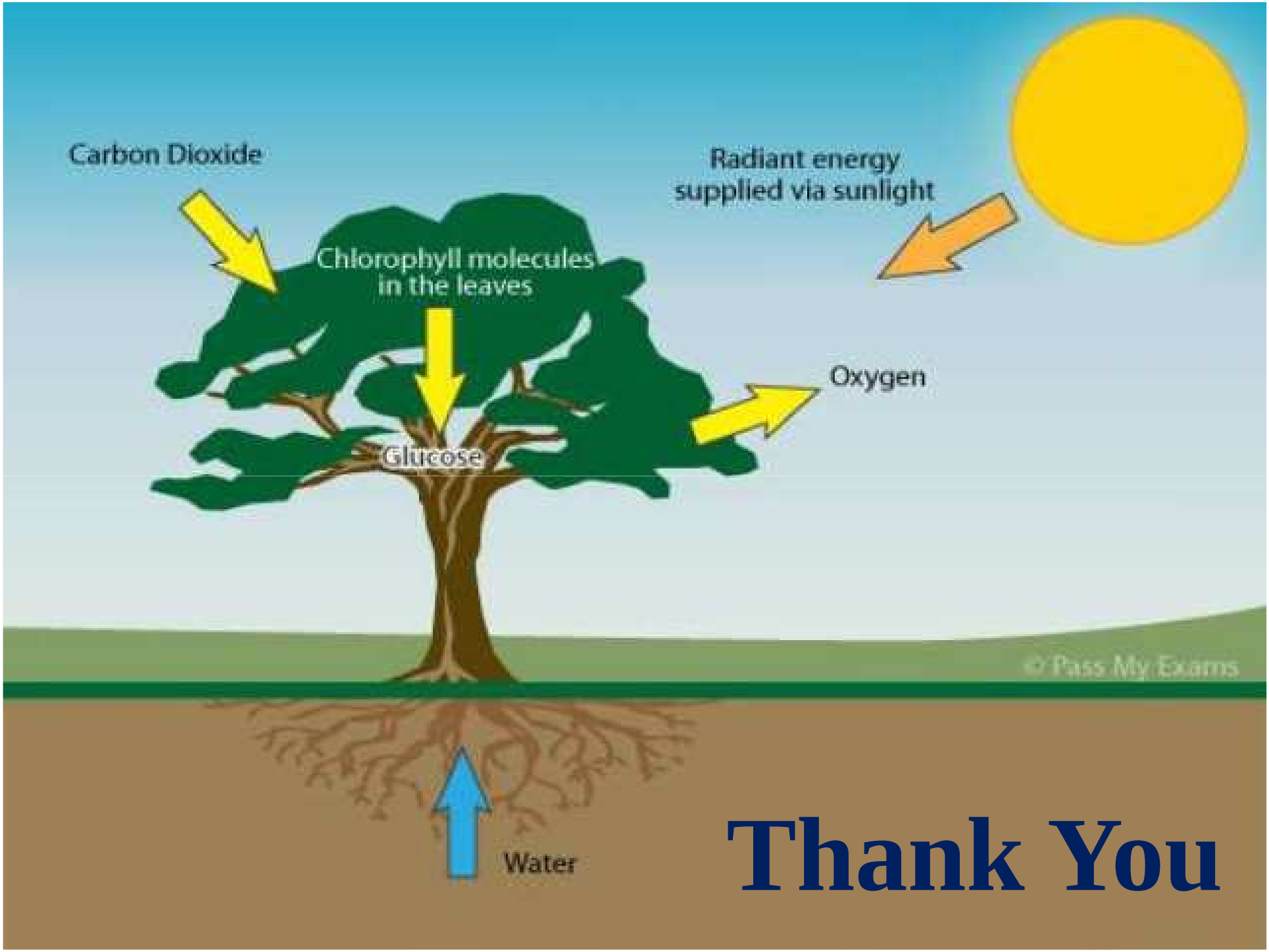
Both transition of excited e- from higher to GS with production of visible radiation due to some cause but other then temp is called Luminescence. (It is also called cold light). It is of two types fluorescence & phosphorescence .
Example:
(a) electro luminescence (EC)is characteristics of material that emits light in response to an electric current.
(b) EL is non thermal conversion of electrical energy into light energy. LED,OLED, Night signal light, computer monitor etc

In Summary


System + light energy (hv)
Photo Process
Increase in thermal energy
Actiavtion or electron excitation
Change in the vibrational and rotational energy of the molecules
Electrons transferred to higher energy levels
Electrons ejected (Photo electric effect)
Revert to the normal state
Instantaneously (Fluorescence)
After some time lag (Phosphorescence)
After producing chemical reactions (Photochemical reaction)
Luminescence

References & further reading

S & Atkins, Oxford Inorganic Chemistry, Fourth Edition
Alagappa university, M. Sc. Chemistry
Pearson, Inorganic chemistry
Fmiza Hammer Synthesis & reaction of organometallic compound


Carbon Dioxide
Radiant energy
supplied via sunlight
Chlorophyll molecules
in the leaves
Oxygen
Glucose
Water
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Thank You