PHOTOCHEMISTRY

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions. The visible and UV radiations (2000-8000Å wavelength) are mainly used in photochemical reactions.

Thermochemical reactions (dark reactions) are brought about by molecular collisions. These reactions are spontaneous and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy.

All ***photochemical reactions*** take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change. For example, in the combination of hydrogen and chlorine,

the first step is: $Cl_2 + h\nu \rightarrow 2Cl^{\bullet}$

The activated chlorine atoms ($Cl^{\cdot}$) then undergoes chemical reaction

It is evident from the above reaction that the second step can occur in absence of light.

Characteristics of photochemical reaction:

1. Photochemical reactions take place by absorption of light.
2. When a light composing number of colours is used, the photochemical reaction may not be initiated by all colours.
3. The free energy change (ΔG) of a photochemical reaction may be either negative or positive.

Differences between photochemical and thermal reactions:

S. No.	Photochemical reactions	Thermochemical reactions
1.	These involve the absorption of light.	These involve either absorption or evolution of heat.
2.	Take place in presence of light.	Take place in dark or in presence of light.
3.	They are independent of temperature.	They are dependent of temperature.
4.	Rate of reactions is dependent on the intensity of the light absorbed.	Rate of reactions is not affected by the intensity of light.
5.	The free energy change is negative or positive.	The free energy change is always negative.

LAWS OF PHOTOCHEMISTRY:

Grotthus-Draper Law (or) The Principle of Photochemical Activation:

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change.

However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be re-emitted as heat or light or it remains unused.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon).

When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

LAMBERT's LAW: When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically, it may be stated as follows

$$-dI/dl \propto I \quad \text{(or)} \quad -dI/dl = kI \quad \text{----------} \ (1)$$

Where I = the intensity if incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating equation 1 and putting $I = I_0$ when $l = 0$, we get

$$\ln I_0/I = kl \quad \text{(or)} \quad I = I_0 e^{-kl} \quad \text{----------} \ (2)$$

BEER's LAW : The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0 e^{-kc} \quad \text{---------- (3)}$$

On combining both laws, we get $\log I_0/I = \varepsilon cl$ ---------- (4)

The equation 4 is termed as mathematical statement of Beer-Lambert's law. In the above equation ε = the molar absorption coefficient

$A = \log I_0/I$ is the absorbance (or) optical density (OD)

Limitations of Beer-Lambert's law : The law is not valid i) when non-monochromatic radiation is used, ii) if temperature changes during measurements, iii) the law is applicable only to dilute solutions.

Some important relations:

Photons	≡	quanta
One molecule absorbs	≡	one photon
One mole of a substance Containing 6.023×10^{23} (Avogadro number) Molecules absorbs	≡	one mole of quanta (or) 6.023×10^{23} quanta of light (or) one Einstein

One Einstein $= Nh\nu$
$= Nhc/\lambda \quad [\therefore \nu = c/\lambda]$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation $E = h\nu = hc/\lambda$, where, h – Planc's constant (6.625×10^{-34} Js; c – velocity of light $= 3.0 \times 10^{8}\ ms^{-1}$; λ – wavelength of light.

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency 'ϕ' is introduced.

Quantum yield is defined as "the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Ǻ; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

Number of einsteins absorbed $= q/(Nhc/\lambda) = q\lambda/Nhc$

$\therefore$ Quantum yield $\phi = n/(q\lambda/Nhc) = nNhc/q\lambda$

In CGS units, $\phi = n/q \times [1.196 \times 10^{16}/\lambda \text{ (in Å)}]$

High (or) Low Quantum Yield:

The quantum efficiency varies from zero to 10^6. If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield $\phi = 1$.

High Quantum Yield: When two or more molecules are decomposed per photon, the quantum yield $\phi > 1$ and the reaction has a high quantum yield.

Low Quantum Yield: When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfil the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.
2. The reactivity of the molecules should be temperature independent.
3. The molecules in the activated state should be largely unstable and decompose to form the products.

Causes (or) Reasons for high quantum yield:

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
2. Formation of intermediate products will act as a catalyst.
3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

Examples:

1. Decomposition of HI: In the primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

$HI + h\nu \rightarrow H + I$ .... Primary reaction

$H + HI \rightarrow H_2 + I$
$I + I \rightarrow I_2$ ....Secondary reaction

Overall reaction : $2HI + h\nu \rightarrow H_2 + I_2$

The overall reaction shows that the two HI are decomposed for one photon ($h\nu$). Thus, the quantum yield (ϕ) = 2

2. Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon and discussed into two Cl atoms. This is followed by the secondary reaction as shown below:

$Cl_2 + h\nu \rightarrow 2Cl$ .... Primary reaction

$Cl + H_2 \rightarrow HCl + H$
$H + Cl_2 \rightarrow HCl + Cl$ .... Secondary reaction

The Cl atom consumed in step 2 is regenerated in step 3, this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

$$2Cl \rightarrow Cl_2$$

Thus the quantum yield varies from 10^4 to 10^6.

Processes of photochemical reactions: The overall photochemical reaction consists of i) *Primary reaction* and ii) *Secondary reaction*.

i. In the primary reaction, the quantum of light is absorbed by a molecule 'A' resulting in the formation of an excited molecule 'A*'.$A + h\nu \rightarrow A^*$
ii. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.$A^* \rightarrow B$

ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS:

Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction.

1. ***Photosensitization***: The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

   i) Atomic photosensitizers : mercury, cadmium, zinc and
   ii) Molecular photosensitizers: benzophenone, sulphur dioxide.

2. ***Quenching***: When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

Examples for photosensitized reactions:

1. ***Dissociation of hydrogen molecule***: UV light does not dissociate H_2 molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.

$$Hg + h\nu \rightarrow Hg^*$$
$$Hg^* + H_2 \rightarrow H_2^* + Hg$$
$$H_2^* \rightarrow 2H$$

2. ***Photosynthesis in plants***: During photosynthesis of carbohydrates in plants from CO_2 and H_2O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO_2 and H_2O molecules, which then react to form glucose.

   In the presence of light and chlorophyll ΔG^o becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG^o for this reaction is +2875 kJ. Since ΔG^o is positive, the above reaction is not possible.

PHOTOPHYSICAL PROCESS: Generally atoms or molecules go to excited state by the absorption of suitable radiation. If the absorbed radiation is not used to cause a chemical reaction, it will be re-emitted as light of longer wavelength. This process is called as photophysical process.

Types of photophysical process: Photophysical process is of two types, i) Fluorescence and ii) Phosphorescence.

i) **Fluorescence**: When a molecule or atom absorbs radiation of higher frequency (shorter wavelength), it gets excited. Then the excited atom or molecule re-emits the radiation of the same frequency or lower frequency within short time (about 10^{-8} sec.). This process is called fluorescence, stops as soon as the incident radiation is cut off. The substance which exhibits fluorescence is called fluorescent substance.

Examples: CaF_2, uranium, petroleum, organic dyes like eosin, fluorescein), chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.

Types of fluorescence:

a) ***Resonance fluorescence***: If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence.

Example, when mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited. Subsequently, when it returns to its ground state, it emits radiation of the same frequency, which it absorbed.

b) ***Sensitized fluorescence***: If the molecule is excited, due to the transfer of part of excitation energy from the foreign substance, it emits the radiation of lower frequency, the process is known as sensitized fluorescence.

Example, if the mercury vapour is mixed with the vapours of silver, thalium, lead or zinc, which do not absorb radiation at 253.7 nm and then exposed to the radiation, a part of the excitation energy from mercury is transferred and gets excited to higher energy state. When it returns to its ground state, it emits radiation of lower frequency.

ii) **Phosphorescence**: When a substance absorbs radiation of higher frequency, the emission of radiation is continuous for some time even after the incident light is cut off. This process is called phosphorescence (or) delayed fluorescence. The substance which shows phosphorescence is called phosphorescent substance.

Examples: Zinc sulphide, alkaline-earth sulphides (eg. CaS, BaS and SrS).

Differences between fluorescence and phosphorescence

Fluorescence	Phosphorescence
1. Its decay period is very short, $10^{-9} - 10^{-4}$ sec.	Its decay period is much longer, $10^{-4} - 100$ s.
2. It is the radiation emitted in a transition between states of same multiplicity.	It is the radiation emitted in a transition between states of different multiplicity.
3. It is not observed in solution at room temperature.	It can be observed in solution at room temperature.
4. Its spectrum is mirror image of the absorption spectrum.	Its spectrum is not mirror image of the absorption spectrum.
5. It is exhibited by some elements in vapour state.	It is rarely observed in gaseous or vapours.
6. Examples: uranium, petroleum, organic dyes, chlorophyll, CaF_2, etc.	Examples: ZnS, sulphides of alkaline earth metals.

Mechanism of Photophysical Processes (or) Mechanism of Fluorescence and Phosphorescence (or) Jablonski Diagram

Most molecules possess an even number of electrons and all the electrons are paired in ground state. The spin multiplicity of a state is given by 2S + 1, where S is the total electronic spin.

i) When the spins are paired (↑↓), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$$S = s_1 + s_2 = (1/2) - (1/2) = 0$$

$\therefore$ 2S + 1 = 1, ie., spin multiplicity is 1. The molecule is in the singlet ground state.

ii) On absorption of a suitable energy, one of the paired electrons goes to a higher energy level. The spin orientation of the two electrons may be either

a) parallel (↑↑), then $S = s_1 + s_2 = (1/2) + (1/2) = 1$, $\therefore$ 2S + 1 = 3, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

b) or anti-parallel (↑↓), then $S = s_1 + s_2 = (1/2) - (1/2) = 0$, $\therefore$ 2S + 1 = 1, ie., spin multiplicity is 1. The molecule is in the singlet (S) excited state.

Since the electron can jump from the ground state to any of the higher electronic states depending upon the energy of the photon absorbed we get a series of

a) singlet excited states ie., S_1, S_2, S_3, etc., (first singlet excited state, second singlet excited state, third singlet excited state, etc.) and
b) triplet excited states ie., T_1, T_2, T_3, etc., (first triplet excited state, second triplet excited state, third triplet excited state, etc.).

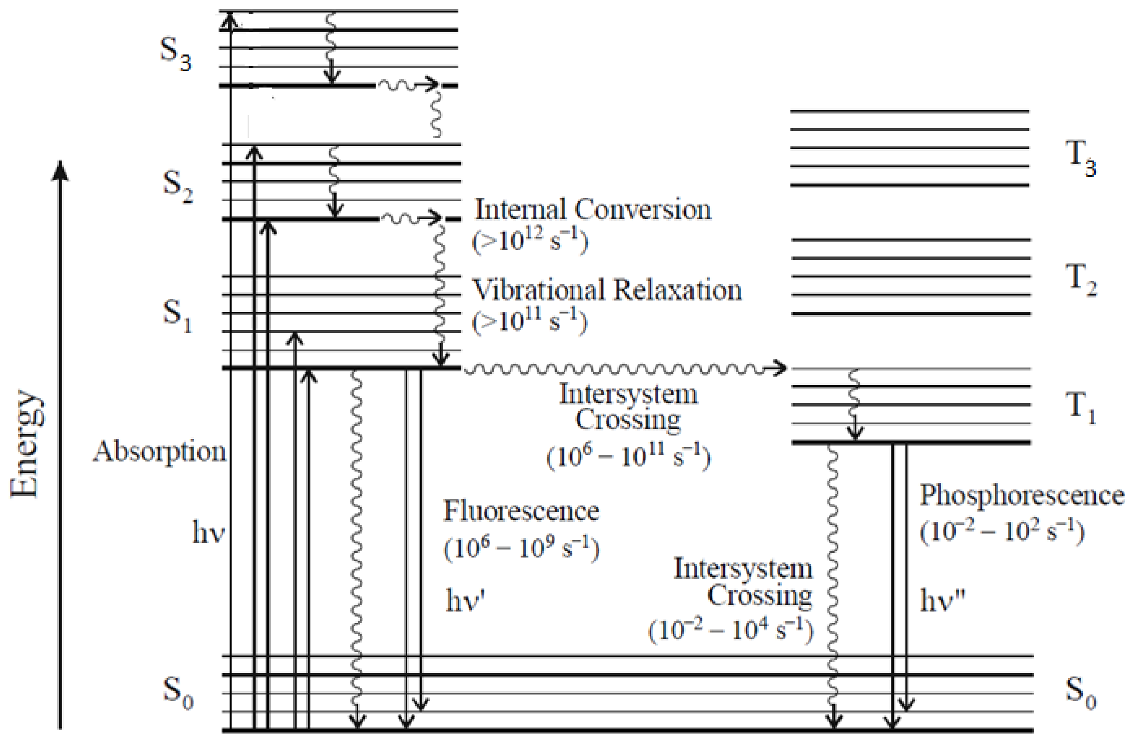
Generally singlet excited state has higher energy than the corresponding triplet excited state. Thus, the energy sequence is as follows: $E_{S1} > E_{T1} > E_{S2} > E_{T2} > E_{S3} > E_{T3}$ and so on.

When a molecule absorbs light radiation, the electron may jump from S_0 to S_1, S_2 (or) S_3 singlet excited state depending upon the energy of the light radiation as shown in Jablonski diagram. For each singlet excited state there is a corresponding triplet excited state, ie.

$$S_1 \rightarrow T_1;\ S_2 \rightarrow T_2;\ S_3 \rightarrow T_3, \text{etc.}$$

The molecule, whether it is in singlet or triplet excited state, is said to be activated. Thus,

$A_0 + h\nu \rightarrow A^*$ where A_0– ground state molecule and A^* - excited state molecule.



The Jablonski diagram.

Types of transitions: The activated molecules returns to the ground state by emitting its energy through the following general types of transitions.

1. **Non-radiative transitions** do not involve the emission of any radiations, so theses are also known as non-radiative or radiationless transitions. Non-radiative transitions involve the following two transitions.

a. ***Internal conversion (IC)***: These transitions involve the return of the activated molecule from the higher excited states to the first excited states, ie.

$S_3 \rightarrow S_1; S_2 \rightarrow S_1$ (or) $T_3 \rightarrow T_1; T_2 \rightarrow T_1$

The energy of the activated molecule is given out in the form of heat through molecular collisions. This process is called internal conversion (IC) and occurs in less than about 10^{-11} second.

b. ***Inter system crossing (ISC)***: The molecule may also lose energy by another process called inter system crossing (ISC). These transitions involve the return of the activated molecules from the states of different spins ie. Different multiplicity ie., $S_2 \rightarrow T_2$; $S_1 \rightarrow T_1$. These transitions are forbidden, occurs relatively at slow rates.

2. **Radiative transitions** involve the return of activated molecules from the singlet excited state S_1 and triplet state T_1 to the ground state S_0. These transitions are accompanied by the emission of radiations. Thus, radiative transitions involve the following two radiations.

a. ***Fluorescence***: The emission of radiation due to the transition from singlet excited state S_1 to ground state S_0 is called fluorescence ($S_1 \rightarrow S_0$). This transition is allowed transition and occurs in about 10^{-8} second.

b. ***Phosphorescence***: The emission of radiation due to the transition from the triplet excited state T_1 to the ground state S_0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition.

3. **Quenching of fluorescence**: The fluorescence may be quenched, when the excited molecule collides with a normal molecule before it fluoresces. During quenching, the energy of the excited molecule gets transferred to the molecule with which it collides. Quenching occurs in two ways.

a. ***Internal quenching***: Quenching may also occur, when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching.

b. ***External quenching***: Quenching may also occur from the addition of an external substance, which absorbs energy from the excited molecule. This phenomenon is called external quenching.

CHEMILUMINESCENCE

Chemiluminescence is a process in which visible light is produced by a chemical reaction at a temperature at which a black body will not give out visible radiation. Thus, chemiluminescence is the reverse of a photochemical reaction. As the emission occurs at ordinary temperature, the emitted radiation is also known as "cold light".

In a chemiluminescent reaction, the energy released during the chemical reaction makes the product molecule electronically excited. The excited molecule then emits radiation, as it returns to the ground state. Examples,

a) The oxidation of ether solution of magnesium p-bromophenyl bromide gives rise to chemiluminescence, the greenish glow that accompanies the exposure of solution to air, being visible in day light.
b) Glow of phosphorous and its oxide, in which the oxide in its excited electronic state emits light.
c) When pyragallol is oxidized by H_2O_2, chemiluminescence is produced.
d) The glow of fire flies is due to the chemiluminescence of a protein (luciferin) oxidation by oxygen in presence of an enzyme (luciferase).

Mechanism of chemiluminescence can be explained by considering anion-cation reactions.

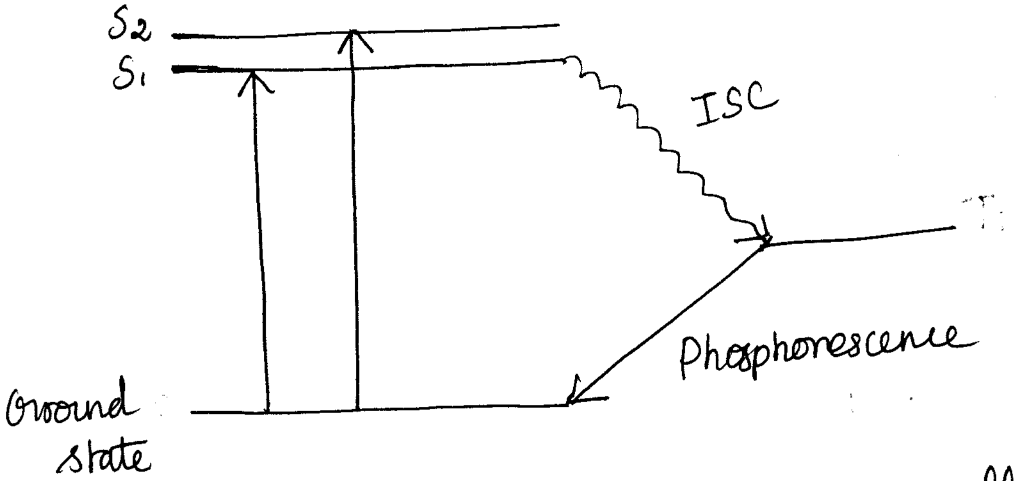
Example, interaction between the aromatic anions (Ar-) and cations (Ar+).

$$Ar^- + Ar^+ \rightarrow {}^1Ar^* + Ar$$

$$^1Ar^* \rightarrow Ar + h\nu$$

The aromatic anion (Ar^-) contains two paired electrons in the bonding molecular orbital (BMO) and one unpaired electron in the antibonding molecular orbital (ABMO). The ABMO of the aromatic cation Ar^+ is empty. When the electron is transferred from the ABMO of the anion (Ar^-) to the ABMO of the cation (Ar^+), the singlet excited state $^1Ar^*$ is formed. The excited state can be deactivated by the emission of photon $h\nu$.

This phenomenon is called Intersystem crossing.



Stern-volmer equation :- (Kinetics of collisional quenching)

A quenching process is defined as one which competes with the spontaneous emission process and there by shortens the lifetime of emitting molecule. These quenching reactions are energy transfer (or) electron transfer process.

In the absence of bimolecular quenching and photochemical reactions, the following steps are important in deactivating the excited molecule back to the ground state.

Reaction	Step	Rate
$S_0 + h\nu \xrightarrow{k_0} S_1$	Excitation	I_a (intensity of activation)
$S_1 \rightsquigarrow \xrightarrow{K_{IC}} S_0 + \text{heat}$	Internal conversion	$K_{IC}[S_1]$
$S_1 \rightsquigarrow \xrightarrow{K_{ISC}} T_1 + \text{heat}$	Intersystem crossing	$K_{ISC}[S_1]$
$S_1 \xrightarrow{k_f} S_0 + h\nu_f$	Flourescence	$k_f[S_1]$

$T_1 \xrightarrow{K_p} S_0 + h\nu_p$ phosphorescense $K_p[T_1]$

$T_1 \xrightarrow{K_{ISC}}$ S_0 + heat Reverse intersystem crossing $K_{isc}[T_1]$

Where

K is the rate constant

$[S_1]$ and $[T_1]$ are concentration of excited singlet state and triplet state molecules respectively.

under the condition of photostationary equilibrium.

Rate of formation of $[S_1]$ = Rate of deactivation of $[S_1]$

$$I_a = \{K_{IC} + K_{ISC} + K_f\} [S_1]$$

$$[S_1] = \frac{I_a}{\Sigma k_i + k_f} \quad \text{—— (1)}$$

$$[S_1] = \frac{I_a}{K_{IC} + K_{ISC} + K_f} \text{ (or)}$$

Hence the quantum yield of flourescence φ_f° in the absence of any external quenching is

$$\varphi_f^\circ = \frac{k_f [S_1]}{I_a} \quad \text{—— (2)}$$

ϕ = No. of ... photo... / No. of absorb... photo... = Rate of emissi... / Rate of absorb...

Substitute eqn (1) in eqn (2) we get,

$$\varphi_f^\circ = \frac{k_f \cdot I_a}{(\Sigma k_i + k_f) \cdot I_a} = \frac{k_f}{\Sigma k_i + k_f} \longrightarrow (3)$$

If another molecule Q is added to the solution which Quenches the flourescence by a bimolecular quenching

$$S_1 + Q \longrightarrow S + Q$$

$$\text{Rate} = k_q [S_1][Q]$$

Then the concentration of the flourescence $[S_1]$ in the presence of quencher is given as

$$[S_1] = \frac{I_a}{\Sigma k_i + k_f + k_q [Q]} \longrightarrow (4)$$

Quantum yield of flourescence process in the presence of quencher,

$$\phi_f = \frac{k_f [S_1]}{I_a} \quad \text{———} (5)$$

Substitute eqn (4) in (5)

$$\phi_f = \frac{k_f I_a}{\Sigma k_i + k_f + k_q [Q] \cdot I_a} \text{———} (6) \Rightarrow \phi_f = \frac{k_f}{\Sigma k_i + k_f + k_q[Q]}$$

The ratio of the yield (ie),

$$\frac{\phi_f^0}{\phi_f} = \frac{k_f}{\Sigma k_i + k_f} \times \frac{\Sigma k_i + k_f + k_q [Q]}{k_f}$$

$$= \frac{\Sigma k_i + k_f + k_q [Q]}{\Sigma k_i + k_f}$$

$$= 1 + \frac{k_q [Q]}{\Sigma k_i + k_f}$$

$$= 1 + k_q \tau [Q]$$

$$= 1 + K_{SV} [Q].$$

This expression is known as Stern-Volmer equation and K_{SV} is Stern-Volmer constant.

K_{SV} is the ratio of bimolecular quenching constant to unimolecular decay constant and has the dimension of litre / mol

$$K_{SV} = \frac{K_q}{\Sigma K_i + K_f}$$

Stern-Volmer expression is linear in quencher concentration and K_{SV} is obtained as the slope of the plot of ϕ_f^0 / ϕ_f (vs) (Q)

Here, τ is the actual life time of the florescence molecule in absence of bimolecular quenching and is expressed as

$$\tau = \frac{1}{K_f + \Sigma K_i}$$

Applications of Stern-Volmer equation :-

① From the knowledge of K_{SV} and τ the rate constant k_q from the bimolecular quenching step can be determined. For an efficient quencher, $K_{SV} \simeq 10^2 - 10^3 \; l \, mol^{-1}$ and of $\tau \simeq 10^{-8} s$

$$k_q = \frac{K_{SV}}{\tau} \simeq \frac{10^2}{10^{-8}} \; l \, mol^{-1} s^{-1} \simeq 10^{10} \; l \, mol^{-1} s^{-1}$$

② The quenching constant can also be calculated from the condition of 50% quenching.

If $[Q]_{1/2}$ is the concentration of the quencher when the solution is half quenches, then

$$\frac{\phi_0}{\phi} = 2 = 1 + K_{SV}[Q]_{1/2}$$

$$K_{SV} = \frac{2-1}{[Q]_{1/2}} = \frac{1}{[Q]_{1/2}}$$

$$K_{SV} = k_q \tau = \frac{1}{[Q]_{1/2}}, \quad \frac{1}{C_h}$$

K_{SV} is the reciprocal of half quenching concentration (or) half value concentration.

Actinometry

To measure the quantum yield, a knowledge of incident light (Io) and the emitted light is needed. (ie) the number of quanta falling per unit time on the reaction vessel and the number of quanta emanating per unit time from the reaction vessel.

Note:

Incident light - no of quanta falling per unit time on the rexn vessel

emitted light - no of quanta emanating per unit time from the rexn vessel.

This method is called Actinometry.

Actinometer is used to determine the intensity of light coming from a reaction cell. The intensity of light is measured with the reaction cell when empty and then with a reaction mixture. The difference b/w the two readings will give the amount of energy absorbed by the reaction system under examination.

The intensity of light can be determined by the following.

(i) Photoelectric cells

(ii) Radiomicrometer

(iii) Chemical actinometer

(iv) Thermopile

(v) Geiger- Muller counder

chemical actinometers :-

Chemical actinometer can be used to measure the indensity of light radiation. A chemical actinometer generally consists of gas mixture (or) Solutions which are sensitive to light. When radiations fall upon to these substances, a chemical reaction will take place and the extent of which is a direct measure of energy absorbed.

There are a number of photochemical reactions which have been employed in chemical actinometers. These are useful within their specific wavelength range.

Following are the main type of chemical actinometers :-

(i) **Eder's actinometer :-**

J. H Eder (1879) utilized the following reaction to determine the absorbed radiations.

$$2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow 2NH_4Cl + 2CO_2\uparrow + Hg_2Cl_2\downarrow$$

The system was exposed to radiations and the Hg_2Cl_2 formed in the reaction was weighed. From the weight of Hg_2Cl_2 (or) CO_2 evolved, The absorbed radiation may be determined quantitatively.

(ii) Uranyl oxalate actinometer:-

This type of actinometer contains a solution of 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When light is incident upon to this solution oxalic acid gets dissociate to form CO, H_2O and CO_2. The extent of the decomposition of oxalic acid is a measure of intensity of the light absorbed. The progress of the reaction is measured by titrating with $KMnO_4$ before and after the exposure.

$$UO_2^{2+} + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{h\nu} CO + CO_2 + H_2O + UO_2^{2+}$$

In actual practice, it becomes essential to standardise this actinometer with the light of different wavelengths and the results are tabulated. These tables may be used for the computation of amount of energy absorbed by the actinometer.

Ex:- The quantum yield obtained from the uranyl oxalate actinometer at 2540 A° is 0.60 while at the same temperature and using light radiation of 3660 A°, the quantum yield falls to

0.049. In this way, the quantum yield changes with the wavelength of light employed.

Thus, the number of quanta absorbed per second can be changed from the known value of wavelength and Intensity of light absorbed; (ie) the amount of light absorbed per second. Knowing the rate of reaction, the quantum yield may be computed.

This actinometer has a range of 2080-4350 Å with an average quantum yield of about 0.5. As UO_2^{2-} ion acts as a photosensitizer for the oxalate decomposition, the light absorption remains constant but rather long exposures are needed for the final accurate oxalate titrations.

(iii) Ferri oxalate actinometer :-

In this actinometer, potassium ferrioxalate solution is used. When this solution is irradiated, the reaction of Fe^{3+} to Fe^{2+} takes place which is estimated colorimetrically by using o-phenanthroline as complexing agent. The optical density at 5100 Å of the deep red colour is compared with the standard. The quantum yield to Fe^{2+} formation is almost constant within the wavelength range and exhibits little variation with solution composition, light intensity and Temperature.

For wavelength upto 4000 A°, a solution of 0.006 M $K_3Fe(OX)_3$ is used.

(IV) MGL - actinomer :- Malachite green leucocyanide is particularly useful in the range 220 - 300nm where it absorbs strongly. On Irradiation MGL is converted into ionized form MG^+ which has a very strong absorption at 6620 A°. The quantum yield for production of MG^+ is 0.91 over the given range.

(V) Reinecke's salt actinometer :-

Reinecke's salt is commercially available as ammonium salt $(NH_4)_3$ or $(NH_3)_2NCS$. This ammonium salt is not employed but its potassium salt is used.

When the solution of pottassium salt of Reinecke's salt is irradiated with light, NCS group in this salt is replaced by water molecule. Hence, quantum yields are calculated as moles of thiocyanate released per Einstein of light absorbed.

Generally, such a concentration of Potassium salt of Reineck's salt is used which should be able to absorb nearly 90 percent of the incident light.

The pH is adjusted b/w 5.3 – 5.5. The quantum yield for the reaction over the visible range lies b/w 0.27 to 0.30.

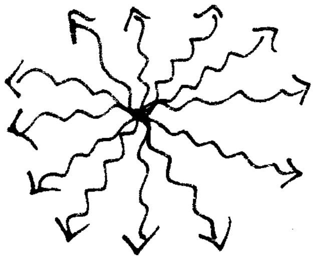
The range of this actinometer is 3160 – 7350 Å and hence it is mainly utilized in the visible region.

LASER

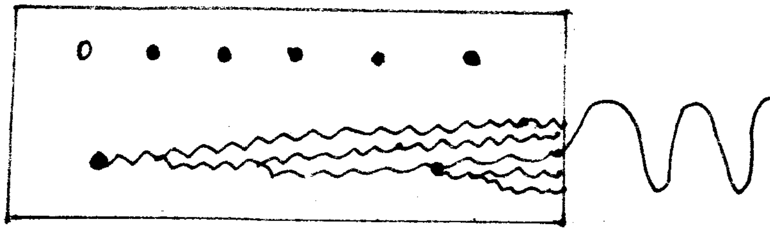
Laser: light Amplification by stimulated emission of Radiation.

The radiation which promotes the molecules to upper energy state is known as pump radiation and the radiation which stimulates emission is known as laser radiation.

When a large percentage of an ensemble of molecules can be brought into an excited state, a way frequently can be found by which large numbers of these excited molecules can be triggered into an almost simultaneous joint transition back to the inactive state, with the resulting emission of a beam of intense coherent radiation. Such an apparatus is now known as a laser, an acronym for light amplification by stimulated emission of radiation.



(a)



(b)

(a) Radiation from a normal source - inhorent beam.

(b) Radiation from a Lazer source - coherent beam

Principle of lazer action :-

To obtain Laser action, the probability of induced emission of the vision region must be increased. At ordinary temperature, ground electronic energy state is Populated. According to Boltzmann law when a stream of proton is allowed to strike on system, Absorption is preferred because Nn (lower state) is large. The population of state m (upper) starts building up and after a time, the rate of absorption becomes equal to the rate of emission.

On the other hand, if by some means the populatio[n] of the excited state is increased the striking proton is more likely to meet an excited particle, than an unexcited one. thereby stimulating emission of a phot[on] rather than its absorption.

To each photon striking on the system, an extra photon gets added to the beam. under the circumstances the emitted intensity will be larger than the incident intensity.

Three kinds of transition involving electromagnetic radiations are possible b/w two energy levels E_1 and E_2 in an atom.

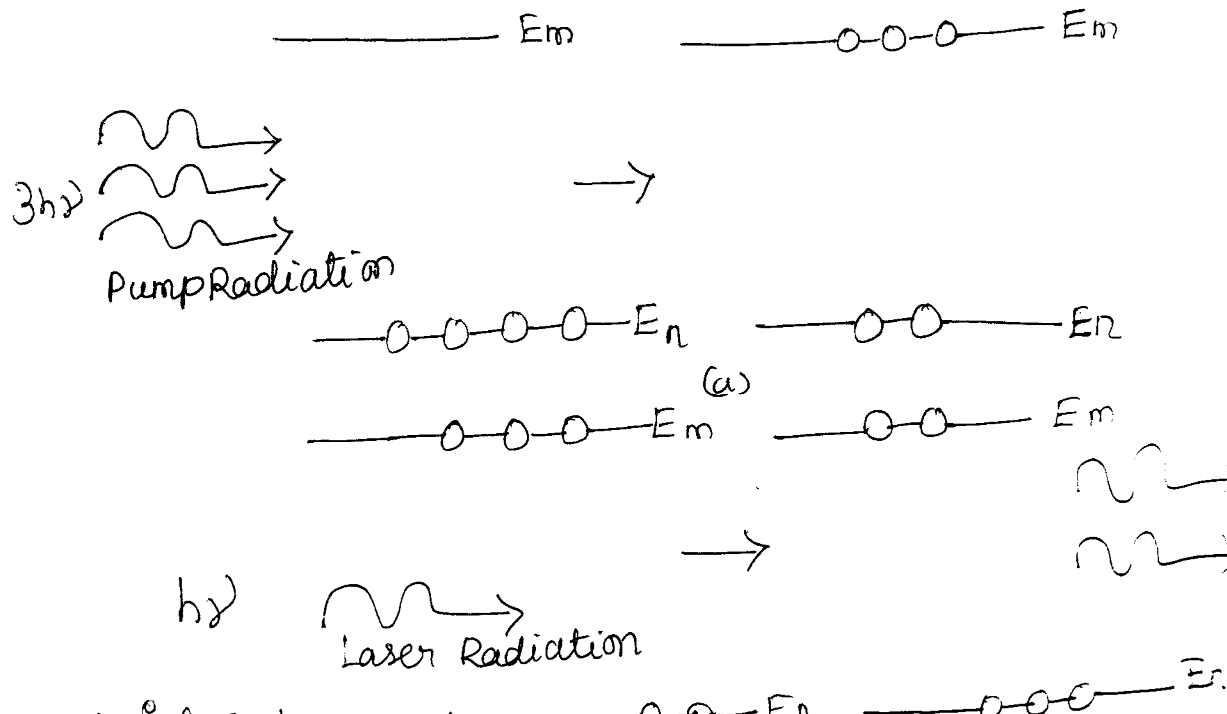
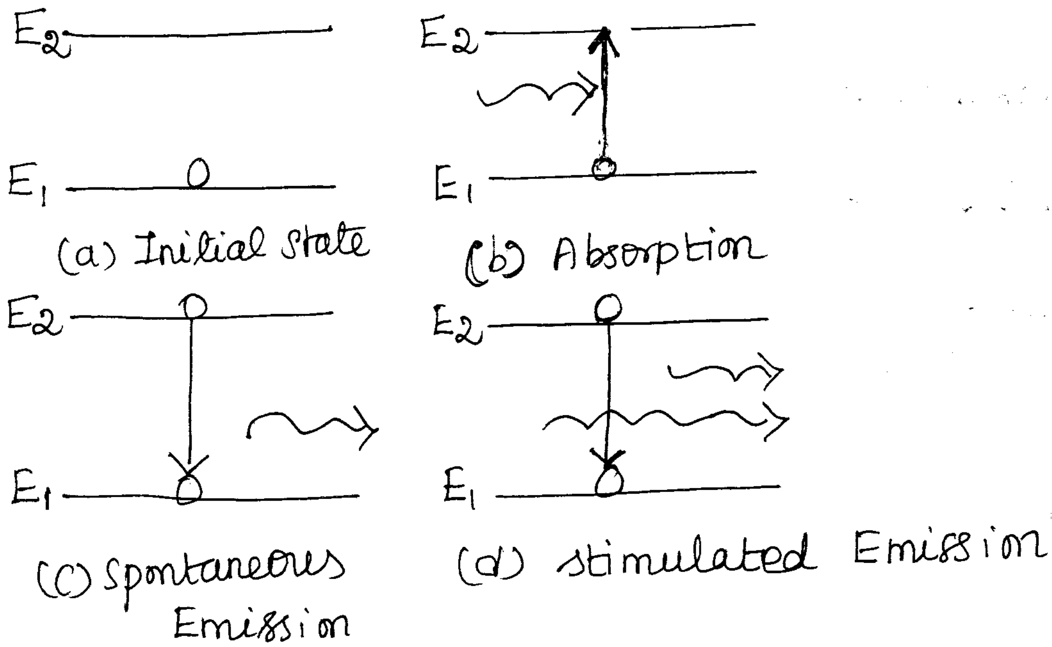


Fig: principle of Laser Action (Population inversion and Laser action).

(i) If the atom is initially in the lower state E_1, It can be raised to E_2 by absorbing a photon of Energy $E_2 - E_1 = h\nu$.

This process is called induced absorption (a)



(ii) If the atom is initially in the upper state E_2, it can drop E_1 by emitting a photon of energy $h\nu$.

This is spontaneous emission (b)

(iii) under certain conditions, it is possible to force in excited atom to emit a photon by another matching photon. This is known as stimulated emission (c).

APPLICATIONS OF LASER

1. Lasers are widely used in manufacturing(industry), e.g. for cutting, drilling, welding, cladding, soldering (brazing), hardening, ablating, surface treatment, marking, engraving, micromachining, pulsed laser deposition, lithography, alignment, etc.
2. Use for the treatment of detached retinas. Use in performing bloodless surgery. Use for the treatment of human and animal cancers and skin tumtors.
3. Optical fiber communication, extensively used particularly for long-distance optical data transmission, mostly relies on laser light in optical glassfibers. Free-space optical communications, e.g. for inter-satellite communications, is based on higher- power lasers, generating collimated laser beams which propagate over large distances with small beam divergence
4. Optical data storage e.g. in compact disks (CDs), DVDs, Blu-ray Discs and magneto-optical disks, nearly always relies on a laser source, which has a high spatial coherence and can thus be used to address very tiny spots in the recording medium, allowing a very high density data storage. Another case is holography, where the temporal coherence can also be important.
5. In Lunar Laser Ranging Experiment, Laser beams are focused through large telescopes on Earth aimed toward the arrays, and the time taken for the beam to be reflected back to Earth measured to determine the distance between the Earth and Moon with high accuracy
6. There are a variety of military laser applications. In relatively few cases, lasers are used as weapons; the “laser sword” has become popular in movies, but not in practice. Some high-power lasers are currently developed for potential use as directed energy weapons on the battle field, or for destroying missiles, projectiles and mines.