Photo chemistry - I

Branch of chemistry with deals with the process involving emission (or) absorption of radiation

Absorption and emission of radiation

According to the classical electromagnetic theory, a system of accelerated charged particles emits radiant energy. when exposed to thermal radiation at a given temp, it absorbs radiant energy. The rates of absorption and emission are given by classical laws. These opposing processes are expected to lead to a state of equilibrium. Einstein in 1916 treated the above problem for atoms and molecules in the following way.

Let us consider two non degenerate stationary states m and n of a system, with energy values E_m and E_n where $E_m > E_n$. According to Bohr's theory, the frequency of the absorbed radiation is given by

$$\nu_{mn} = \frac{E_m - E_n}{h}$$

Let us assume that the system is in the lower state n and exposed to radiation density ρ. The probability per unit time that it will absorb the radiation and will there by be raised to the upper state m, is [Proportional to the number of Particles N] in the state n and the (density o radiation of frequency ν_{mn}. Hence

Rate of absorption $= B_{nm} N_n \rho(\nu_{mn})$

where B_{nm} is the proportionality constant and is known as Einstein's co-efficient of absorpti

The probability of emission from $m \rightarrow n$ consists of two parts, one which is spontaneous and hence independent of radiation density and the other proportional to it. If N_m be the no. of particles in the upper state m at any ti then

Rate of emission $= A_{mn} N_m + B_{mn} N_m \rho(\nu_{mn})$

where A_{mn} is Einstein's co-efficient of spontaneous emission and B_{mn} as Einstein's co-efficient of induced emission

At equilibrium, the two rates will be equal.

$$B_{nm} N_n \rho(\nu_{nm}) = A_{mn} N_m + B_{mn} \cdot N_m \varphi(\nu_{mn})$$

on rearranging
$$\frac{N_n}{N_m} = \frac{A_{mn} + B_{mn} \rho(\nu_{mn})}{B_{nm} \rho(\nu_{nm})} \quad ①$$

The ratio of the no. of particles in the states n & m with energy E_n & E_m, can also be obtained from the Boltzmann distribution Law.

$$\frac{N_n}{N_m} = e^{-(E_n - E_m)/kT} = e^{h\nu/kT} \quad ②$$

solving for $\rho(\nu_m)$ and substituting for N_n/N_m from ① & ② we have

$$\rho(\nu_{nm}) = \frac{A_{mn}}{B_{nm} e^{h\nu/kT} - B_{mn}}$$

Franck - Codon Principle:

At normal temperatures most of the molecules reside in the zero vibrational level of the ground state & few molecules occupying the higher vib. states

The wave function for the zero vib. level has a maximum in the centre, indicating the region of maximum Probability (Fig. 1) Therefore, the most Probable transition during the act of light absorption is that which originates from the Centre of $\nu = 0$ vib. level. The time taken for an electronic transition is of the order of 10^{-15} s, the reciprocal of the radiation frequency. On the other hand, the time period for vibration is about 10^{-13} s which is nearly 100 times as slow.

As a consequece, the internuclear distance do not change during the act of light absorption Hence, the transition process can be represented by a vertical line which is Parallel to the potential energy axis & originates from the lower potential curve to the upper curve. This fact forms the basis of formulation of the Frank - Codon Principle which stated that "[Electronic transitions are so fast (10^{-15} s) in comparison to the nuclear motion (10^{-13} s) that immediately after the transition, the nuclei have nearly the same relative position and momentum as they did just before the transition"]

This principle implies that the most Probable transitions between different electronic and vibrational levels are those for which the momentum and the position of the nuclei do not change very much.

This most Probable transition appears as the most intense absorption line at a frequency given by Bohr relationship $\Delta E = h\nu$. Few transitions are also possible from the other positions of the $\nu = 0$ level adding to the width of the absorption band. since they are less Probable, these absorption lines are of lower intensities.

If a transition occurs to a position corresponding to energy greater than the excited state dissociation energy, the molecules dissociates directly on excitation. and discrete Vibrational bands are not observed. Fig1.c. a Continuum is more likely to appear for simple diatomic molecules.

For the internuclear geomtry as represented by the P.E surfaces of the G.S and E.S in Fig1.b. the Vibrational excitation to $v' = 2$ level is coupled with the electronic transition, giving an intensity distribution Pattern as shown. If a different equilibrium bond length is indicated in the excited state the shape of the absorption curve will change accordingly.

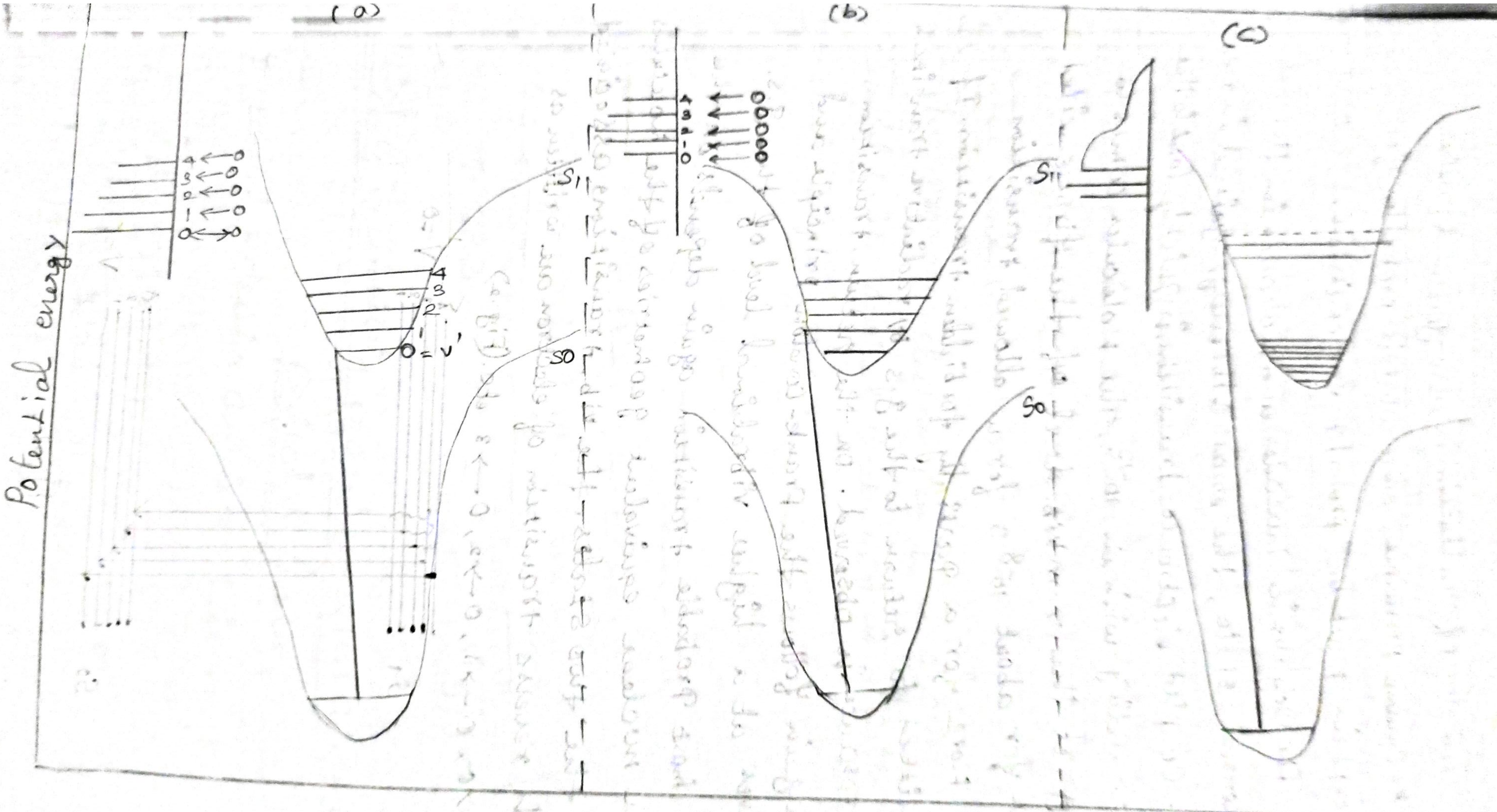


Fig-1

The emission of radiation is also goverened by the Frank-Condon principle. since what is probable for absorption must be probable for emission.

For Polyatomic molecules and molecules in the condensed state, the excess vib. energy gained in a vib. coupled electronic transition, is quickly lost to th surrounding with in 10^{-13} s. The molecules comes to stay at the zero vib. level of the first excited state for about 10^{-8} s for an allowed transition and more for a partially forbidden transition. If Permitted to return to the g.s by radiative transi fluoresance is observed. On the return, transition, it again follows the Frank-Condon principle and arrives at a higher vibrational level of the g.s. The most probable transition again depends on the inter nuclear equivalent geometries of the molecul in the two states. the vib. transitions associate with reverse transition of electron are written as 0→0, 0→1, 0→2, 0→3 etc. (Fig.2)

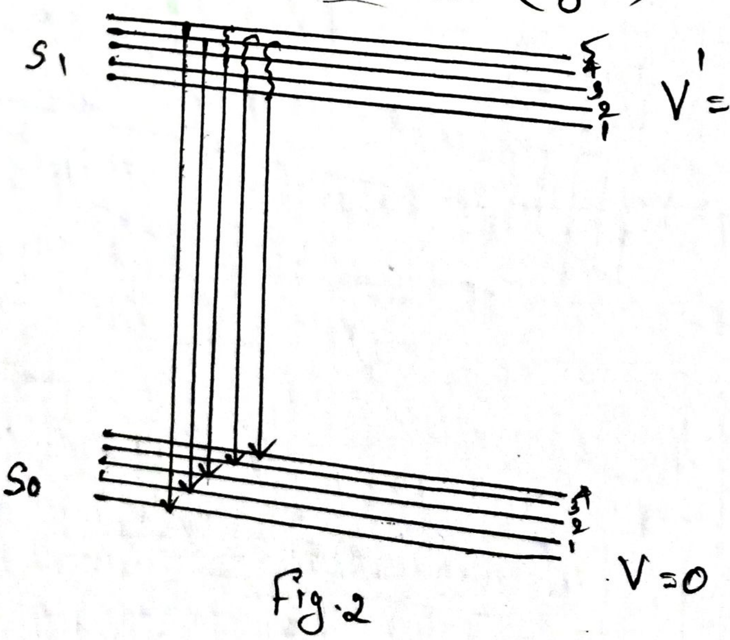


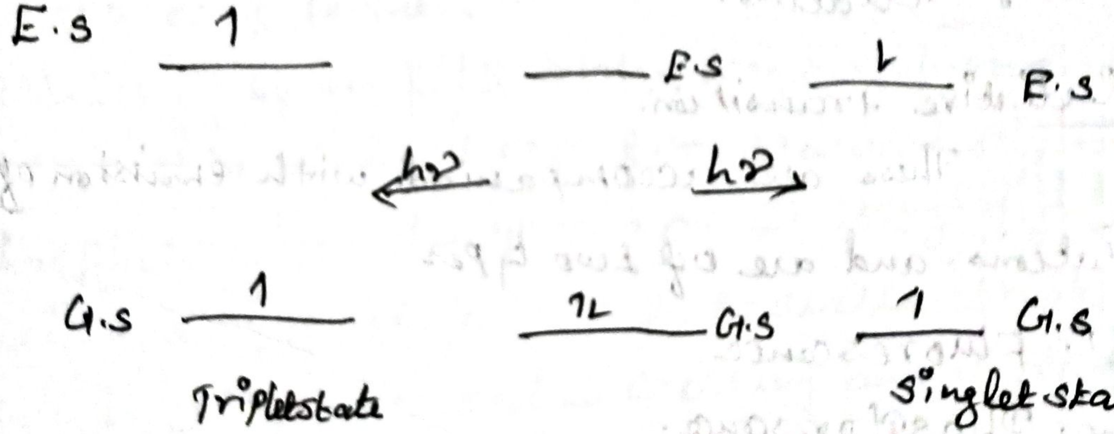
Fig.2

Singlet and Triplet states

When the molecule in the ground singlet state absorbs U.V (or) Visible radiations of proper frequency, one electron passes into the vacant orbitals present in higher energy level. During such transition two spin relationship are possible.

1. The promoted electron can have a spin antiparallel to its original partner, this is called excited singlet state. (or)

2. The promoted electron can have a spin parallel to its original partner, this is called excited triplet state.



Decay of electronically excited states (or) Fate of excited molecules

The excited molecules can lose their energy in two ways.

1) by non-radiative transition or.

2 by radiative transition

1. Non-radiative transition: The transition from excited singlet state (S_1) to ground state (S_0) i.e $S_1 \rightarrow S_0$ are called non-radiative transition. It is also called internal conversion (I.C). It can also takes place b/w triplet states in the same manner. eg: $T_2 \rightarrow T_1$ i.e from higher triplet state (T_2) to the lower triplet state (T_1)

In some molecules, there is a triplet state (T_1) close to an excited singlet state (S_1) and as a result the molecule can crossover to triplet state such type of transition i.e $S_1 \rightarrow T_1$ is called intersystem crossing (I sc) and is also a non radiative transition. The non-radiative transitions do not emit any radiations.

2. Radiative transition:

These are accompanied with emission of radiations and are of two types

1. Fluorescence
2. Phosphorescence.

1. Fluoresance: when the molecules are exposed to U.V or visible light of the appropriate frequency it will be absorbed in a femto sec (10^{-15} sec) and the molecules moves from the ground singlet state to the first excited singlet state. Since the average life time of this excited singlet state is very very small (10^{-9} - 10^{-6} sec) a direction transition from the excited singlet state back to the singlet ground state

may takes place with the emission of Photons (radiations). This kind of emission of radiation is called fluorescence. The mechanism

$$\text{Molecule} \xrightarrow[\text{absorption}]{h\nu} S_1 \xrightarrow{\text{Radiation}} S_0 + h\nu'$$

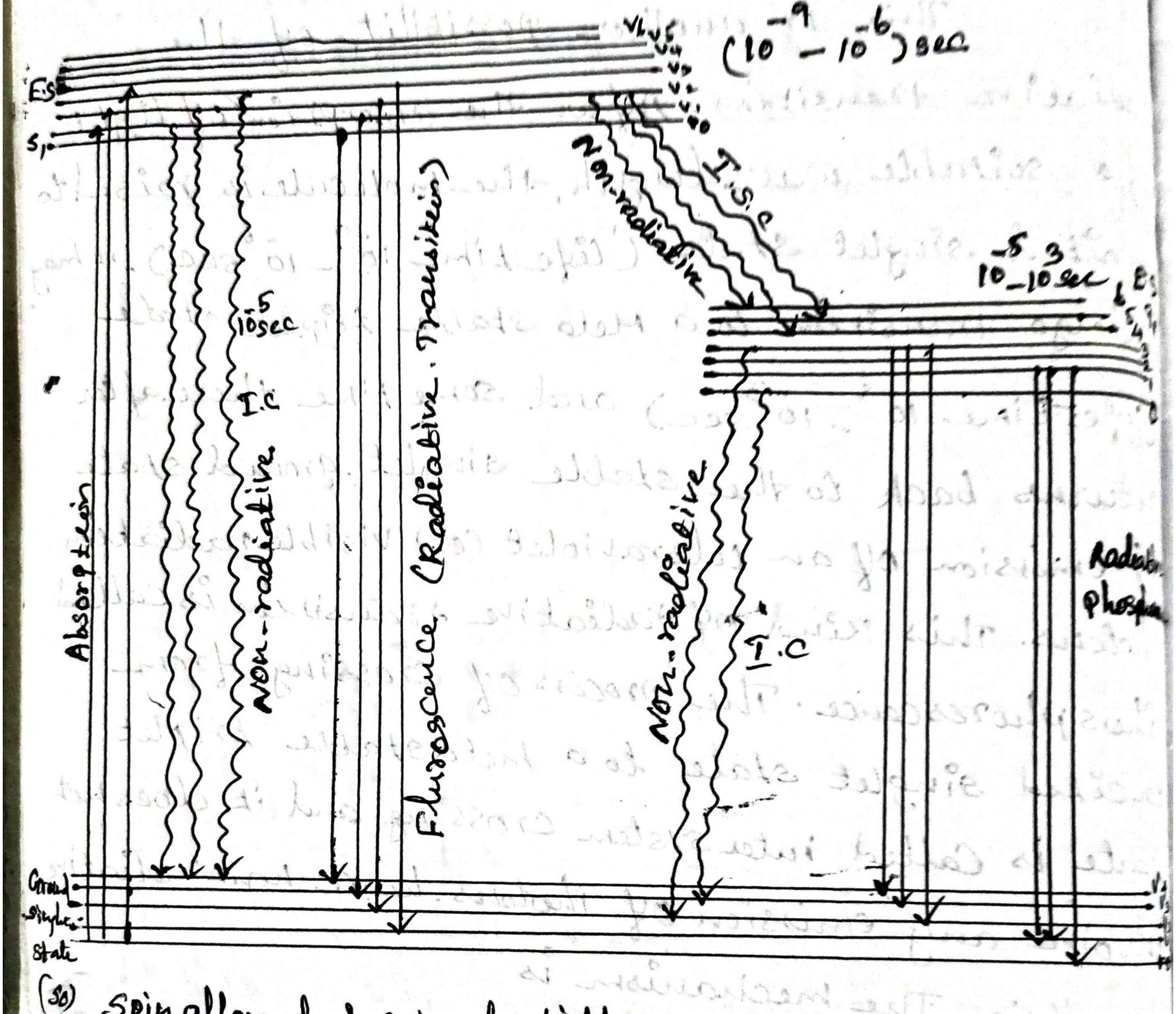
2. Phosphorescence.

This is another possibility of the radiative transition. Aifter the absorption of light of a suitable wave length, the molecule is raised to excited singlet state (life time 10^{-9} - 10^{-6} sec). it may undergo transition to a Meta stable triplet state (life time 10^{-5} - 10^{-3} sec) and some time thereafter returns back to the stable singlet ground state by emission of an ultraviolet (or) visible radiation Photons. This kind of radiative transition is called Phosphorescence. The Process of Crossing, from excited singlet state to a metastable triplet state is called inter system crossing and it does not involve any emission of Photons, hence non-radiative transition. The mechanism is

$$\underset{\substack{(GS)\\ S_0}}{\text{Molecule}} \xrightarrow[\text{absorption}]{h\nu} S_1 \xrightarrow[\text{ISC}]{\text{Non-radiative}} T_1 \xrightarrow{\text{Radiative}} S_0 + h\nu'$$

Life time of fluorescence & phosphorescence.

As per spin conversion rule the decay (emission) from excited triplet state to Ground singlet state is forbidden and is therefore very slow. Hence life time of Phosphorescence ($T_1 \rightarrow S_0$) is much longer than fluorescence ($S_1 \rightarrow S_0$)



Spin allowed & spin forbidden Transition

Spin conservation rule

This rule states that transitions between states of different multiplicity are forbidden. For example, from singlet to triplet and vice versa are forbidden. i.e., such transitions have very small probability of occurence in practice

Photo sensitisation

* In many Photo chemical reactions the reactant molecule does not absorb the radiation required for the reaction.
* By a third substance which transfers the absorbed energy to the reactants.
* This third substance which itself does not undergo any change.

“ A species which can both absorb and transfer radiant energy for activation of the reactant molecule is called Photo sensitizer and process is known as Photosensitization.

* Among the Photo sensitizers in common use are the atomic sensitizers such as Hg, cd and zn and the molecular photosensitizers such as benzophenone and Sulphur dioxide.

Function of Photosensitizer

* The function of Photosenitizer is to be absorb light become excited and then excited atom collides with a reactant molecule and transfer to it the excitation energy. This energy is enough to activate the molecule. Photosensitizer returns to the original unactivated state.

example

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + A \rightarrow A^* + Hg$$

Meachanism of Photosensitization

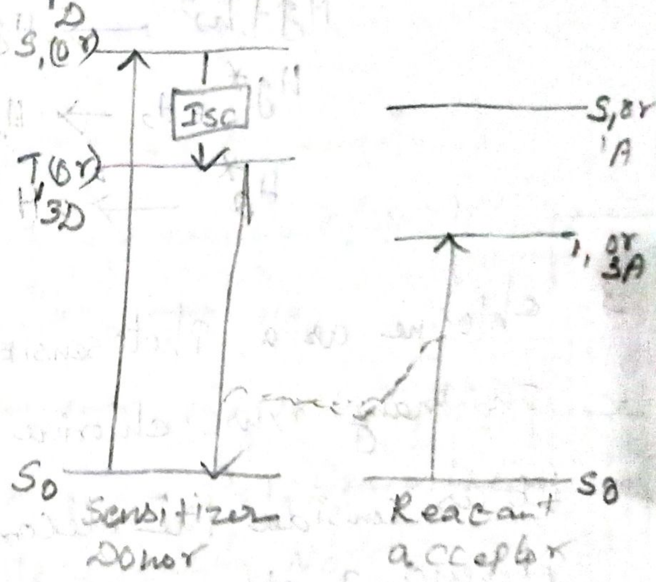
- The Sensitizer (donar D) absorbs the incident Photon and the triplet state of the donor is higher in energy than the triplet state off the acceptor A reactant.
- Absorption of the Photon Produces the singlet excited state of the donor ^1D which, via intersystem crossing Isc gives the triplet excited state of the donor ^3D.
- This triplet excited state then Collides with the acceptor producing the triplet excited state of the acceptor, ^3A and the ground state of donor
- ^3A gives the desired products, then the mechanism is called Photosentization

$$D + h\nu \rightarrow {}^1D$$

$${}^1D \xrightarrow{Isc} {}^3D$$

$${}^3D + A \rightarrow D + {}^3A$$

$${}^3A \rightarrow \text{products}$$



Examples of Photosensitized reaction

a) Reaction between H_2 and O_2. This reaction is Photosensitized by mercury Vapour. The Product is H_2O_2

$Hg + h\nu \rightarrow Hg^*$ primary absorption

$Hg + H_2 \rightarrow 2H + Hg$ Energy transfer

$$\left.\begin{array}{l} H + O_2 \rightarrow HO_2 \\ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \end{array}\right\} \text{Reaction}$$

b) Reaction between H_2 and Co mercury vapour is used as Photosensitizer. The product is formaldehyde HCHO

$Hg + h\nu \longrightarrow Hg^*$ primary absorption

$Hg + H_2 \longrightarrow 2H + Hg$ energy transfer

$H + CO \longrightarrow HCO$

$HCO + H_2 \longrightarrow HCHO + H$

$2HCO \longrightarrow HCHO + CO$

Reaction

2. Dissociation of H_2 Molecule

Irradiation of a mixture of hydrogen gas and mercury vapour with light of wavelength 253.7 nm brings about dissociation of hydrogen molecule into hydrogen atoms.

$Hg + h\nu \longrightarrow Hg^*$

$Hg^* + H_2 \longrightarrow H_2^* + Hg$

$H_2^* \longrightarrow 2H^{\cdot}$

3. chlorine as a Photosensitiser

In many rxns, chlorine acts as a Photosensitiser let us consider the decomposition of ozone in the Presence of Chlorine

Quenching of fluorescence

when photochemically excited atom undergoes collisions with another atom or molecule before it has chance to show fluorescence, the intensity of fluorescent radiation may be diminshed or stopped. This whole phenomenon known as quenching of fluorescence. (shorten the lifetime of the emitting molecule)

Mechanism of Quenching

i) Electronic energy transfer to the added gas molecules resulting in excitation of the later such transfer may result in the characteristic emission from the added gas with continous quenching of Hg

eg $Hg^* + Tl \longrightarrow Hg + Tl$

ii Energy transfer in the Vib. modes of the quencher (E → V transfer) $^3Hg_1 \longrightarrow {}^3Hg_0$

Quenching cross section and the energy difference Vib. energy spacing $\Delta\nu$ of $\nu=0 \rightarrow \nu=1$ transition the quencher. simple molecules like NO, CO, N_2 we found to be effecient quenchers. i.e strong interaction b/w the ex. atom and the quencher must be essential to Quenching.

iii Quenching by inert gases like Ar & Xe

These gases are good quenches of ex. states. In these cases electronic excitation energy can be dissipated as translational energy (E-T transfer) iv Quenching due to abstraction of H atom

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow H_2^* + Hg$$

$$H_2^* \rightarrow 2H.$$

Static and dynamic quenching

- ✱ The Quenching Process is defined as one which competes with the spontaneous emission process and thereby shorten the life time of the emitting molecule.
- ✱ Basically these quenching rxns are energy transfer or e^- transfer processes.
- ✱ In some cases transient complex formation in the excited state may be involved (exciplex formation)
- ✱ These excited state complexes may or may not emit their own character emission which is likely to be different from that of the original.

Static quenching.

- ✱ In solution there is a possibility of weak complex formation in the G.S is also present.
- ✱ Hence there is just a position of flurocent and quencher molecules with in the solvent cage at the moment of excitation.
- ✱ This may cause immediate loss electronic energy is called static quenching.

Since there is no competition with emission processes the life time is not affected.

- Ground state complex formation reduces fluorescence intensity by competing with the uncomplexed molecules for the absorption of the incident radiation. This is called the inner filter effect.

- The ordinary quenching process is otherwise called Dynamic quenching.

The dynamic & static quenching may be distinguished by the following mode of action

$$\begin{tikzcd}
 & & & A+Q+h\nu' \\
\text{Dynamic} & A^{*}+Q \arrow[r, leftrightharpoons] & (A\cdot Q)^{*} \arrow[ur] \arrow[dr] & \\
 & & & A+Q+\Delta \\
\text{Static} & A+Q \arrow[uu, "h\nu"] \arrow[r, leftrightharpoons] & (AQ) \arrow[uu, "h\nu"'] &
\end{tikzcd}$$

Stern - Volmer equation

- The rate of formation of an excited molecule A^* is equal to its rate of deactivation and the Conc'n $[A^*]$ remains constant.

$$\frac{d[A^*]}{dt} = 0$$

The conc^n/. of A^* in the absence of any bimolecular Quenching step

$$[A^*]^0 = \frac{I_a}{k_f + k_{Ic} + k_{ISC}} = \frac{I_a}{k_f + \Sigma k_i}$$

where I_a is the rate of absorption (Or) Rate of formation the activated molecule, k_f is the rate constant for fluoresance and Σk_i, the sum of rate constants for all the unimolecular deactiting step such as IC, and ISC which originate from this energy state.

If another molecule Q is added to the solution which Quenches the fluorescence by a bimolecular Quenching step

$$A^* + Q \rightarrow A + Q$$

$$\text{Rate} = k_q [A^*] [Q]$$

then the concentration of the fluorescence $[A^*]$ in presence by the Quencher is given as

$$I_a = \left[\Sigma k_i + k_f + k_q [Q] \right] A^*$$

$$A^* = \frac{I_a}{k_f + \Sigma k_i + k_q Q}$$

If $[A^*]^0$ and $[A^*]$ are fluorescence concentrations in absence and in presence of the Quencher, the respective Quantum yield are

$$\phi_f^0 = \frac{k_f [A^*]^0}{I_a} = \frac{k_f}{k_f + \Sigma k_i}$$

$$[A^*]^0 = \frac{I_a}{k_f + \Sigma k_i} = \frac{k_f}{\cancel{I_a}} \times \frac{I_a}{k_f + \Sigma k_i}$$

$$\phi_f = \frac{k_f [A^*]}{I_a} = \frac{k_f}{\cancel{I_a}} \times \frac{I_a}{k_f + \Sigma k_i + k_q Q}$$

$$= \frac{k_f}{k_f + \Sigma k_i + k_q (Q)}$$

the ratio of the two yield is

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

$$\frac{\phi_f^\circ}{\phi_f} = \frac{k_f+\Sigma k_i+k_q(Q)}{k_f+\Sigma k_i} \Rightarrow \frac{k_f+\Sigma k_i}{k_f+\Sigma k_i} . \frac{k_q(Q)}{k_f+\Sigma k_i}$$

$$= 1 + \frac{k_q(Q)}{k_f+\Sigma k_i}$$

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

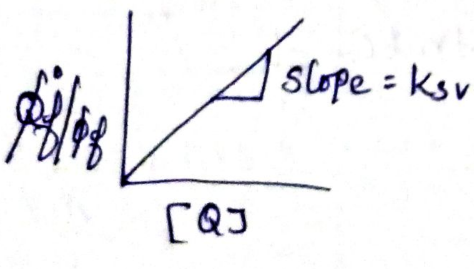
$$= 1 + K_{sv}[Q]$$

This expression is known as the stern-Volmer equation and ksv as Stern Volmer Constant.

* Ksv is the ratio of bimolecular quenching constant to unimolecular decay constant. It implies a competition b/w the two decay pathways and has the character of an equilibrium constant.

Verification of Stern Volmer expression

* The stern-volmer expression is linear in quencher concentration and k is obtained as the slop of the plot of ϕ_f°/ϕ_f Vs [Q]. The assumed mechanism of quenching is operative.



τ is the actual life time of the fluores Molecule in absence of bimolecule Quenching and expressed as

$$\tau = \frac{1}{k_f + \Sigma k_i}$$

If τ is measured independently then from the known value of k_{sv}, the rate constant k_q for the bimolecular quencher step can be determined. For an efficient quencher.

$$k_{sv} \simeq 10^{2} - 10^{3} \text{ lit. mol}^{-1}$$

$$T \simeq 10^{-8} \text{ s} \quad \text{then}$$

$$k_q = \frac{k_{sv}}{T} = \frac{10^{2}}{10^{-8}} \simeq 10^{10} \text{ lit mol}^{-1} \text{s}^{-1}$$

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-Quenched then

$$\frac{\phi^{0}}{\phi} = 2 = 1 + k_{sv}[Q]_{1/2}$$

$$k_{sv}[Q]_{1/2} = 1$$

$$k_{sv} = \frac{1}{[Q]_{1/2}} = k_q T = \frac{1}{c_h}$$

k_{sv} is the reciprocal of half-quenching Concentration or having wave Concentration c_h.

For weak quenchers all the encounters may not be fruitful and collisional quenching p is less than unity, so that

$$k_{SV} = pT k_q$$

For ionic solution, ionic strength is an important parameter, affecting the quenching constant. The rate constant for bimolecular quenching collision should be corrected to the limiting value k_q^0 according to Bronsted theory

$$\log k_q = \log k_q^0 + 0.5 \, \Delta z^2 \sqrt{M}$$

where μ is the ionic strength, $\Delta z^2 = z_{AQ}^2 - (z_A^2 + z_Q^2)$ and z_{AQ}, z_A, z_Q are number and nature of charges on the intermediate complex AQ, the fluorescer A and the quencher Q respectively. with rise in ionic strength the quenching action may increase, decrease or remain unchanged depending on the sign of Δz^2

Excimer formation

* Excimer is a transient Complex formation occurs b/w the excited state molecule and G.S molecule of the Same kind

$$\underset{\text{Excited state molecule}}{A^*} + \underset{\text{G.S Molecule}}{A} \longrightarrow \underset{\text{Excimer Complex}}{AA^*}$$

$$A + A \xrightarrow{h\nu} A^* + A \longrightarrow \underset{\text{Excimer Complex}}{AA^*}$$

* In same cases simultaneously with the Quenching of the normal fluorescence, a new structureless emission band appears at about 6000 cm^{-1} to the red side of the monomer fluorescence spectrum. This phenomenon was due to transitory complex formation in the excited state. These short lined excited state dimers are called excimers.

* The eximers dissociate when they return to the g.s by emission, giving rise to a structureless envelope for the emission spectrum. This show that the G.S P.E surface must be repulsional.

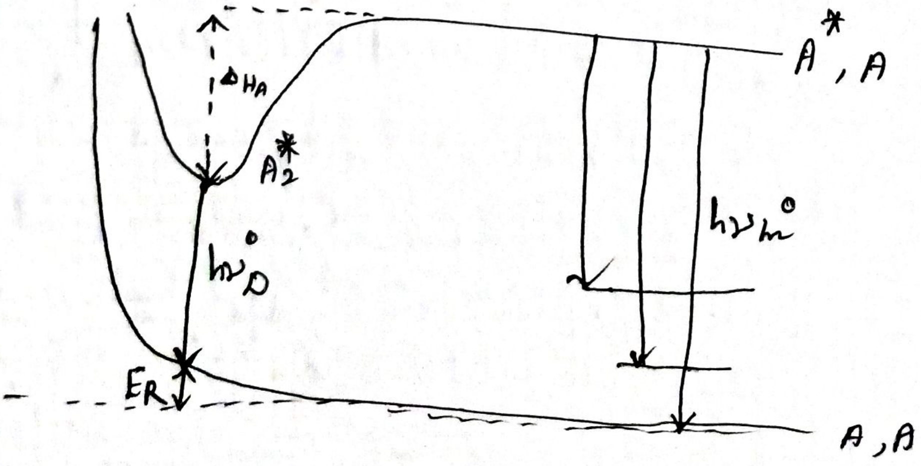


Fig. Potential energy surfaces for monomer and excimer emission. ν^0_M, ν^0_D monomer & excimer emission frequency, A_2^* excimers ΔH_A enthalpy of excimer formation.

Conditions excimer emission

* Excimer emission is often observed from Planar molecules. when the two molecules are placed in Parallel configuration. The conditions are that

1) The two Planar molecules approach with in a d/s ≃0.33 nm of each other

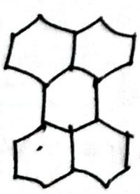
2) The concentration is high enough for interaction to occur with in the excited life time.

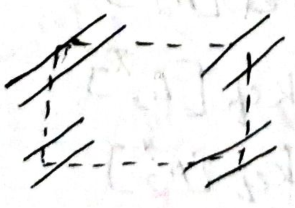
3. The interaction energy b/w an excited and a normal molecule is attractive such that ΔH^* (excited state enthalpy) is greater than RT Thermal energy.

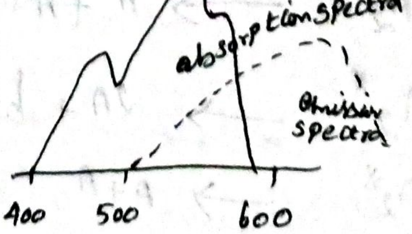
example :

i) The excimer emission is obsewed in planar aromatic hydrocarbon.

ii Pyrene gives emission structureless band in the visible region, very similar to that observed in concentrated solutions. the crystals lattice of Pyrene consists of two overlaping molecules.







iii Emission from the biopolymer deoxyribose nucleic acid (DNA) is due to excimer formation b/w the constituent base

Excimer emission is known to occur in inert gases He

* Besides the prompt excimer emission, delayed excimer emission has been observed. The mechanism is thro triplet-triplet annihilation process

diatomic process

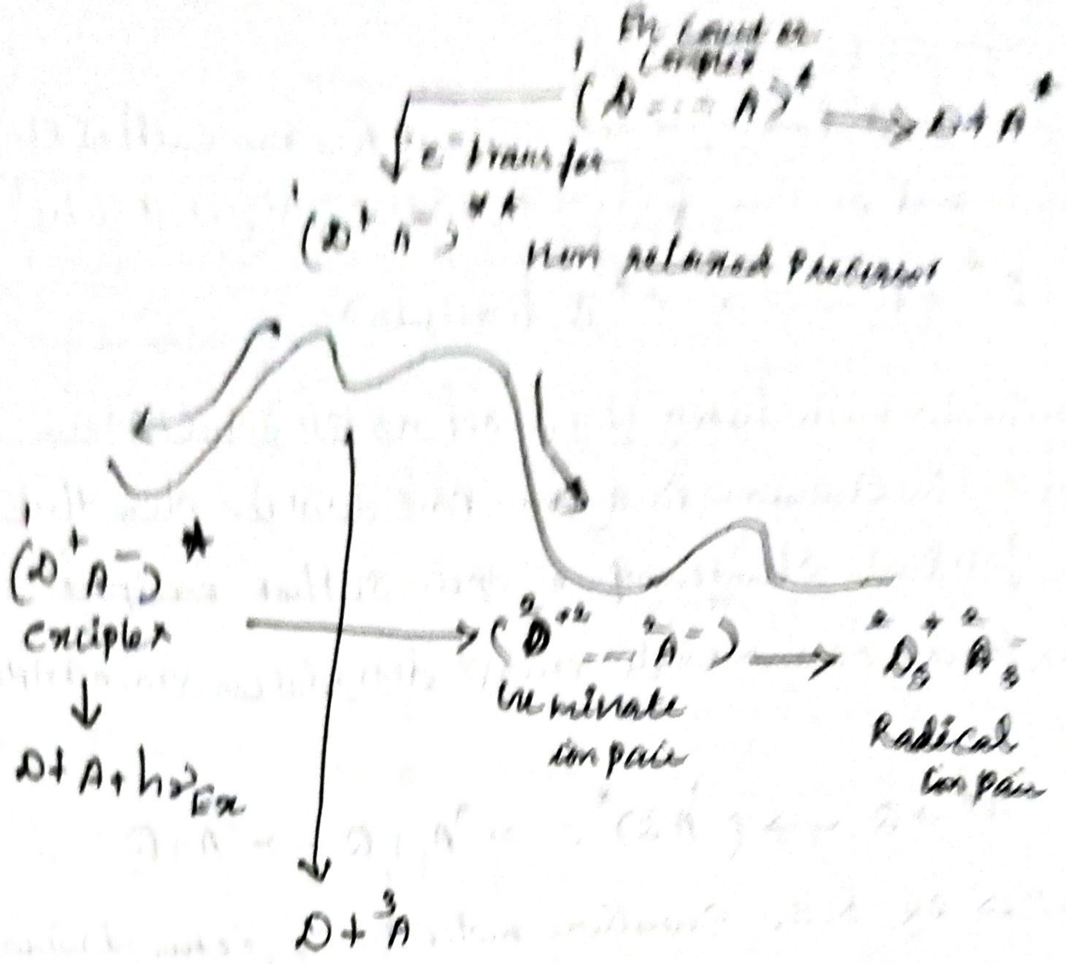
$$\begin{tikzcd} {}^3A + {}^3A \arrow[r] & A_2^* \arrow[r] \arrow[d] & A^* + A \arrow[d] \\ & h\nu_{ex} & h\nu_{DF} \end{tikzcd}$$

The excimer is formed as an intermediate which may dissociate into an excited singlet & a g.s singlet

Excimer formation has been assumed to be a necessary step in conc/ quenching. It is not essential that the excimer shall be always fluorescent (step 7) It may promote radiationless processes with in the molecule (step 8) the various steps involved in conc/ quenching are

		Rate
1.	$A + h\nu_a \longrightarrow A^*$	I_a
2	$A^* \longrightarrow A + h\nu_f$	$k_f [A^*]$
3	$A^* \longrightarrow A$	$k_{IC} [A^*]$
4	$A^* \longrightarrow {}^3A$	$k_{ISC} [A^*]$
5.	$A^* + A \longrightarrow A_2^*$	$k_{ex} [A^*][A]$
6.	$A_2^* \longrightarrow A^* + A$	$k_{ed} [A_2^*]$
7.	$A_2^* \longrightarrow 2A + h\nu_D$	$k_{ef} [A_2^*]$
8	$A_2^* \longrightarrow A + A$	$k_{er} [A_2^*]$

Step 5 is the excimer formation step. Step 6 which is the reverse process involving the dissociation of the excimer into an es & a g.s



An intermediate non-relaxed $\bar{e}$ transfer state (${}^1D^+_s$ is produced by e^- transfer in the encounter compl which relaxes to the exciplex state after readjustment of co-ordinate & solvent orientation. Triplet formation and ion pair formation may occur in Competition to exciplex formation and also as a mode of relaxation of exciplex. The ~~geminate~~ generate ion pair (${}^2D^+ \ldots {}^2A^-$) lead to radical ion-pair which decays via Triplet state.

An example of exciplex emission is the syst anthracene and biphenyl and an easily oxidised aniline N-N'-diethyl aniline.

PHOTOELECTROCHEMICAL CELL:

I Yr/VM

A photoelectrochemical cell can be constructed by placing two redox couples of graded potentials on either side of the membrane and dipping metal electrodes in each of them. On completing the circuit by suitable device, photo current is generated on excitation of the membrane by light energy.

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The alternative sequence of reactions initiated by light can be summarized as follows

$Chl + h\nu \longrightarrow Chl^{-+}$ (exciton formation)

$H_2O - Chl^{-+} \longrightarrow e^-_{aq} + Chl^+$

$A - Chl^+ \longrightarrow A^- - Chl^+ \longrightarrow A^- + Chl^+$

$e_{aq} + A \longrightarrow A^- + H_2O$

$H_2O - Chl^{-+} \longrightarrow h^+_{aq} + Chl^-$

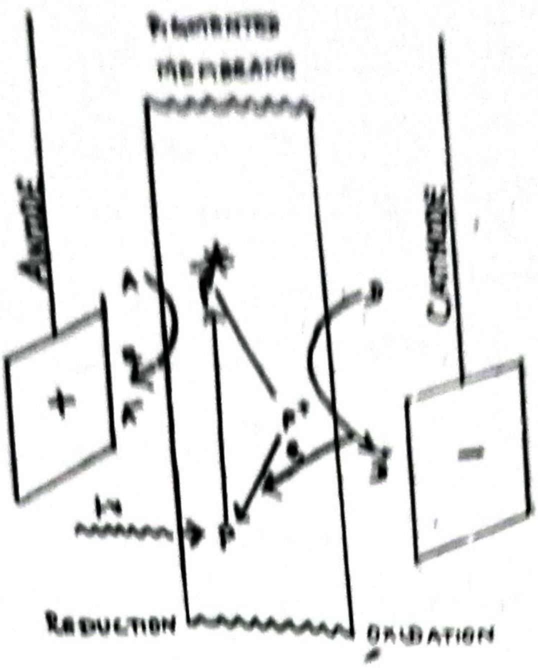
$D - Chl^{-+} \longrightarrow D^+ + Chl \longrightarrow D^+ + Chl^-$

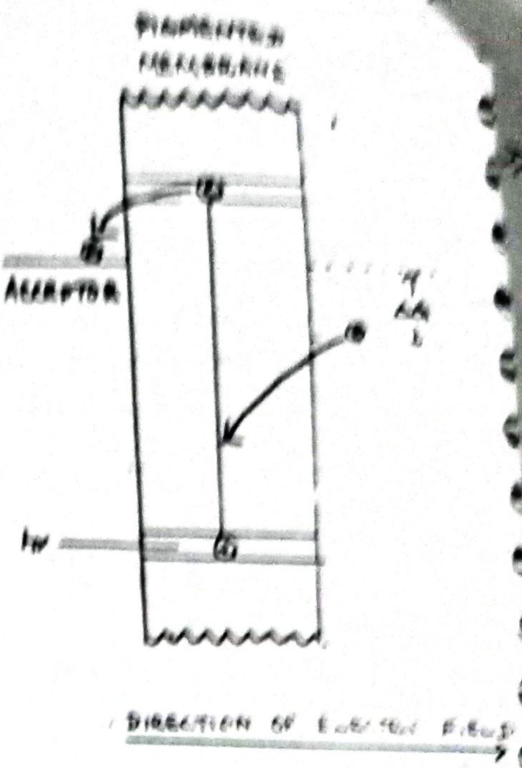
h^+ or $Chl^+ + \frac{1}{2}H_2O \longrightarrow Chl + H^+ + \frac{1}{4}O_2$

$Chl^- + Chl^+ \longrightarrow 2Chl + h\nu'$

Here Chl denotes a photosynthetic pigment, (−, +) is an electron-hole pair or exciton, e^-_{aq} is hydrated e^-, h^+_{aq} is hydrated hole. $A^- = Chl^+$ and $D^+ = Chl^-$ are charge transfer cplx with an e^- acceptor A and an e^- donor D, respectively. The last step is responsible for delayed emission from chloroplast.

It has been postulated that cplxs of





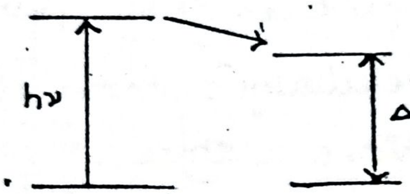
electron-transfer proteins in a membrane are of graduated redox-potential. The e^- transfer occurs through channels provided by a cplx sequence of ligand and bonds are conjugated molecules like carotenoids. These proteins are able to accept e^{-ns} from excited chl on one membrane side (anode) and donate them to an acceptor of more positive redox potential on the other side (cathode). The membrane provides a resistance for an Ion current from anode to cathode which closes the electrochemical circuit, and converts excitation energy into chemical free energy 'ΔG'.

SOLAR ENERGY CONVERSION AND STORAGE:

Solar energy conversion device are based on two objectives energy by Suitable energy storing i.e., endergonic photochemical reans.

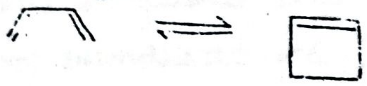
a) Conversion of light energy into electrical energy by Suitable photoelectrochemical devices.

(1) The energy storing photoreactions occur with +ve free energy change ($+\Delta G$) and are hence thermodynamically unstable.

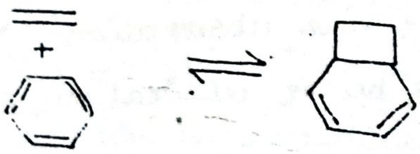


$$R \underset{\text{Thermally forbidden}}{\overset{\text{Photochemically allowed}}{\rightleftharpoons}} P$$

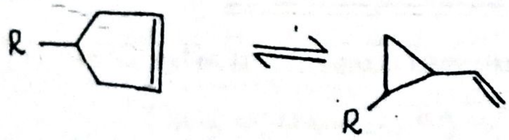
a) Valence Isomerization :-



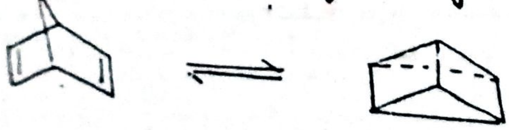
b) Cycloaddition



c) Sigmatropic Effect



d) norbornadiene to quadricyclene conversion.



If the reverse back rean is prevented or is forbidden by other considerations, the energy remains stored in the photoproducts. Some

Woodward - Hoffman rules have been found which rules provide the stereochemical course of [illegible] photo rearrangement based on symmetry properties of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. A rean which is photochemically allowed may be thermally forbidden. From the principle of microscopic reversibility, the same will be true for the reverse rean also. Thermally forbidden back rean will produce stable photoproducts.

Such electrolytic rearrangements are given above. A rean which can store about 260 cal per gram in material and has shown some promise is valence isomerization of norbornadiene (NBD) to quadricyclene. The disadvantage is that it does not absorb in the visible region and therefore the sunlight efficiency is poor. By attachment of chromophoric gps or by use of suitable sensitizers it might be possible to shift the absorption region towards the visible for better utilization of solar energy.

DECOMPOSITION OF WATER :-

The decomposition of water to H_2 and O_2 is highly endothermic process.

$$H_2O(l) \longrightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta H^\circ = +295\,kJ \qquad \Delta G^\circ = +237\,kJ$$

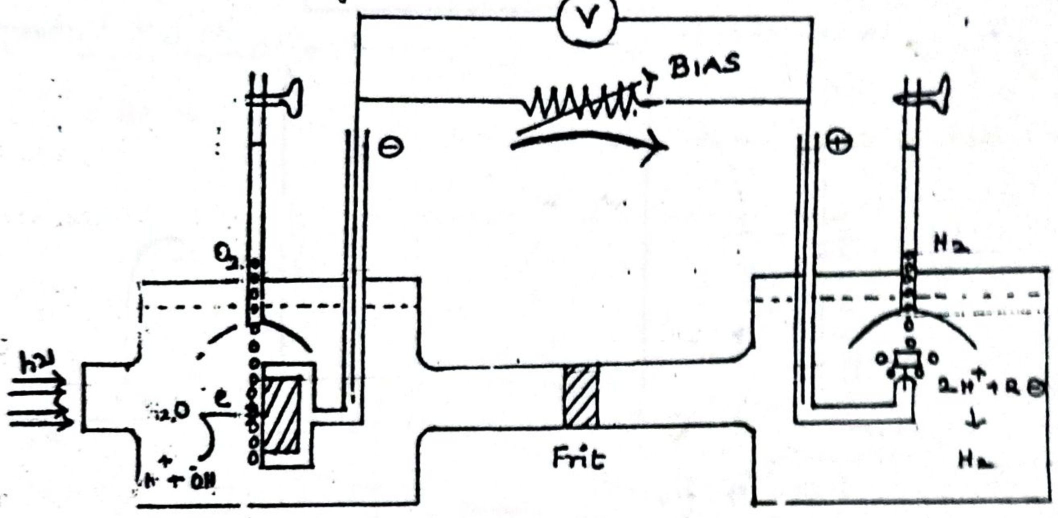
Hydrogen is a non polluting fuel which burns in air to produce water again releasing large amount of heat. Alternatively, H_2 and O_2 may be made to [illegible] electrodes are

$$TiO_2 \cdot 2h\nu \longrightarrow 2e^- + 2h^+ \text{ (hole)}$$

$$2h^+ + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ \text{ (at } TiO_2 \text{ electrode)}$$

$$2e^- + 2H^+ \longrightarrow H_2 \text{ (at Pt electrode)}$$

Hydrogen and oxygen can be collected separately and combined again in a fuel cell to obtain electrical energy.



TiO_2
Semiconductor Electrode

platinized platinum Counter Electrode.

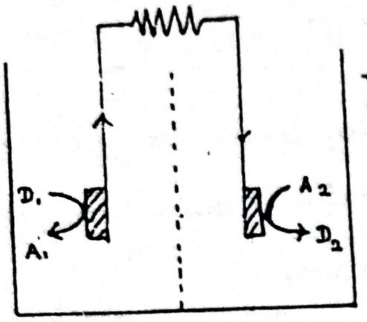
PHOTOELECTROCHEMICAL DEVICES:

Photoelectrochemical devices to convert light energy to electrical energy implies construction of a battery which undergoes cyclical charging and discharging processes.

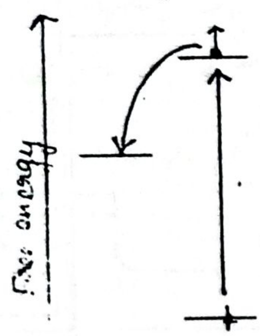
PHOTOGALVANIC CELL:

On illumination the cell is charged. Light energy is converted into chemical energy by driving a suitable redox reacn against the potential gradient.

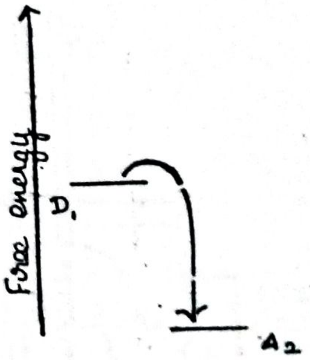
$$\underset{ox_1}{A_1} + \underset{red_2}{D_2} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \underset{red_1}{D_1} + \underset{ox_2}{A_2}$$



(a) Cell charge



(b) Cell discharge



$D_2 \xrightarrow{h\nu} D_2^*$

$D_2^* + A_1 \longrightarrow A_2 + D_1$

Photochemical reacn followed by pdt separation

$D_1 + A_2 \longrightarrow D_2 + A_1$

b) Thermodynamically spontaneous.

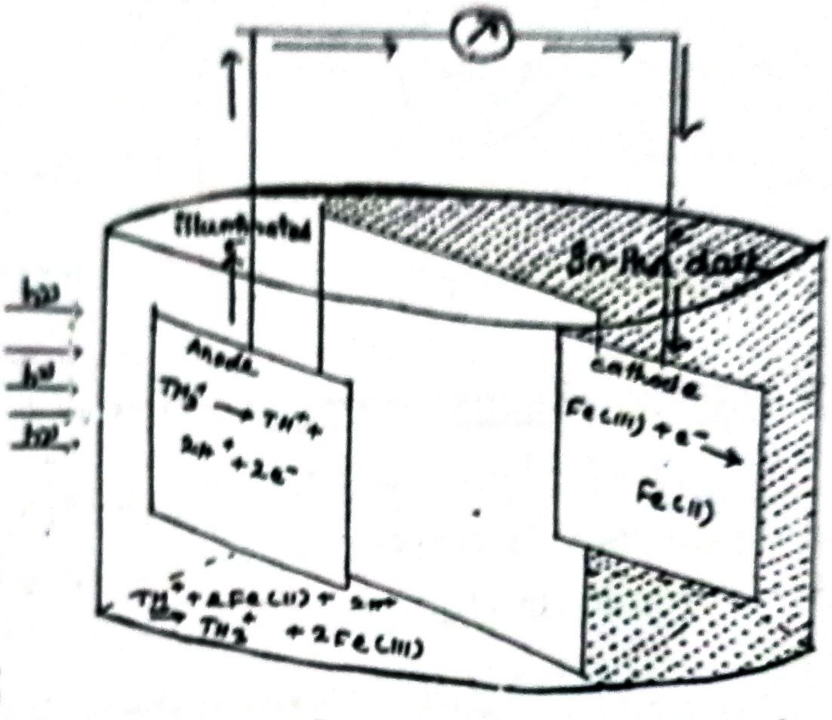
Where D and A represent the reduced forms and the oxidized forms of the donar-acceptor system respectively. The reacn reverses spontaneously in the dark using the external circuit for e^- transfer. In the process chemical energy is converted into electrical energy and the cell is discharged. No consumption of chemicals occurs during the charge-discharge cycle. Therefore in an ideal system, the system shd funcn as a rechargeable battery without any loss of efficiency. These are known as photogalvanic cells. An example of such a reacn is the reversible photobleaching of technique by and can be represented as TH⁺, overall reaction is

$$TH^+ + 2Fe^{3+} + 3H^+ \underset{dark}{\overset{h\nu}{\rightleftharpoons}} TH_2^+ + 2Fe^{2+}$$

DRAWBACKS:

The efficiency of photogalvanic devices for solar energy conversion is not very good mainly due to difficulties in preventing the spontaneous back recombination reaction.

2) They cannot utilize the total solar spectrum.



primitive Iron-thionine photogalvanic cell.

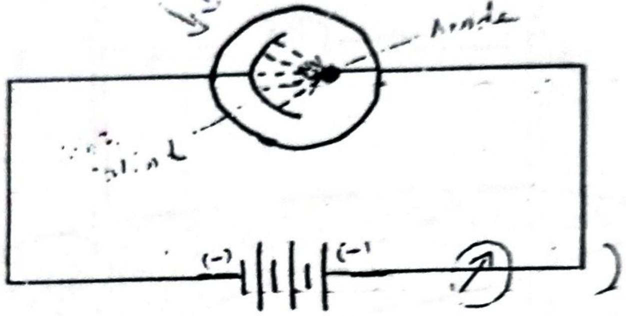
PHOTOVOLTAIC CELL:-

Silicon solar cells have been found to be the most efficient quantum conversion devices. They are photovoltaic cells in which the light energy is directly converted into electrical energy without the intermediate chemical reaction. The photocurrent is used to charge a storage battery. In a typical

[illegible]

Semiconductors like silicon. 'Si' can also be used.

When the radn falls on the cathode plate e^{-ns} are emitted, these are attracted towards the anode, the photocurrent is used to charge a storage battery. Since silicon are very high purity is required. They are expensive.



INORGANIC REDOX SYSTEMS:

Photoinduced e^{-n} transfer in an aqueous solution of tris-(2,2'-bipyridine) ruthenium (II) has been found to decompose water into a mixture of H_2 and O_2. The cplx can serve both as an e^{-n} donor and e^{-n} acceptor in the excited state. The efficiency is low because of barrier of to e^{-n} transfer. When spread as a monolayer on glass slides after attaching to a surfactant chain, visible evolution of gases occur when a battery of about 20 to 80 slides are exposed to sunlight.

Many reducing cations in aqueous soln can photoreduce water in low yields when irradiated in their charge transfer bands. Similarly,

Kinetics of photochemical rxns.:

A photochemical rxn. is defined as any rxn. which is induced or influenced by the action of light (2000 - 8000 A°) on the system.

These are two approaches

(i). Non steady treatment
(ii). steady state treatment.

steady state treatment:

According to this approach, the conc. of a free radical or intermediate or a chain carries is constant at any instant

$$\frac{d[R]}{dt} = 0$$

R. free radical or intermedi
or chain carrier.

consider the rxn.

$$A \longrightarrow B$$

The photochemical rxn. takes place with an absorption of photochemical energy.

The various possible steps involved in the photochemical rxn. are as follows.

(i). $A + h\nu \xrightarrow{k_1} A^*$

(ii). $A^* \xrightarrow{k_2} B$ ~~[illegible]~~

(iii). $A^* + A \xrightarrow{k_3} 2A$

step:

(i). Is the 1° Process where as the steps (ii) & (iii). represent the dissociation and deactivation process.

[illegible]

by,

$$\frac{d[B]}{dt} = k_2[A^*] \text{ —— ①}$$

The rate of formation of the activated cpx. A*

$$\frac{d[A^*]}{dt} = k_1 I_{abs} \qquad = k_3 [A^*][A]$$

The rate of deactivation of the A*.

$$-\frac{d[A^*]}{dt} = k_2[A^*] + k_3[A^*][A]$$

According to steady state principle:

the rate of formation = the rate of deactivation.

$$\frac{d[A^*]}{dt} = -\frac{d[A^*]}{dt}$$

$$k_1 I_{abs} = k_2[A^*] + k_3[A^*][A]$$

$$= [A^*]\{k_2 + k_3[A]\}$$

$$[A^*] = \frac{k_1 I_{abs}}{k_2 + k_3[A]}$$

This value substitute in equ. (1)

$$\frac{d[B]}{dt} = \frac{k_2 k_1 I_{abs}}{k_2 + k_3[A]}$$

If one molecule of B is formed from one molecule of A by absorbing light, then the quantum efficiency [φ]

$$\phi = \frac{d[B]}{dt} \Big/ I_{abs}$$

$$= \frac{k_1 k_2 \, I_{abs}}{\{k_2 + k_3[A]\} \, \cancel{I_{abs}}} = \frac{k_1 k_2}{\{k_2 + k_3[A]\}}$$

from the kinetics of photochemical rxn/. to determine the following things.

(i). To measure the quantum yield.

(ii). To determine the order of rxn/.

(iii). To determine the influence of conc/.

(iv). To determine the influence of light intensity.

photochemical rxns/. may be divided into the following two types.

1. Rxn/. which donot involve chains
2. Rxn/. which involve chains.

(I). <u>photo chemical chain rxn/.</u>

(a). <u>combination of H_2 & Cl_2</u>:

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

<u>Mech/.</u>

<u>In absence of oxygen</u>:

(a). 1° Process (initiation)

(i). $Cl_2 + h\nu \xrightarrow{k_1} 2Cl$ Rate = $k_1 I_{abs}$.

(b). <u>secondary process</u>:

1. <u>chain propagation</u>

(ii). $Cl + H_2 \longrightarrow HCl + H$ $k_2[Cl][H_2]$

(iii) $H + Cl_2 \longrightarrow HCl + Cl$ $k_3[H][Cl_2]$

2. <u>chain termination</u>:

(iv). $Cl + \text{wall} \longrightarrow \frac{1}{2}Cl_2$ $k_4[Cl]$

Net rate of formation of Cl = (Rate of formation of Cl) − (Rate of removal of Cl)

$$\frac{d[Cl]}{dt} = k_1 I_{abs} + k_3[H][Cl_2] - k_2[Cl][H_2] - k_4[Cl]$$

But at steady state principle:

$$\frac{d[Cl]}{dt} = 0$$

$$\therefore k_1 I_{abs} + k_3[H][Cl_2] - k_2[Cl][H_2] - k_4[Cl] = 0 \text{ — ①}$$

III^{ly}

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0 \text{ — ②}$$

$$k_1 I_{abs} - k_4[Cl] = 0$$

$$[Cl] = \frac{k_1}{k_4} I_{abs} \text{ — ③}$$

From equ. ②

$$k_2[Cl][H_2] = k_3[H][Cl_2] \text{ — ④}$$

Net rate of formation of HCl is given by

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \text{ — ⑤}$$

$$\frac{d[HCl]}{dt} = 2k_2[Cl][H_2] \text{ — ⑥}$$

$$\boxed{\frac{d[HCl]}{dt} = 2\left(\frac{k_1 \cdot k_2}{k_4}\right) I_{abs}[H_2]} \text{ — ⑦}$$

equ. ⑦ is the rate law of the over all rxn.

Quantum Yield:

$$\varphi = \frac{\frac{d[HCl]}{dt}}{k_1 I_{abs}} = \frac{2\cancel{k_1} k_2 \cancel{I_{abs}}[H_2]}{k_4} \times \frac{1}{\cancel{k_1} \cancel{I_{abs}}}$$

$$\boxed{\varphi_{HCl} = \frac{2k_2[H_2]}{k_4}}$$

upon the [illegible] of time over which the fluorescence is emitted and the mode, whereby the fluorescence arises.

Prompt fluorescence is normally emitted with in 10^{-8} s after the exciting radiation is distinguished. It results from the S_1 state molecules, which are produced initially on excitation reverting to G.S.

Delayed fluorescence is usually emitted over a much longer period of time than prompt fluorescence (typically $> 10^{-6}$ s) and results from the radiative conversion to the G.S of S_1 state molecules, which are formed by rxn of corresponding T_1 state molecules.

Since the delayed fluorescence depends upon the conversion of T_1 state species into S_1 state species. This type of fluorescence can be seen throughout the life time of the molecule under study.

Delayed fluorescence has longer life time where as prompt fluorescence has shorter life time.

Prompt fluorescence can arise by radiative emission from either (a) an 'S_1' state molecule (b) an eximer formed by interaction of an S_1 state molecule with an S_0 State molecule.

The term eximer is used to denote the excited state dimeric species. The two processes giving rise to prompt fluorescence are represented below.

(a). $S_1 \longrightarrow S_0 + h\nu_F$

(b). $S_1 + S_0 \rightleftharpoons (S_1 S_0)^* \longrightarrow 2S_0 + h\nu_F$

excimer emission

Fluorescence emission of the excimer $(S_1 S_0)^*$ can differ from that of the free S_1 state molecule. The delayed fluorescence can be formed by either

(a). Thermal exitation of a "T_1" state molecule (or)

(b). collision of two T_1 state molecules.

The process leading to delayed fluorescence are shown below.

(a). $T_1 \xrightarrow{\text{Thermal exitation}} S_1 \longrightarrow S_0 + h\nu_F$

(b). $T_1 + T_1 \longrightarrow S_1 + S_0$

$S_1 \longrightarrow S_0 + h\nu_F$

The Ist step in the mech, (b). above referred to as "energy pooling" since two state combine their energy to form a 3rd state of higher energy. Normally the form of the delayed fluorescence spectrum is the same as that of the prompt fluorescence originating from the free S_1 state molecule.

Delayed fluorescence is further classified into E-type delayed fluorescence and P-type delayed fluorescence.

E-type decay fluorescence is observed when the singlet - Triplet energy gap (ΔE state) is small as in the case for dye molecules.

In the process thermal excitation of "T" to "S" State occure from S_1 state, they decay radiatively by emitting E type delayed fluorescence.

The rate (or) rate constant for E-type delayed fluorescence is temp/. depr dependent.

$$k_{E.D} : A \cdot e^{(-\Delta E_{ST} / RT)}$$

A. frequency factor.

$$T_1 \xrightarrow[\text{exitation}]{\text{Thermal}} S_1 \longrightarrow S_0 + h\nu_{E.D}$$

ΔE_{S_1} - activation energy equal to 0-0 diff/. b/w singlet and triplet level.

This type of emission was first observed in deoxygenerated solu/. of eosin in glycol glycerol and ether at room temp. and hence it is designated as E type (or) eosin type.

Quantum efficiency of E-type delayed fluorescence is given by

$$\varphi_{E.D} = \varphi_T \varphi_F \cdot \frac{k_{ED}}{k_P + k_{ISC} + k_{BP}}$$

Here one proton is enough for the rxn to occur. Hence it is φ mono protonic process.

E.T.P.P is independent of the intensity of the absorption (I_a). P-type delayed fluorescence is observed when the energy gap b/w T & S state is large. It is so called because it was first observed in pyrene and phenatharacen solu/.

$$T_1 + T_1 \longrightarrow S_1 + S_0$$

$$S_1 \longrightarrow S_0 + h\nu_P$$

It depends on the intensity of absorption.

$$I_{pD} \propto I_a^2 \left(\phi_{pD} = \frac{\text{rate of emission}}{\text{rate of absorption}} = \frac{I_e}{I_a} \times I_a \right)$$

Here two photons are needed for this process to occur. So it is a biphotonic in nature. Intensity of D.T.P.P should decrease with viscosity.

Eg. of phosphorescence:

1. The common, substances that exhibit this phenomenon are sulphides of Ca, Ba, Sr.
2. Minerals eg: Ruby emerald are the Indensity egs. of phosphorescent substance.

Exciplex formation:

Hence a transient cpx. formation occurs b/w the excited state molecule and another foreign molecule of different kind.

$$A^* + Q \longrightarrow A^* Q \text{ (exciplex)}$$

Molecules with heavy atoms act as quenches by an exciplex mech. Quantum considerations show that they facilitate change of e^- spin. so that exciplex dissociation occurs with energy degradation. via a triplet level.

$$^1A^* + \underset{\text{(heavier atoms)}}{Q} \longrightarrow (^1AQ)^* \longrightarrow {}^3A + Q \longrightarrow A' + Q$$

eg. of such quencher molecules are Xenon, bromo benzene, bromides and iodides and some Rare earth cpds. In the absence of heavy atom effect and where the extent