

Introduction

Photochemistry is the branch of physical chem. with study of chemical reaⁿ which are caused by absorption of light radiations. Only absorbed radiation can cause a chemical reaⁿ. The light radiation of visible and UV region lying betⁿ 800 to 2000 nm.

Photochemical reaⁿ — Reaⁿ which occurs by absorption of light radiation in uv and visible region. When reaⁿ occurs by an absorption of light radiation in region other than uv and visible, then such reaⁿ are known as radiation induced reactions.

Photochemical Reaⁿ

- ① Reaⁿ occurs by an absorption of light energy.
- ② These reaⁿ are carried out only in the presence of light.
- ③ Rate of reaⁿ depends upon the conc. of reactant and intensity of incident light and independent of temperature.
- ④ Energy of activation for reactant molecule is provided by light energy.
- ⑤ For photochemical reaⁿ both \uparrow increase in free energy and \downarrow decrease in free energy may be observed.
- ⑥ e.g. $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$.
- ⑦ $-\Delta G$ +ve or -ve

Thermal Reaⁿ

- ① Reaⁿ occurs by absorption of heat energy.
- ② These reaⁿ are carried out in both light and dark.
- ③ Rate of reaⁿ depends upon the conc. of reactant and temp.
- ④ Energy of activation is provided by heat energy.
- ⑤ "In thermal reaⁿ, there is always decrease in free energy."
- ⑥ e.g. $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$
exothermic reaⁿ.
- ⑦ ΔG must be +ve

◦ Importance: In the field of research, photochemistry plays very imp. role. It has made sufficient contribution in solving problems of redⁿ kinetics. The synthesis of complex molecules like proteins and nucleic acids can occur through photochemical redⁿ betⁿ CO_2 , NH_3 and CH_4 , formation of vit-D, formation of ozone from oxygen in earth's atmosphere formation of smog and also development of skin cancer are examples of photochemical reactions. Another branch of photochemistry i.e. photobiology deals with study of various biological reactions.

Photochromic materials show a particular property of changing colour when exposed to radiation of suitable wavelength. These substances reverse their absorption characteristics on withdrawal of incident radiation. Spiropyrans which are photochromic are used in photochromic sun glasses and also in production of the information, storage and self-developing self-erasing films in digital computers.

Phenomena like fluorescence and phosphorescence have useful applications in development of x-ray, television screen, fluorescent tubelights, optical brighteners, luminescent watch dials, microanalytical reagents used for tracing river course through cover.

✓ LASER (Light Amplification by Stimulated Emission of Radiations) constitutes intense, monochromatic, coherent radiation which can be focused on a tiny spot and used for boring diamonds, cancer treatment, cutting of metals.

Photochemistry also helps in solving "Energy Crisis". Solar energy conversion can be achieved by manufacture of solar batteries which operate on the principle of photovoltaic effect.

◦ Absorption of light and nature of absorption spectra —

For the study of nature of light, the basic is the interaction betⁿ light and matter. To study the nature of light, the light should be incident on matter and it reflected, absorbed and transmitted and this helps us to understand the behaviour of light.

All light measuring devices are based on the interactions between light and matter. In some interactions, light behaves as a particle while in some cases it shows wave character, hence light shows a dual nature.

Photochemistry is based on the same laws. These are related to the absorption of radiation and chemical reactions various laws were proposed.

Law (i): Grothus and Draper law —

The light absorbed and chemical change occurring in photochemical reaction are closely related. This relation can be stated in terms of generalisation, which was made by T. Von Grothhus in 1817 and latter by J.W. Draper in 1841. As a result of expt. on union of hydrogen and chlorine. It is known as Grothus and Draper law.

obj — It is also known as first law of photochemistry. "only those radiations are absorbed by reaction system, which are effective in producing a chemical change."

$$I = I_a + I_r + I_t$$

Here, I_a is only useful for chemical reaction. Although a photochemical reaction can only results from the absorption of light. It does not mean that all absorbed light is effective for chemical change but some part of it may be converted into heat and some may be re-emitted as light of same or different frequency. This emission of radiation is known as fluorescence.

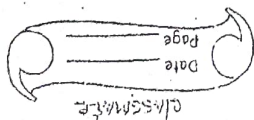
Law (ii): Lambert's law —

"When a beam of monochromatic light passes through transparent medium, the rate of decrease of intensity of light with thickness of absorbing medium is directly proportional to the intensity of incident light."

Whenever light is incident on absorbing medium the intensity of light get reduced. The rate of these decrease is proportional to intensity of incident light."

$$-\frac{dI}{dt} \propto I$$

$$-\frac{dI}{dt} = KI$$



$$dI/I = -k \cdot dt \quad \text{--- (1)}$$

where, $-dI/dt$ = rate of decrease of intensity with thickness.

I = intensity of incident light.

k = absorption coefficient.

The value of ' k ', depends on the wavelength of incident light radiation and nature of absorbing medium.

Integrating above eqⁿ, we get,

$$\int_{I_0}^I \frac{dI}{I} = -k \int_0^t dt$$

$$\therefore [\ln I]_{I_0}^I = -kt$$

$$\therefore \ln \frac{I}{I_0} = -k \cdot t$$

$$\therefore \log_{10} I/I_0 = -k \cdot t / 2.303$$

$$\therefore \log_{10} I/I_0 = -\alpha t$$

where, α is called as extinction coefficients.

Lambert's law is applicable to only solids.

Law (ii): Beers Law — (Lambert-Beers law)

"When a beam of monochromatic light passes through a solⁿ of an absorbing substance, the rate of rate intensity with thickness of absorbing medium is proportional to the intensity of light as well as concⁿ of the solution."

$$\frac{-dI}{dt} \propto I \cdot c$$

When a beam of monochromatic radiation of suitable frequency passes through a solⁿ. It is absorbed by the solⁿ due to which the intensity of emergent light is considerably reduced.

If I_0 is the intensity of incident light and I_t is intensity of transmitted light then intensity of absorbed light I_a is given by,

$$I_a = I_0 - I_t$$

The intensity of light is defined as, "the energy falling on unit area perpendicular to the beam per unit time." It is proportional to the no. of photons incident on unit area in unit time.

Beer's law can be given as, $\frac{-dI}{dt} \propto I \cdot c$

$$\therefore \frac{-dI}{dt} = k' I \cdot c$$

$$\therefore \frac{dI}{I} = -k' c \cdot dt$$

where, $-dI/dt$ = rate of decrease of intensity with thickness.

c = concⁿ of solⁿ in mole/dm³.

I = intensity of incident radiation.

k' = const called as molar absorption coefficient.

The value of k' depends upon nature of absorbing material and wavelength of incident light radiation.

Integrating above eqⁿ, we get,

$$\int_{I_0}^I \frac{dI}{I} = -k' c \int_0^t dt$$

$$\ln I/I_0 = -k' c \cdot t$$

$$\log_{10} \frac{I}{I_0} = \frac{-k'}{2.303} c \cdot t$$

$$\log_{10} I/I_0 = -\epsilon \cdot c \cdot t$$

where, ϵ = molar extinction coefficient.

Beer's law mainly applicable to solutions.

Molar extinction coefficient

We have, $\log_{10} I/I_0 = -\epsilon \cdot c \cdot t$

$$I/I_0 = 10^{-\epsilon \cdot c \cdot t}$$

When, $I/I_0 = 10^{-1}$ then $\epsilon \cdot c \cdot t = 1$

Hence, molar extinction coeff. can be defined as, "the reciprocal of thickness of one molar solⁿ, when the intensity of incident light radiation is reduced to $(1/10)^{\text{th}}$ of its original value"

• Limitations of Lambert-Beers law :

- (i) Lambert-Beers law is not obeyed in absence of monochromatic light.
- (ii) The law does not hold good for temp. variations, this is because increase in temp. has bathochromic effect on ions in solⁿ i.e. absorption band shift towards longer wavelengths.
- (iii) Beers law is applicable for dilute solutions only. At higher concⁿ ions of solute (in case of an electrolyte) are so close that charge distribution of their neighbouring ions get disturbed. This interionic interaction alters the ability of solute to absorb given wavelength. Also, at higher conc. the value of $R \cdot T \cdot (n)$ of solⁿ also changes. It is found that the quantity $(n/(n+2)^2) \cdot \epsilon$ remains constant. Hence, large deviation are observed when the factor $n/(n+2)^2$ changes with the change in the concentration.

• Light and Radiations :

The light can be considered as, a stream of energy packets or particles travelling with very high velocity. These energy packets are called as photons. The frequency (ν) of wave and energy (E) of photon are related by following eqⁿ:

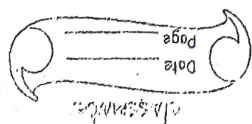
$$E = h\nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \bar{\nu}$$

where, E = energy of photon, h = Planck's const.

c = velocity of light, λ = wavelength

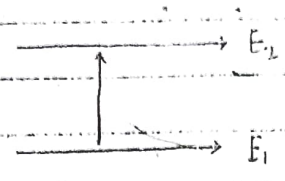
$\bar{\nu}$ = wave number.

ν = freqⁿ of radiation.



The electromagnetic spectrum is divided into various regions: Radio, FM/AM, Television, Radio, Microwave, Infrared, Visible, Ultraviolet, X-rays, Gamma rays, cosmic rays.

The energy of atoms and molecules is quantised. An absorption spectrum is a result of excitation of atoms or molecules from the lower energy level to next higher energy level by an absorption of one quantum of energy.



$$\Delta E = E_2 - E_1$$

$$\therefore \Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} = \text{transition energy.}$$

The absorption and emission of radiations by a sample molecules through which radiation passes, is a basis of spectroscopy.

According to Einstein-Planck's relation, eqⁿ, in any beam of radiation of freqⁿ (ν), each photon carries energy $E = h\nu$. This means that the energy of monochromatic light radiation depends only on the intensity of its beam. This beam is may be more or less intense depending upon the no. of photons per unit time per unit area, but quantum energy remains same for define freqⁿ of radiation.

It is found that, a photon in UV region carry more energy than that in IR region. Thus, shorter the wavelength (greater freqⁿ) greater will be energy of photons and hence more powerful will be radiation.

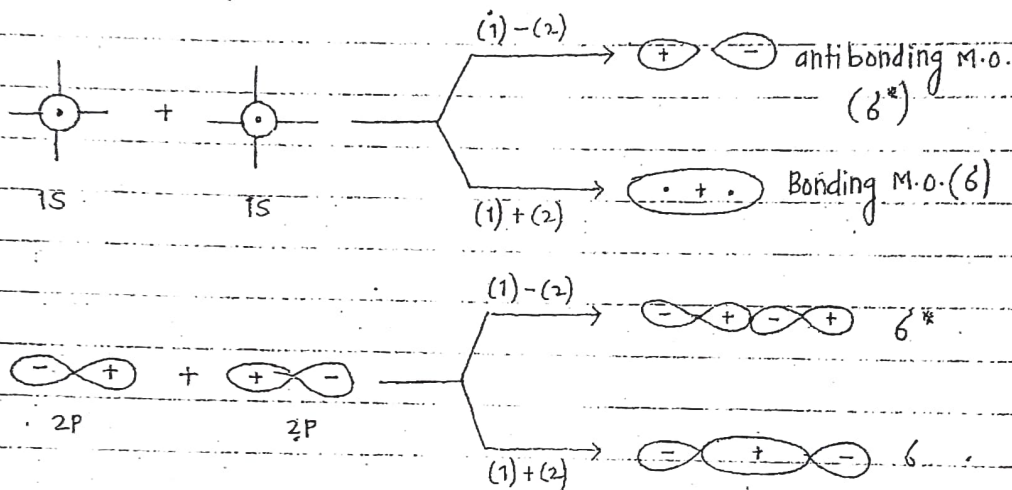
Imp **Types of molecular orbitals:**

"An atomic orbital is a region around the nucleus where the probability of finding an electron density is maximum."

A molecular orbital is formed by the combination of atomic orbitals participating in molecular formation, get disturbed as a concerned nuclei approach each other, they mix up to form an equivalent no. of new orbitals called as molecular orbitals.

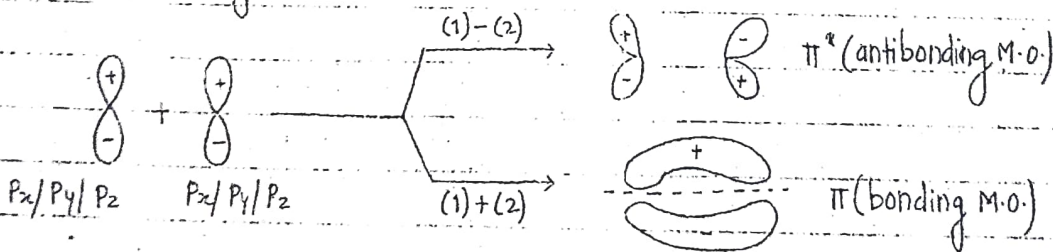
The different types of molecular orbitals are as follows -

1) sigma orbital - sigma orbital may be formed by combination of two atomic orbitals lying along the axis joining the atoms. The molecular orbitals resulting from combination of 1s and 2p atomic orbitals are as shown below. Bonding and anti-bonding sigma orbitals are designated by σ and σ^* resp.



The difference in energy betⁿ bonding and antibonding orbitals is normally such that the promotion of electron from σ orbital to σ^* orbitals requires absorption of radiation in the wavelength range 100-200 nm.

2) Pi (π) orbital - π -orbitals are formed by sidewise or lateral overlap of atomic orbitals which results into formation of bonding π and antibonding π^* orbitals as shown -



The difference in energy betⁿ π and π^* orbital is less than that betⁿ σ and σ^* orbitals, hence $\pi \rightarrow \pi^*$ transition gives rise to absorption in longer λ .

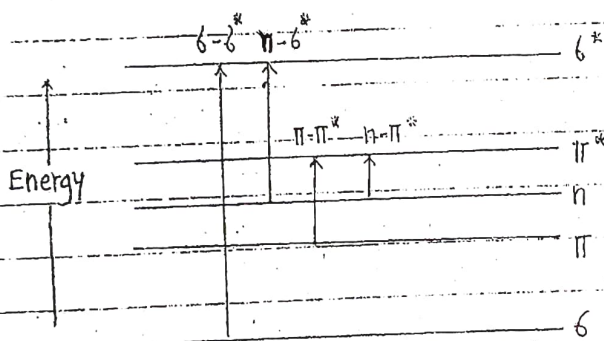
into an absorption band 200 nm

3) Non bonding orbitals — The molecules containing heteroatoms have electrons in the orbitals associated with hetero atoms which are not involved in the bonding system of molecule.

e.g. In case of carbonyl compounds, there are two electrons in non-bonding orbitals on oxygen atom. Absorption of radiation can lead to promotion of one of these electrons into σ^* or π^* orbitals. Such transitions are known as $n \rightarrow \sigma^*$ or $n \rightarrow \pi^*$ transitions.

Electronic Transitions :

Whenever energy from electromagnetic radiations is absorbed, changes are produced in electronic energy of molecules due to transitions of valence electron in a molecule.

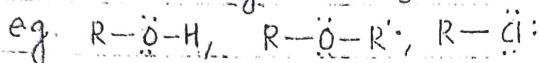


1) $\sigma \rightarrow \sigma^*$ transition — "A transition of an electron from bonding σ -M.O. to higher energy antibonding σ^* orbitals is known as $\sigma \rightarrow \sigma^*$ transition." As σ -orbitals are held much more strongly, more energy is necessary for their excitation, hence $\sigma \rightarrow \sigma^*$ transition requires maximum energy and very short wavelength.

e.g. In alkanes, only σ -electrons are present and hence in alkanes only $\sigma \rightarrow \sigma^*$ transitions are possible. The study of this transition should be done, in vacuum UV region. This is because below 200 nm, the oxygen present in air being to absorb the radiation.

2) $n \rightarrow \sigma^*$ transition - "A transition of an electron from non-bonding molecular orbital to an higher energy antibonding σ -orbital is called as $n \rightarrow \sigma^*$ transition"

These transitions are found in saturated comp. containing hetero atom with a lone pair or unshared electrons. These transitions requires comparatively less energy than $\sigma \rightarrow \sigma^*$.



eg. sat. halides, alcohols, ether, aldehyde, ketones. These transitions are very sensitive to hydrogen bonding. Alcohols which form hydrogen bond with the solvent molecule absorbs at lower wavelength. such association occurs due to the presence of non-bonding electron on hetero atom and hence transition requires greater energy.

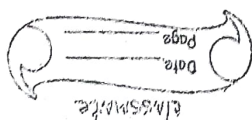
In sat. alkyl halides the energy required for $n \rightarrow \sigma^*$ transition decreases with increase in size of halogen atom or decrease in the electronegativity.

3) $\pi \rightarrow \pi^*$ transition - "A transition of an electron from π -bonding orbital to higher energy antibonding π -orbital is called as $\pi \rightarrow \pi^*$ transition." The transition is available in unsaturated compounds like simple alkene, aromatics and carbonyl comp.

This transition requires less energy than $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions. In simple alkenes though several transitions occurs and absorption band around 170 to 190 nm in unconjugated alkene is due to this transition.

4) $n \rightarrow \pi^*$ transition - "A transition of electron from unshared electron pair on hetero atom to π -antibonding molecular orbital. is known as, $n \rightarrow \pi^*$ transition. This transition requires lowest energy and hence it gives rise to an absorption band at longer wavelength."

In saturated aliphatic ketones (eg. acetone) $n \rightarrow \pi^*$ transition around 280 nm is the lowest energy transition.



Atomic Spectra
Spectroscopy is a study of interactions betⁿ atoms or molecules and electromagnetic radiations. The atomic spectra involves only a transition of an electron from one (lower) electronic level to other. Hence, atomic spectra are only line spectra.

Molecular spectra involves transition betⁿ rotational and vibrational energy levels in addition to electronic transitions. Hence, molecular spectra are band spectra and are much more complicated than the atomic spectra, but at the same time molecular spectra provides much more informations about rotation and vibration.

The effect of absorption of electromagnetic radiation on the molecule is as follows -

microwave - induced molecular rotation.

IR - induced molecular vibration.

visible - excite electron of valence orbital breaking of weak bonds.

UV - Breaking of bonds.

x-ray - excite electron from deep inner orbital of atom.

γ -ray - cause of nuclear change.

o Molecular Spectra :

It is found that, similar to electronic energy levels rotational and vibrational energies are also quantised i.e. they have discrete values.

consider, the energy-level diagram of molecules. Each electronic level consists of no. of vibrational levels represented by vibrational quantum no. 'v'. The various values of 'v' i.e. $v = 0, 1, 2, 3, \dots$ etc. gives vibrational subenergy levels in the same electronic level.

Each vibrational level further consist of no. of rotational sub-energy levels represented by rotational quantum no. 'J'. Various values of 'J' i.e. $J = 0, 1, 2, 3, \dots$ gives various rotational subenergy levels in same vibrational level.

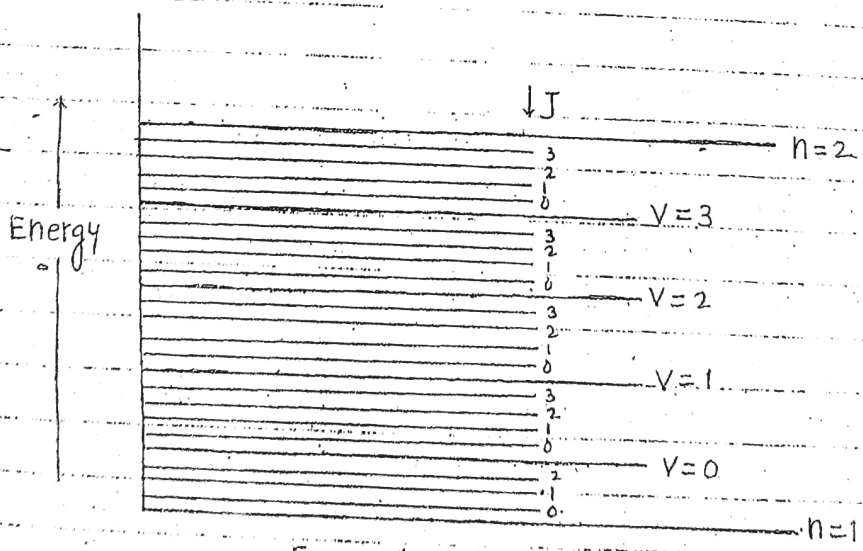
As shown in figure, if the excitation energy is very small then the transition from one rotational quantum level to another level takes place.

Here, vibrational and electronic levels are remains same as excitation energy is not enough to cause vibrational or electronic transition. Hence, the spectra obtained corresponds to change in rotational quantum no. by. Such spectrum is known as rotational spectrum.

These spectra occurs in microwave region or far IR region.

If the excitation energy is sufficiently large to cause transition from one vibrational level to another then the electronic energy levels are remains same. But the rotational levels are also involved along with the vibrational level in transition and hence the spectrum consist of vibrational levels along with the fine rotational levels. Such, a spectrum consist of is known as vibrational-rotational spectrum. This, spectrum is observed in IR-region.

If still higher excitation energy is applied, then the electronic transition takes place. This brings about the change in vibrational as well as rotational subenergy levels. Such a spectrum is very complex because it contains the line due to the electronic, vibrational and rotational transitions. This spectrum is called as electronic band spectrum. These spectra are observed in UV and visible region.

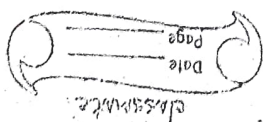


Energy level diagram

where, n = electronic energy level.

v = vibrational energy level.

J = Rotational energy level.



Stark-Einstein law of photochemical equivalence

This is also called as second law of photochemistry.

obj "In a photochemical reaction, each molecule absorbs one quantum of energy."

One quantum of light is absorbed per molecule of absorbing and reacting substance that disappears."

As one mole of substance contains avogadro's number of molecules i.e. 6.023×10^{23} molecules. The no. of quanta absorbed by one mole of substance will be equal to 6.023×10^{23} . Here for convenience another unit has been introduced.

$$1 \text{ Einstein} = 6.023 \times 10^{23} \text{ quanta.}$$

Quantum yield:

To express the efficiency of any photochemical reaction, the term quantum yield or quantum efficiency is used. "It is the ratio of total no. of molecules reacted in the given time to total number of quanta absorbed in same time."

$$\text{Quantum yield} = \frac{\text{Total no. of molecules reacted in given time.}}{\text{Total quantum no. absorbed in the same time.}}$$

Quantum yield is represented by ϕ .

The quantum efficiency is also defined as the ratio of no. of moles of reactant reacted in given time to the total no. of einstein absorbed in same time.

$$\text{i.e. } \phi = \frac{\text{Total no. of moles reacted in given time}}{\text{Total no. of einstein absorbed in same time.}}$$

According to the Stark-Einstein law of photochemical equivalence quantum yield of every photochemical process is equal to unity. However, the value of ϕ varies from 0.5 to 10^6 .

The concept of quantum yield was first introduced by Einstein. Because of frequent complexity of photochemical reaction, the variation in quantum yield was observed.

When high intensity light source as lasers were used, biphotonic photochemical effects were observed (absorption of two photons).

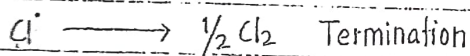
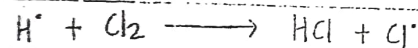
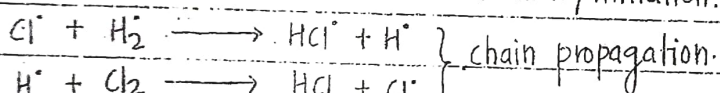
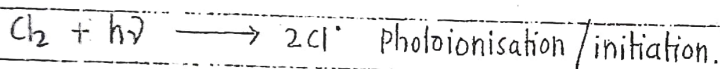
Here, the second photon of longer wavelength by the metastable species (triplet or radical) produced by action of first photon.

The nature of photoproduct and quantum yield depends on light intensity.

Quantum yield can be defined alternatively as,

$$\phi = \frac{\text{Rate of process}}{\text{Rate of absorption}}$$

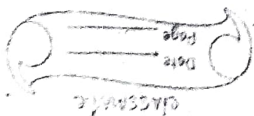
It is very important to specify the process while reporting the value of quantum efficiency. The reason for this can be given as - consider, the following reaction,



The quantum yield for primary process i.e. photoionisation can not be greater than two. Since, maximum only two chlorine atoms can be produced by absorption of one quantum. On the other hand quantum yield for consumption of $\text{H}_2 + \text{Cl}_2$ is extremely high because of chain reactions occurring in second and third step.

• Frank-Condon principle:

"Electronic transitions are so fast (10^{-15} sec) in comparison to nuclear motion (10^{-13} sec), that immediately after the transition, nuclei have nearly same relative position and momentum as they did just before the transition."



at room temp most of the molecules remain in lowest vibrational level of ground state while very few molecules occupy higher vibrational levels. Wave function for zero vibrational level has maximum in the centre indicating the region of maximum probability. Due to difference in time required for electronic transition and that for vibration, the internuclear distance do not change during light absorption.

According to Frank-Condon principle, it is difficult to convert the electronic energy rapidly into vibrational kinetic energy and most probable transitions are those for which the momentum and position of nuclei do not change very much. Due to maximum value of wave function at the centre of zero vibrational level, a transition always starts from the centre of zero vibrational level to various vibrational levels of excited states.

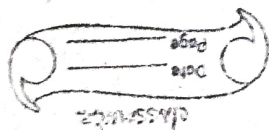
• Selection Rule :

The probability of occurrence of an electronic transition and hence the intensity of associated absorption band depends on various factors. All these are included in selection rule which governed whether the transition is allowed or forbidden.

Transitions obeying selection rule can give rise to very intense absorption band and transitions which do not conform to the selection rules either do not occur or probability of their occurrence is so low, that they give rise to very weak bands in the absorption spectrum.

selection rule of polyatomic molecule can be summarised in relation to oscillator strength F_o of fully allowed $\pi \rightarrow \pi^*$ transition by the equation, $F = P_s P_o P_p P_m f_a$

where, F = oscillator strength for transition under consideration and P_s, P_o, P_p and P_m are probability factor taking an account for change in electron spin, orbital symmetry, parity and momentum which occur as result of electronic transition.



1) Electronic spin (P_s) - $P_s = 10^{-2}$ for singlet \rightarrow triplet.

selection rule predict that the transitions which involves change in spin of an electron during excitation process are forbidden. A change in electron spin causes change in the multiplicity and consequently the transitions from singlet to triplet and vice versa are forbidden:

2) Orbital symmetry (P_o) -

The spatial properties of orbitals involved in electronic transition are important in the determination of intensity of absorption band.

If two orbitals involved in the transition do not simultaneously possess large amplitude in same region of space then transitions are called overlap or space forbidden.

For carbonyl compound, $P_o = 10^{-2}$

3) Parity (P_p) - When a wavefunction of molecules changes sign on reflection through centre of symmetry, it is called as ungrade (u), whereas if it does not change its sign is called as grade (g). Bonding π and antibonding π^* orbitals in ethylene provides example of wave function which are ungrade and grade respectively.

Parity selection rule state that electron transitions from $g \rightarrow u$ and $u \rightarrow g$ are allowed but those from $g \rightarrow g$ and $u \rightarrow u$ are forbidden.

Aromatic hydrocarbons $P_p = 10^{-1}$

4) Momentum (P_m) - Any transitions resulting in large change in linear or angular momentum of molecule is called as momentum forbidden e.g. for condensed ring comp. probability factor P_m lies in the range 10^{-1} to 10^{-3} .

Electronic state or multiplicity (singlet or triplet)

The multiplicity of an electronically excited state is defined by the expression $2S+1$ where S is the algebraic sum of spin quantum numbers of the e^- in system. The spin quantum numbers can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

As a consequence of Pauli's exclusion principle, electrons in the same orbital must have their spins paired i.e. one will have the spin quantum number $+\frac{1}{2}$ (It is represented by \uparrow) and other $-\frac{1}{2}$ (represented by \downarrow). In the molecule where all electrons are paired in orbital, sum 's' of the spin quantum numbers must be equal to zero and hence multiplicity will be one. The molecule is then said to be in singlet ground state. This state is designated by the symbol 's'. The ground state of majority of organic molecules are singlet states.

Upon absorption of photon of suitable energy ' $h\nu$ ', one of the paired electron goes to higher energy level or the excited state. If the promoted electron retains its spin configuration, the sum of the spin quantum number will be equal to zero and hence multiplicity will remain unity. However the molecule will be in an excited singlet state.

If the spin configuration of promoted electron is changed on excitation, the spin promoted electron will not be paired with spin of electron in the vacant orbital. Thus, two electrons will have parallel spin. In such cases algebraic spin of quantum no. will be one and multiplicity of the state will be three. Thus, a molecule with two unpaired electrons is described as being in triplet state. These states are designated by symbol 'T'.

Molecules have the minimum electronic energy when in the ground state and when this is in a singlet state, it is represented as ' S_0 '.

The singlet state are invariably of higher energy than corresponding triplet states because of greater electronic repulsion in singlet state.

Singlet $S=0$
 $2S+1=1$

Triplet $S=1$
 $2S+1=3$

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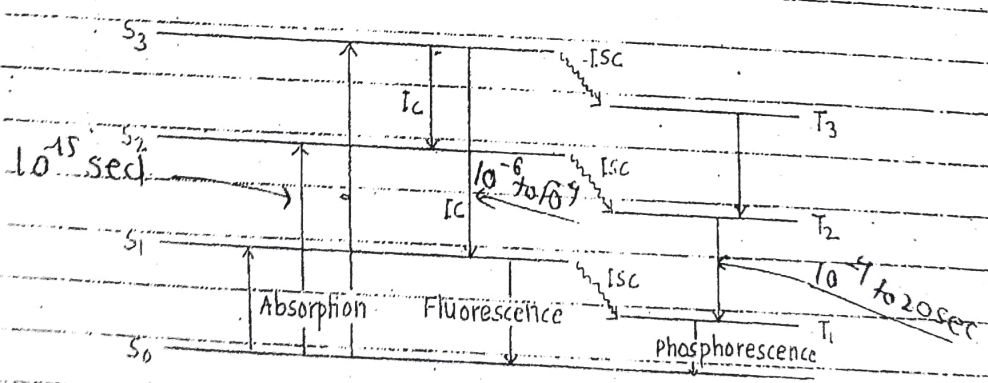
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Joblonski Diagram :-

Molecules have more than one nuclei. These nuclei can vibrate with respect to each other and also they can rotate around molecular axis. As the vibrational and rotational energies are quantised, they give rise to discrete energy levels which can be calculated from Schrodinger's equation. Difference in quantised energy levels for vibrational and rotational energy levels are smaller than those for electronic energy levels. All these depends on the nature of molecule. According to Hund's rule, the triplet state is lowest energy excited state. The state diagrams are represented by all singlet levels expressed as horizontal lines, one above the other and triplet levels are drawn slightly shifted in space, maintaining the order of energy values. The ground state is arbitrarily assigned a zero value for the energy. Such diagrams are known as 'Joblonski diagram' and it is useful in representing the various photophysical processes that may occurs after initial absorption of radiation.

Here, S_1, S_2, S_3, \dots etc. are known as 1st, 2nd, ... singlet excited states, second, third and so on.

Similarly, T_1, T_2, T_3, \dots etc. are 1st, 2nd, ... triplet excited states.

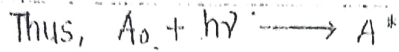


where, I_c = Internal Conversion.

ISC = Inter System Crossing.

on absorption of light photon electron from orbiting molecule may jumps from S_0 to S_1 , S_0 to S_2 depending upon the energy of light photon absorbed as shown in the Jablonski diagram

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



where, A_0 = molecule in ground state.

A^* = molecule in excited state.

The activated molecule returns to ground state by dissipating its energy through following general types of processes -

1) **Non-radiative transitions** - These transitions involves return of an activated molecule from higher excited state (S_3, S_2, S_1 or T_3, T_2) to first excited state (S_1 or T_1). These transitions do not involves emission of any radiation and hence these are known as non-radioactive or radioactionless transitions.

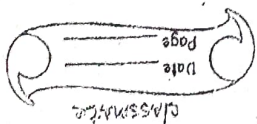
Energy of activated molecule is dissipated in the form of heat through molecular collision. This process is known as internal conversion (IC) and occurs in less than about 10^{-11} second.

Activated molecule may also use its energy by another process called as intersystem crossing (ISC). It involves the transition between the states of different spins i.e. different multiplicity. These transitions are spectroscopically forbidden, they do ~~not~~ occurs at relatively slow rates.

2) **Radioactive / Radiative transitions** - These transitions involves the return of activated molecule from singlet excited state (S_1) or triplet excited state (T_1) to ground state (S_0), such transitions are accompanied by emission of radiations. Transition from S_1 to S_0 is spectroscopically allowed transitions and occurs in about 10^{-8} second, emission of radiation in this transitions is known as fluorescence.

The transition from triplet excited state (T_1) to ground state (S_0) is rather slow as it is forbidden transitions. The emission of radiation in this transition is known as phosphorescence. Life time of phosphorescence

are much longer being of the order 10^{-3} sec or greater, as the transitions involves spin inversion which need time for its occurrence.



magic

Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light because some part of light energy absorbed by the molecule is dissipated in the form of heat during the non-radioactive transitions.

3) Chemical Reactions - Activated molecules may also lose energy by undergoing a chemical reaction. As molecule in singlet excited state returns quickly to the ground state and there is no chance to react chemically, however the molecule in triplet excited state returns slowly to ground state, thus there is an opportunity for activated molecule to react chemically. Thus, a molecule which undergoes a chemical reaction is always previously in triplet excited state.

• Kasha's Rule :

"The fluorescence emission is normally observed from zero vibrational level of 1st excited state of molecule."

The non-radioactive or radiationless energy transfer involves two steps -

1) The vertical transfer of energy at isoenergetic point from zero point level of higher electronic energy state to high vibrational level of lower electronic state.

2) The rapid loss of excess vibrational energy after transfer, this is known as vibrational relaxation.

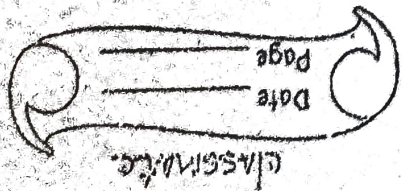
On absorption of energy an electron from zero vibrational level of ground state is excited to various vibrational levels of 1st excited state. As soon as this transition occurs, the excited molecule rapidly loses its energy non-radioactively and the electron returns to zero vibrational level of 1st excited state. This process is called as 'Relaxation'.

Hence, the fluorescence emission is normally observed from zero vibrational level of 1st excited state of the molecules.

• Fluorescence :

The absorption of UV or visible radiation by a molecule results in the formation of excited state. Such high energy states are relatively short lived and rapidly lose the absorbed energy to return to stable ground state. There are two types of processes by which molecules can lose their excess energy. These are -

- 1) Radioactive process - as energy is lost by emission of radiation.
- 2) Non-radioactive process - as radiation is not emitted during the loss of energy.

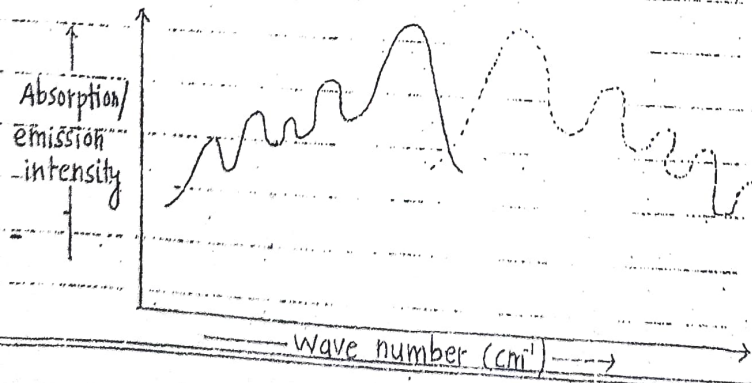
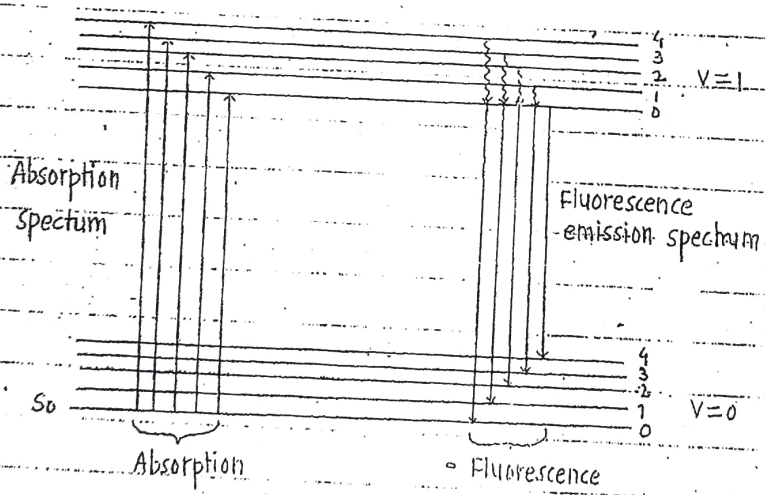


Radioactive process gives rise to emission spectra. A radiation emitted during a radioactive transition is called as 'Fluorescence'. When transition takes place betⁿ states of same multiplicity. The emitted radiation is fluorescence for the transition $S_1 \rightarrow S_0$.

A relationship betⁿ spectrum of a molecule with a singlet ground state and its fluorescence spectra is as shown in fig.

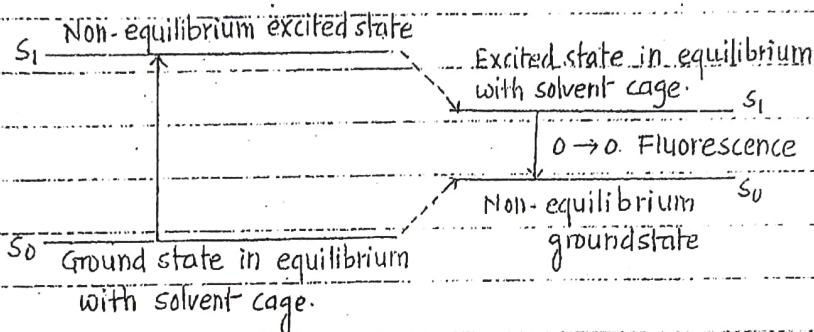
On absorption of radiation the molecule may be excited to the upper vibrational level of singlet excited state. (The excess vibrational energy is rapidly lost by collisional deactivation and the molecule occupies the lowest vibrational level of first excited singlet state.

The fluorescence arises from the radioactive transitions from lowest vibrational level of S_1 state to various vibrational levels in the excited states. are similar to these in the ground state, then there will be an approximate mirror image relationship betⁿ absorption and fluorescence spectra.



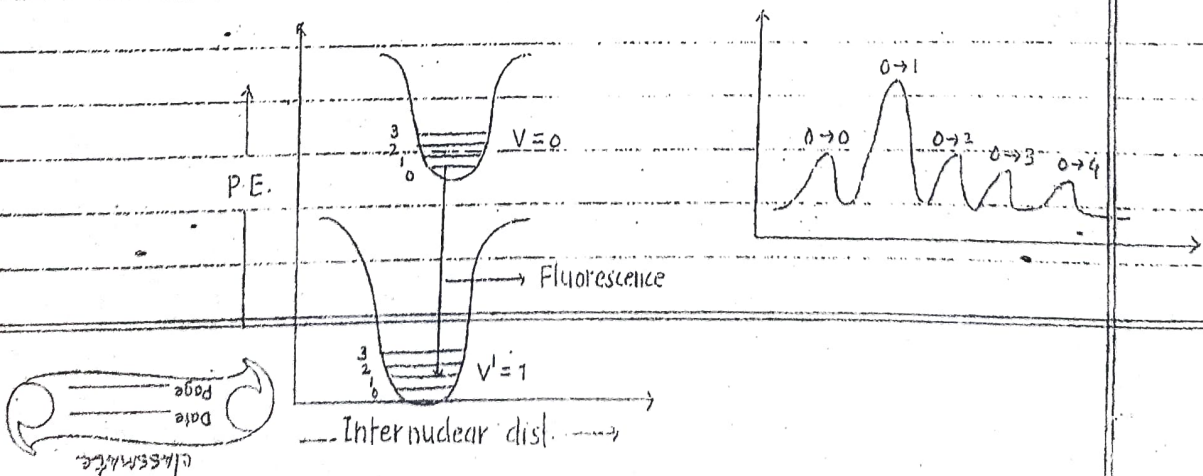
The spacing betⁿ the bands in the absorption spectrum is equal to the difference in energy betⁿ the vibrational levels of the excited states, while the spacing betⁿ bands in fluorescence spectrum is equal to difference in energy between vibrational levels of ground state.

In above diagram, $0 \rightarrow 0$ transition in absorption and fluorescence are shown to have same energy, however it may not be the case and the bands arising from $0 \rightarrow 0$ transition in absorption and fluorescence spectra may be slightly displaced.



If the excited state (S_1) has different solvated equilibrium from ground state (S_0) then there will be re-orientation of the solvent cage after excitation and more stable equilibrium state S_1 will be formed. The fluorescence emission from this will give a non-equilibrium ground state. Thus, $0 \rightarrow 0$ fluorescence transition will be of lower energy (lower wave number or higher λ) than the original $0 \rightarrow 0$ absorption transition.

The intensity of vibrational band vary with bands in absorption spectra. A typical potential energy curves for S_0 and S_1 states of diatomic molecule are shown in figure.



Here, the excited state curve is displaced to the greater internuclear distance or separation than groundstate curve. Frank-Condon principle is applicable to emission as well as absorption processes and emission processes can be represented by vertical lines connecting initial and final states. In this case $0 \rightarrow 1$ transition is most probable and the fluorescence spectrum obtained is as shown above.

* Characteristics of fluorescence :

- (i) This phenomenon is instantaneous and starts immediately after the absorption of light and stops as soon as the incident light is cut off. Fluorescence is stimulated by light of UV or visible region of spectrum. Line, band and continuous spectra of emitted light of fluorescence are observed. The character of the spectrum depends on the states of aggregation of the substances.
- (ii) It is the general phenomenon and is exhibited by gases, liquids and solids. No fluorescence will be observed in gases unless the pressure is low.
- (iii) Different substances have fluorescence light of different wavelengths. Thus, fluor spar produces blue light, chlorophyll with red light, Uranium glass with green light and so on.
- (iv) Fluorescent light from the solⁿ is polarised and the degree of polarisation depends on concentration of solⁿ in some cases.
- (v) Extent of fluorescence depends on nature of solvent and the presence of certain anions in the solⁿ. Thus, thiocyanate iodide and bromide ions show considerable quenching effect.
- (vi) According to Stock's law, during the fluorescence light is absorbed and it should be emitted at greater wavelength (lower freq/energy).
- (vii) Quantum yield of fluorescence is a ratio of no. of photons of luminescent radiation to no. of photons absorbed from stimulating light upon a fixed wavelength. Quantum efficiency of fluorescence increases with wavelength of absorbed radiation. After, reaching its maximum value in certain interval of λ_{max} , efficiency decreases rapidly to zero with further increase in the wavelength.

Fluorescence is a secondary effect resulting from primary process of absorption of quantum of light by an atom or molecule.

• Factors affecting Fluorescence :

(i) All molecules can not show phenomenon of fluorescence. Only these molecules which are able to absorb UV or visible radiations show this phenomenon. In general greater the absorbance of a molecule, more intense will be luminescence.

The molecules having conjugated double bonds are particularly exhibiting this phenomena. On the other hand aliphatic, saturated and cyclic organic compounds are not suitable.

(ii) The pH exhibits marked effect on fluorescence of compound. e.g. Neutral or alkaline solⁿ of aniline shows fluorescence in visible region. However, if solⁿ is acidic visible fluorescence disappears. Aniline shows fluorescence in UV region, regardless of pH value.

(iii) Substituents often exhibits marked effect on fluorescence.

a) Electron donating groups — -NH_2 , -OH often enhances the fluorescence while group like $\text{-SO}_3\text{H}$, NH_2^+ and alkyl groups do not have much effect on fluorescence.

b) Electron withdrawing groups like -COOH , -NO_2 , -N=N- and halides decreases or even destroy fluorescence.

c) If high atomic no. is introduced into π electron system, fluorescence is decreased.

• Relation between Fluorescent intensity and concentration :

Beer-Lambert's law can not be applied to fluorescent radiation directly as it is emitted by a substance. To explain the fluorescent radiation following reaction relation has been developed.

$$F \propto (I_0 - I)$$

$$F = k(I_0 - I) \quad \text{--- (i)}$$

where, 'F' is intensity of fluorescent radiation.

'k' is proportionality constant.

Delayed Fluorescence and Prompt Fluorescence:

"If emission process takes place with emission of radiation then it is called as radioactive process."

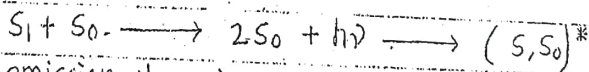
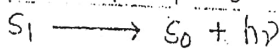
Fluorescence can be classified as either prompt or delayed depending upon the period of time over which the fluorescence is emitted and the mechanism by which it arises. prompt fluorescence is normally emitted within 10^{-6} sec.

Delayed fluorescence is usually emitted over much longer period of time than prompt fluorescence. The delayed fluorescence is emitted within 10^{-3} sec. A delayed fluorescence results from the radioactive conversion to ground state of S_1 which are formed from corresponding T_1 molecule. As delayed fluorescence depends upon conversion of T_1 state species into T_1 .

Prompt fluorescence may arise by the radioactive emission from either -

- 1) 1st excited singlet / S_1 state molecule.
- 2) an excimer formed by interaction of S_1 state molecule with S_0 state molecule.

The term excimer represent an excimer state dimeric species two process giving rise to prompt fluorescence are -

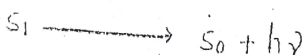
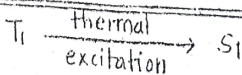
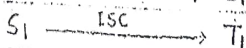
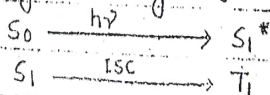


Fluorescence emission of excimer $(S_1, S_0)^*$ can differ from that of free S_1 state molecule and presence of excimer can be detected recording a fluorescence spectrum with different conc. of solute.

Delayed fluorescence can be formed either by -

- i) Thermal excitation of T_1 .
- ii) Collision of two T_1 state molecule.

A process leading to delayed fluorescence may be represented as,



(ii) P-type delayed fluorescence

This is known as p-type delayed fluorescence as it was first observed in pyrene and phenanthracene solutions. In case of aromatic hydrocarbons singlet-triplet splitting is large and hence thermal activation to excited singlet state from room temp. is not possible.

The mechanism was first proposed by Parker and Hatchard based on the observation that, the intensity of emission of delayed fluorescence was proportional to square of intensity of absorption of light I_a

$$I_{pp} \propto I_a^2$$

Quantum yield for the process is given by,

$$\phi_{PD} = \frac{\text{Rate of emission}}{\text{Rate of absorption}} = \frac{I_a^2}{I_a} = I_a$$

As quantum yield of fluorescence is independent of I_a , the ratio of intensity of p-type delayed fluorescence should show a clear dependence on absorption intensity. This dependence indicates the necessity of two photons for delayed emission and hence it is called as biphotonic process. It has been observed in fluid solution of many compounds and also in vapour state. The intensity of p-type delayed fluorescence should decrease with viscosity and it should be observed with very low efficiency in a rigid media.

• Phosphorescence:

"When a light radiation is incident on the certain substances they emits light continuously, even after the incident light is cut off. This type of emission is known as phosphorescence." and such substances are called as phosphorescent substances.

Characteristics of phosphorescence

- (1) The life time of phosphorescence is much longer than that of fluorescence.
- (2) Generally, the material exhibiting fluorescence re-emits the excess radiation within 10^{-6} to 10^{-8} sec. of absorption, while the material exhibiting phosphorescence re-emits excess radiation within 10^{-4} to 10 second or even excess longer.
- (3) The phenomenon of phosphorescence is caused mainly by UV and visible part of spectrum.
- (4) This phenomenon is mainly shown by solids.
- (5) Magnetic and dielectric properties of phosphorescent substances are different before and after illumination.
- (6) The time for which the light is emitted depends on the nature of substance and temp. changes.
- (7) Different colours may be obtained by mixing different phosphorescent substances.

Theory of Phosphorescence :

In order to understand the theory of phosphorescence we have to understand meaning of singlet and triplet state.

(i) Singlet state - The multiplicity of electrically excited state is defined by expression $(2s+1)$, where 's' is an algebraic sum of spin quantum numbers of an electron in system.

Most of the molecule in their ground state have their electron paired. Thus, the algebraic sum of spin quantum numbers must be zero and hence, multiplicity will be one. This is called as singlet state and has been represented by symbol 'S'.

(ii) Triplet state - Upon absorption of energy, its spin configuration of promoted electron is changed, then its spin will not be paired with spin of electron in vacant orbital. In such cases the algebraic sum of spin quantum no. will be one and multiplicity will be three.

This is called as triplet state and represented by 'T'.

Singlet state are of higher energy than corresponding triplet state because of greater repulsion (electron) in singlet state.

When a molecule absorbs UV or visible radiation of proper freq. then it get excited to 1st excited singlet state (ie. S_1 state). Then by the process of vibrational relaxation the molecule returns to the zero vibrational level of S_1 state.

Now the molecule may undergoes a transition to a metastable triplet state by the process of intersystem crossing and then returns to S_0 state ie. ground state by emission of UV or visible radiation which is called as phosphorescent emission.

The transition from triplet to singlet ground state (S_0) ie. $T_1 \rightarrow S_0$ is forbidden by spin symmetry and hence the process is slow. Hence, the lifetime of phosphorescence is much longer than that of fluorescence is inhibited by competitive radioactive process like impurity, quenching or internal conversion.

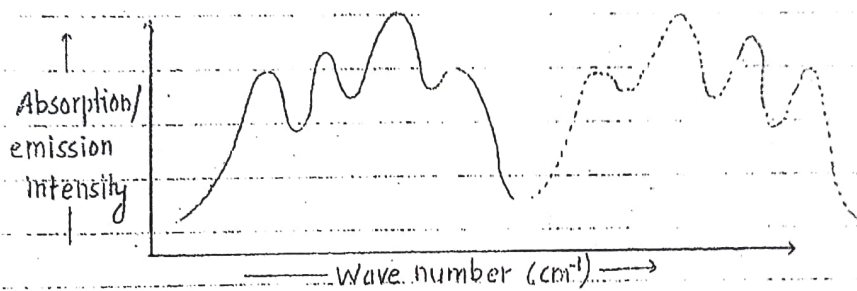
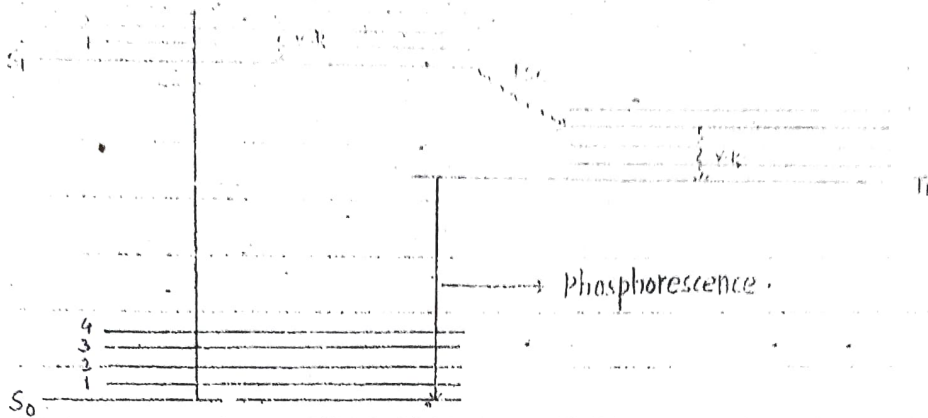
Due to spin forbidden character, phosphorescence has low probability of emission of long radioactive lifetime.

At low temp. and in rigid solvents, the probability of phosphorescence emission is high.

After crossing to triplet energy state at isoenergetic point by non-radioactive process of 'Intersystem crossing', the excited molecule quickly relaxes to zero vibrational level of triplet state. From this it can be return to S_0 state by -

- ① Phosphorescence emission (Radioactive process)
- ② By intersystem crossing (non-radioactive process)

According to the Hund's rule T_1 lies always lower than S_1 state and hence phosphorescence spectrum is not a mirror image of an absorption spectrum and it occurs at longer wavelength compared to absorption and the fluorescence spectrum.



A phosphorescent radiations are shorter freqⁿ than the exciting light because some part of light energy which is absorbed by the molecule is dissipated in the form of heat energy during the non-radioactive transitions.

Phosphorescence is rarely observed in gases. It is almost never observed at room temp.

• Factors affecting phosphorescence :

- ① Only those molecules which are able to absorb UV or visible radiation shows the phosphorescence.
- ② substituent exhibits marked effect on phosphorescence of the molecule
e.g. i) The group like $-\text{SO}_3\text{H}$, $-\text{NH}_4^+$ and alkyl groups do not have much effect on phosphorescence.
- ③ If a higher atomic number atom is introduced into π -electron system, it enhances phosphorescence.

• Applications of phosphorescence :

- (1) Determination of aspirin (Acetyl salicylic acid) in blood serum with high sensitivity, by phosphorimeter at liq. nitrogen temperature. Using this method 0.02 - 1 mg aspirin per ml can be analysed.
- (2) Low concⁿ of procaine, cocaine, phenobarbitol and chlorpromazine in blood serum can be determined by phosphorimetry in combination with extraction procedure.
- (3) Using phosphorimetry cocaine and atropine in urine can be measured.

• Difference between —

Delayed Fluorescence

Phosphorescence

- | | |
|---|--|
| (1) In case of delayed fluorescence the transition of an excited e^- occurs from 1st excited singlet state (S_1) to ground state (S_0) | (1) In case of phosphorescence excited e^- returns to ground state from excited triplet state (T_1) to ground state (S_0) i.e. $T_1 \rightarrow S_0$. |
| (2) The lifetime of delayed fluorescence emission is 10^{-3} second. | (2) Life time of phosphorescence emission is 10^4 to 10 second. |
| (3) In delayed fluorescence, there involve process of intersystem crossing and the reverse inter system crossing bet ⁿ T_1 and S_1 . | (3) In phosphorescence, there is no reverse intersystem crossing from T_1 to S_1 state. |
| (4) Delayed fluorescence is mirror of absorption spectrum. It occurs at slightly larger wavelength compared to absorption. | (4) Phosphorescence spectrum is not mirror image of absorption spectrum and it occurs at very long wavelength compared to absorption. |
| (5) It may be exhibited by the solids, liquids and gases. | (5) Phosphorescence is mainly shown by solid and by gases rarely. |
| (6) The intensity of delayed fluorescence is high as the transition $S_1 \rightarrow S_0$ is allowed. | (6) The intensity of phosphorescence is very low as transition $T_1 \rightarrow S_0$ is forbidden i.e. not allowed. |



Fluorescence Quenching

When a photochemically excited atom has a chance to undergo a collision with another atom or a molecule in fluorescence, then intensity of fluorescent radiation may be diminished or stopped. This phenomenon is called as quenching of fluorescence."

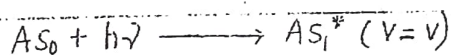
The quenching of fluorescence occurs because of the energy transfer from excited state species to a molecule with which it collides.

A quenching which is produced when a molecule changes from singlet excited state to triplet excited state is known as internal quenching.

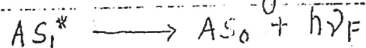
Quenching also may be results from presence of externally added species which takes up energy from the excited state species. This phenomenon is called as external quenching.

Kinetics of Bimolecular quenching -

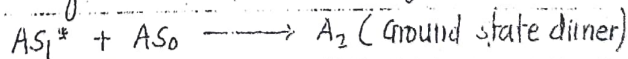
Consider a molecule in ground state level S_0 . On absorption of radiation of appropriate frequency the molecule get excited to 1st excited singlet state S_1 . Depending on the amount of energy absorbed it acquires various vibrational levels.



After absorption of energy, by process of vibrational relaxation, the molecule returns to zero vibrational level of S_1 state. This molecule may exhibits fluorescence by returning to ground state S_0 .

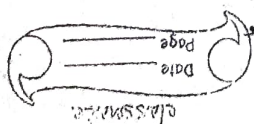


However, before exhibiting fluorescence, if a molecule collides with another molecule in a ground state, then transfer of energy occurs and a ground state dimer is formed.



The formation of ground state dimer takes place only at higher concentration.

The quenching produced due to this process is called as unimolecular quenching or colloidal quenching as it occurs due to collision between two molecules.

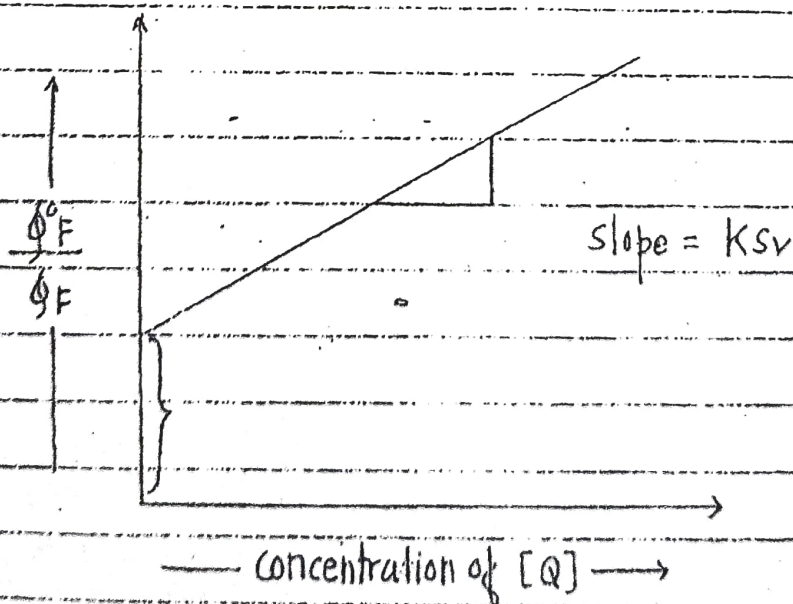


$$\frac{\phi_F^0}{\phi_F} = 1 + K_{SV} [Q]$$

where, $K_{SV} = \frac{k_Q}{\sum k_i + k_F}$ — (iv)

Equation (iv) represents Stern-Volmer eqⁿ. The term K_{SV} is called Stern-Volmer const. and it is a ratio of bimolecular quenching const. to unimolecular decay const. and has a dimension of dm^3/mole or lit./mole . This implies competition betⁿ two decay pathways and has a character of an equilibrium constant.

The Stern-Volmer expression is linear in quencher concentration and when a graph of ϕ_F^0/ϕ_F is plotted against concentration of quencher $[Q]$ then slope of graph gives value of Stern-Volmer constant (K_{SV}).



Half Quenching Concentration

When a concentration of quencher is 1/2 the value of half of the original value, the relationship between half quenching concⁿ $[Q_{1/2}]$ and k_{sv} can be established.

From eqⁿ (iv) we write,

$$\frac{\phi_F^0}{\phi_F} = 1 + k_{sv}[Q]$$

At half quenching concⁿ we have,

$$[Q_{1/2}] = 10^{-3} \text{ M}$$

$$\frac{\phi_F^0}{\phi_F} = 2 \text{ and } [Q] = [Q_{1/2}]$$

$$\therefore 2 = 1 + k_{sv}[Q_{1/2}]$$

$$1 = k_{sv}[Q_{1/2}]$$

$$\boxed{[Q_{1/2}] = \frac{1}{k_{sv}}}$$

A relationship between ^{intensity} fluorescence and concentration of a fluorescent substance is given by,

$$\boxed{F = \phi_F \cdot 2.303 I_0 \cdot \epsilon \cdot c \cdot l}$$

where, F = Intensity of fluorescence.

ϕ_F = quantum efficiency of fluorescence.

I_0 = Intensity of incident light.

ϵ = molar extinction coefficient.

c = concentration.

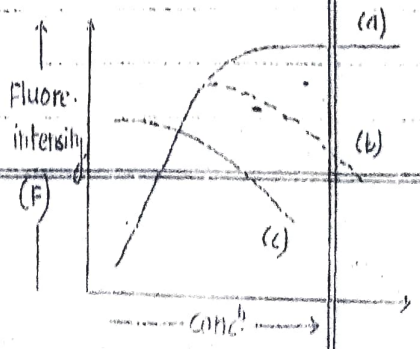
l = thickness of path.

At very high concⁿ where all incident light is absorbed, above equation reduces to, $F = \phi_F \cdot I_0$

Fluorescent intensity should remain const. for any further increase in concentration. (curve @)

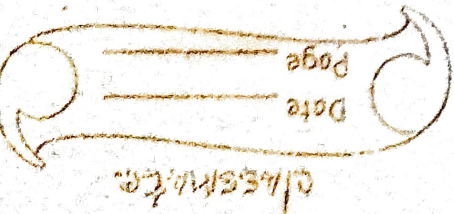
A plot of fluorescence intensity (F) vs concⁿ should be of nature (a).

However, for many comp. intensity 'F' start decreasing after reaching critical concⁿ resulting into (b).



Excimer :

In certain cases of fluorescence quenching, along with normal quenching of fluorescence, a new structureless band appears at 6000 cm^{-1} to red side of the monomer fluorescence spectrum. This phenomenon is first observed in pyrene solⁿ by Forster. This band appears due to transitory complex formation betⁿ ground and excited



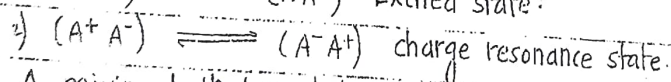
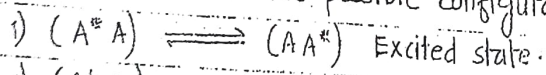
state molecules, as absorption spectrum is not modified by an increase in conc. The microscopic experiments gave negative results for presence of ground state dimers. These short lived excited state dimers are known as 'Excimers'.

[The excimers dissociates when they returns to ground state by emission giving rise to structureless band] This shows that the ground state potential energy of surface is repulsional.

Excimer emission is often observed from the planer molecules when two component molecules are placed in a parallel configuration. The conditions are —

- (i) The two planer molecules approach within dist. ≈ 0.35 nm of each other.
- (ii) The conc. is high enough, for the interaction to occur, within the lifetime of excited state.
- (iii) The interaction energy betⁿ normal and excited molecule is attractive such that excited state enthalpy ΔH^* is greater than the thermal energy.

The excimer binding energy can be explained as quantum mechanical interaction betⁿ two possible configuration.



A mixing betⁿ two states creates 'bound excimer state'. In some molecules, the interaction can develop into stronger force and inter-planer distance further reduced to form a stable photodimer through

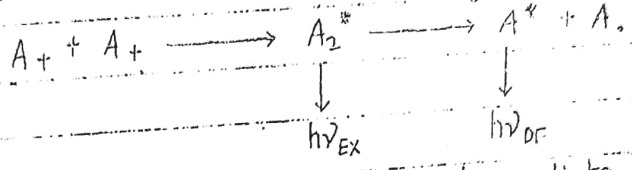
e.g. Anthracene forms a photodimer and no excimer emission is observed while some of its derivatives with bulky substituents (which hinders close approach) giving excimer fluorescence.

In 9-methyl anthracene neither forms photodimer nor emits excimer fluorescence due to steric hinderance.

Similarly type of emission is observed from some crystalline hydrocarbons.

the characteristic of the excimer formation but the constitutional basis.
 Excimer emission is also observed in gases like He and Xe. The ability of xenon as a source of continuous high intensity radiation is due to this emission.

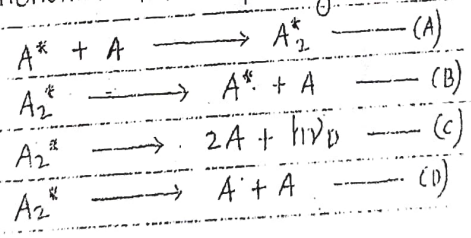
Beside prompt excimer emission, delayed excimer emission has also been observed. The mechanism is through triplet-triplet annihilation.



Here, the excimer formed as an intermediate which may dissociate into a excited state singlet and ground state singlet. A delayed excimer emission is a biphotonic process while the prompt excimer emission is monophotonic.

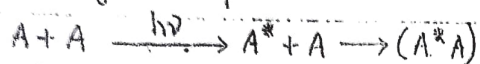
The excimer formation is assumed to be a necessary step in concentration quenching. It is not essential that the excimer must be fluorescent step (c). It may promote radiationless process within the molecule (d).

The step (A) is excimer formation step. step (B) which is reverse process which involves a dissociation of excimer into excited and ground state monomer. This step may be require an energy of activation.



7019 Excimer

- ① Dissociates in ground state.
- ② Dimerisation follows at the act of absorption.



- ③ Radioactive transition weak.
- ④ No absorption is observed.

⑤ Observed for planer aromatic hydrocarbon.

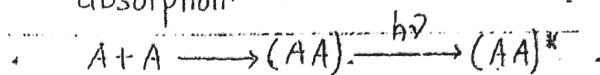
⑥ Emission characteristics -

① Broad structureless band is shifted to 6000 cm^{-1} to red side of monomer fluorescence band.

② Emission is concentration dependent.

Excited state dimer

- ① stable: in ground state at room temp.
- ② Dimerisation proceeds the act of absorption.



- ③ Radioactive transitions are strong.
- ④ Intensity of dimer absorption band increases with concentration.

⑤ Observed for ionic form of dyes.

⑥ Emission characteristics -

① Give sharp emission on long waveside of corresponding dimer absorption.

② Usually this is dependent of concentration.

- Defⁿ @ mark sheet bid

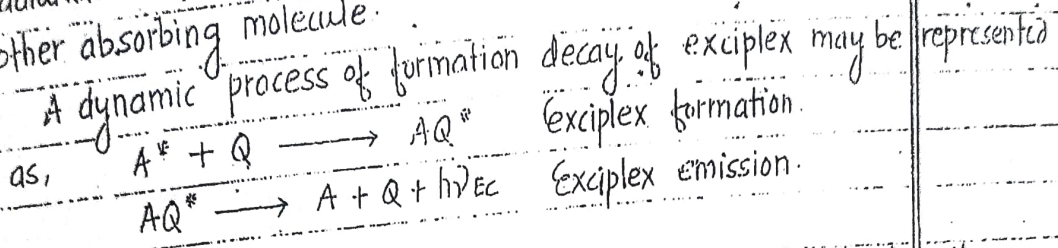
✓ **Exciplex**: This is one of the photophysical pathway for excited molecule to return to ground state and involves a bimolecular process. A quenching process can be defined as, "a process which competates with spontaneous emission process, and hence resulting into shortening of lifetime of emitting molecule."

Usually, these quenching reactions are energy transfer or electron transfer processes. In some cases a transient complex formation in excited state may be involved. This is the exciplex formation. These excited state complexes may or may not emits their own characters emission which is likely to be different from original molecule.

In solution, there is also possibility of formation of weak complex in ground state. Due to side by side placing of fluorescer and quencher molecule within the solvent cage, at the moment of excitation.

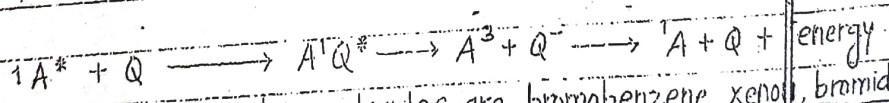
static quenching. As there is no competition with the emission process, the life time is not affected.

The ground state complex formation reduces the fluorescence intensity by comparing with uncomplexed molecule for absorption of an incident radiation. This is called as "inner filter effect" similar to presence of other absorbing molecule.



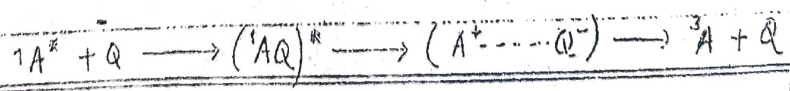
Whenever, there is a collision betⁿ two dissimilar molecules, the attractive tendencies are usually greater depending upon polar and polarisable properties.

"The interaction involves some degree of charge transfer frequently formed complexes, betⁿ excited fluorescent molecule and added foreign molecule are called as exciplexes." The absorption spectrum remains unchanged in contrast with the ground state interactions because of short life of complexes. The molecules with heavy atoms acts as a quencher by exciplex mechanism. The quantum consideration shows that they facilitate a change of electron spin, so that exciplex dissociation occurs with dissipation of energy through a triplet level.



(The example of quencher molecules are bromobenzene, xenon, bromides and iodides and some rare earth compounds).

When the extent of charge transfer is high and the heavy atom effect is absent, exciplex lifetimes may be long enough for them to degrade by the light emission. However, the dissociation may occur via ion-pair complex which was first suggested by Weiss.



An intramolecular complex is formed in nitraceinboaxant. Aniline group is not co-planar with phenanthrene but is oriented perpendicular to it. electron located on its p atom interact with excited π electron system and intramolecular complex is formed in rigid medium where the rotation is restricted.

• Energy transfer in photochemical reactions :

1) **Photosensitisation** — Some chemical reactions takes place by absorption of light, not by one of the reactant but by the third substance which transfer the absorbed energy to the reactants. The third substance which itself doesnot undergo any change is called as photosensitizer and such process is known as 'photosensitization'.

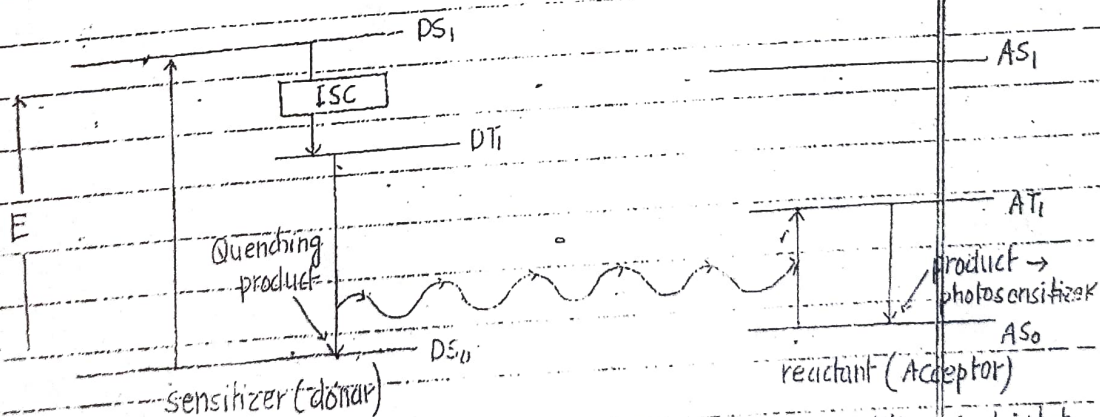
Commonly used photosensitizers are,

i) Atomic photosensitizer — Hg, Cd, Zn.

ii) Molecular photosensitizer — Benzophenone, SO₂.

consider, a general donor-acceptor system where only donor (D) i.e. sensitizer absorbs the incident light.

Mechanism of photosensitization —



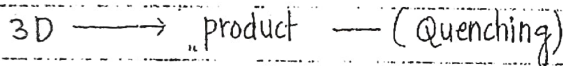
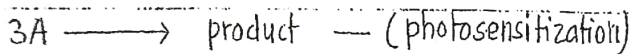
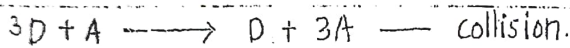
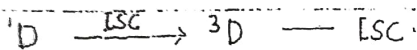
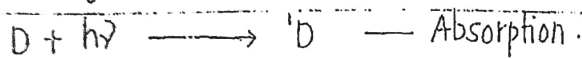
In case of photosensitization process, the necessary condition is triplet state of donor is higher than triplet state of acceptor (A) i.e. reactant.

The absorption of radiation produces singlet excited state of donor (D) which gives the triplet excited state (3D) of donor through intersystem crossing. This triplet state then collides with acceptor producing the triplet excited of acceptor 3A and ground state of donor (D_0).

i) If triplet excited state of acceptor i.e. A^3 gives desired product then the process is called as photosensitization.

ii) If desired product are obtained from 3D , then acceptor A is called as quencher and process is quenching.

The reactions representing photosensitization and quenching may be given as follows -



Here, it should be remembered that, triplet excited state of sensitizer (D) must be higher in energy than triplet excited state of reactant (A), so that the excess available energy is enough to raise the reactant molecule to its triplet excited state. The dotted line in figure indicate the transition in which sensitizer loses energy with that in which the reactant gains energy.

2. **Photosynthesis** — This is the very imp. photochemical reaⁿ, which involves the formation of carbohydrates, in plants from CO_2 and H_2O . In this photosynthesized reaction the green colouring matter chlorophyll acts as photosensitizer.

In photosynthesis, neither CO_2 nor H_2O can absorb any radiation in the visible region, however chlorophyll can absorb the radiation in visible region. It absorbs the visible light of almost any wavelength in the range of 400-700 nm. The energy of light absorbed by chlorophyll



where, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ represents a carbohydrate like cellulose or sugar. In absence of light ΔG° of redⁿ is +2878 KJ. As it is very large positive value, equilibrium lies to left. In presence of light absorbed by chlorophyll, ΔG° becomes -ve causing reaction to proceed to right. The chlorophyll contains extensively conjugated system of alternate single and double bonds which helps the chlorophyll molecule to absorb visible radiation. The process of photosynthesis requires eight photons per molecule of CO_2 consumed. The efficiency of conversion of light of 600 nm into the chemical energy is about 30% in this process.

According to Melvin Calvin (1961, Nobel prize winner) of chemistry for this contribution to mechanism of photosynthesis.)

Photosynthesis proceeds through two main stages 'Light reactions' and 'dark reactions'. First stage i.e. light reaⁿ involves, the reaⁿ taking place on absorption of light and being completed within 10^{-12} to 10^{-10} second.

The second stage of dark reaction (as they occurs in absence of light) is R.D.S for overall redⁿ. The exact mechanism of photosynthesis occurring in plants is not fully known.

3) Pre-dissociation — V. Henri in 1924 found that, in certain electronic bands with a discontinuous structure is observed due to quantisation of vibration, however instead of fine rotational structure, the bands show diffuse appearance. This is called as pre-dissociation spectra. It is observed particularly for the polyatomic molecule like SO_2 , NO_2 , NH_3 , acetaldehyde methyl halide etc.

The pre-dissociation spectra is a result of absorption of radiation in this region, where the molecule is raised to higher electronic level and at the same time there are the vibrational transitions, so that the vibrational bands appears in the spectrum.

With the molecule exhibiting this phenomena, it is supposed that within a short period, the energy redistribution takes place leading to another excited state in which the available energy is sufficient to bring about dissociation. If the time period betⁿ acquisition of necessary energy and its redistribution resulting into ~~distribution~~ dissociation is small, compared with the period of rotation of molecule (10^{-11} sec), then the dissociation will take place, before complete rotation can occur and there will be radiation fine structure.

Thus the absorption of radiation in pre-dissociation region can lead to dissociation. However, the resulting atom or radicals may recombine immediately leading to low overall efficiency. In regions of discrete fine structure, the radiation absorbed by the molecule, resulting into transition of molecule from lower to higher electronic level with simultaneous vibrational and rotational changes. If the excited molecule has energy insufficient for breaking a bond, then the excited molecule will lose its additional energy within 10^{-7} to 10^{-3} sec, either in the form of heat or as a fluorescence.

If excited molecules possess sufficient energy for the dissociation to occur as consequence of redistribution of energy within the molecule then the dissociation of a molecule may occur spontaneously or as a result of collision with another molecule, either of a same kind or different.

As life time of an excited molecule is at least 10^{-8} sec. It may undergo various vibrations and rotations before its dissociation and the spectrum will exhibit a definite structure. This is also referred to as a pre-dissociation even though the absorbing molecule doesn't exhibit pre-dissociation type of spectrum.

It is possible to distinguish betⁿ spontaneous and induced pre-dissociation by observing the effect of increasing the press. or by adding inert gas. If these changes increase the photochemical yield then the arrangement of energy within the molecule is induced while in case of spontaneous predissociation, the yield is unaffected.

fluorescence or in deactivating collisions with the frequency of fluorescence increases while deactivating collisions decrease

Photoisomerization

8 mark
2015

Photodissociation -- The chemical behaviour of molecules generally depends on most weakly bound electrons. A molecule in an excited state differs from the ground state molecule with respect to both energy and the electron wave function and hence show different characteristic. An irradiation to produce excited electronic state, alters the reactivity of a molecule in number of ways which decide the nature of photochemical reaction.

As the nuclei are often weakly bound in an excited state than in ground state, the molecule may be dissociated more easily in excited state. If it is excited to a repulsive state, then the dissociation may occur with unit efficiency (photodissociation). Photodissociation is also called as photofragmentation. A direct dissociation of molecule, on absorption of quantum of energy becomes very probable, when the energy absorbed is equal to or greater than the bond dissociation energy. A molecule excited to continuous region of absorption spectrum dissociates immediately, with unit quantum efficiency. Whenever a molecule dissociates from an excited state then it is called as photolysis.

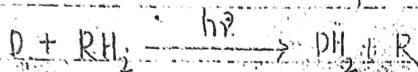
Photooxidation

4 mark
2014

Photoreduction -- The prototype of photoreduction reaction is the hydrogen abstraction by carbonyl comp in presence of suitable "H-donors" such H-atom transfers may occur by the transfer of an electron followed by proton transfer. An electron deficient centre is the seat of reaction and the efficiency of reduction depends on the nucleophilic nature of donor.

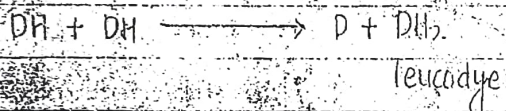
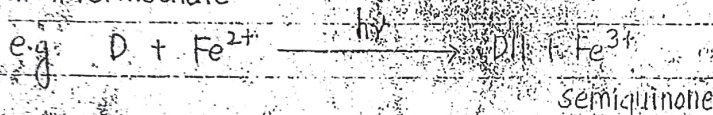
Photo-reduction of dyes by two electron transfer process

Photoredox reactions are observed for some dyes in which the dye appears to become white in light. The colour of light dye may or may not reappears in dark. In such reduction processes, two H-atoms or two electrons and two protons are added to the dye (D)

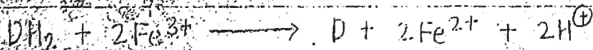
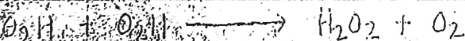
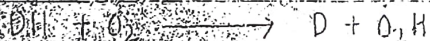
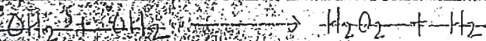
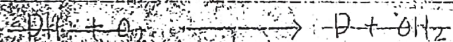


where, RH_2 represents a reducing agent, $D = \text{dye}$.

The reaction occurs into one electron step giving the semiquinone as an intermediate.



In certain cases, the redⁿ may be reversed by H_2O_2 or atmospheric O_2 or by photo-oxidised reductant itself.



From thermodynamic consideration the course of such redox reaction may be expressed in terms of redox potentials of two couples E_D and E_R .

