WEST BENGAL STATE UNIVERSITY
SYLLABUS FOR CHEMISTRY (HONOURS) ON PHOTOCHEMISTRY
UNDER CHOICE BASED CREDIT SYSTEM
SEM VIH

Photochemistry
(15 Lectures) Marks: 14
Lambert-Beer‟s law: Characteristics of electromagnetic radiation, Lambert-Beer‟s law and its limitations, physical significance of absorption coefficients; Laws of photochemistry, Stark-Einstein law of photochemical equivalence, quantum yield, actinometry, examples of low and high quantum yields

Photochemical Processes: Potential energy curves (diatomic molecules), Frank-Condon principle and vibrational structure of electronic spectra; Bond dissociation and principle of determination of dissociation energy (ground state); Decay of excited states by radiative and non-radiative paths; Pre-dissociation; Fluorescence and phosphorescence, Jablonskii diagram

Rate of Photochemical processes: Photochemical equilibrium and the differential rate of photochemical reactions, Photostationary state; HI decomposition, H_2-Br_2 reaction, dimerisation of anthracene; photosensitised reactions, quenching; Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence

Books to follow:

- *McQuarrie, D. A. & Simons, J. D. Physical Chemistry: A Molecular Approach, Viva Press*
- *Atkins, P. W. & Paula, J. de Atkins' Physical Chemistry, Oxford University Press*
- *Rakshit, P.C., Physical Chemistry, Sarat Book House*
- *Laidler, K. J. Chemical Kinetics, Pearson*
- *Castellan, G. W. Physical Chemistry, Narosa*

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Photochemistry

The ***photochemistry*** would logically appear to be a subdivision of ***Radiation chemistry***. It is the science of the chemical effects of light, where light includes the infrared and ultraviolet, as well as the visible regions of the spectrum, i.e., the range of wavelength from about 100 nm to 10,00 nm. The energies of quanta in this range vary from about 1 to 10 eV, or 23 to 230 kcal per mole. These energies are comparable in order of magnitude with the strengths of chemical bonds.

On the other hand, if a 1,000,000 eV γ-ray photon or photon from x-ray traverses a medium, thousands of molecules may become activated along its trajectory. As we shall see, these activations often result in ionization of the molecules, whereas in the photochemical region, ionization would be a rare occurrence. Radiations like a, α, β, γ rays, neutrons, and cyclotron beams, are therefore called ionizing radiations. Usually, when we speak of ***Radiation chemistry*** we mean the science of the chemical effects of such highly energetic, ionizing rays.

❖ Photochemistry

A branch of Chemistry that deals with the study of chemical reaction which proceed in the presence of light. This branch also includes the study of the reactions that are accompanied by the emission of chemical energy as radiation.

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

$$CH_3 - CH = CH_2 + HBr \xrightarrow{Dark} CH_3 - CH(Br) - CH_3$$

$$\downarrow h\nu$$

$$CH_3 - CH_2 - CH_2Br$$

Example:

(i) Photosynthesis in plants

$$6CO_2 + 6H_2O \xrightarrow[chl]{h\nu} C_6H_{12}O_6 + 6O_2$$

(ii) Vison

Our retina has two different types of cells that detect and respond to light—rods and cones. These cells that are sensitive to light are called photoreceptors. Rods are activated when we're in low or dim light. Cones are stimulated in brighter environments. Cones contain photo pigments, or color-detecting molecules. Humans typically have three types of photo pigments—red, green and blue. Each type of cone is sensitive to different wavelengths of visible light.

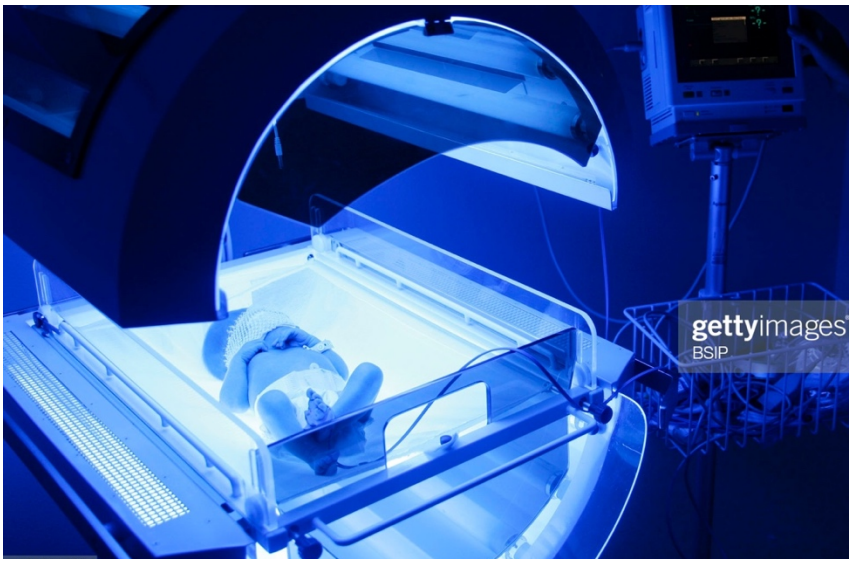
(iii) Bioluminescence in fire fly

(iv) Phototropism

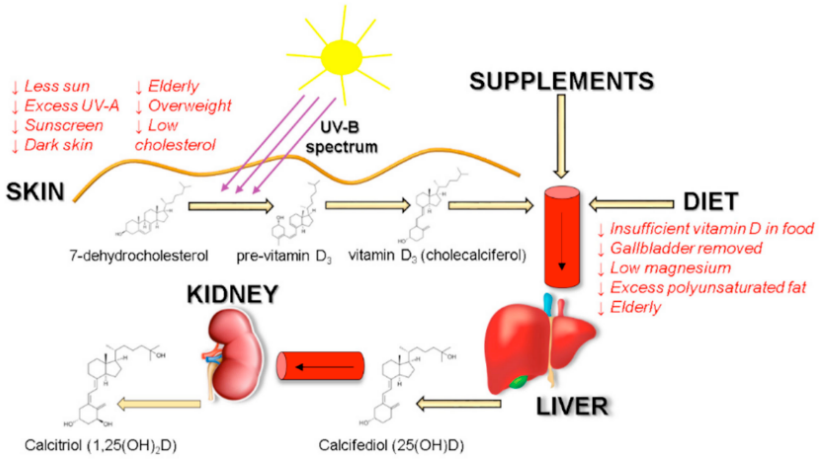
Orientation of plants towards the direction of sunlight

(v) Treatment of Jaundice of Newborn babies

Phototherapy is sometimes used to treat newborn jaundice by lowering the bilirubin levels in baby's blood. One way is to converts a substantial fraction of the normal toxic 4Z, 15Z form of less toxic bilirubin to the 4Z, 15E. Moreover, photo-oxidation adds oxygen to the bilirubin so it dissolves easily in water. This makes it easier for your baby's liver to break down and remove the bilirubin from their blood.



(vi) Biosynthesis of Vitamin D



(vii) Photochromism

The reversible transformation of molecules between two isomeric forms induced by the absorption of light. Cis–trans isomerization is the most common photochromic transformation.

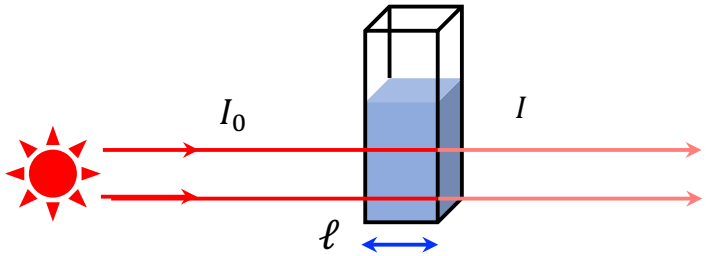
(viii) Polymerization or de-polymerization

❖ Difference between thermal and photochemical reaction

Photochemical Reaction	Thermal Reaction
(i) Photo activation with radiation of sufficient large energy (200-800 nm) leads to electronic excitation followed by a reaction.	(i) Thermal energy gets distributed mainly amongst different translational, rotational and vibrational excitations, very small fractions lead to electronic excitations.
(ii) The energy required for a successful reaction, is gained by absorption of quanta from UV/Visible region.	(ii) The energy of activation is provided by molecular collision or the collision with reaction vessel wall.
(iii) Many photochemical reactions proceed with increase (non-spontaneous) in free energy.	(iii) The thermal reactions proceed with decrease in free energy (spontaneous). If increase in free energy is involved, no reaction is possible.
(iv) The rate of photochemical reaction depends on the intensity of the radiation absorbed.	(iv) The rate of thermal reaction depends on temperature.
(v) Photochemical reaction is more selective than thermal reaction. Using a monochromatic light, only one species in a mixture can be excited.	(v) By heating a reaction mixture, translational energies of all the species in the mixtures are increased.

❖ Lambert's Law

The rate of decrease in intensity of incident radiation with the thickness of absorbing media is proportional to the intensity of the penetrating radiation.



If We consider a thin layer of the medium of thickness dℓ and let, I be the intensity of the radiation entering it then

$$\frac{dI}{d\ell} = -kI$$

Now, if I_0 is the intensity at $\ell = 0$ and I is the intensity at distance ℓ then

$$or \int_{I_0}^{I} \frac{dI}{I} = -\int_{0}^{\ell} k\, d\ell \qquad or\ ln\frac{I}{I_0} = -k\ell$$

$$I = I_0 e^{-k\ell}$$

$$Altenatively, 2.303\ log\frac{I}{I_0} = -k\ell$$

$$log\frac{I}{I_0} = \frac{-k}{2.303}\ell = -0.4343k\ell$$

$$\log\frac{I}{I_0} = -a\ell, \qquad here\ a = -0.4343k$$

$$I = I_0 10^{-a\ell}, \qquad a\ is\ termed\ as\ extinction\ coefficient$$

❖ Beer's Law

The rate of decrease in intensity of the incident radiation with the thickness of the absorbing media is proportional to the intensity of the penetrating radiation and the concentration of the absorbing media.

$$\frac{dI}{d\ell} = -k'CI, k' \text{ is called as molar absorbance coefficient}$$

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{0}^{\ell} k'C\, d\ell \qquad or\ ln\frac{I}{I_0} = -k'C\ell$$

$$I = I_0 e^{-k'C\ell}$$

$$Altenatively, \qquad 2.303\ log\frac{I}{I_0} = -k'C\ell$$

$$log\frac{I}{I_0} = \frac{-k'C}{2.303}\ell = -0.4343k'C\ell$$

$$\log\frac{I}{I_0} = -\epsilon C\ell, \qquad here\ \epsilon = -0.4343k'$$

$$I = I_0 10^{-\epsilon C\ell}, \qquad \epsilon \text{ is termed as molar extinction coefficient}$$

The molar absorption coefficient depends on the frequency of the incident radiation and is greatest where the absorption is most intense. Its dimensions are 1/(concentration × length), and it is normally convenient to express it in cubic decimeters per mole per centimeter ($dm^3.mol^{-1}.cm^{-1}$).

❖ Relation between Transmittance and absorbance:

The ratio of the transmitted intensity, I, to the incident intensity, I_0, at a given frequency is called the transmittance, T, of the sample at that frequency:

$$T = \frac{I}{I_0}$$

We can also introduce the term the absorbance, A, of the sample at a

given wavenumber as

$$A = log \frac{I_0}{I}$$

Therefore,

$$A = log \frac{1}{T} = -\log T$$

$$or \quad A = log \frac{100}{\%T} = 2 - \log T$$

❖ Deviation from Beer's Law can be observed:

(i) If the light used is not monochromatic

(ii) If the concentration of the absorbing solute is greater than 0.02 (M), in that case Beer's law is not correct. This is due to the interaction among the solute particles which changes the value of molar extinction coefficient (ϵ)

(iii) Aggregation: If the solute is partially soluble in a solvent, in that case if may form aggregation at high concentration. The absorption spectra of the aggregation may be different from that of the monomers.

e.g. At concentration 10 mg/ml phenol blue is appears as red whereas at lower concentration is is blue. Depending on the chosen wavelength for observation, the deviation from Beer's law may be positive or negative.

(iv) Scattering of Light: Biological samples are mostly turbid due to presence of macromolecules or formation of large aggregates, therefore light is scattered by the turbid solution. The optical density (O D) due to scattering is proportional to $^1/_{\lambda^4}$ $(Rayleigh\ Scattering)$ and may be easily recognized as background absorption which mat increase rapidly with increase in wavelength of the radiation.

(v) Fluorescence: If the optical density of the sample is high and the absorbing species is itself is fluorescent in that case the deviation from Beer's law is observed because here emitted light can reach directly to the detector.

(vi) If the optical density of the solute in the solution is measured when it is present in equilibrium between two forms, then the concentration of the particular solute decreases and deviation is observed.

(vii) The factors are due to the intrinsic property of the sample. Besides, the instrument artifacts may provide the optical density of the sample which may be nonlinear with the concentration.

❖ Laws of Photochemistry

1st Law or Grotthuss-Draper Law: Only the light which is absorbed by the reaction system can be effective in producing the chemical change.

It is trivial that photochemical reaction is the result of absorption of light but absorption of light does not commence photochemical reaction all the time. Sometimes absorption of light may increase the thermal energy of the system and absorbed radiation may also emit in the form of fluorescence.

2nd Law or Stark-Einstein Law: For each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction.

This law is concerned with primary step of activation through absorption of one quantum of radiation by one molecule. So, there is one to one correspondence between number of quanta and the number of molecule, therefore, this law is also known as "*Law of photochemical equivalence*".

What is "one Einstein"?

The energy corresponds to one mole of photon or Avogadro number of photons is called "one Einstein".

According to Einstein, the energy of a photon with frequency ν can be expressed as

$$\varepsilon = h\nu; h\ is\ planck's\ constant$$

So, one Einstein photon of energy is

$$E = Nh\nu = Nh\frac{c}{\lambda}$$

$$= \frac{6.023\times10^{23}\times6.625\times10^{-27}\times2.298\times10^{10}}{\lambda}$$

$$= \frac{119.59729\times10^{6}}{\lambda}\ ergs/mole$$

$$= \frac{28.583\times10^{4}}{\lambda}\ kCal/mole$$

Law of equivalence does not mean that one molecule would react per photon absorbed.

(i) There are several molecules which are activated by absorbing one quanta of energy and then breaks up into many fragments, which can take part in chemical reaction.

(ii) If molecules get excited after absorbing photon and after that they may deactivated without any reaction.

(iii) During excitation with very intense laser, e.g. Two Photon absorption

However, the efficiency of photochemical process is often expressed in terms of **quantum Yield (ϕ)**. This can really establish a relation between the number of quanta absorbed and the number of molecules reacting. Quantum yield may vary from 0 to ~10^6.

$$\phi = \frac{The\ number\ of\ molecule\ reacting\ in\ the\ given\ time}{The\ number\ of\ quanta\ of\ light\ absorbed\ in\ the\ same\ time}$$

$$\phi = \frac{The\ number\ of\ moles\ reacting\ in\ the\ given\ time}{The\ number\ Einstein\ of\ photon\ absorbed\ in\ the\ same\ time}$$

$$\phi = \frac{Rate\ of\ the\ process\ (formation\ or\ decomposition)}{Rate\ of\ absorption}$$

More conveniently, if we measure the rate of formation of X in molecules per second, $\frac{dN_X}{dt}$, then

$$\phi = \frac{\frac{dN_X}{dt}}{Number\ of\ quanta\ absorbed/second}$$

The number of quanta absorbed per second is simply the absorbed intensity, I_A

$$\phi = \frac{\frac{dN_X}{dt}}{I_A}$$

When quantum yield has low value?

(i) Non utilization of the excited molecules in the photochemical reaction
(ii) Activated molecules may loss their activity through collision with normal molecules
(iii) The decomposed fragments may recombine to form the initial reactants
(iv) The primary photochemical reaction may be reversed
(v) Molecules may not have sufficient amount of energy to undergo a successful reaction

Example

(a) In absence of sensitizer during photodecomposition of oxalic acid, the quantum yield is 0.001, which is very low at radiation wavelength 265 nm to 365 nm.

When quantum yield has high value?

(i) The activated molecule may undergo chain reaction where a large number of molecule undergo reaction.
(ii) During intermediate formation by the catalyst in a photochemical reaction
(iii) The activated molecule may collide with normal molecules to activate them, which can participate in subsequent reaction.
(iv) The reaction may be exothermic one, therefore heat evolved may activate the normal molecule to react further

Example

(a) For the combination of H_2 and Cl_2 to produce HCl, quantum yield value is 10^5 at excitation wavelength 400 nm. This reaction follows chain mechanism.

(b) During decomposition of HI, one photon is absorbed, which leads to decomposition of two HI molecules. Therefore, quantum yield of this reaction is 2.

$$HI + h\nu \longrightarrow H^{\cdot} + I^{\cdot}$$

$$H^{\cdot} + HI \longrightarrow H_2 + I^{\cdot}$$

$$I^{\cdot} + I^{\cdot} \longrightarrow I_2$$

❖ Actinometry

A device that measures the total amount of incident radiation on sample is called an actinometer, and the measurement method is known as actinometry.

Two types of actinometer are commonly used.

One is Thermopile: It consists of a number of thermocouples connected in series, with their hot junction imbedded at a blackened surface which absorbs almost all the incident light and converts it into heat. Calibrated lamps of known energy are available from National Bureau of Standards. The e.m.f. developed by the Thermofile is measured with the standard lamp and then with the source of radiation of unknown intensity. The reaction vessel is mounted between Thermofile and the light, and the radiation absorbed by the reacting system is measured by the difference between filled and empty.

Instead of Thermofile, it is possible to employ relative methods of actinometry, which is based on chemical change produced. One of the most reproducible reaction is the decomposition of oxalic acid photosensitized by Uranyl salts. Uranyl ion UO_2^{++} absorbs radiation from 250 nm to 450 nm, becoming an excited ion $(UO_2^{++})^*$, which decomposes oxalic acid. This reaction has quantum yield (ϕ) 0.50

$$UO_2^{++} + h\nu \longrightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO_2 + H_2O + CO$$

The oxalic acid concentration is easily followed by titration with permanganate. A quartz vessel filled with the uranyl oxalate mixture can be used exactly like the thermopile, the light absorbed being calculated from the oxalic acid decomposed and the known quantum yield.

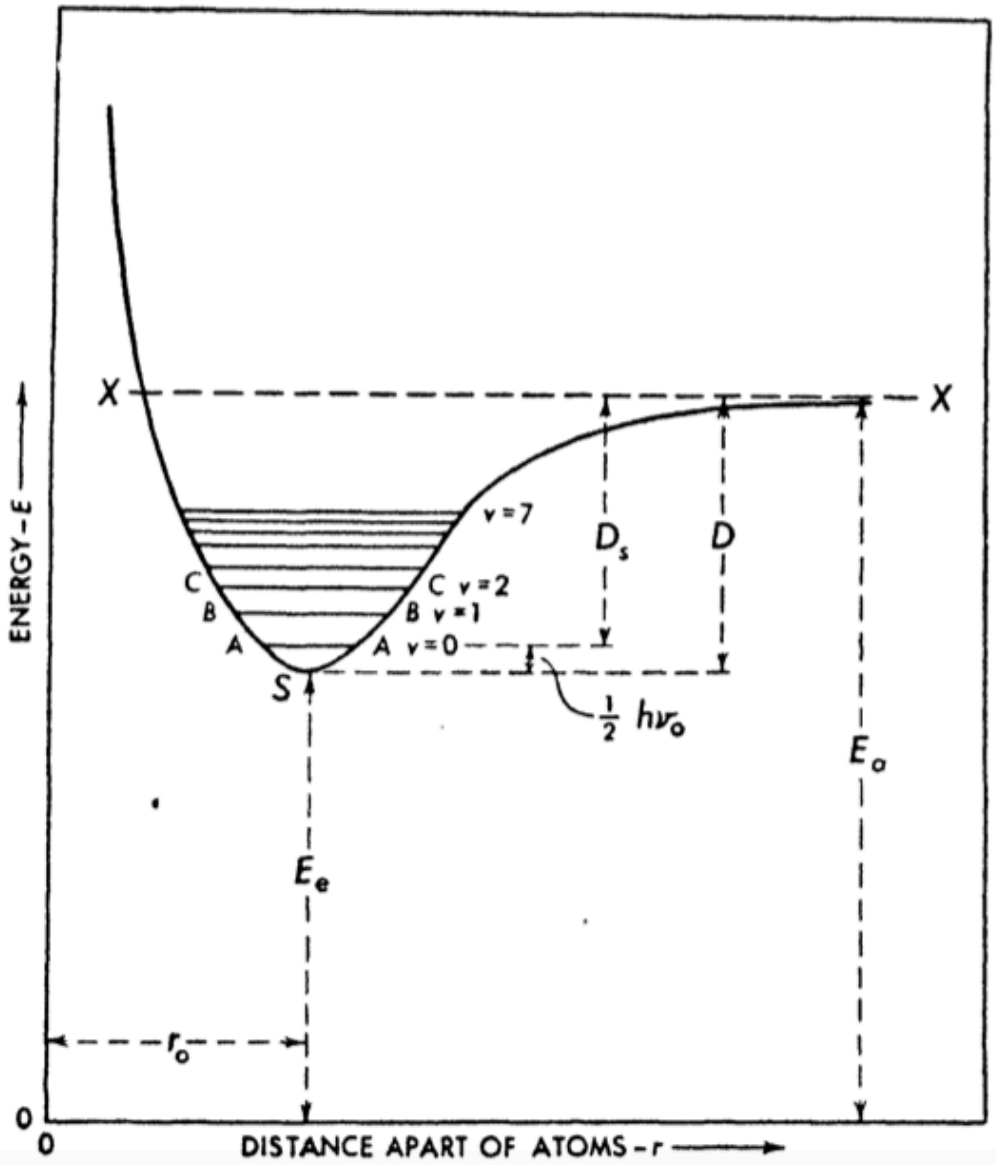
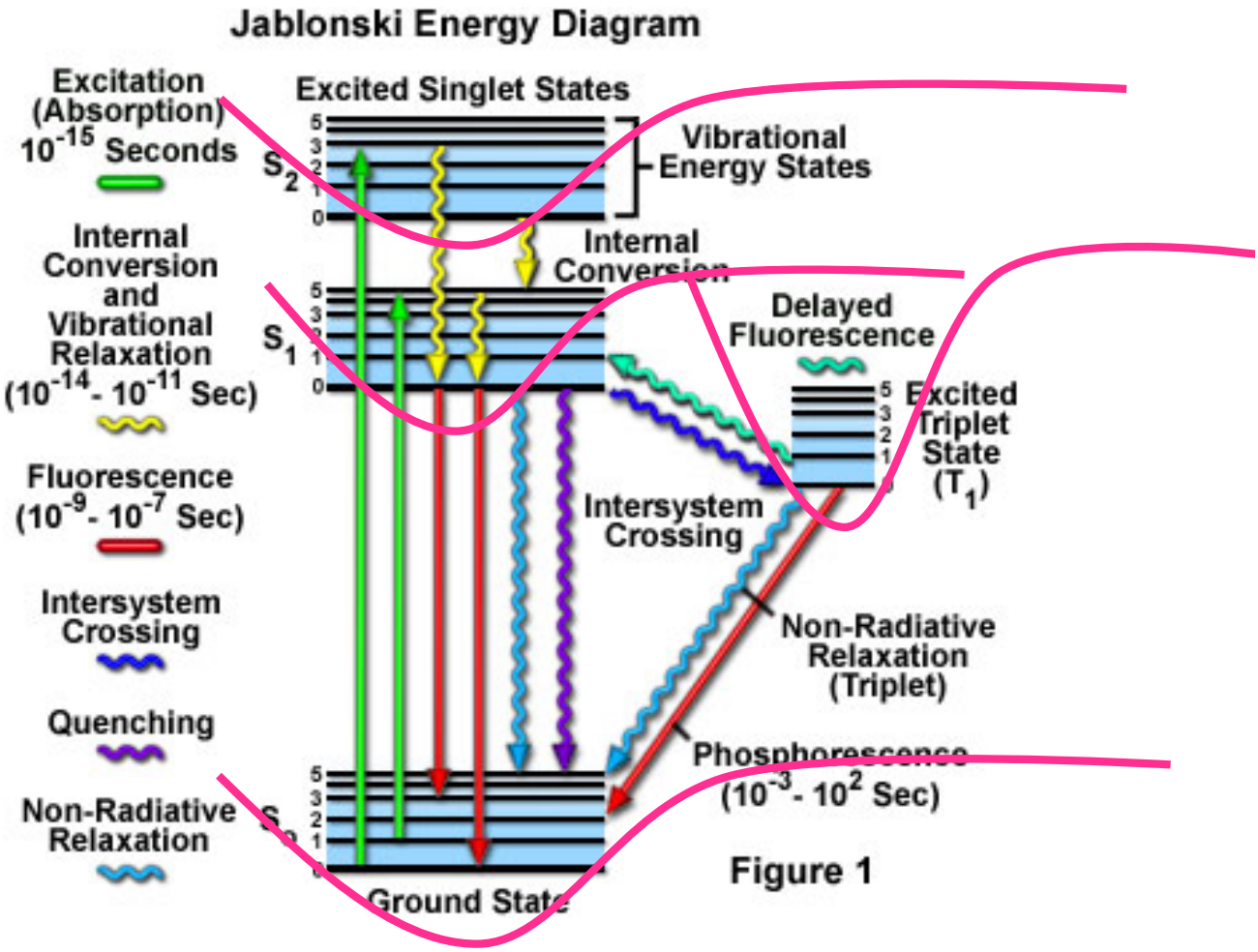


Fig. 4. Potential Energy Diagram of Diatomic Molecule



If a molecule is excited from ground singlet state, a set of photo-physical processes occur before it returns to the ground state. All photo-physical process occur can be conventionally depicted with the help of Jablonski's diagram. In the above diagram S_1, S_2 represent higher singlet electronic state and T_1 represents higher triplet states with S_O denoting singlet ground state. Each of states is accompanied with the series of vibrational fine structure levels.

When a molecule is given sufficient amount of energy then it can absorb that energy and will very quickly excited to higher singlet state at femtosecond timescale ($\sim 10^{-15}\, Sec$). An excited molecule will release energy with various ways.

If the excitation energy is such that the promoted molecule reaches to the higher vibrational energy level of S_1. In that case molecule tends to be

vibrationally relaxed by releasing the excess absorb energy and will come to the lowest vibrational state of S_1. This excess energy can be lost by collision with other molecules, this phenomenon is called vibrational relaxation. The excited state can be vibrationally relaxed very rapidly ($10^{-14} - 10^{-12}\ Sec$) before the operation of any other loss process. The molecule at lowest vibrational level in S_1 can release energy to reach their original ground electronic state by radiative or non-radiative processes. During non-radiative transition the energy can be lost by collision and will be appeared as heat in the system. This type of return is called internal conversion. Internal conversion is a Radiationless transition between states of same multiplicity. Energy can be released rapidly by emitting a radiation, this type of return is known as radiative process, i.e. called fluorescence which occurs at the timescale of $10^{-9} - 10^{-7}\ Sec$. So, fluorescence is an emission process between two states of same spin multiplicity.

Typical time scales of the various processes by which a molecule in an excited electronic state can relax.

Process	Transition	Change in spin multiplicity	Time scale
Fluorescence	Radiative $S_1 \rightarrow S_0$	0	10^{-9} s
Internal conversion	Collisional $S_1 \rightarrow S_0$	0	10^{-7}–10^{-12} s
Vibrational relaxation	Collisional		10^{-14} s
Intersystem crossing	$S_1 \rightarrow T_1$	1	10^{-12}–10^{-6} s
Phosphoresence	$T_1 \rightarrow S_0$	1	10^{-7}–10^{-5} s
Intersystem crossing	$T_1 \rightarrow S_0$	1	10^{-8}–10^{-3} s

A spin forbidden transition also may happen if excited molecule transit from S_1 to T_1 state. This might be accounted due to the reason that their potential energy surface intersects with each other. At the point of intersection of two curves, the nuclear geometries and energy are identical. At this instant the molecule may cross without any radiation from S1 to T1 state, this process is known as intersystem crossing (ISC). So, radiationless

transition between states of different spin multiplicity is called intersystem crossing. It is observed due to spin orbital coupling. In case of moderately heavy atom (e.g. ZnS), the spin orbital coupling is large in that case ISC is appreciable. Now, the molecule at T_1 try to loose energy to return to the original ground state either by non-radiative processes or by a radiative process, latter process is called phosphorescence.

In case of phosphorescence, energy is lower than fluorescence therefore phosphorescence has longer wavelength. The duration of fluorescence ($10^{-9} - 10^{-7}\,Sec$) is faster than phosphorescence ($10^{-9} - 10^{-1}\,Sec$). In case of phosphorescence since the path followed is spin forbidden, the rate constant is much smaller than that of fluorescence, T_1 state has the lifetime of $10^{-5} - 10^{-3}\,Sec$ and therefore phosphorescence lasts longer than fluorescence.

Electronic Spectroscopy: As a first approach of electron spectroscopy we can use Born-Oppenheimer Approximation:

$$\psi_{sys} = \psi_{ele,spin}\psi_{vib}\psi_{rot}$$

$$E_{tot} = E_{ele,spin} + E_{vib} + E_{rot}$$

The approximate orders of magnitude of these changes are

$$\Delta\varepsilon_{ele} \approx 10^3\Delta\varepsilon_{vib} \approx 10^6\Delta\varepsilon_{rot}$$

therefore, we see vibrational changes will produce coarse structure and rotational changes a fine structure on the spectra of electronic transition. We should also note that pure rotational spectra are shown by molecules possessing a permanent electric dipole moment and vibrational spectra requires a change of dipole during the motion, electronic spectra are given by all molecules since changes in the electronic distribution in a molecule are always accompanied by a dipole change.

An electronic transition is made up of vibrational bands, each of which is in turn made up of rotational lines. Initially we will ignore rotational fine structure and discuss Vibronic transitions. The intensities of the various vibrational bands are determined by three factors: the intrinsic strength of the electronic transition, the population of vibrational levels, and the squared overlap integral of the two vibrational wavefunctions, called Franck-Condon factor. Franck-Condon factor result from the application of a more general rule called the Franck-Condon Principle. This principle has both classical and

quantum mechanical versions. ***Franck-Condon states that an electronic transition takes place so rapidly that a vibrating molecules does not change its internuclear distance appreciably during the transition.*** On a potential energy diagram therefore electronic transitions occur vertically at same internuclear separation as ground vibrational state from where it has been excited to. The quantum mechanical version of Franck-Condon principle is based on the fact that the intensity of the transition is proportional to the square of the transition moment integral:

$$TMI = \int \psi_{ele,spin,vib}^{final} \hat{\mu} \psi_{ele,spin,vib}^{initial} \, d\tau$$

Now, applying Born-Oppenheimer approximation, We get

$$TMI = \int \psi_{ele,spin}^{final} v_{vib}^{final} \hat{\mu} \psi_{ele,spin}^{initial} \, v_{vib}^{initial} d\tau$$

The dipole moment operator can be broken into an electronic part and a nuclear part namely,

$$\mu = \sum q_i r_i = \sum_j q_j r_j + \sum_k q_k r_k$$

in which the sum over the charged particles in the molecules is broken into a sum over electrons (index j) and a sum over nuclei (index k). Then

$$TMI = \int \psi_{ele}^{final} v_{vib}^{final} (\hat{\mu}_{ele} + \hat{\mu}_{Nuc}) \psi_{ele}^{initial} \, v_{vib}^{initial} d\tau$$

$$TMI = \int \psi_{ele}^{final} \hat{\mu}_{ele} \psi_{ele,s}^{initial} \, d\tau_{ele} \int v_{vib}^{final} v_{vib}^{initial} \, d\tau_{Nuc} + \int \psi_{ele}^{final} \psi_{ele}^{final} d\tau_{ele} \int v_{vib}^{final} \, \hat{\mu}_{Nuc} \, v_{vib}^{initial} d\tau_{Nuc}$$

The electronic wavefunctions of two different states belong to same orthonormal state therefore they are orthogonal. Hence, $\int \psi_{ele,s}^{final} \psi_{ele,s}^{initial} \, d\tau_{ele} = 0$, whereas, $\int v_{vib}^{final} v_{vib}^{initial} \, d\tau_{Nuc} \neq 0$, as two vibrational wavefunctions belong to two different excited state so they are not orthogonal to each other. Finally, we obtain TMI as

$$TMI = \int \psi_{ele}^{final} \hat{\mu}_{ele} \psi_{ele}^{initial} \, d\tau_{ele} \int v_{vib}^{final} v_{vib}^{initial} \, d\tau_{Nuc}$$

$$or \quad TMI = \langle \psi_{ele}^{final} | \widehat{\mu_{ele}} | \psi_{ele}^{initial} \rangle \langle v_{vib}^{final} | v_{vib}^{initial} \rangle$$

in which first term is known as R_e, electronic transition dipole moment and second term is vibrational overlap integral, $\langle v_{vib}^{final} | v_{vib}^{initial} \rangle$. The intensity of Vibronic transition is proportional of the transition moment integral, namely

$$I \propto |R_e|^2 \left| \langle v_{vib}^{final} | v_{vib}^{initial} \rangle \right|^2$$

Here, R_e value measures the intrinsic strength of an electronic transition, while Franck-Condon factor determines how the intensity is distributed among the vibrational levels.

- ❖ Franck-Condon Principle predicts the relative intensities of Vibronic Transition

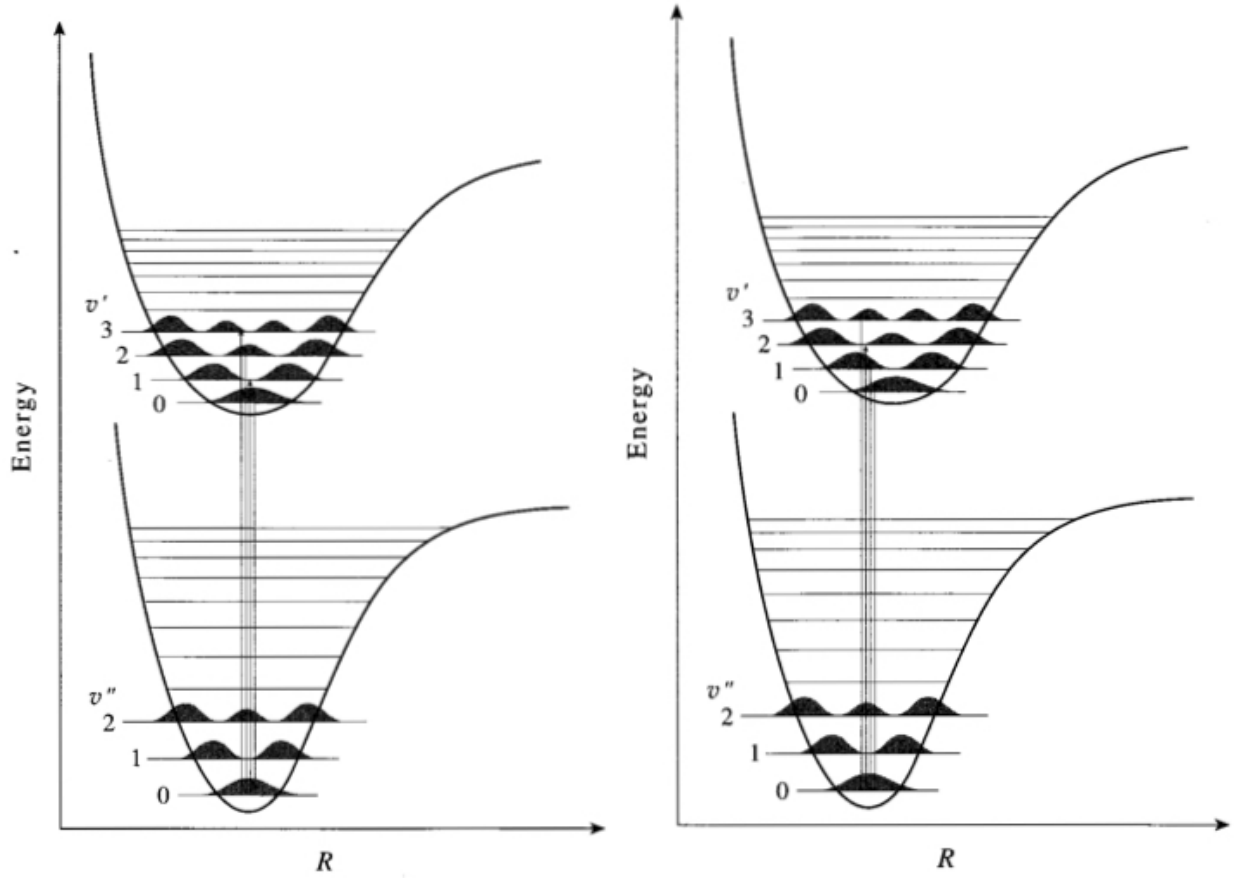


Figure 5: Two electronic potential energy curves showing the vibrational states associated with each electronic state. (a) The minimum of the upper curve lies almost directly over the minimum of the lower curve. (b) the minimum of the upper curve occurs at a somewhat greater value of the internuclear separation than for the lower curve. The shaded areas represent the harmonic-oscillator probability densities for each vibrational state. The vertical lines represent a series of $0 \rightarrow \upsilon'$ *vibronic transitions.*

When an electron makes a transition from one electronic state to another, the nuclei do not move appreciably during the transition. Electronic transitions can therefore be depicted as vertical lines in the diagram such as figure 5. In figure 5(a) the minima of the two electronic states lie very nearly above each other i.e. the equilibrium bond distances are same at vibrational ground state of both ground and excited electronic state. As the relative intensities of $0 \rightarrow v'$ transition is proportional to the product of vibrational wave functions of two vibrational state thus we will obtain a distribution of intensities like Figure 6(a) for this system.

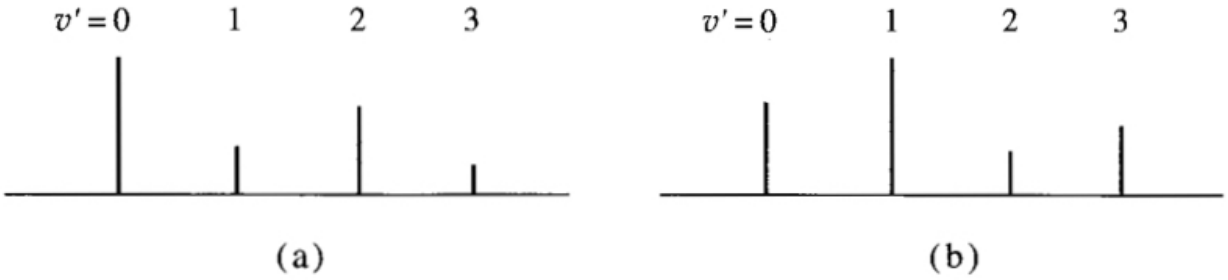


Figure 6: The distribution of intensities of the vibronic transitions for the case shown in (a) Figure 5(a) and (b) Figure 5(b).

Another commonly occurring case, in which the minimum of the upper potential energy curve lies at a somewhat greater value of the internuclear separation than for the lower curve. In that case $0 \rightarrow 0$ transition is not the most intense transition. The most intense transition as shown in figure 5(b) is the $0 \rightarrow 1$ transition, and the distribution of intensities for this case is like that given in figure 6(b).

Selection Rule of Spin multiplicity: We know

$$TMI = \int \psi_{ele,s}^{final} \hat{\mu}_{ele} \psi_{ele,s}^{initial} \, d\tau_{ele,s} \int v_{vib}^{final} v_{vib}^{initial} \, d\tau_{Nuc}$$

The above equation can be written out more completely as follows

$$TMI = \int \psi_{ele}^{final} \hat{\mu}_{ele} \psi_{ele}^{initial} \, d\tau_{ele} \int \psi_{s}^{final} \psi_{s}^{initial} \, d\tau_{s} \int v_{vib}^{final} v_{vib}^{initial} \, d\tau_{Nuc}$$

This equation is the basis of the electronic selection rules. If any of the integrals is zero, the transition is formally forbidden. We say, therefore, that there are vibrational, orbital, and spin selection rules for electronic transitions. The spin selection rules, based on above equation, states that the integral $\int \psi_{s}^{final} \psi_{s}^{initial} \, d\tau_{s}$ must be nonzero if the transition is to be allowed. In practice, this is the easiest selection rule to apply because a

transition is spin-allowed if and only if the multiplicities of the two states involved are identical. No change in spin multiplicity occurs during a transition i.e. $\Delta S = 0$. Singlet to singlet and triplet to triplet transition are allowed but singlet to triplet or triplet to singlet are forbidden.

As an example, we will show that the triplet→singlet transition involving the spin functions ${}^{1}/_{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ (singlet) and $\alpha(1)\alpha(2)$(triplet) is forbidden,

$$\int \psi_s^{final}\psi_s^{initial}\, d\tau_s = \frac{1}{\sqrt{2}}\int_{e\ 1,2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(1)\alpha(2)]\, d\tau_{e\ 1,2}$$

$$= \frac{1}{\sqrt{2}}\left[\int_{e\ 1,2}\alpha(1)\beta(2)\alpha(1)\alpha(2)d\tau_{e\ 1,2} - \int_{e\ 1,2}\beta(1)\alpha(2)\alpha(1)\alpha(2)d\tau_{e\ 1,2}\right]$$

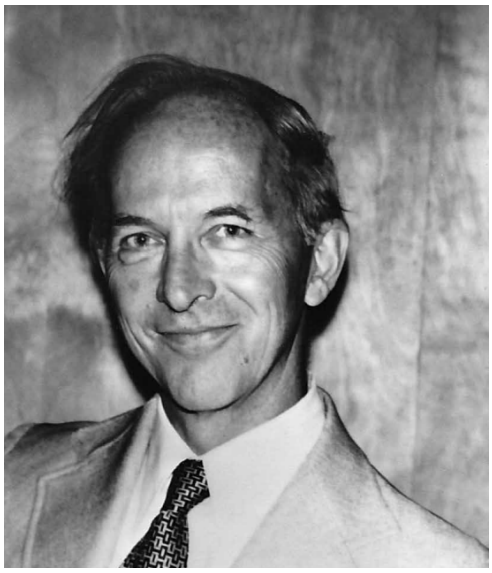
$$= \frac{1}{\sqrt{2}}\left[\int_{e\ 1}\alpha(1)\,\alpha(1)d\tau_{e\ 1}\int_{e\ 2}\beta(2)\alpha(2)d\tau_{e\ 2} - \int_{e\ 1}\beta(1)\alpha(1)d\tau_{e1}\int_{e\ 2}\alpha(2)\alpha(2)d\tau_{e\ 2}\right]$$

$$= \frac{1}{\sqrt{2}}[(1)(0) - (0)(1)]$$

$$= 0; \quad Spin\ forbidden$$

Kasha's rule:

Kasha' Rule, states that fluorescence will always originate from the vibrational ground state of the lowest excited singlet level, the S_1, while phosphorescence will originate from the vibrational ground state of the lowest excited triplet level, the T_1, regardless of which initial level the molecule is excited too.



Michael Kasha (1920 – 2013)

Azulene and some thiocompounds observed to violate Kasha's rule. For these molecule transition occurs directly from S_2 to S_O state. Because energy gap between S_2 and S_1 is higher than the energy gap between S_1 and S_O. For these reason fluorescence originates from S_2 state competes over internal conversion from S_2 to S_1.

Why fluorescence intensity decreases due to temperature rise?

With increase in temperature, the intensity of fluorescence decreases. Since the molecule in the excited state (S_1) may follow inter system crossing (ISC) to reach the T_1 state. Thus lower proportion of molecule remain in the S_1 state to undergo radiative process from S_1 to S_O. As a result, fluorescence intensity decreases.

Resonance fluorescence:

When the frequency of the emitted radiation due to fluorescence is identical with that of the absorbed radiation. The phenomenon is called resonance fluorescence.

e.g. When the Hg-vapour atoms are excited at 253.7 nm and if pressure is lowered in that case excited molecules come back to ground state by emitting radiation at 253.7 nm.

E-Type delayed fluorescence:

Molecules get excited from S_O to S_1 state after absorption of sufficient energy. The excited molecule can cross over to the triplet state via inter system crossing mechanism. Now, if the energy gap between S_1 and T_1 is very smaller then excited molecules at T_1 state can be prompted to the S_1 state again which is known as reverse intersystem crossing. Then excited molecules at S_1 state come back to S_O state through radiative process. This type of fluorescence takes a longer time and called as E-type delayed fluorescence.

P-Type delayed fluorescence:

Molecules get excited from S_O to S_1 state after absorption of sufficient energy. The excited molecule can cross over to the triplet state via inter system crossing mechanism. Now, interaction of the two molecule in the

triplet states (triple-triplet annihilation) sends one molecule to the first excited singlet state and other molecule returns to the singlet ground state. Now the excited molecule at first excited singlet state will return to ground singlet state with delayed fluorescence. This type of delayed fluorescence known as P-type delayed fluorescence.

Photosensitized reaction:

When in a mixture, a special type of molecule called donor (D) which absorb energy from light of a particular wavelength (characteristic of donor molecule) and becomes excited. Subsequently transform its excitation energy to another type of molecule present in the mixture, called acceptor (A) and then donor molecule returns to its ground state. Now, acceptor molecule become excited and emits radiation or undergo reaction photo-chemically. This transfer of energy from donor (D) to acceptor (A) followed by emission of energy is known as photosensitization.

The transfer of energy from Donor to Acceptor is possible under the following condition:

(i) The donor excited state must have sufficiently longer lifetime to be able to transfer its excitation energy to the acceptor molecule. Since triplet state has the longer lifetime than singlet state therefore photosensitization is more favorable for former than latter.

(ii) The energy of the donor molecule should be higher than the acceptor. The common sensitizes is Benzophenone. Its energy for S_1 and T_1 state is 356 kJ and 291 kJ.

(iii) The multiplicity of the donor and acceptor should be same during energy transfer

$$D(S_O) \xrightarrow{h\nu} D^*(S_1) \xrightarrow{ISC} D^*(T_1) \xrightarrow{A(T_1)} D(S_O) + A^*(T_1)$$

$$\Big\downarrow A(S_O)$$

$$D(S_O) + A^*(S_1)$$

Sensitized fluorescence:

Taking two molecules, one exhibit fluorescence and one does not under same condition, if these two molecules are mixed and irradiated with a particular wavelength of radiation then both exhibit fluorescent. This phenomenon is known as sensitized fluorescence.

e.g. Hg-vapor show resonance fluorescence when irradiated with 253.7 nm wavelength light source. But Thallium (Tl) does not exhibit fluorescence under same condition. Now, if the mixture of Hg-vapor and Tl are irradiated at a wavelength 253.7 both exhibit fluorescence.

$$Hg + Tl \xrightarrow{h\nu} Hg^* + Tl \longrightarrow Hg + Tl^*$$

Photosensitized decomposition:

Sometimes a normal molecules absorb so much energy from a photosensitizer molecule that it can decomposes and photosensitizer molecule returns to their ground state. This phenomenon is known as photosensitized decomposition.

e.g. H_2 molecule do not dissociate with irradiation at 253.7 nm light. But if a mixture of Hg-vapor and H_2 molecule are irradiated with 253.7 nm light source then Hg atom gets excited. Then ectied mercury atom transfer its energy (112000 cal) by collision to hydrogen molecule. 103000 cal energy is then used up by H_2 molecule to decomposes to H-atom

$$Hg + H_2 \xrightarrow{h\nu} Hg^* + H_2 \longrightarrow Hg + 2H$$

❖ Quenching

Fluorescence quenching refers to any process which decreases the fluorescence intensity of any sample or may stopped the fluorescence from any sample. A variety of molecular interaction can result in quenching. These include excited-state reactions, molecular rearrangement, energy transfer, ground-state complex formation, and collisional quenching.

If the excited molecule undergo collision with another molecule the fluorescence will be quenched., i.e. the intensity of the emitted radiation for fluorescence may be reduced or stopped. The quenching of fluorescence is due to transfer of energy from the excited molecule to that one with which it

collides. At low pressure, the number of molecule per unit area is small and the excited molecule take longer time to collide with other molecule. In that case excited molecule releases excess energy as fluorescence. But when the pressure increases, the number of molecule per unit area increases, therefore, the probability of collision is higher. In that case appreciable quenching of fluorescence is observed. In case of liquid collisions are very frequent due to presence of large number of molecule per unit area. The quenching of fluorescence is appreciable.

We will primarily discuss two types of quenching

(i) Dynamic or collisional quenching:

The collisional encounter between fluorophore and quencher decreases the intensity of radiation of the emitted photon for fluorescence, this type of quenching process is known as dynamic or collisional quenching.

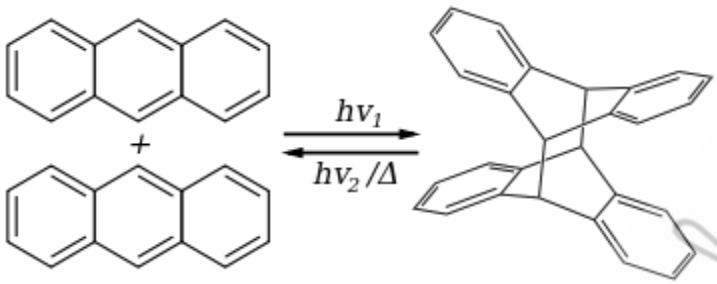
(ii) Static quenching:

Quenching can occur as a result of the formation of a nonfluorescent complex between fluorophore and quencher without presence of any excitation light source. When this complex absorbs light, it immediately returns to the ground state with emission of a photon.

❖ The Photostationary State

Absorbed light has an interesting effect on a system in chemical equilibrium. The absorption of light by a reactant can increase the rate of the forward reaction without directly influencing the rate of the reverse reaction; this disturbs the equilibrium. The concentration of products increases somewhat, increasing the rate of the reverse reaction. In this way the rates of the forward and reverse reaction can be brought into balance with the system This new state in not an equilibrium state but a stationary state, called a Photostationary state.

The dimerization of anthracene offers a convenient example, The reaction



occurs upon irradiation of a solution of anthracene by ultraviolet solution.

The plausible mechanism of the dianthracence formation is

$$A + h\nu \longrightarrow A^* \qquad Rate = I_a$$

$$A^* + A \xrightarrow{k_2} A_2$$

$$A^* \xrightarrow{k_3} A + h\nu'$$

$$A_2 \xrightarrow{k_4} 2A$$

The net rate of formation of A_2 is

$$\frac{d[A_2]}{dt} = k_2[A][A^*] - k_4[A_2]$$

In the steady state,

$$\frac{d[A^*]}{dt} = I_a - k_2[A^*][A] - k_3[A^*] = 0$$

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

In the Photostationary state we have additional requirement that,

$$\frac{d[A_2]}{dt} = 0$$

$$or \;\; k_2[A][A^*] - k_4[A_2] = 0$$

$$or \;\; [A_2] = \frac{k_2[A][A^*]}{k_4}$$

$$or \;\; [A_2] = \frac{k_2[A]}{k_4}\frac{I_a}{k_2[A] + k_3}$$

$$or\ [A_2] = \frac{1}{k_4}\ \frac{I_a}{\frac{k_2[A]+k_3}{k_2[A]}}$$

$$or\ \ [A_2] = \frac{1}{k_4}\ \frac{I_a}{1+\frac{k_3}{k_2[A]}}$$

If the concentration of monomer [A] is very high, then $1 + \frac{k_3}{k_2[A]} \approx 1$

$$[A_2] = \frac{I_a}{k_4}$$

The concentration of diantharcene is independent of monomer concentration and for the usual equilibrium $[\mathrm{A}_2] = \mathrm{K}[\mathrm{A}]^2$.

Secondary photochemical processes: initiation of chain reactions:

Decomposition of HI: If a molecule is dissociated into fragments as a consequence of absorbing a quantum of radiation, extensive secondary reactions may occur. For example, if HI molecule is brought about by the radiation of light in the range of 200-330 nm. The chain reaction is initiated by photolysis; many reactant molecules might be consumed as a result of absorption of a single photon. The overall quantum yield, Φ, for such reactions, the number of reactant molecules consumed per photon absorbed, might exceed 1. The mechanism is

$HI + h\nu \longrightarrow H + I$	$Rate = I_a$
$H + HI \longrightarrow H_2 + I$	$Rate\ constant = k_2$
$I + I \longrightarrow I_2$	$Rate\ constant = k_3$

Other possible elementary reactions either have much higher activation energies or require three-body collisions.
The rate of disappearance of HI is

$$-\frac{d[HI]}{dt} = I_a + k_2[H][HI]$$

The steady state requirement is

$$\frac{d[H]}{dt} = I_a - k_2[H][HI] = 0$$

$$or \quad [H] = \frac{I_a}{k_2[HI]}$$

Combining these two equation we obtain

$$-\frac{d[HI]}{dt} = 2I_a$$

By definition quantum yield

$$\phi = \frac{-\frac{d[HI]}{dt}}{I_a} = 2$$

In a variety of experimental situations, the observed value of ϕ is 2.

The interesting point about photochemical reaction is that the rate of the reaction is simply the twice the absorbed intensity and is not directly dependent on the concentration of HI.

For example, if a mixture of chlorine and hydrogen is exposed to light in the continuous region of the absorption spectrum of chlorine (λ < 480 nm) an extremely rapid reaction to hydrogen chloride ensues.

After irradiation of photon of 480 nm, chlorine molecule reaches to the higher energy, the maximum instability level of the molecule then it dissociates into Cl atoms and then Cl atom participate into a chain reaction. The quantum yield of this reaction is 10^4 to 10^6. Quantum yield of this reaction deceases if the impurity is present in the medium. The impurity can react with H and Cl atoms to terminate the chain reaction. Quantum yield also can decrease if reaction occurs at the walls of vessel.

$$Cl_2 + h\nu \longrightarrow 2Cl \qquad\qquad Rate = I_a$$

Efficiency of this step is one as one photon is absorbed and one molecule of Cl_2 dissociates.

$$\phi_1 = \frac{rate\ of\ the\ process\ (or\ rate\ of\ decomposition\ of\ Cl_2)}{Rate\ of\ absorption}$$

$$Cl + H_2 \xrightarrow{k_2} HCl + H$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl$$

$$Cl \xrightarrow{k_4} \frac{1}{2}\ Cl_2$$

If we set up the steady-state expressions for [Cl] and [H] in the usual way Then

$$\frac{d[Cl]}{dt} = \phi_1 I_a - k_2[Cl][H_2] + k_3[H][Cl_2] - k_4[Cl] = 0$$

$$or \quad [Cl] = \frac{\phi_1 I_a + k_3[H][Cl_2]}{k_2[H_2] + k_4}$$

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

$$k_2[Cl][H_2] = k_3[H][Cl_2]$$

Now, we can obtain for the rate of HCl production,

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

$$or \quad \frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_2[Cl][H_2]$$

$$or \quad \frac{d[HCl]}{dt} = 2k_2[Cl][H_2]$$

$$or \quad \frac{d[HCl]}{dt} = 2k_2 \frac{\phi_1 I_a + k_3[H][Cl_2]}{k_2[H_2] + k_4}[H_2]$$

$$or \quad \frac{d[HCl]}{dt} = 2\frac{\phi_1 I_a + k_3[H][Cl_2]}{1 + \frac{k_4}{k_2}[H_2]}$$

The Photochemical reaction between H_2 and Br_2

Using light of wavelength less than 511 nm, the photochemical reaction between H_2 and Br_2 can be initiated, which follows following mechanism.

$$Br_2 + h\nu \longrightarrow 2Br; \qquad Initiation$$

$$\phi_i = \frac{rate\ of\ the\ process\ (formation\ or\ decomposition)}{Rate\ of\ absorption}$$

$$rate\ of\ the\ process\ (formation\ or\ decomposition) = \phi_i \times I_a$$

Where, $I_a$is the intensity of the light absorbed per unit volume and per unit time.

$$\left.\begin{aligned} Br + H_2 &\xrightarrow{k_2} HBr + H \\ H + Br_2 &\xrightarrow{k_3} HBr + Br \end{aligned}\right\} \quad Chain\ Propagation$$

$$HBr + H \xrightarrow{k_{-2}} Br + H_2 \qquad Inhibition$$

$$Br + Br \xrightarrow{k_{-1}} Br_2 \qquad Termination$$

The steady hypothesis must be applied to the two intermediates Br and H both of which are present at very low concentrations. The steady state equation for bromine atom is now,

$$\frac{d[Br]}{dt} = \phi_i I_a - k_2[Br][H_2] + k_3[H][Br_2] + k_{-2}[H][HBr] - k_{-1}[Br]^2 = 0 \qquad (a)$$

The steady state equation for H atom is

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_{-2}[H][HBr] = 0 \qquad (b)$$

Now adding equation (a) and equation (b)

We have,

$$\frac{d[Br]}{dt} + \frac{d[H]}{dt} = \phi_i I_a - k_{-1}[Br]^2 = 0$$

$$[Br] = \sqrt{\frac{\phi_i I_a}{k_{-1}}}$$

also

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_{-2}[HBr]}$$

An expression for [H] can be obtained by inserting the expression for [Br]

$$[H] = \frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]} \qquad (c)$$

Here, the rate of formation of HBr is

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_{-2}[H][HBr] \qquad (d)$$

From equation (b), we know

$$k_2[Br][H_2] - k_{-2}[H][HBr] = k_3[H][Br_2]$$

Therefore, equation (d) becomes

$$\frac{d[HBr]}{dt} = 2k_3[H][Br_2]$$

$$or \quad \frac{d[HBr]}{dt} = 2k_3\frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]}[Br_2]$$

$$or \quad \frac{d[HBr]}{dt} = 2k_3\frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]}[Br_2]$$

$$or \quad \frac{d[HBr]}{dt} = 2\frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{1 + \frac{k_{-2}}{k_3}\frac{[HBr]}{[Br_2]}}$$

The quantum yield of the overall reaction is

$$\phi = \frac{\frac{d[HBr]}{dt}}{I_a} = \frac{2k_2\sqrt{\frac{\phi_i}{k_{-1}}}[H_2]}{\sqrt{I_a}\left(1 + \frac{k_{-2}}{k_3}\frac{[HBr]}{[Br_2]}\right)} = \frac{k_2'[H_2]}{I_a^{\frac{1}{2}}\left(1 + k_{-2}'\frac{[HBr]}{[Br_2]}\right)}$$

Quantum yield is inversely proportional to the square root of the intensity. As intensity increases, a greater proportion of the bromine atoms formed are converted to Br_2 instead of entering the chain; most of the additional quanta

therefore are wasted, and the process is less efficient. Because k_2 is very small, the quantum yield is less than unity at room temperature in spite of the fact that the HBr is formed in a chain reaction. As the temperature increases, the increase in k_2 increases the quantum yield.

Rate of this reaction is rate of the consumption of H_2, which is

$$v_p(t) = -\frac{d[H_2]}{dt} = k_2[Br][H_2] - k_{-2}[H][HBr]$$

$$or \quad v_p(t) = -\frac{d[H_2]}{dt} = k_3[H][Br_2]$$

$$v_p(t) = k_3 \frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]}[Br_2]$$

$$v_p(t) = \frac{k_2\sqrt{\frac{\phi_i I_a}{k_{-1}}}[H_2]}{1 + \frac{k_{-2}}{k_3}\frac{[HBr]}{[Br_2]}}$$

❖ Luminescence:

It is generally observed that when a metal is heated to a high temperature, it initially becomes red hot and then white. Here light is emitted by the application of heat.

But if the emission of radiation occurs from a body by the application of agencies other than heat that phenomenon is called luminescence. E.g. Fluorescence, phosphorescence.

❖ Chemiluminescence: This is a reverse process of photo-chemical reaction. In a photochemical reaction chemical reaction occurs after the absorption of light, but chemiluminescence is a phenomenon in which emission of light by a system at ordinary temperature is possible as a result of some chemical reactions. These chemical reactions yield the product at excited electronic state, decay of these excited state may produce the emission of radiation at the temperature which is normally expected. These reactions are electron transfer or oxidation reactions.

Most chemiluminescent reactions involve singlet excited state. The energy required for excitation is as a result of exothermic reaction.

Example: When phosphorous is oxidized in O_2 or air at low low pressure and at temperature between -10. The greenish white luminescence is observed due to the formation of an oxide in an excited state. These molecules when return to their ground state resulting in emission of light in visible range.

- Bioluminescence: This is due to biochemical reaction. The intensity of the emitted radiation is weak and the spectra observed are broad and structureless. The intensity varies with time.

Example: The oxidation of protein luciferin in presence of enzyme luciferase in fireflies, produces excited complex. Once it falls back down to a ground state a photon is released.

$$Luciferin + O_2 + ATP \xrightarrow{Luciferase} Oxyluciferin + ADP + PPi + Light$$