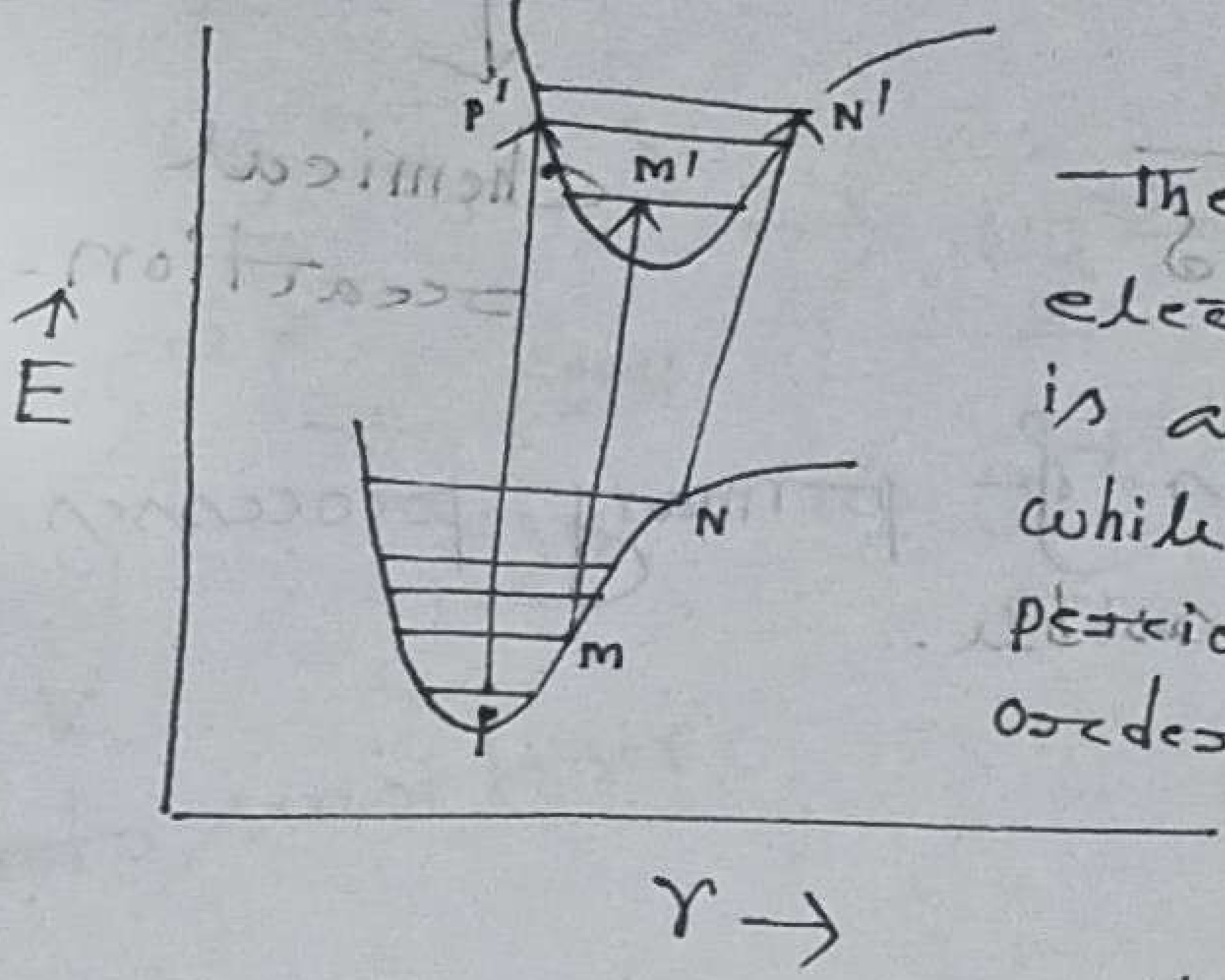
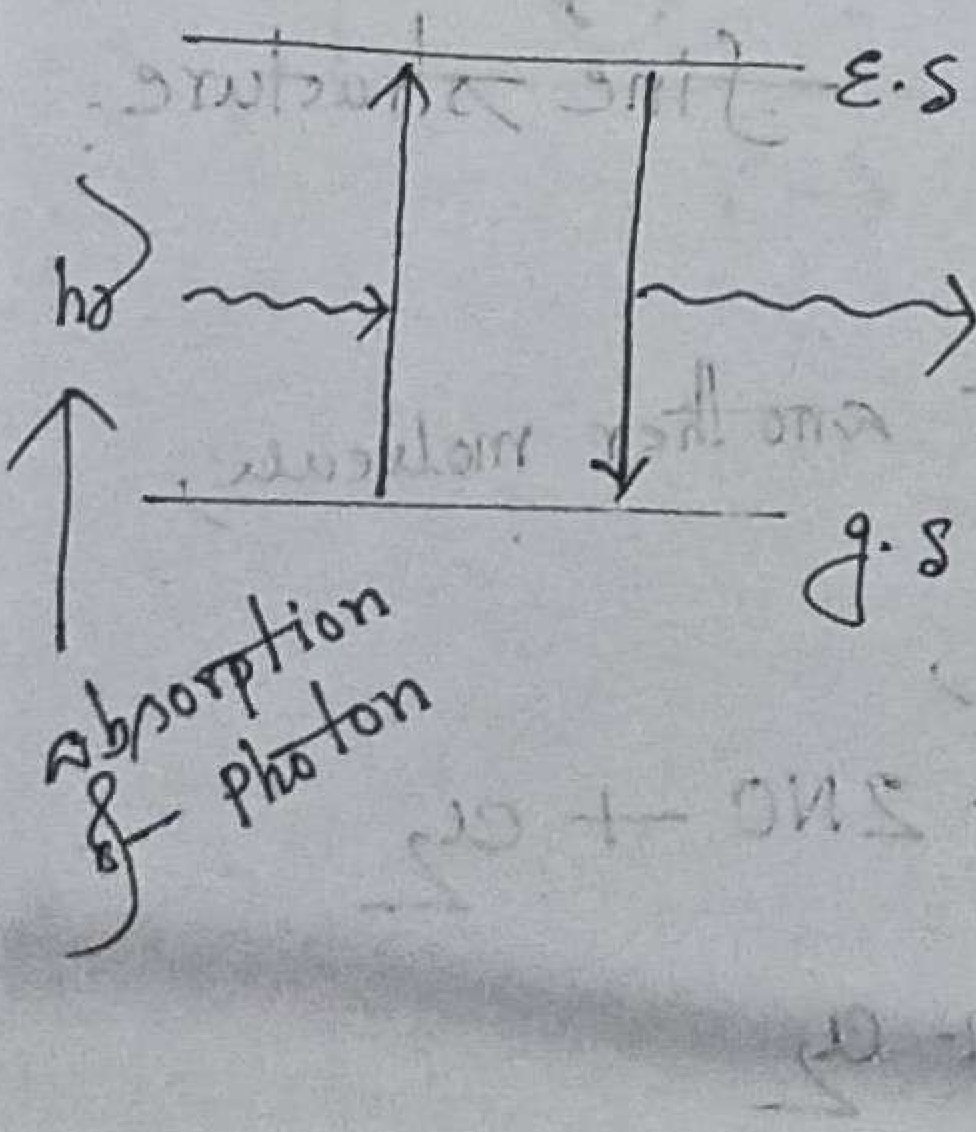
Primary Process in photo chemical reactions.

Franck-condon principal



The period for electronic transition is about 10^{-16} sec while vibrational period is of the order of 10^{-13} sec. This suggest ~~that~~ nuclei will not change ~~their~~ position when electronic configuration changes.

Photo physical process:



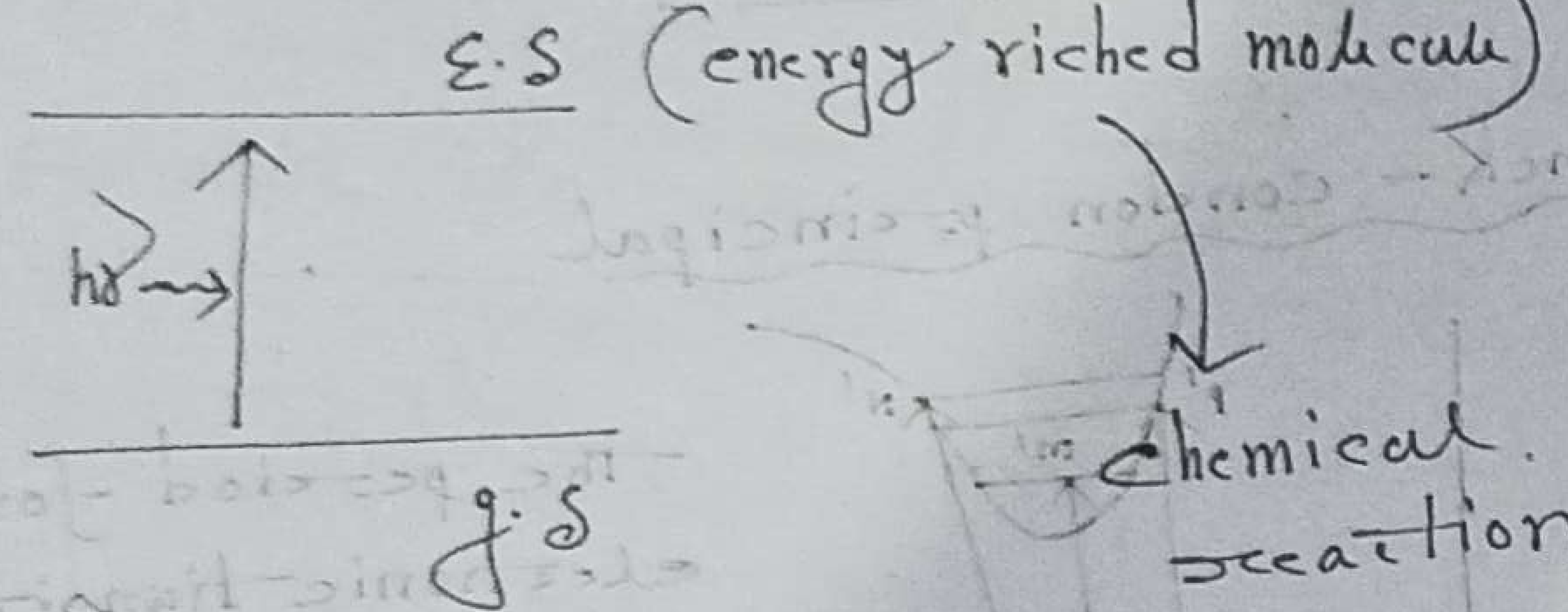
Re-emits radiation

✓ Fluorescence

✓ Phosphorescene

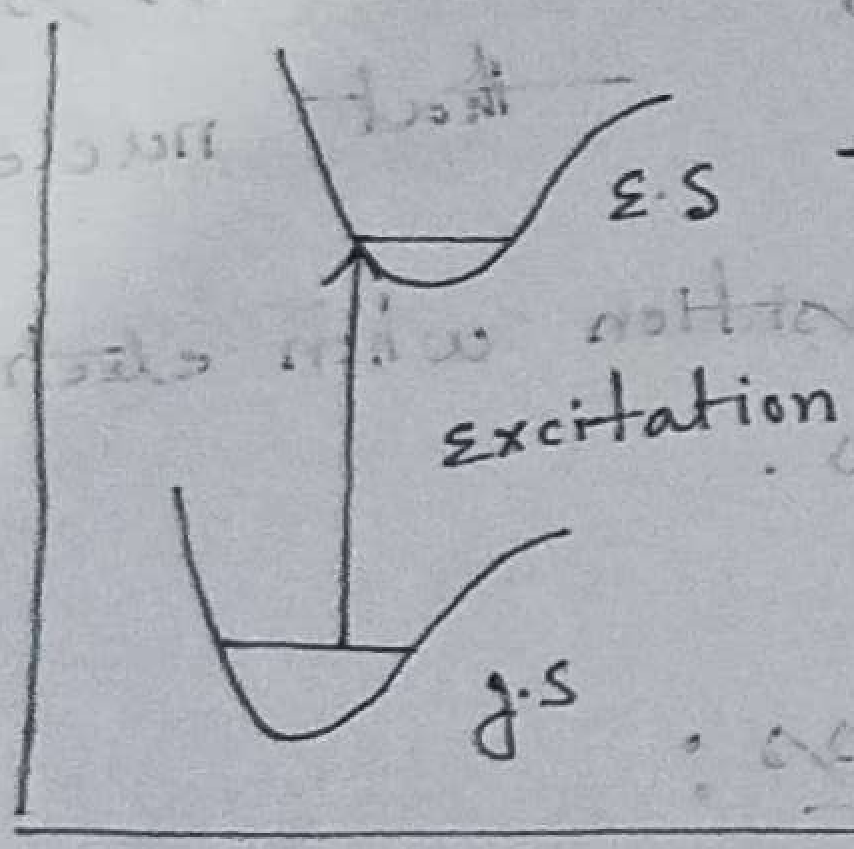
✓ Resonance Radiation

Photo chemical process

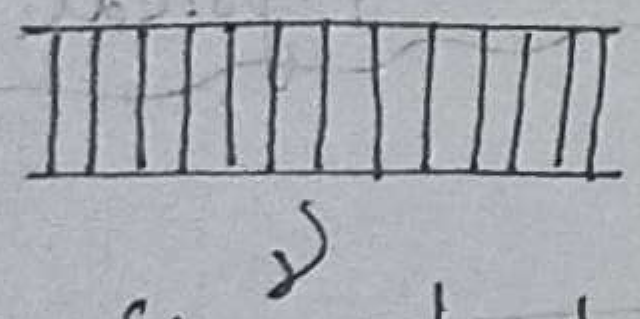


Four types of primary processes are possible.

Type I :-



→ stable
No direct dissociation of the molecule.



fine structure.

a) By combination, with another molecule,

$NOCl + h\nu \rightarrow NOCl^*$,

$NOCl + NOCl^* \rightarrow 2NO + Cl_2$

$NOCl + NOCl^* \rightarrow 2NO + Cl_2$

$\phi = 2.$

b) By transferring the excitation energy to another molecule

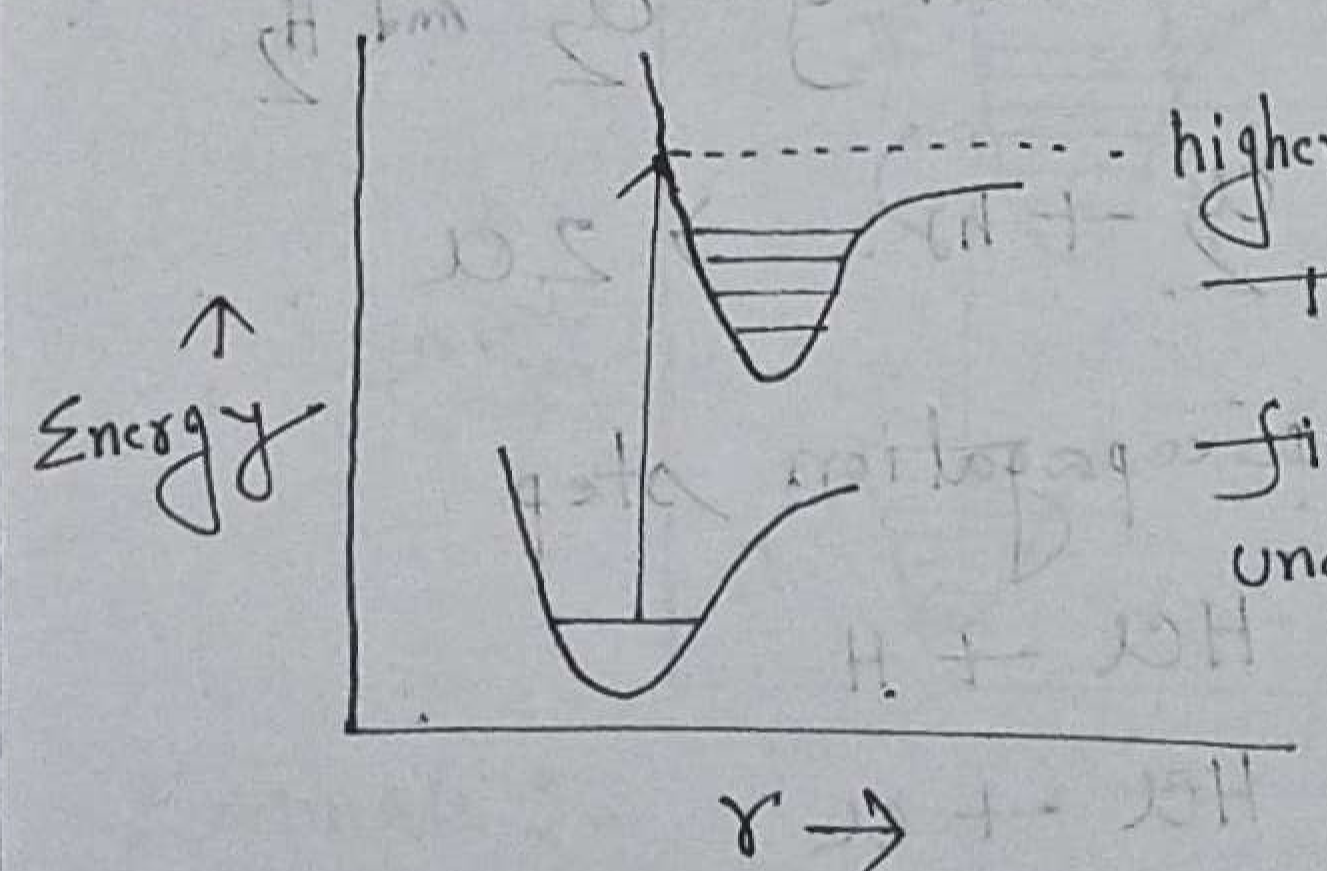
example: Decomposition of oxalic acid by UO_2^{++} ion:

$UO_2^{++} + h\nu \rightarrow UO_2^{+2*}$

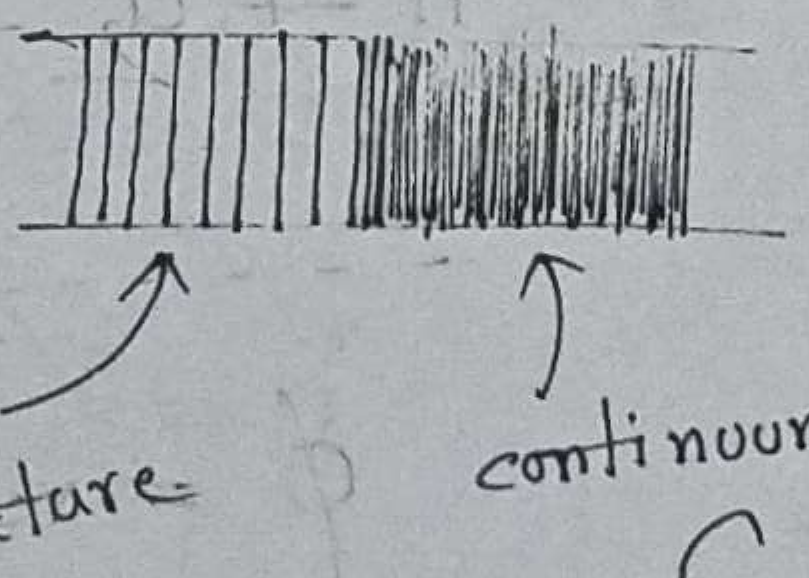
$UO_2^{+2*} + \begin{matrix}CO_2H\\|\\CO_2H\end{matrix} \rightarrow UO_2^{+2} + CO + CO_2 + H_2O$

↓ Photo sensitiser.

Type —(III)



The molecule in its first oscillation will undergoes dissociation.



ⓐ Thermal chemical reaction

Primary step: $HI + h\nu \rightarrow H + I$

(Light absorbing step)

Secondary thermal process:

$H + HI \rightarrow H_2 + I$

$I + I \rightarrow I_2$

$\phi = 2.$

ⓑ chain reaction

Photo chemical reaction of Cl_2 and H_2

Primary step: $Cl_2 + h\nu \rightarrow 2Cl$

Secondary chain propagation step

$Cl + H_2 \rightarrow HCl + H$

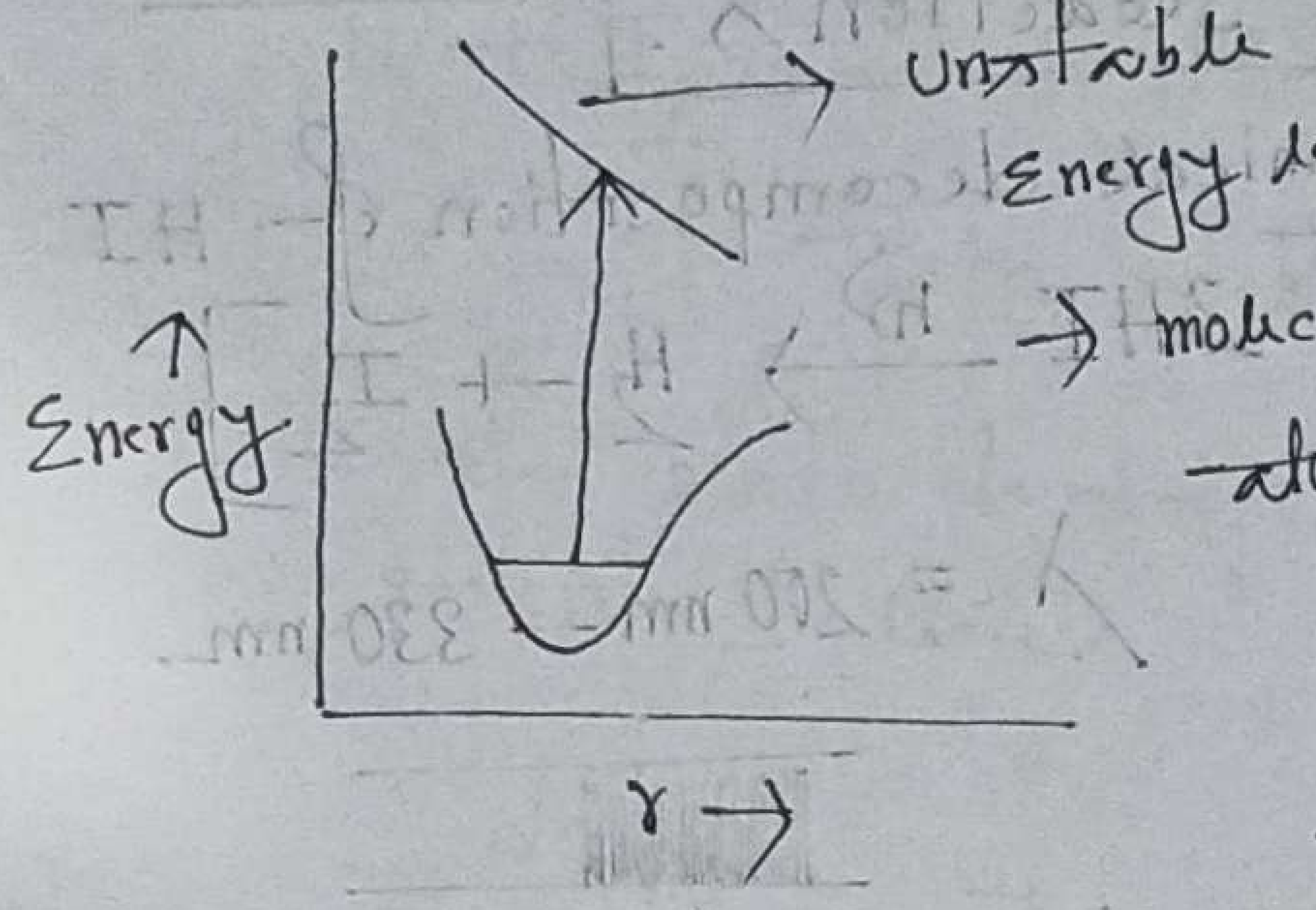
$H + Cl_2 \rightarrow HCl + Cl$

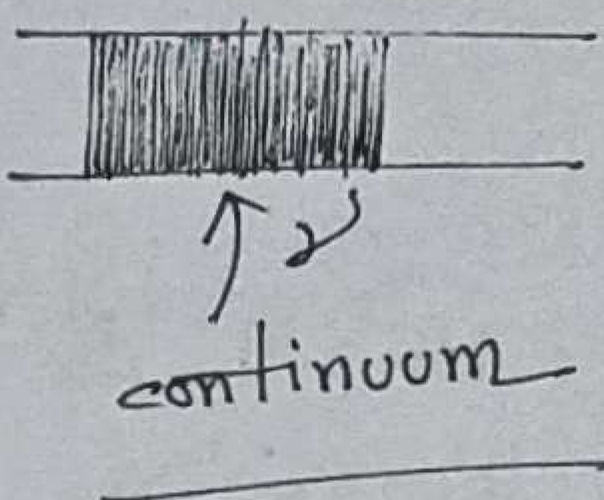
- - - - - - - - - - - - -

- - - - - - - - - - - - -

ϕ = very high

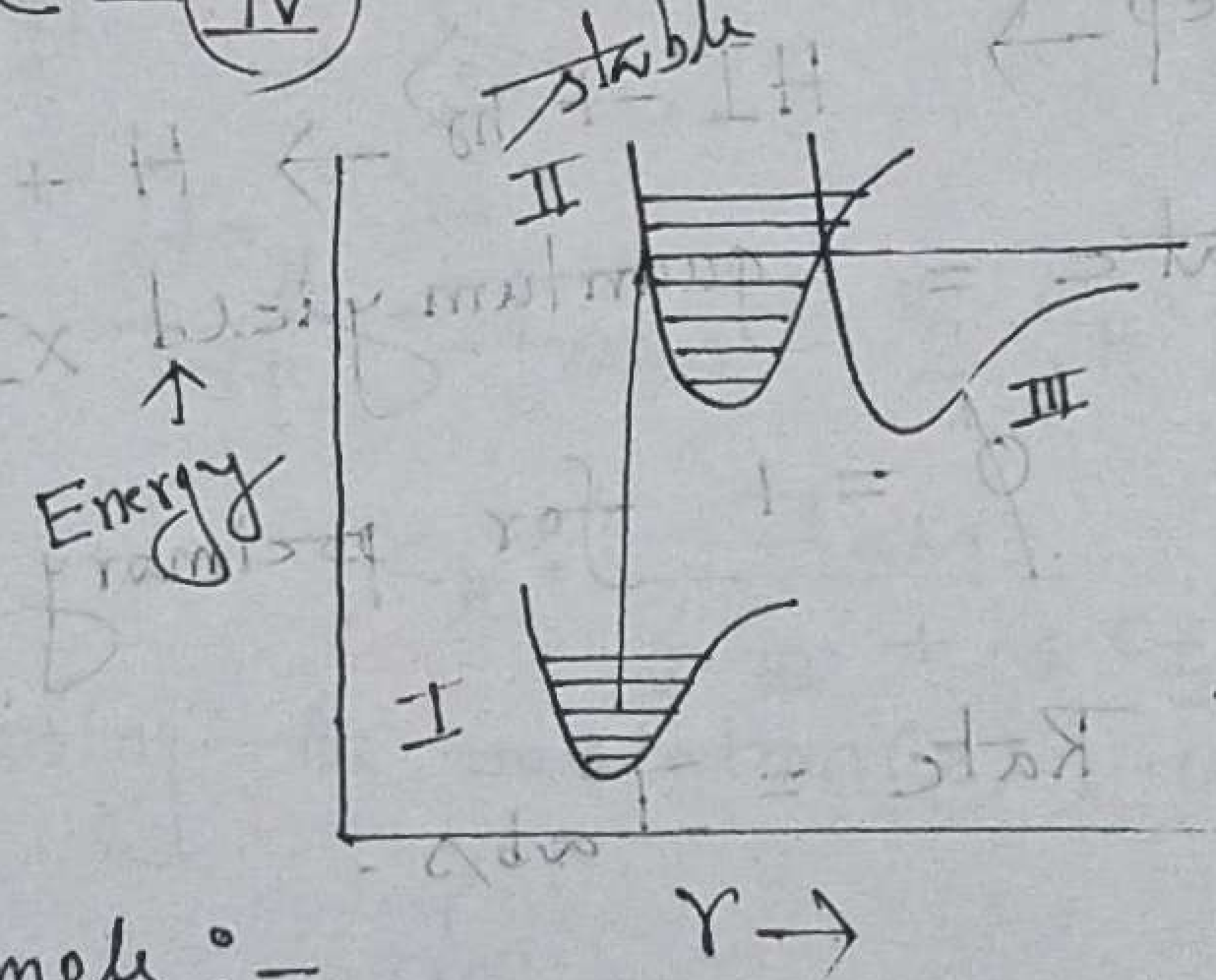
Type – ⟨III⟩

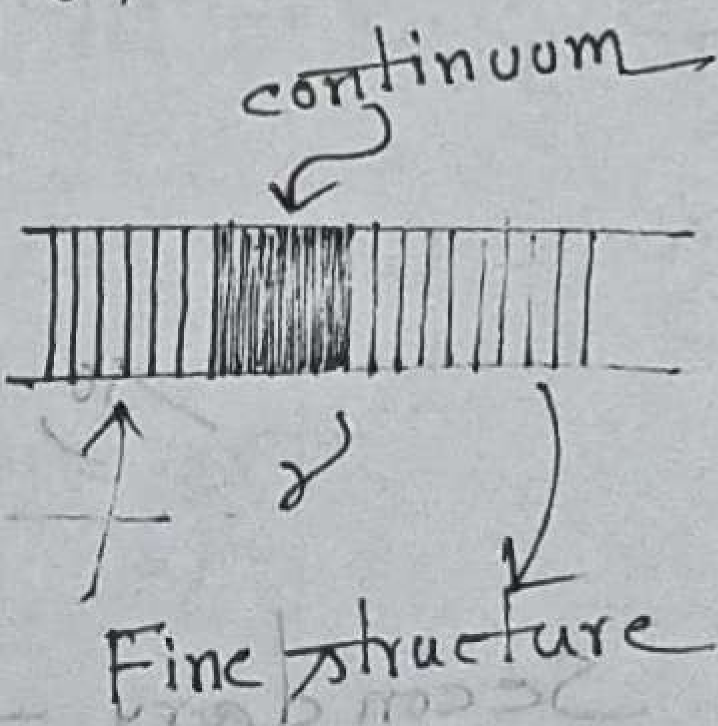




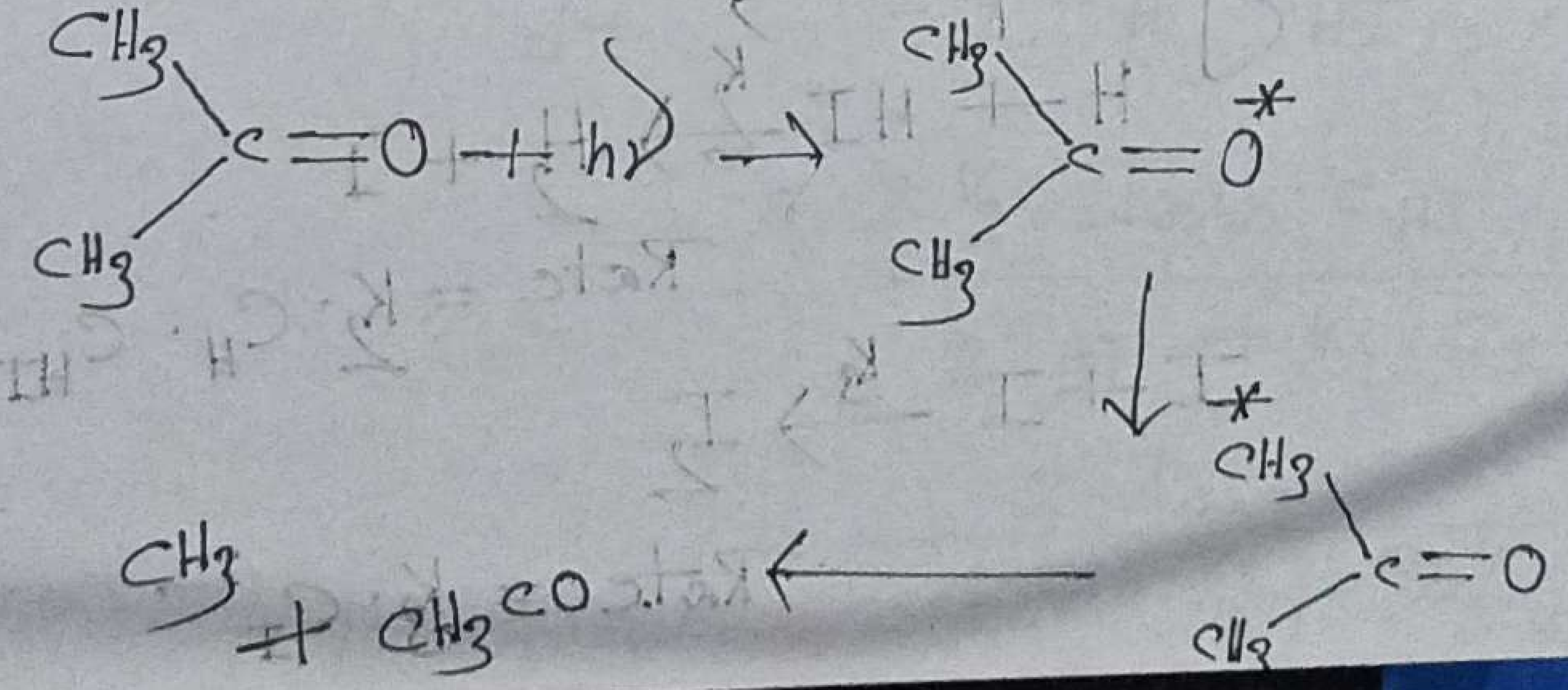
The secondary steps similar to type – ⑪.

Type – (IV)





Example :-

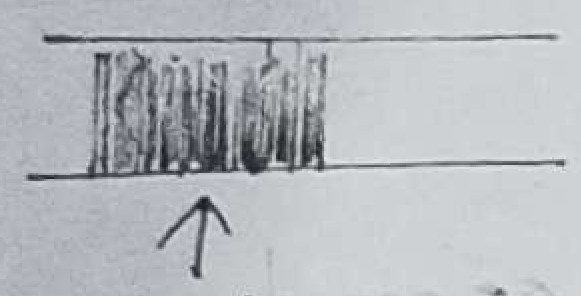


Some typical photo chemical reactions.

1) Photo chemical decomposition of HI

$$\left[2HI \xrightarrow{h\nu} H_2 + I_2\right]$$

λ = 200 nm — 330 nm



continuum
200 nm — 330 nm.

Decompⁿ study (282 nm and 253 nm)

Primary step → $HI + h\nu \rightarrow H + I$

Rate = quantum yield × $I_{abs.}$

$\phi = 1$ for primary step.

so, Rate = I_{abs}.

Secondary steps →

$$H + HI \xrightarrow{K_2} H_2 + I$$

Rate = $K_2 \cdot C_H \cdot C_{HI}$

$$I + I \xrightarrow{K_3} I_2$$

Rate = $K_3 \cdot C_I^2$

Inhibition steps

$$H + I_2 \xrightarrow{K_4} HI + I$$

Rate = $K_4 \cdot C_H \cdot C_{I_2}$

Rate of photo decomposition of HI is given bellow

$$\frac{dC_{HI}}{dt} = I_{abs} + K_2 \cdot C_H \cdot C_{HI} - K_4 \cdot C_H \cdot C_{I_2} \quad \cdots ①$$

using steady state approximation of H atom and we get,

$$\frac{dC_H}{dt} = I_{abs} - K_2 \cdot C_H \cdot C_{HI} - K_4 \cdot C_H \cdot C_{I_2}$$

$$C_H = \frac{I_{abs}}{K_2 C_{HI} + K_4 \cdot C_{I_2}} \qquad = 0 \cdots ②$$

using the relation (2), we get

$$-\frac{dC_{HI}}{dt} = 2K_2 \cdot C_H \cdot C_{HI}$$

$$= \frac{2K_2 \cdot I_{abs} \cdot C_{HI}}{K_2 C_{HI} + K_4 \cdot C_{I_2}}$$

$$= \frac{2 \cdot I_{abs}}{1 + \left(\frac{K_4}{K_2}\right) \cdot C_{I_2}/C_{HI}} \cdots ④$$

We know, the quantum yeild (ϕ) of the process,

$$\phi = \frac{(-dc_{HI}/dt)}{I_{abs}}$$

$$= \frac{2}{1+\left(\frac{K_4}{K_2}\right)\cdot C_{I_2}/C_{HI}}$$

at the Initial stage of reaction, C_{I_2}/C_{HI} = small

So, $\phi = 2$

But at the latter stage of the reaction, C_{I_2}/C_{HI} = not small/ not negligible

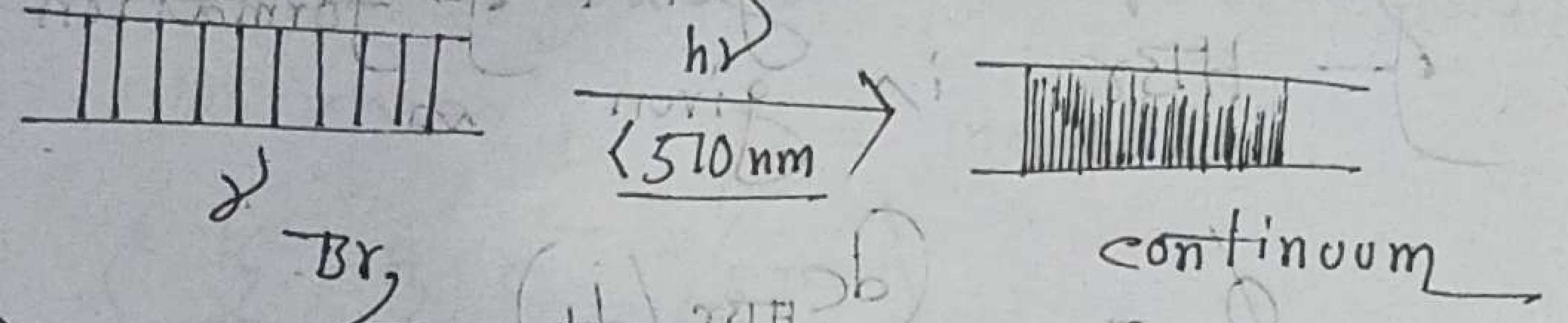
So, $\phi < 2$

—o—

Photochemical combination of H_2 and Br_2

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

λ = Less than 510 nm.



→ Primary step

$Br_2 + h\nu \rightarrow 2Br^{\cdot}$; Rate = I_{abs}.

Secondary step → ⟨$\phi = 1$⟩

ⓐ $Br + H_2 \xrightarrow{K_2} HBr + H$
Rate = $K_2 \cdot C_{Br} \cdot C_{H_2}$

ⓑ $H + Br_2 \xrightarrow{K_3} HBr + Br$
Rate = $K_3 \cdot C_H \cdot C_{Br_2}$

ⓒ $H + HBr \xrightarrow{K_4} H_2 + Br$
Rate = $K_4 \cdot C_H \cdot C_{HBr}$

ⓓ $Br + Br \xrightarrow{K_5} Br_2$
Rate = $K_5 \cdot C_{Br}^2$

The rate of formation of HBr

$$\frac{dC_{HBr}}{dt} = \frac{2K_2\left(\frac{2I_{abs}}{K_5}\right)^{1/2} \cdot C_{H_2}}{1+\left[\left(K_4/K_3\right)\cdot \frac{C_{HBr}}{C_{Br_2}}\right]}$$

The quantum yeild of formation of HBr is given as

$$\phi = \frac{(dC_{HBr}/dt)}{I_{abs}}$$

$$= \frac{1}{\sqrt{I_{abs}}} \cdot \frac{2K_2\cdot(2/K_5)^{1/2}\cdot C_{H_2}}{1+\left[\left(\frac{K_4}{K_3}\right)\cdot\frac{C_{HBr}}{C_{Br_2}}\right]}$$

i) $\frac{dC_{HBr}}{dt} \propto (I_{abs})^{1/2}$

ii) $\phi = 0.01$ (Photo synthesis of HBr at low/ordinary tempr.)

<u>Chain mechanism</u>

Q. ϕ = Low ?

$Br + H_2 \xrightarrow{K_2} HBr + H$ ⟨2ndary step⟩

soln $E_a = 18$ Kcal/mole.

= high_ value

$Br + Br \xrightarrow{K_5} Br_2$

This reaction happend and ϕ = Low.

But when:

Tempr increases

The rate of the step, $Br + H_2 \xrightarrow{K_2} HBr + H$, increases, ϕ = increases.

⟨ $K_2 = A_2 \cdot e^{-E_2/RT}$ ⟩

iii) intensity of radiation increase

$Br + Br \longrightarrow Br_2$

$\xrightarrow{\times}$ Chain reaction

ϕ = decreases.

Photo synthesis of Hydrogen chloride

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

$\lambda < 480$ nm

Primary step: $Cl_2 + h\nu \rightarrow 2Cl$

Rate = I_{abs} , $\phi = 1$

Secondary steps:

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

Rate $= k_2 \cdot C_{Cl} \cdot C_{H_2}$

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

Rate $= k_3 \cdot C_H \cdot C_{Cl_2}$

$Cl + \text{wall} \xrightarrow{K_4} \text{Destruction}$

Rate $= K_4 \cdot C_{Cl}$

Rate of formation of HCl,

$$\frac{dC_{HCl}}{dt} = k_2 \cdot C_{Cl} \cdot C_{H_2} + k_3 \cdot C_H \cdot C_{Cl_2}$$

Applying steady state condition for conc of H and Cl, we have

$$\frac{dC_H}{dt} = k_2 \cdot C_{Cl} \cdot C_{H_2} - k_3 \cdot C_H \cdot C_{Cl_2} = 0 \quad ..(A)$$

And

$$\frac{dC_{Cl}}{dt} = 2I_{abs} - k_2 \cdot C_{Cl} \cdot C_{H_2} + k_3 \cdot C_H \cdot C_{Cl_2} - K_4 \cdot C_{Cl} = 0 \quad ......(B)$$

Adding these above two equation and we get,

$$2I_{abs} - K_4 \cdot C_{Cl} = 0$$

or, $$C_{Cl} = \frac{2I_{abs}}{K_4} \quad ......(C)$$

From the equation (A), we get

$$\frac{dC_H}{dt} = k_2 \cdot C_{Cl} \cdot C_{H_2} - k_3 \cdot C_H \cdot C_{Cl_2} = 0$$

so, $$k_2 \cdot C_{Cl} \cdot C_{H_2} = k_3 \cdot C_H \cdot C_{Cl_2}$$

Thus, $$\frac{dC_{HCl}}{dt} = 2 \cdot k_2 \cdot C_{Cl} \cdot C_{H_2}$$

Putting the value of C_{Cl} from the equation (C).

we get, $$\frac{dC_{HCl}}{dt} = 2k_2 \times \left(\frac{2I_{abs}}{K_4}\right) \times C_{H_2}$$

$$= \left(\frac{4k_2}{K_4}\right) \cdot I_{abs} \cdot C_{H_2}$$

$$\phi = \left(dC_{HCl}/dt\right) / I_{abs}$$

$$\phi = \left(\frac{4k_2}{K_4}\right) \cdot C_{H_2}$$

rate $\propto I_{abs}$

$\propto C_{H_2}$

i) But when the chain termination step is the gas phase recombination of Cl-atoms with a third body,

$$Cl + Cl + M \xrightarrow{K_5} Cl_2 \; (M)$$

$$\frac{dC_{HCl}}{dt} = 2K_2 \cdot C_{H_2} \cdot \left(\frac{2 I_{abs}}{K_5 \cdot C_m} \right)$$

ii) a small amount of oxygen is present in the reaction mixture, the main chain termination step becomes,

$$H + O_2 \rightarrow HO_2$$

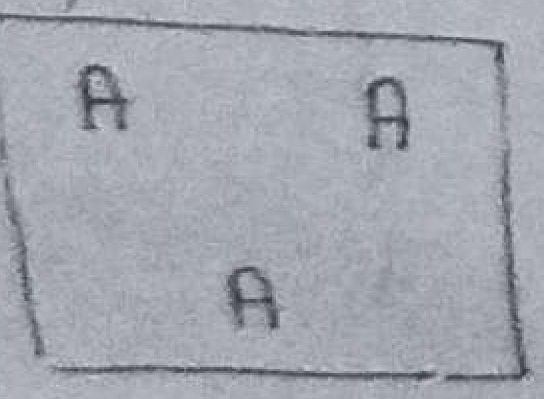
$$\frac{dC_{HCl}}{dt} = K \cdot \frac{I_{abs}}{C_{O_2}} \cdot C_{Cl_2}$$

Photo Dimerisation of Anthracene

$$2A \xrightarrow{h\nu} A_2$$

in Benzine solution

i) When C_A is low:



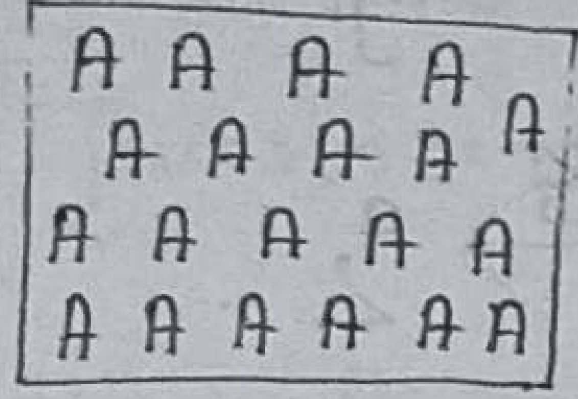
Chance of collision of A^* with A → very small.

— Life-time of A^* 10^{-8} sec

— The excited energy are emitted in the form of fluorescence

ψ = high

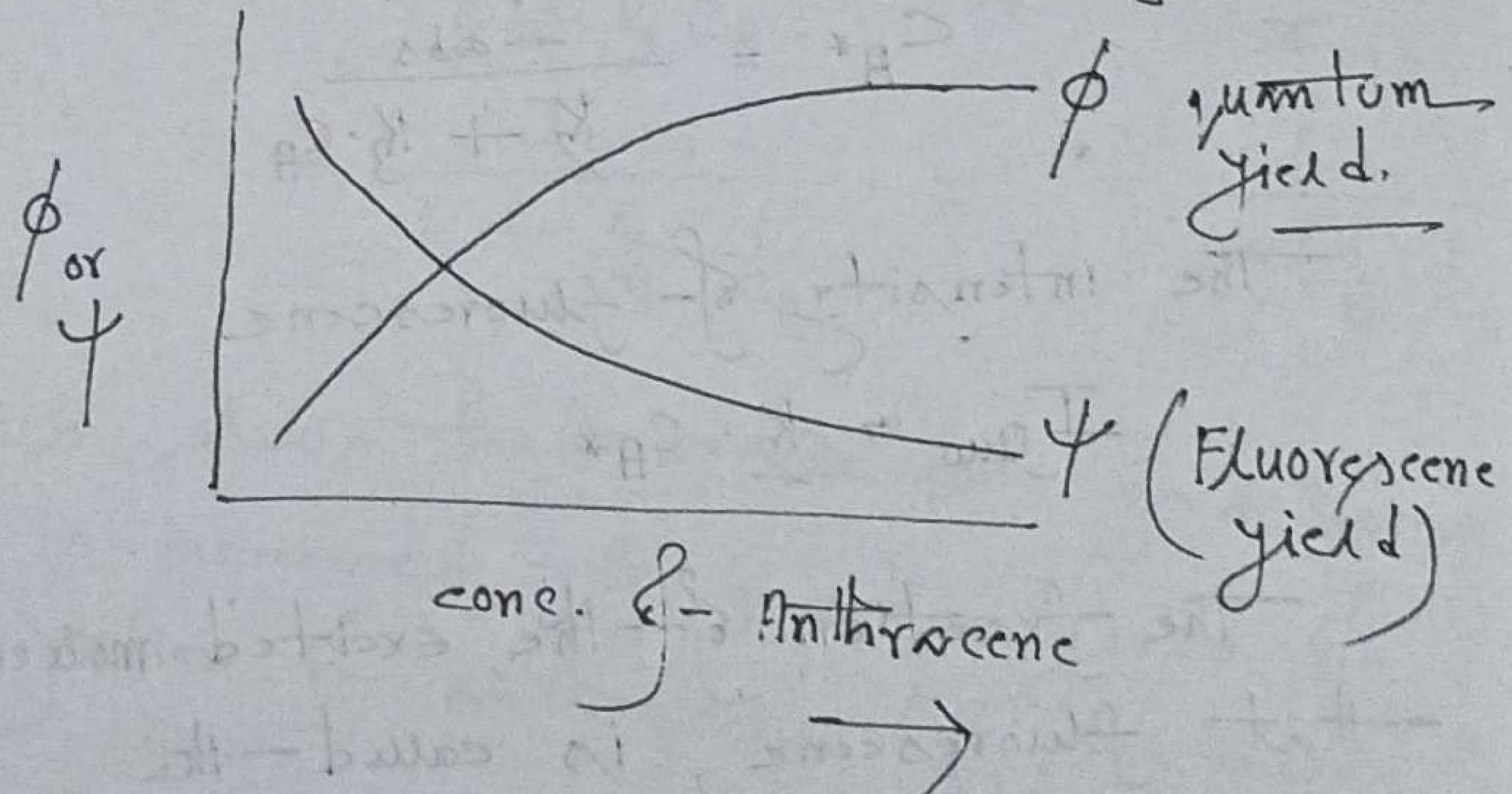
ii) When C_A is high



— chance of collision of A^* with A — increases

— formation of dimer increases

so, ϕ = high



~~Absorption Phenomena~~

Proposed mechanism of the process.

Absorption step / primary step:

$$A + h\nu \longrightarrow A^* \text{ (excited-state)}$$

Fluorescene step : $A^* \xrightarrow{k_2} A + h\nu_f$

quenching step
or Dimerization step $A^* + A \xrightarrow{k_3} A_2$

Appling the steady state for A^*

$$\frac{dc_{A^*}}{dt} = I_{abs} - k_2 \cdot c_{A^*} - k_3 \cdot c_{A^*} \, c_A = 0$$

$$c_{A^*} = \frac{I_{abs}}{k_2 + k_3 \cdot c_A}$$

The intensity of fluorescene

$$I_{fluo} = k_2 \cdot c_{A^*}$$

The fraction of the excited molecules that fluorescene, is called the fluorescence yield (ψ).

$$\psi = \frac{I_{fluo}}{I_{abs}}$$

$$\psi = \frac{k_2 \cdot c_{A^*}}{(k_2 + k_3 \cdot c_A) \, c_{A^*}}$$

$$= \frac{1}{1 + \left(\frac{k_3}{k_2}\right) \cdot c_A}$$

This shows that as the conc. of anthracene (c_A) is increased, fluorescence yield (ψ) is decreased.

Again, the rate of dimerization

$$\frac{dc_{A_2}}{dt} = k_3 \cdot c_{A^*} \cdot c_A$$

$$= \frac{k_3 \cdot c_A \cdot I_{abs}}{k_2 + k_3 c_A} \qquad \phi = \frac{(dc_{A_2}/dt)}{I_{abs}}$$

$$= \frac{I_{abs}}{1 + \frac{k_2}{k_3} \cdot \frac{1}{c_A}} \qquad = \frac{1}{1 + \left(\frac{k_2}{k_3}\right)/c_A}$$

This shows that as the conc. of anthracene (c_A) is increased, the quantum yield of dimerization of anthracene (ϕ) increases.

When c_A is very large, $\phi \rightarrow 1$

Photo chemical Equilibrium or photo-stationary state.

If either or both the reactions of a reversible chemical change are sensitive to light, a photo chemical equil^m or photo-stationary state will be developed when the rates of the forward and back-ward reactions are equal.

Examples: Dimerisation of Anthracene ($C_{14}H_{10}$) in benzene solution with UV-Light.

$$2\cdot C_{14}H_{10} \underset{\text{thermal}}{\overset{\text{Light}}{\rightleftharpoons}} (C_{14}H_{10})_2$$

Rate of forward reaction ⇌ Rate of backward reaction

Thus at photo chemical equil^m,

$$I_{abs} = K\cdot C_{A_2}$$

or, $C_{A_2} = I_{abs}/K$

Dif. with ordinary thermal equil^m

1) In photochemical equil^m, conc of the dimer is independent of the conc of the monomer. But in thermal equil^m, conc. of dimer, $C_{A_2} = K\cdot C_A^2$, where K is equil^m const of the reaction.

2) If the source of the light is removed, Photo chemical equil^m is disturbed and change into thermal equil^m.

3) photo chemical equil^m is almost unaffected by the change of tempr of the system but thermal equil^m is sensitive to tempr change.

* $2SO_2 + O_2 \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} 2SO_3$

* UV-Light

* Depends on the intensity and wavelength of the light absorbed.

Photo sensitisation reactions :-

Reactant ⟶ not sensitive to the Light — No absorption of Light

↓ + small amount of foreign substance

Reaction starts.

Why this is happend :-

Foreign substance $\xrightarrow{h\nu}$ Foreign substance* (excited state)

↓

This is known as photo-sensitizer.

$\xrightarrow{E}$ Reactant

↓

Reaction starts (dissociation)

Similarity with catalyst :

i) like catalyst, photosensitiser remains unchanged after the reaction.

Difference with catalyst.

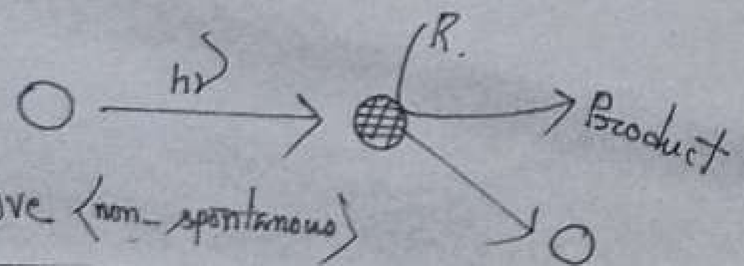
ii) It induces the change of other substances.

R ⟶ P

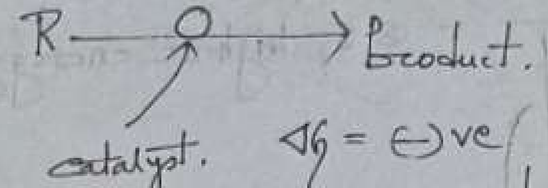
ΔG = (−)ve
spont.

or,

ΔG = (+)ve ⟨non-spontaneous⟩



in case of catalyst :



ΔG = (−)ve only in case of spont. reaction — catalyst can do.

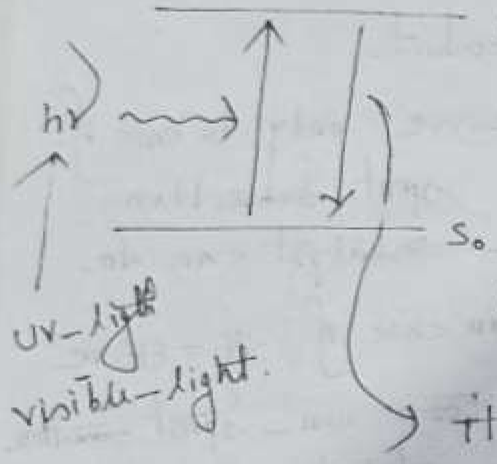
But in case of ΔG = (+)ve For non-spont. reaction — catalyst can not do any thing.

Example :—

$$UO_2^{+2} + h\nu \rightarrow UO_2^{+2*} \langle \text{Excited} \rangle$$

$$UO_2^{+2*} + \begin{array}{c} CO_2H \\ | \\ CO_2H \end{array} \rightarrow UO_2^{+2} + CO + CO_2 + H_2O .$$

Primary Photophysical process.



E.S / highest energy state

G.S / ground energy state

It return to its ground electronic state by dif: photo-physical process.

— — — — — — — — — — —.

Singlet state (S) and Triplet state (T)

These two terms represent the multiplicity of the spin vector (J) and is equal to $J = 2S+1$

S = total spin quantum number
$= s_1 + s_2$

$\boxed{i}$ For arrangement of opposite spins

$s_1 = \frac{1}{2}$, $s_2 = -\frac{1}{2}$, $S = \frac{1}{2} - \frac{1}{2} = 0$

so, $J = 2 \times 0 + 1 = 1$

Singlet state.

$\boxed{ii}$ For an arrangement of two parallel spins, the value of $S = s_1 + s_2$
$= \frac{1}{2} + \frac{1}{2}$
$= 1$

Thus the spin multiplicity $= 2S+1$
$= 2 \times 1 + 1$
$= 3.$

Triplet state.

Jablonsky – Potential energy diagram

Let the system in initially in the ground state (S_0) with electrons in pair (in ground singlet state). Absorption of one quantum radiation unpairs of electrons and promote to an excited electronic state (first excited singlet state S_1^{ν}). The vertical axis measures the energy of the system. Radiative transitions are indicated by solid lines while non-radiative transitions by wavy-lines. Because of Franck–Condon principle, the molecule most likely be in excited vibrational level, collision with other molecules takes away this excess vibrational energy and comes to zero-vibrational level (v=0) of the excited singlet state (S_1).

Allowed electronic transition

Singlet → Singlet or
Triplet → Triplet.
Allowed transition.

Singlet → Triplet
Forbidden Transition.

internal conversion (IC)

The crossing over of the molecule from singlet to singlet or Triplet to Triplet is known as internal conversion (IC).

*
singlet → triplet or
Triplet → singlet
(ISC) inter system crossing