
WELCOME!

JABLONSKI DIAGRAM

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- ❖A molecule excited to higher energy state unless it gets involved in a photo chemical reaction and loses its identity.
- ❖There are more than one pathways available to the excited molecule for dissipation of excitational energy.

$$A + h\nu \rightarrow A'^{*}$$

Where A'^{*} is either an electronically excited molecule with excess vibrational energy in S_1 state or a molecule excited to higher singlet state S_2, S_3 etc..

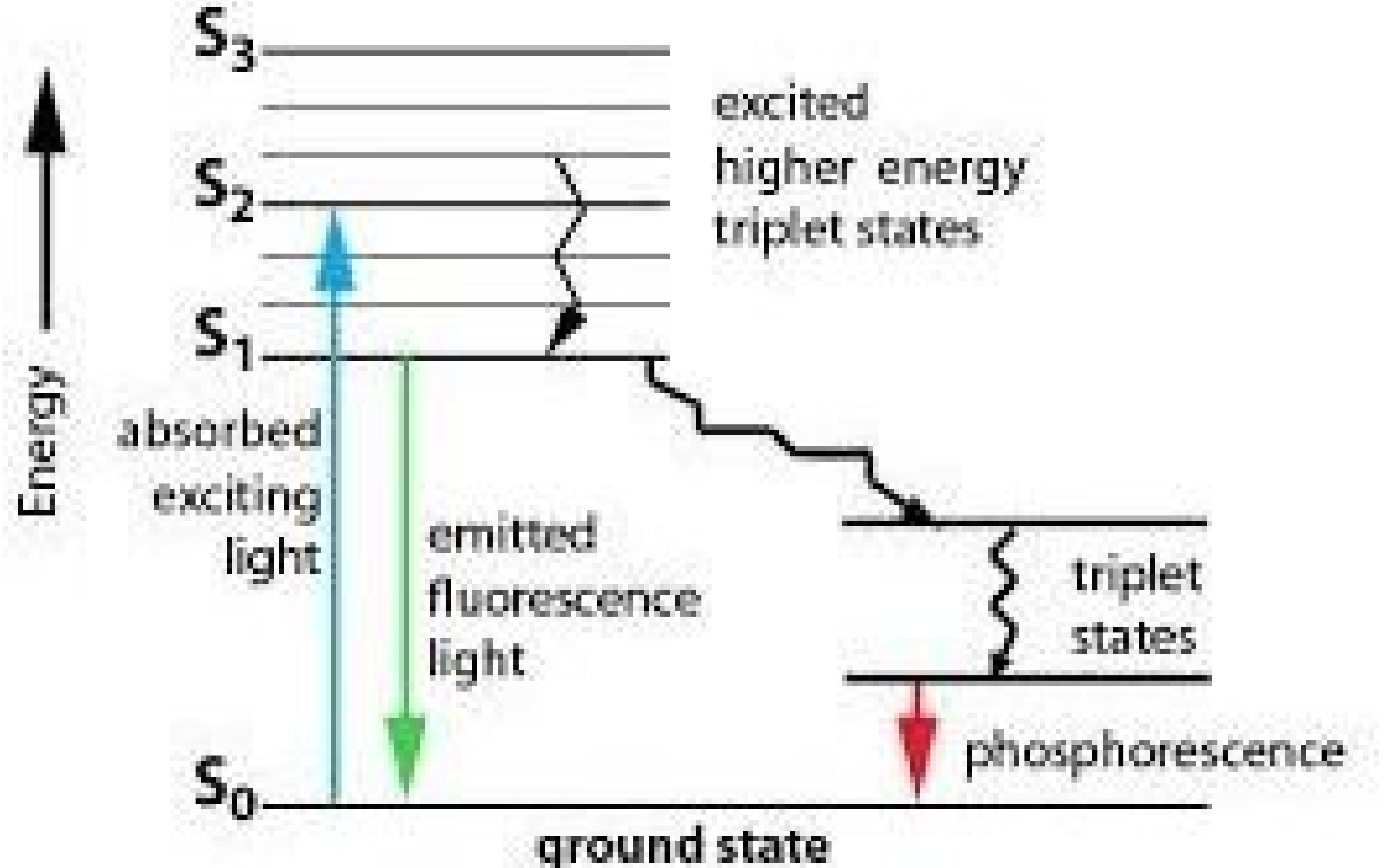
- The initial absorption may promote a molecule to higher energy states S_2, S_3 etc.. to higher vibrational levels of the S_1 state in time period 10^{-15} s ($k=10^{15}$ s^{-1}) obeying Frank-Condon Principle.

- The electronic energy of S_2, S_3 states or excess vibrational energy of S_1 state is quickly lost to the surroundings by a mechanism known as Internal Conversion (IC).

- The rate constant of internal conversion is ~10^{13}-10^{12} s^{-1}
- Inter system crossing (ISC) involves non radiative transition from singlet to triplet state

- Rate constant for ISC should also be 10^{12} s^{-1} but due to spin restriction factor, it varies from 10^{11} to10^{7} s^{-1}.

DIAGRAM:


S_3
S_2
S_1
S_0
Energy
excited higher energy triplet states
absorbed exciting light
emitted fluorescence light
triplet states
phosphorescence
ground state

The Quantum Yield of a photo chemical process is defined as

$$\varphi = \frac{\text{NO.of molecules that react}}{\text{No.of quanta of radiation absorbed}}$$

$$= \frac{\text{No. of moles that react}}{\text{No. of einstein of radiation absorbed}}$$

$$= \frac{\text{Rate of process}}{\text{Intensity of light absorbed}} = \frac{\gamma}{I_{abs}}$$

FLUROSCENCE EMISSION

- **Fluroscence emission is normally observed from the first excited singlet state of the molecule.**
- **The rate constant for Fluroscence emission k_f is defined as,**

$$K_f=1/\tau_N = 1/\tau_f^0$$

- **In the presence of other competitive deactivating processes, the average lifetime is much reduced and actual lifetime τ_f is**

$$\tau_f = 1/k_f+€k_t$$

- **Where $€k_t$ is the rate constant for the i^{th} competitive process assumed to be uni-molecular.**

The Quantum yield of Fluroscence Φ_f is defined as

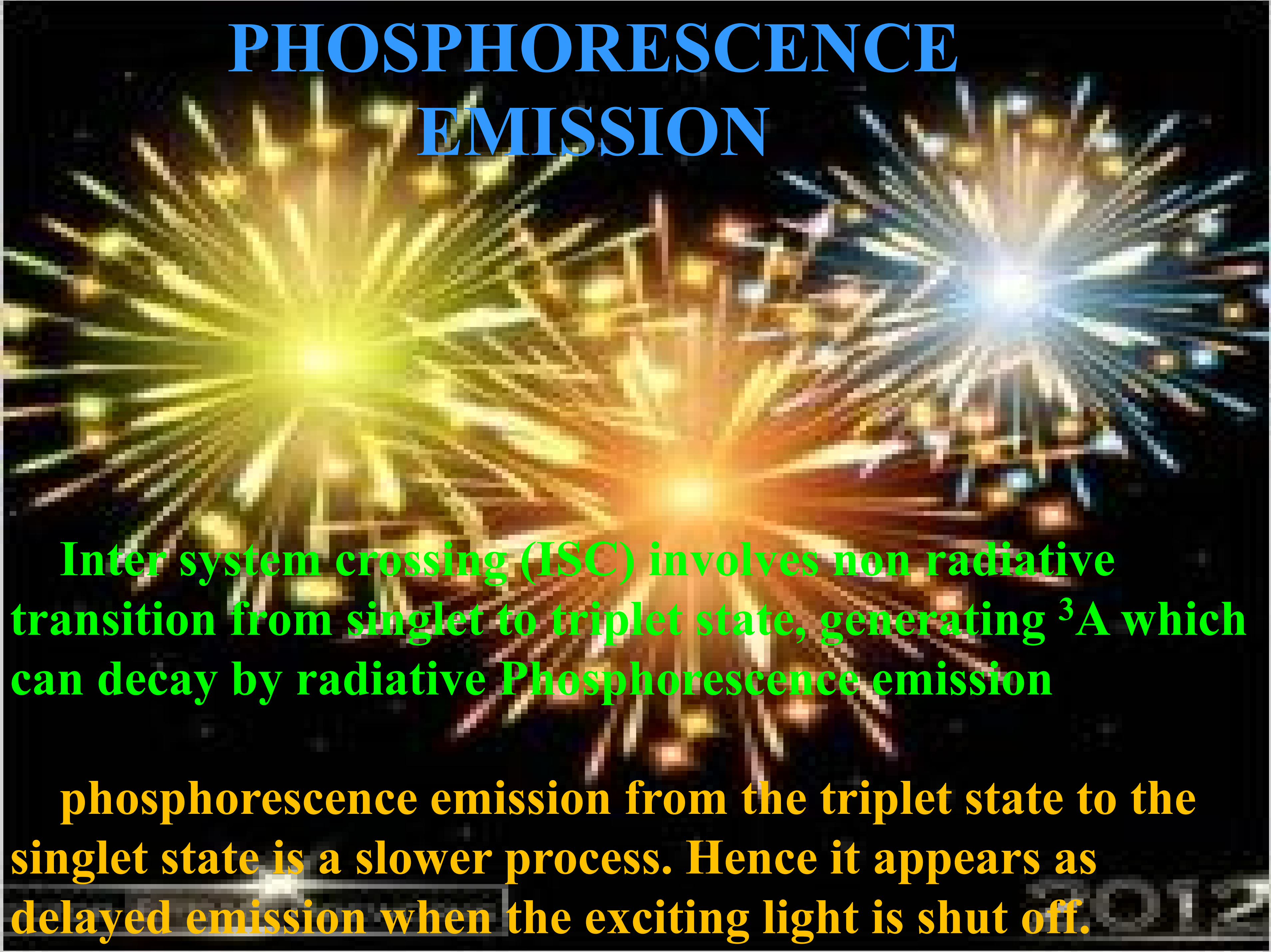
$$\varphi_f = \frac{No.of\ quanta\ emitted\ /s/cm^2}{No.of\ quanta\ absorbed/s\ \ /cm^2} = \frac{n_f(h\gamma_f)}{n_a(h\gamma_a)}$$

$$= \frac{Intensity\ of\ emission}{Intensity\ of\ absorption} = \frac{F\ einstein\ s^{-1}cm^{-2}}{I_a einstein\ s^{-1}cm^{-2}}$$

$$= \frac{rate\ of\ emission}{rate\ of\ absorption} = \frac{k_f[s_1]}{I_a}$$

S_1 is the concentration of the lowest excited singlet molecules. It is independent of the exciting wavelength except when chemical changes occur.

PHOSPHORESCENCE EMISSION



Inter system crossing (ISC) involves non radiative transition from singlet to triplet state, generating ^3A which can decay by radiative Phosphorescence emission

phosphorescence emission from the triplet state to the singlet state is a slower process. Hence it appears as delayed emission when the exciting light is shut off.

The quantum yield of Φ_p is defined as

$$\varphi_p = \frac{T_1 \rightarrow s_0\,\text{transition}}{\text{Number per second of quanta absorbed ins}_1 \leftarrow s_0\,\text{transition}}$$

$$= \frac{\text{rate of phophorescence}}{\text{rate of absorption}} = \frac{k_p[T_1]}{I_a}$$

$$= \frac{\text{intensity of phophorescence emission}}{\text{intensity of absorption}}$$

$$= \frac{P\ \text{einstein}\ s^{-1}}{I_{a\ \text{einstein}\ s^{-1}}}$$

T_1 is the concentration of the triplet state.

Because of the forbidden nature of T_1 S_0 transition, T_1 is long lived and subjected to rapid collisional deactivation and thermal relaxation. As a result phosphorescence is not observed at room temperature except for a few cases. It is observed at low temperatures only in rigid glassy solutions.

The intrinsic lifetime of triplet T_1 state τ_p^0 is the reciprocal of the rate constant for phosphorescence emission and the actual lifetime τ_p is the reciprocal of the sum of all the steps which deactivate the triplet

$$\tau_p^o = \frac{1}{k_p} \qquad \tau_p = \frac{1}{k_p + k_{ISC}^T}$$

$$\frac{\tau_p}{\tau_p^0} = \frac{k_p}{k_p + k_{ISC}^T} = \frac{k_p / I_a}{k_p + k_{ISC}^T / I_a} = \frac{\varphi_p}{\varphi_T}$$

Where k^T_{ISC} is the rate constant for inter system crossing from triplet to ground state. ϕ_p and ϕ_T are quantum efficiencies of phosphorescence emission and triplet formation respectively.

ϕ_T is identical with ISC efficiency ϕ_{ISC} assuming that all the molecules which do not fluoresce are transferred to the triplet state.

The phosphorescence lifetimes may vary from 10 s to more than a second


Thank you