PHYSICAL CHEMISTRY

PHOTOCHEMISTRY

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CONTENTS

Photochemical reactions are of great importance to life on Earth. Nature has made tremendous use of radiations. For example, some chemical changes taking place in atmospheric gases are initiated by radiations and modified by the suspended particles. These are very useful for the support of life. The formation of complex organic molecules, which act as precursor of life and then emergence of life itself, from the simplest elements are very intimately connected to photochemical reactions. Formation of carbohydrates and liberation of oxygen in the atmosphere from carbon dioxide and water is another useful application of harvesting Sun's energy. One of the most important senses, for Man and many other species besides, is vision, which is also photochemical in origin. It is not only the nature which has utilized radiations man has also tried to harness it for his utility. The applications are ranging from the synthesis of new and complex organic species through various kinds of imaging and photographic processes to gathering and storage of solar energy, lasers and laser technology etc.

Chemistry by itself is of great interest at the most fundamental level and thus photochemistry does not only involve the science of applications, either by Nature or Mankind, but involves the understanding of many chemical reactions, like dissociations, isomerizations and optical emissions from many electronically excited states. Further, species in these excited states possess higher energies and different electronic structures in comparison to ground state. The interactions of radiation with atoms or molecules open up new and interesting areas. In other words studying photochemistry is as challenging as studying chemistry by itself and these interests are different for different chemists. The

physical chemists are more interested in studying the detailed dynamics of photodissociation process and the progress of these changes on a time scale of picoseconds. On the other hand, interest of organic chemists lie in better understanding of the relationships between reactivity and electronic and molecular structure through these photochemical reactions.

In general the photochemical reactions involve a number of questions. Few of them, which are very fundamental, are:

(i). What is the detailed fate of the excitation energy pumped into a molecule during excitation?
(ii). What is the chemical nature of the various electronically excited states?
(iii). From the knowledge of the answers to questions 1 and 2, how can one predict the course of a chemical reaction?

From above observations it is clear that it is not easy to summarize all the processes for the understanding of photochemical processes in one unit. In this unit we shall give a brief summary of the terms involved in the photophysical processes by which the electronically excited molecules lose their energy and return to the ground state. At the end some typical photochemical reactions and their applications will be discussed in brief.

Difference between Thermal and Photochemical Reactions

Photochemical reactions take place on the absorption of radiations (photons) by molecules, whereas thermal reactions are initiated by the absorption of heat energy, manifested by an increase of temperature. The former reactions also include the study of reverse processes in which the energy of the chemical reaction is emitted as radiation. Thermal reactions differ from photochemical reactions in number of ways.

(1). Thermal activation takes place by collision between the reactive species with itself or with other reactants or even with vessel containing the reaction mixture. There is no way of controlling the energies of the colliding molecules and thermal energy may be distributed among all the modes of excitation in the species. In a molecule these modes include translational, rotational and vibrational excitations. The electronic excitation mode can be excited but its population at room temperature will be negligibly small and can be confirmed from the Boltzmann's distribution, i. e. if n_1 and n_2 are the population of the molecules in the ground and first excited singlet state populated by the 500 nm photon (corresponds to energy commonly used in chemical reactions) the population ratio in these two non-degenerate states is given by the equation

$$n_2 / n_1 = \exp(-\Delta E/RT)$$

where $\Delta E = N_{av} h \nu = N_{av} h c/\lambda$, where N_{av} is Avogadro's number, h is Planck's constant and ν (or λ) is frequency (or wavelength) of the photon.

$$\Delta E = (6.02\times10^{23}) (6.626\times10^{-34} \text{ J s}) (3\times10^{8} \text{ m s}^{-1})/ 500\times10^{-9} \text{ m})$$

$= 238.3 \text{ kJ mol}^{-1}$

$n_2 / n_1 = \exp(-238.3 \times 1000 / 8.314 \times 298) = 2.66 \times 10^{-42}$

The same calculations suggest that to have 1% population in the above excited state one needs 6260 K. Normal experience suggests that all the molecules would undergo rapid decomposition at this temperature in the ground state. Whereas in a photochemical reaction molecules can be excited electronically, using 500 nm radiation at room temperature. The concentration of the molecules produced in the excited state depends up on a number of factors, e. g. intensity of the radiation source and rate of decrease of excited molecules by many competing processes (discussed later). Further a particular species can be excited in the presence of large number of other molecules which do not absorb radiation in the same region. If this energy is used in the bond rupture of the molecule, the chemical reactions can take place.

(2). In most of the chemical reactions, the activation energy observed in the ground electronic state is nearly of the same magnitude as used in the electronic excitation process. If it is assumed that the electronic excitation energy is used partly or completely to overcome the activation energy, then it may be expected that the electronically excited molecules will react much faster at room temperature than the molecules in the ground state.

Thus the photochemical reactions can be distinguished from thermal reactions, firstly by relatively large concentrations of highly excited species, which may react faster than the ground state species and may even participate isothermally in the processes that are endothermic for the latter and secondly, the electronic excitation may lead to the new electronic configuration of the molecule (for example cis-trans isomerization).

(3). Thermal reactions take place mainly in the rotationally-vibrationally excited states while remaining in the ground electronic state. The energy is distributed between molecules according to the Maxwell-Boltzmann's distribution law (In the molecular beam reactions the reactions can be mono-energetic, but such studies are very recent and involve sophisticated methods). In photochemical reaction energy can be located in any one particular quantum state and hence a particular bond can be broken in a molecule if it absorbs mono-chromatic radiation of an appropriate frequency. The energy of absorption is given by the well known Bohr's relation: $\Delta E = h \nu$.

(4). Pyrolysis of complex molecules leads to large number of free radicals and molecular fragments with Maxwell-Boltzmann's distribution of energies. These free radicals at high temperatures are highly reactive and short lived and hence have a very low concentration. Photochemically, with selection of a proper wavelength, a selective bond rupture can be achieved even at low temperature with large concentrations.

Absorption of Radiation

It is well known that a particular molecule absorbs radiation of certain wavelengths or frequencies. The frequency (ν) of radiation photon absorbed by a molecule is given by Bohr's frequency rule:

$$\nu = \frac{E_2 - E_1}{h} \qquad (1)$$

where E_2 and E_1 are the energies of the final and the initial states respectively. The energy absorbed is generally expressed in terms of '*Einstein*'. *This corresponds to the amount of energy of one mole of photons of a given frequency absorbed by the system*. Obviously, the value of the einstein depends on the frequency and can be calculated from Planck's relation. Thus:

$$\text{One einstein} = N_{av}\, h\, \nu = (N_{av}\, h\, c) / \lambda$$

$$= (6.626\text{x}10^{-34}\ \text{J s} \times 3\text{x}10^{8}\ \text{m s}^{-1} \times 6.02\text{x}10^{23}) / \lambda\text{x}10^{-9}\ \text{m}$$

$$= (119666 / \lambda)\ \text{J mol}^{-1} \qquad (2)$$

where λ is expressed in nm. The energy equivalent of einstein corresponding to various wavelengths is given in the Table 1. It can be seen that in ultraviolet and visible regions the energy is comparable to the bond energy in a large number of organic and inorganic molecules.

Table 1: Energy Conversion Table.

λ (nm)	ν (10^{14} Hz)	einstein (kJ mol^{-1})
200	15.0	598.3
250	12.0	478.6
300	10.0	398.9
400	7.5	299.2
500	6.0	239.3
600	5.0	199.5
700	4.286	170.9

Example 1: Calculate the energy of an einstein associated with a wavelength of 275 nm.

Using equation (2):

1 einstein = 119666 / λ kJ mol^{-1} and λ = 275 nm,

1. einstein = 119666 / 275 = 435.2 kJ mol^{-1}

Absorption Spectrum

Molecules in their ground electronic states, generally exist in their lowest vibrational level (i.e. v = 0, where v is the vibrational quantum number). When radiation is absorbed, the molecules are excited both electronically and vibrationally (molecules are also excited in their rotational states but since the rotational quantum is so small, especially in polyatomic molecules that it becomes difficult to resolve and thus are omitted). As a

result instead of single line a broad band is observed and the intensity distribution of the broad band is governed by Franck-Condon principle. Classically this principle states that "*the electronic excitation in a molecule occurs so rapidly (~ 10^{-15} s) that the nuclei retain their relative positions and velocity unchanged*", also known as *vertical transition*. In other words when an electron absorbs a photon of proper energy, it goes from lower quantum state to an upper quantum state. The time required in this absorption act (electronic excitation) is very small (i.e. 10^{-15} s) and thus the relative positions and velocities of the nuclei before and after the electronic transition are nearly same. Whereas according to quantum mechanics, the intensity distribution of each band is proportional to the square of the transition moment integral <M>, defined as:

$$\langle M \rangle = \int \Psi_{ini} \sum er_i \Psi_{fin} \, d\tau$$

Ψ_{ini} and Ψ_{fin} are the wave functions of the initial and final quantum states respectively and er_i is the electronic dipole moment operator. Transition is allowed if $\langle M \rangle \neq 0$ and not allowed (forbidden) if $\langle M \rangle = 0$. Due to this absorption transitions from any vibrational level of the ground electronic state to any vibrational level of the upper electronic state will be observed so long <M> is finite. Hence a number of transitions are observed. Since the value of each integral is different for different combination of initial and final quantum states, the intensity of each transition will be different. The probability of a transition between different vibrational levels is not equal and the intensity of the transition is represented by the height of the arrow in the spectra (Figure 1).

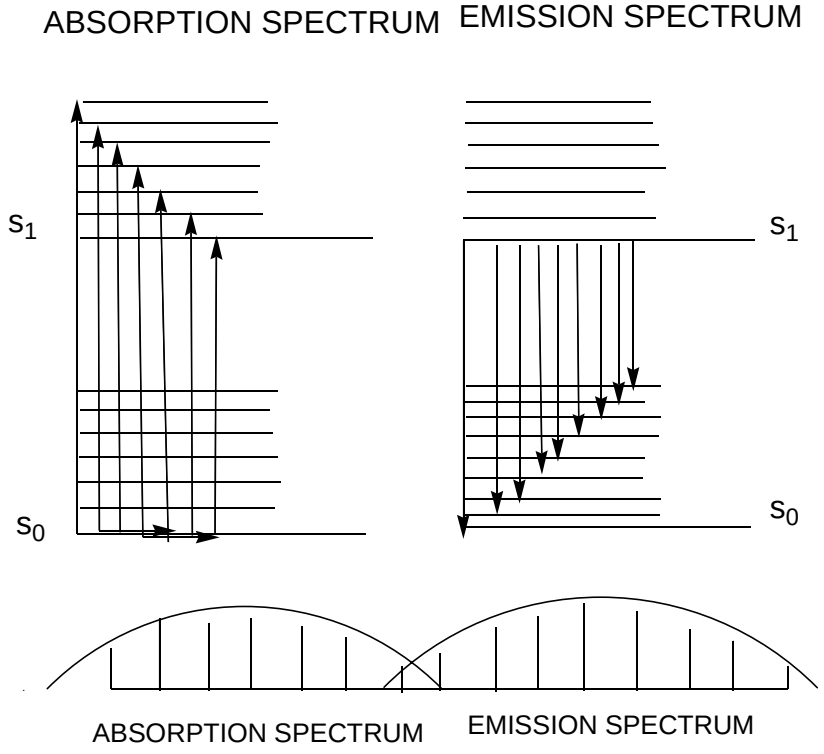


Figure 1: Absorption and emission spectrum and their vibrational distribution.

Every molecule possesses many electronic states or molecular orbitals (m. o.) and energy levels corresponding to each electronic state. The general classification depicts three

kinds of m. o.'s, i.e. σ, π and n (non-bonding), as shown in Figure 2. Figure 2 also depicts the two kinds of anti-bonding orbitals (σ^*, π^*) of energies larger than their respective bonding orbitals. Different types of transitions are observed when the electron is excited from different bonding or non-bonding m. o. and are broadly classified as: n π^*, n σ^*, π π^* σ σ^* etc. Observation of these transitions is governed by the selection rules, based on quantum mechanical expressions. In general n π^* and n σ^* are forbidden (or weak) transitions possessing molecular extinction coefficient of ~ 10- 10^2 cm^{-1} mol^{-1} cm^3. On the other hand σ σ^* and π π^* are very strong transitions, but in some cases these can be

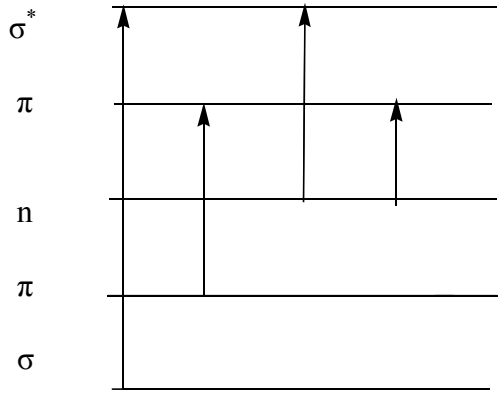


Figure 2: Molecular orbitals and their approximate energy levels. Arrows show different transitions which can be possible forbidden also. For example, the smallest energy (or longest wavelength) transition in benzene is forbidden based on symmetry selection rules, but becomes allowed if vibrational motion is also considered.

It is evident from Figure 2 that the energy gap between different m. o.'s are in order of ΔE (n π^*) < ΔE (π π^*) < ΔE (σ σ^*), i.e. λ_{max}, (n π_*) > λ_{max} (π π_*) > λ_{max} (σ σ_*). σ σ^* transition are generally observed in vacuum UV and are thus of no practical interest. Further normally available radiation sources do not contain photon of these frequencies. The wavelengths and intensities of these transitions are affected by the presence of different substituents on the parent molecules and sometimes reversal of n π^* and π π^* transitions can take place. For details about the electronic absorption spectrum, books on UV/Visible absorption spectrum can be considered.

Laws of Photochemistry

There are two laws of photochemistry:

Grotthus Drapper Law: Although the importance of radiations involved in many chemical or biological processes (for example, photo-fading of coloured materials, photosynthesis in plants, blackening of silver halides etc.) was well known but all the results used to be expressed qualitatively. It was only in 1817 that Grotthus and Drapper had formulated a law of photochemistry which stated that "**only the radiation absorbed by the system can be effective in producing the chemical change**" The radiation absorbed (I_{abs}) is given by:

$$I_a = I_0 - I \quad (3)$$

where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. These are related by the well known Beer-Lambert's law.

$$I = I_0 \exp(-\varepsilon' C l) \quad (4)$$

where 'C' is the concentration of the absorbing species in moles litre^{-1}, '*l*' is the path length in cm and ε' the natural molar extinction coefficient and is a function of the frequency of radiation. The SI units for C, *l* and ε' are mol dm^{-3}, mm and m^2 mol^{-1}. For historical purpose, the Lambert- Beer law is the combination of two laws, i. e. **Lambert law** which states that *the fraction of incident radiation absorbed by a transparent medium is independent of the intensity of the incident radiation and each successive layer of the medium absorbs an equal fraction of incident radiation,* whereas the **Beer's law** states that *the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation, that is the concentration 'C' of the absorbing species.* Combining the equations (3) and (4)

$$I_a = I_0 - I = I_0 - I_0 \exp(-\varepsilon' C l) = I_0 [(1 - \exp(-\varepsilon' C l))] \quad (5)$$

In absorption spectroscopy, the intensity of any absorption transition is measured as absorbance (A) or optical density (OD), defined as;

$$A = \log (I_0/I) = \log [I_0 / I_0 \exp(-\varepsilon' C l)] = \varepsilon' C l / 2.303 = \varepsilon C l \quad (6)$$

ε is the molar extinction coefficient used commonly in absorption spectroscopy and two quantities are related through ε' = 2.303 ε. Just for information, in existing literature ε' has also been used. One should be careful while consulting the existing literature. The Beer-Lambert laws can also be written in the following forms and thus depending upon the situation one can use any form.

$$I = I_0 \exp(-\kappa C' l) \quad (7)$$
$$I = I_0 \exp(-\sigma N l) \quad (8)$$

In equation (7) the concentration is expressed in SI units as mol m^{-3}, path length in m and κ as m^2 mol^{-1}. In equation (8) N is expressed as number of molecules per m^3, *l* in m and σ has the unit m^2, known as *absorption cross section*. Relation between σ and ε can be derived by comparing the equations (5) and (8) after adjusting the dimensions.

$\varepsilon' C l = (\sigma x 10^4 \text{ cm}^2)(N x 10^{-6} \text{ cm}^3)(l x 10^2 \text{ cm})$ [*$N\ m^{-3} = Nx10^{-6}\ cm^{-3}$ and $\sigma\ m^2 = \sigma x10^4\ cm^2$*]

$$= \sigma N l = \sigma C N_{av} l / 1000 \qquad [N = C N_{av} / 1000]$$

where N_{av} is Avogadro's number. The above equation can be written as:

$$\sigma = \varepsilon' 1000 / N_{av} = 2303\ \varepsilon / N_{av} \quad (9)$$

If the absorbing components at a given wavelength are more than one the absorbance is defined as $\sum (\varepsilon_i C_i l)$, where ε_i is the molar extinction coefficient at frequency ν_i for the ith component whose concentrations is C_i assuming the path length to be '*l*'. Thus the measured absorbance is:

$$A_{total} = A_1 + A_2 + A_3 \qquad (10)$$

Example 2: 0.25 mg of compound A with molecular weight 140 g mol^{-1} was dissolved in 50 mL of the solvent. If the absorbance of this solution at wavelength 310 nm is 0.35, calculate the molecular extinction coefficient at 310 nm.
Molarity of compound A: ($0.25x10^{-3}$ g / 140 g mol^{-1}) (1000 mL L^{-1} / 50 mL)

$$= 3.57x10^{-4} \text{ mol } L^{-1}$$

$\varepsilon = A / C l = \{0.35 / (1 \text{ cm}) (3.57x10^{-4} \text{ mol } L^{-1}) = 980 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Example 3: Absorbance of a solution containing compounds A and B at wavelengths 310 and 370 nm are 0.45 and 0.25 respectively. Calculate the concentrations of A and B from the following data. ε_A (310 nm) = $1.2x10^4$ L mol^{-1} cm^{-1}, ε_A (370 nm) = $0.25x10^4$ L mol^{-1} cm^{-1}, ε_B (310 nm) = $0.2x10^4$ L mol^{-1} cm^{-1}, ε_B (370 nm) = $2.5x10^4$ L mol^{-1} cm^{-1}.
Before the above problem is solved we have to derive the relation depicting the concentration of each species. For the binary (two component) system the absorbance are measured at two wavelengths. According to equation (10) the following relations can be written:

$$A(\lambda_1) = \varepsilon_A(\lambda_1) C_A l + \varepsilon_B(\lambda_1) C_B l \qquad (11)$$
$$A(\lambda_2) = \varepsilon_A(\lambda_2) C_A l + \varepsilon_B(\lambda_2) C_B l \qquad (12)$$

Multiply equation (11) by $\varepsilon(\lambda_2)$ and equation (12) by $\varepsilon(\lambda_1)$ and subtract.

$$A(\lambda_1) \varepsilon_A(\lambda_2) - A(\lambda_2) \varepsilon_A(\lambda_1) = [\varepsilon_B(\lambda_1) \varepsilon_A(\lambda_2) - \varepsilon_B(\lambda_2) \varepsilon_A(\lambda_2)] C_B l$$

So

$$C_B = [A(\lambda_1) \varepsilon_A(\lambda_2) - A(\lambda_2) \varepsilon_A(\lambda_1)] / [\varepsilon_B(\lambda_1) \varepsilon_A(\lambda_2) - \varepsilon_B(\lambda_2) \varepsilon_A(\lambda_1)] l \qquad (13)$$
$$C_A = [A(\lambda_1) \varepsilon_B(\lambda_2) - A(\lambda_2) \varepsilon_B(\lambda_1)] / [\varepsilon_A(\lambda_1) \varepsilon_B(\lambda_2) - \varepsilon_A(\lambda_2) \varepsilon_B(\lambda_1)] l \qquad (14)$$

Using equation (14)

$C_A = [(0.45) (2.5x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) - (0.25) (0.2x10^4 \text{ L mol}^{-1} \text{ cm}^{-1})] / [(1.2x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) (2.5x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) - (0.25x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) (0.2x104 \text{ L mol}^{-1} \text{ cm}^{-1})] [1 \text{ cm}]$
$= [(1.125 - 0.05) x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}] / [(3.0 - 0.05) x10^4 \text{ L}^2 \text{ mol}^{-2} \text{ cm}^{-1}]$
$= 1.075x10^4 \text{ mol } L^{-1} / 2.95x10^8 = 3.65x10^{-5} \text{ mol } L^{-1}$

$C_B = [(0.45) (0.25x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) - (0.25) (1.2x10^4 \text{ L mol}^{-1} \text{ cm}^{-1})]/[(0.2x10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}) (0.25x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) - (2.5x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) (1.2x10^4 \text{ L mol}^{-1} \text{ cm}^{-1})] [1 \text{ cm}]$
$= [(0.1125 – 0.3x10^4) x10^4 \text{ L mol}^{-1} \text{ cm}^{-1}] / [(0.05 – 3.0) x10^8 \text{ L}^2 \text{ mol}^{-2} \text{ cm}^{-1}]$
$= 0.1875x10^4 \text{ mol } L^{-1} / 2.95 = 6.35x10^{-6} \text{ mol } L^{-1}$

Example 4: The percentage radiation transmitted by a solution containing 2-aminonicotinic acid at pH 3.6 and 298 K at 320 nm is 72.4% for a solution $2x10^{-5}$ mol L^{-1} in a one cm cell. Calculate: (a) the absorbance at 320 nm, (b) the molecular extinction coefficient, (c) radiation transmitted if the cell length is 5 cm and (d) absorbance cross section.

(a) $A = \log (I_0 / I) = \log (100 / 72.4) = 0.14$
(b) $\varepsilon = A / C\,l = 0.14 / (2x10^{-5}\ \text{mol}\ L^{-1})\ (1\ \text{cm}) = 7x10^{3}\ L\ \text{mol}^{-1}\ \text{cm}^{-1}$
(c) $\log (I_0 / I) = \varepsilon C\,l = (7x10^{3}\ L\ \text{mol}^{-1}\ \text{cm}^{-1})\ (2x10^{-5}\ \text{mol}\ L^{-1})\ (5\ \text{cm})$
$= 0.7$
$I_0 / I = 5$ and thus $I / I_0 = 20\%$
(d) $\sigma = 2303\ \varepsilon / N_{av} = (2303)\ (7x10^{3}\ L\ \text{mol}^{-1}\ \text{cm}^{-1}) / 6.022x10^{23}\ \text{mol}^{-1}$
$= 2.68x10^{-20}\ \text{cm}^2$.

*Stark-Einstein' Law***:** The second law was first stated by Stark in 1908 and later by Einstein in 1912. The combined law states that "*One quantum of light is absorbed per molecule of absorbing and reacting substance that disappears."* This law is valid for normal sources of radiation, where the average number of photon quanta emitted from such sources is between 10^{13} to 10^{15} s^{-1}. A number of exceptions to the above law have been observed using very intense laser radiation, known as multi-photon excitation.

Behavior of the Excited State Molecules

Depending on the excitation wavelength, the molecule can be raised to one of the several different vibrational levels of the excited states. The various ways in which this excited molecule can behave are shown in Figure 3, known as **Jablonski diagram.** These processes can be broadly divided in to two categories:

Photophysical Process: In this process the molecule returns to the ground state without change in the structure of the molecule. This includes non-radiative and radiative processes.

Photochemical Process: The excited molecule decomposes into atoms or radicals and these intermediates may take part in further reactions. Unlike the above processes, this process is generally accompanied either with change of mass in the reactants or change in the molecular structure (for example, isomerization).

(a) Primary Process: Primary process is defined as a sequence of steps which starts with the absorption of radiation and ends up with any of the process mentioned below.
(i). Radiative: This involves two kinds of processes. One is fluorescence and the other phosphorescence.
(ii). Non-radiative: This process also can be classified into internal conversion and intersystem crossing.
(iii). Chemical reactions: This process may directly lead to the products or may decompose involving intermediates.
(iv). Quenching.
(v). Energy Transfer

The primary process is generally named after the last step. For example if the primary step is emission of light then the primary step is either fluorescence or phosphorescence. If the last step is deactivation without emission of radiation, it can be either internal conversion or intersystem crossing. Similarly several mechanisms for dissociation are recognized and these are classified as *optical dissociation, pre-dissociation, induced predissociation,* and so on.

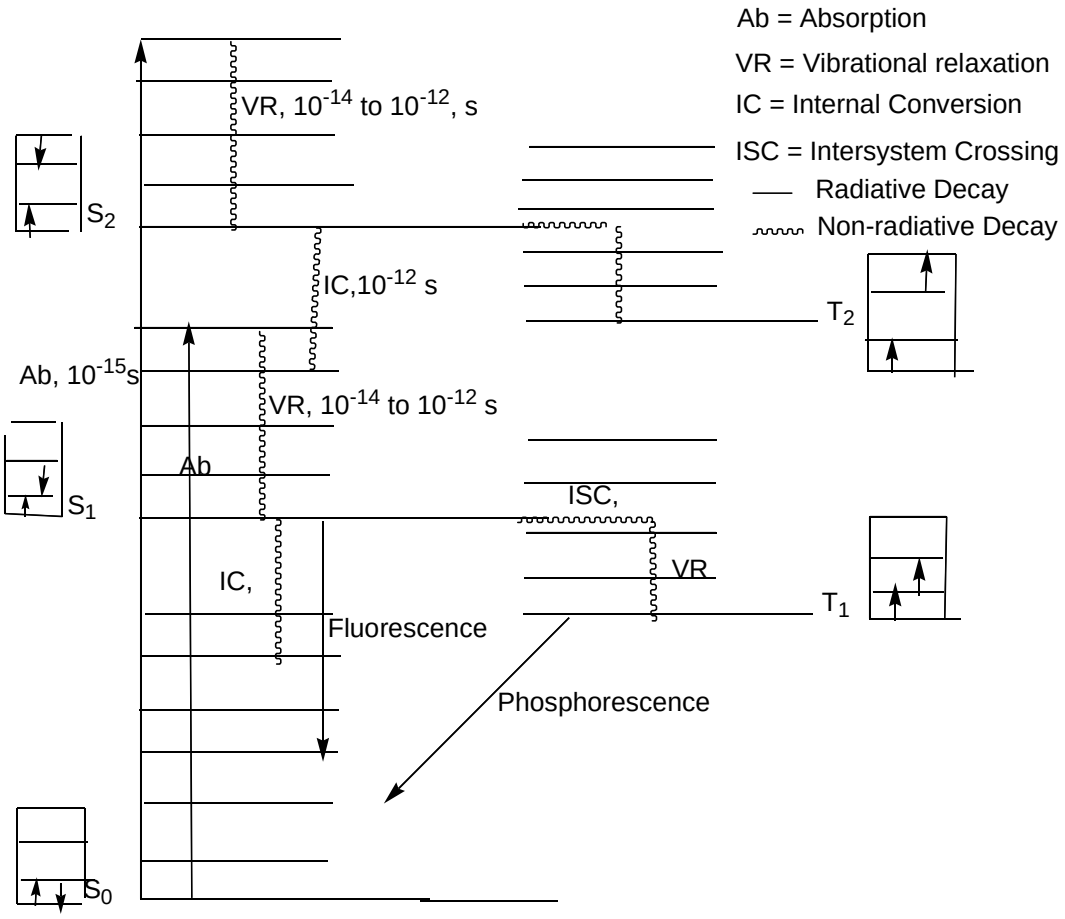


Figure 3: Jablonski diagram showing the fate of polyatomic molecule on photo-excitation.

(b) Secondary Process: It is quite common that some species formed in the primary steps further react to form the final products of different chemical nature. Such transformations are called *secondary steps* or secondary (thermal) reactions. The most common example is the formation of free radicals or atoms by dissociation of excited molecules and their further reactions with other molecules. For example in the photochemical reaction between chlorine and hydrogen as given below:

$$Cl_2 + h\nu \rightarrow 2\,Cl \qquad (A)$$

$$Cl + H_2 \rightarrow HCl + H \quad (B)$$

The step (A) is primary step whereas the step (B) is the secondary step. Any further reactions of hydrogen atom will also be secondary step.

Efficiency or Quantum Yield

The quantum yield or efficiency of a photophysical or photochemical process is of great help. It provides information about the extent of particular process occurred after excitation. As originally understood, *it was the number of molecules of reactant consumed for each photon of light absorbed*, i.e.

Φ = number of molecules undertaking the process / number of photons absorbed (15)

Quantum yield defined by equation (15) is very misleading because the product can be formed in primary as well as secondary steps, whereas equation (15) does not tell whether the quantum yield is for primary step or for total reaction. As suggested by Einstein-Stark law that not more than one molecule is decomposed in the primary step, quantum yield greater than one means that secondary reactions are also accompanying the primary process. Thus one should consider two yields separately. As mentioned earlier that chemical reaction is not the only path followed by the photo-excited molecule, the quantum yield should be defined separately for each process. Thus: "**Sum of quantum yields of all the primary processes should be equal to one"**.

Efficiency: Efficiency (η) of a step is defined as the ratio of the rate at which a particular step occurs to the total rate by which that particular state is being depopulated. In other words, η describes the probability of that particular step relative to the other steps by which that excited state is removed.

Let the scheme depicting the depopulation of the excited state is as follows:

$$^1M_0 + h\nu \rightarrow {}^1M^* \quad \text{Photoexcitation } (I_a) \quad (16)$$

$$^1M^* \rightarrow {}^1M_0 + h\nu_f \quad \text{Fluorescence } (k_f) \quad (17)$$

$$\rightarrow {}^1M_0 \quad \text{Internal Conversion } (k_{IC}) \quad (18)$$

$$\rightarrow {}^3M^* \quad \text{Intersystem Crossing } (k_{ISC}) \quad (19)$$

$$^3M^* \rightarrow {}^1M_0 + h\nu_{Ph} \quad \text{Phosphorescence } (k_{Ph}) \quad (20)$$

$$^3M^* \rightarrow {}^1M_0 \quad \text{Intersystem Crossing } (k_{GT}) \quad (21)$$

Here $^1M_0$ and $^1M^*$ are the molecules in the ground and first excited singlet states, $^3M^*$ are the molecules present in the first triplet state and k_i are the rate constants for the various processes mentioned in the reaction scheme. Then

$$\eta = R_i / \sum R_i \quad (22)$$

where R_i is the rate of the jth step and the summation is over the rate of all the steps involved in depopulating the particular excited state. From the above reaction scheme, the efficiency of phosphorescence is given by:

$$\eta_{Ph} = R_{Ph} / (R_{Ph} + R_{GT}) \quad (23)$$

thus η_{Ph} represents the fraction of all the molecules in triplet state undergoing phosphorescence. When all the steps involved are of first order, the efficiency will be independent of concentrations.

$$\eta_{Ph} = k_{Ph} / (k_{Ph} + k_{GT}) \quad (24)$$

or $$\eta_i = k_I / \sum k_j \quad (25)$$

where k represents the first order rate constants. If the steps involved in depopulating the excited state are of mixed order, the concentration terms do arise in the expression for η. For example, if the reaction scheme given above also includes the following quenching step then the efficiency of phosphorescence is given by:

$$^3M^* + Q \rightarrow {}^1M_0 \qquad k_q \quad (26)$$

$$\eta = k_{Ph} / (k_{Ph} + k_{GT} + k_q [Q]) \quad (27)$$

Comparing the equations (24) and (27), one can see that the former is independent of the concentration of any species and depends only on the physical factor like temperature and nature of solvent, whereas the latter depends on the concentration of the quenching species.

The value of η can have values ranging from 0 to 1. Further the sum of the efficiencies of all the steps that depopulate the particular excited state will be unity. When efficiencies depend on concentrations, obviously the sum will be unity only if the efficiencies refer to same concentrations. Finally since it does not involve the absorption of radiation so the name quantum needs not to be used.

Thus for a process the quantum yield gives the performance of any process per photon absorbed, i.e. it gives a mode of account-keeping for partition of absorbed quantum into various pathways. This concept was first given by Einstein.

Kinetic Parameters of Unimolecular Photophysical Processes

Kinetic parameters are very important quantities in finding the quantitative information about any event which takes place. In this section we will only discuss the unimolecular photophysical processes which are followed by the excited molecule. The kinetic parameters of these photophysical processes can be calculated by two methods.

(1) *Using steady state radiation source*. In this case the continuous radiation source is used and the emission (both fluorescence and phosphorescence) are recorded under steady state environments, i.e. emission spectra are recorded while the radiation source is on. Only those processes, in the above scheme, where the excited molecules are deactivated by physical processes are considered. Considering only the reactions of singlet state molecules, the differential rate equation for the deactivation of excited singlet state process can be written as:

$$- d[^1M^*]/ dt = k_f [^1M^*] + k_{IC} [^1M^*] + k_{ISC} [^1M^*] - I_a \quad (28)$$

Applying the steady state approximation, $- d[^1M^*] / dt = 0$, the equation (28) reduces to

$$I_a = (k_f + k_{IC} + k_{ISC}) [^1M^*] \quad (29)$$

Fluorescence quantum yield (Φ_f) can be obtained by the expression

Φ_f = (number of fluorescence quanta emitted)/ number of photons absorbed (30)

$$= k_f [^1M^*] / I_a = k_f [^1M^*] / (k_f + k_{IC} + k_{ISC}) [^1M^*]$$

$$= k_f / (k_f + k_{IC} + k_{ISC}) = k_f/k_{M,}, \text{ where } k_M = k_f + k_{IC} + k_{ISC} \quad (31)$$

That is the fluorescence quantum yield can be defined as the ratio of the rate constant for radiative decay and the total rate of deactivation for the excited singlet state under going these processes.

Transient Conditions: Under these conditions the molecule is excited at t = 0 with radiation following δ function, i.e. radiation of very short duration pulse or flash of negligible duration and the excited molecules are produced at initial concentration of $[^1M^*]_0$. The rate equation at t > 0 will be:

$$-d[^1M^*]/dt = k_M [^1M^*] \quad \text{so that,} \quad [^1M^*] = [^1M^*]_0 \exp(-k_M t) \quad (32)$$

The *fluorescence response function i(t)* of any molecular system is defined as the fluorescence quantum intensity at a time t, following such a δ-function excitation, i.e.

$$I_M(t) = k_f [^1M^*]/[^1M^*]_0 = \{k_f [^1M^*]_0 \exp(-k_M t)\}/ [^1M^*]_0$$
$$= k_f \exp(-k_M t) \quad (33)$$

Integrating the total fluorescence quantum intensity, we get

$$\Phi_f = {}_0^{\infty}\int i_M(t)\, dt = {}^{\infty}_0\int k_f \exp(-k_M t)\, dt = (-k_f / k_M) [\exp(-k_M t)]^{\infty}_0$$
$$= (-k_f / k_M) [\exp(-k_M \infty) - \exp(-k_M 0)] = k_f / k_M \quad (34)$$

This is in agreement with the relation derived using steady state excitation. We can now define certain relations:

fluorescence lifetime (τ_M) = $1 / k_M$ and *radiative lifetime* (τ_f) = $1 / k_f$

and $\Phi_f = k_f / k_M = \tau_M / \tau_f$ (35)

Phosphorescence Parameters

In this case, a dilute solution of a system of molar concentration of $[^1M]$ is excited to $[^1M^*]$ using radiation source of low light intensity (I_{ab}). The molecules from the first excited singlet state can go to triplet state by intersystem crossing (equation 19) path. The molecules in the triplet state can be deactivated to ground state through the processes described in equations (20) and (21). The rate equation of phosphorescence decay can be written as:

$$d[^3M^*]/dt = k_{ISC} [^1M^*] - k_T [^3M^*] \quad (36)$$

where $k_T = k_{Ph} + k_{GT}$

Light of low intensity is used to avoid the triplet-triplet annihilation. Under the steady state conditions, equation (36) can be equated to zero, i.e.

$$k_{ISC} [^1M^*] - k_T [^3M^*] = 0 \rightarrow k_{ISC} = k_T [^3M^*]/ [^1M^*] \quad (37)$$

The triplet quantum yield or intersystem crossing quantum yield (Φ_{ISC}) can be defined as:

$$\Phi_{ISC} = k_{ISC} [^1M^*] / I_{ab} = k_{ISC} [^1M^*] / k_M [^1M^*] = k_{ISC} / k_M \quad (38)$$

Combining equations (37) and (38)

$$\Phi_{ISC} = k_T [^3M^*] / k_M [^1M^*] \quad (39)$$

The phosphorescence quantum efficiency (η_{Ph}) is defined as the ratio of the number of phosphorescence photons emitted and the number of molecules excited to T_1 state and is given as:

$$\eta_{Ph} = k_{Ph} / k_T \quad (40)$$

The phosphorescence quantum yield is defined as

Φ_{Ph} = number of phosphorescence quanta emitted/ number of quanta absorbed

$$= k_{Ph} [^3M^*] / I_{ab} = k_{Ph} [^3M^*] / k_M [^1M^*] \quad (41)$$

From equation (39) $[^3M^*] / [^1M^*] = \Phi_{ISC} k_M / k_T$ and substituting it in equation (41)

$$\Phi_{Ph} = (k_{Ph} / k_M) (\Phi_{ISC} k_M / k_T) = (k_{Ph} / k_T) \Phi_{ISC} = q_{Ph} \Phi_{ISC} \quad (42)$$

On similar lines as discussed in case of transient behavior of excited singlet state, the transient behavior of the triplet state can be considered by exciting the system by a δ-function light flash at t = 0. This type of radiation produces an initial concentration $[^1M^*]_0$ of the excited molecules. The subsequent rate equations can be written as:

$$d [^1M^*] / dt = -k_M [^1M^*] \quad (43)$$

$$d [^3M^*] / dt = k_{ISC} [^1M^*] - k_T [^3M^*] \quad (44)$$

Solving equations (43) and (44) and using the initial conditions, $[^1M^*] = [^1M^*]_0$ and $[^3M^*] = 0$, at t = 0,we get

$$[^3M^*] = \{(k_{ISC} [^1M^*]_0) / (k_M - k_T)\} [\exp(-k_T t) - \exp(-k_M t)] \quad (45)$$

Using the response function for phosphorescence the phosphorescence quantum yield can be written as:

$$\Phi_{Ph} = \{ \int_0^\infty k_{Ph} [^3M^*] dt\} / [^1M^*]_0 \quad (46)$$

Substituting the value of $[^3M^*]$ from equation (45) in equation (46) and integrating it we get

$$\Phi_{Ph} = (k_{Ph} k_{ISC}) / (k_T k_M) = q_{Ph} \Phi_{ISC} \quad (47)$$

A similar relation has also been obtained earlier (42). Further knowing Φ_f and Φ_{ISC}, τ_M and τ_T (defined as $1 / k_T$) we can obtained all the kinetic parameters for the fluorescence and phosphorescence emissions.

Example 5: The photophysics of a compound 'A' has been studied using steady state and time dependent spectrofluorimeter. The following data have been obtained. $\Phi_f = 0.6$ $\Phi_{ISC} = 0.2$, $\tau_M = 5$ ns and $\tau_T = 4\mu s$. Compound A also undergoes decomposition in the first excited singlet state and quantum yield of decomposition is 0.05. Calculate k_f, k_{IC}, k_{ISC}, and k_{Ph} if the quantum efficiency of phosphorescence is 0.5.

(a). Using equation (35): $\Phi_f = k_f / k_M = k_f \tau_M$,

$k_f = \Phi_f / \tau_M = 0.6 / 5x10^{-9}$ s $= 0.12x10^9$ s^{-1}.

(b). Similarly $\Phi_{ISC} = k_{ISC} / k_M = k_{ISC} \tau_M$

$k_{ISC} = \Phi_{ISC} / \tau_M = 0.2 / 5x10^{-9}$ s $= 0.04x10^9$ s^{-1}

(c). Since the total quantum yield of the primary processes is equal to unity, then

$\Phi_{IC} = 1 - \Phi_f - \Phi_{ISC} - \Phi_D = 1 - 0.6 - 0.2 - 0.05 = 0.15 = k_{IC} / k_M = k_{IC} \tau_M$

$k_{IC} = 0.15 / 5x10^{-9}$ s $= 0.3x10^9$ s^{-1}

(d). Using equation (40), $\eta_{Ph} = k_{Ph} / k_T = k_{Ph} \tau_T$

$k_{Ph} = 0.5 / 4x10^{-6} s = 0.125x10^{6} s^{-1}$.

Photophysical Processes

As mentioned above, the absorption of radiation (photon) by the molecules leading to one of the several possible vibrational levels of one of its electronically excited states is complete in 10^{-15} second. The sequence of events that lead to the deactivation of the excited molecule to the ground state is relatively slower, taking 10^{-14} to several seconds. In comparison to many physical processes (to be discussed later) return of these excited molecules to the ground state by emission is among the slowest processes in the electronically excited states, requiring 10^{-9} to few seconds. Based on the time scale the processes leading to the deactivation of the excited molecules will be discussed in this section.

Vibrational and Solvent Relaxation

After absorption of photon, the excited molecules may be present in the vibrationally excited levels (i. e. in $v > 0$). These excited molecules then oscillate with the frequency pertaining to the electronically excited state. These excited molecules can lose their excess vibrational energy either by stepwise emission of infrared frequency or in the form of kinetic energy given to other molecules during the collisions among themselves or with other molecules. With in the lifetime of few vibrations the molecules lose their excess vibrational energy, returns to the zero vibrational level of the electronically excited states. Loss of excess vibrational energy in any electronically excited state is a very fast process and is complete with in 10^{-14} to 10^{-12} seconds. This process (i.e. loss of excess vibrational energy) is called *vibrational relaxation* and the state where molecules are present after this process is known as *vibrationally relaxed state*.

When a molecule is excited electronically, the charge densities at different atoms of the molecule are different from those of the ground state. This leads to change in the polarity of the molecule in the excited state. Thus the interactions between the excited molecule and the solvent molecules are different from those present in the ground state. Because of these changes rearrangement of the solvent molecules around the excited molecules takes place which is different from that in the ground state. This is known as *solvent relaxation* (Solvent relaxation is a complicated phenomenon but many useful information about environments of fluorophore can be obtained from this study) and the period of solvent relaxation varies from 10^{-12} to 10^{-6} seconds, depending upon the viscosity and other characteristics of the solvents. In the viscous solvents, period of solvent relaxation is very large as compared to the lifetime of the molecules in the excited state. In other words loss of excitation energy via solvent interactions will be slow and the fluorescence is observed from higher energy as compared to that in less viscous solvents. For example, the fluorescence band maximum observed in case of 2-quinoxalinone in water, ethylene glycol and glycerol are at 421, 414 and 409 nm respectively. Extreme case of high viscosity is sample present in solid state or at liquid nitrogen temperature.

Following these two processes, the electronically excited molecules present in the Franck-Condon state attain thermal equilibrium with the environment. The electronically excited state is known as *thermally relaxed excited state.* On the energy level scale these processes are depicted in Figure 4.

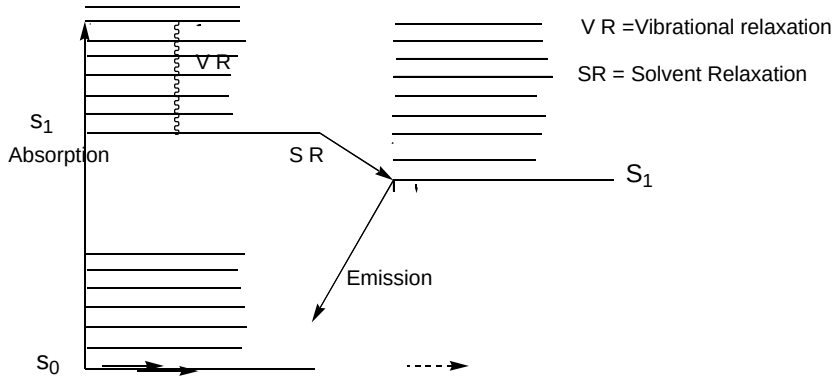


Figure 4: Vibrational and solvent relaxation processes.

Thermodynamically, even arriving at the zeroth vibrational level of the lowest excited singlet state, the electronically excited isolated molecule still has the tendency to loose energy in order to come to the zeroth vibrational level of the ground electronic state, as this process is favourable. There are number of ways by which this energy loss can take place. We will divide these two processes into two broad categories. One that emits radiations while releasing energy and the other that does not emit radiations while losing energy. The former is known as *radiative* processes and the latter *non-radiative* processes.

Non-Radiative Processes: There are two non-radiative processes by which the excited molecule can lose its excess energy.

Internal Conversion

Internal conversion (IC) is defined as the process by which the molecules from the higher excited state cross over to the lower state of the same spin multiplicities ($\Delta S = 0$) through the vibrational coupling. Internal conversion is generally observed from singlet to singlet states but this process is also observed from higher triplet to lower triplet. In this process the radiation is not emitted and is thus called as non-radiative one. It can be achieved by two ways.

(1). If the lower vibrational levels of the upper electronic state overlap with higher vibrational levels of the lower electronic state, there will be a transient thermal equilibrium and this will allow the transfer of the molecules from the upper electronic state to the lower one. In this overlap the nuclear configuration of the two states will be the same and the total energy (i.e. sum of the electronic and the vibrational energy) of the upper state is equal to that of the lower state. Thus this transformation is also called as *horizontal transition*. After this the vibrational relaxation of the lower electronic state follows as mentioned earlier.

(2). In some cases there is a small gap (of few vibrational quanta) between the lower vibrational levels of the upper electronic state and the upper vibrational levels of the lower electronic state (there is no overlap, like that mentioned in the first process). The excited molecules from the upper electronic state revert to lower electronic state by a

process known as *tunneling*. Tunneling is observed in many processes like radioactivity, solid state phenomenon, and electron and proton transfer reactions. This phenomenon is explained by quantum mechanical concepts. Although the detailed picture of tunneling is beyond the scope of this chapter, but the probability of tunneling decreases as: (i) the difference in energy between the upper vibrational levels of the lower electronic state and the lower vibrational levels of upper electronic state increases and, (ii) also as the mass of the particle increases.

In both the above processes, it is clear that the efficiency of internal conversion depends on the difference in energy between the upper electronic state and the lower electronic state and the vibrational levels associated with each state. The presence of vibrational levels in both the electronic states is more important as the overlap of these states leads to internal conversion. If the number of vibrational levels in the lower electronic state of the molecule is large, then the overlap between the lower vibrational levels of the upper electronic state and the upper vibrational levels of the lower electronic state will increase. This will lead to the higher probability of dissipation of the excitation energy and hence increase in the internal conversion. The molecules which possess flexibility in their structure possess large degree of vibrational modes and large number of vibrational energy levels. In other words internal conversion process is predominant in these kinds of molecules. Thus fluorescence is rarely observed in aliphatic hydrocarbons and similar molecules. On the other hand aromatic hydrocarbons are rigid molecules and thus possess very few vibrational degrees of freedom as compared to aliphatic hydrocarbons and thus often show fluorescence.

In the electronic absorption spectrum, especially of aromatic hydrocarbons, overlap of the absorption bands due to higher electronic states is commonly observed (i.e. gap between the successive electronic absorption bands decreases with the increase in the quantum number of the excited state). In other words it suggests that the rate of internal conversion between the second excited singlet state to the first excited singlet state will be greater than that between the first excited singlet state to the ground state and so on. **Thus fluorescence is generally observed from the first excited singlet state.** Exceptions to these statements are there. The first one was azulene and its derivatives, where the fluorescence is observed from the second excited singlet state. The main reason is that the gap between the second singlet and the first singlet is nearly same (14,100 cm^{-1}) as in the first singlet and the ground state (14,200 cm^{-1}).

Lastly the internal conversion process is very fast and is generally complete in 10^{-12} s. As said earlier, the average lifetime of the excited molecule is approximately 10^{-9} s. Thus if the internal conversion process is not occurring in the molecule, some other processes may be competing with the fluorescence process occurring from the lowest excited singlet state.

Intersystem Crossing

It has been mentioned in the last section that rate of internal conversion is very fast if the gap between the two electronically excited singlet states is small and the excess excited energy is converted into molecular vibrations. If the gap between the lowest excited singlet state and the ground state is substantial, then the excited molecules may lose their

excess energy by emitting radiation in the form of fluorescence. But there is another path by which the excited molecules may lose energy without emitting radiation, i. e. by another radiationless process called *intersystem crossing (ISC)*. *The main difference between internal conversion and intersystem crossing is that in the former process,* $\Delta S = 0$*, whereas in the latter process* $\Delta S \neq 0$*,* i.e. $S_1 \rightarrow T_1$, $T_1 \rightarrow S_0$ etc.

It is well know that the electrostatic repulsion between the two electrons is smaller when these possess the parallel spin than when these electrons are anti-parallel to each other, i.e. electronic repulsion in any given triplet state is less than that in the singlet state of the same electronic configuration. In other words energy of the triplet state will be lower than its singlet state and thus will lie below the excited singlet state. In general there is substantial overlap between the lowest vibrational energy levels of the lowest excited singlet state and the upper vibrational levels of the triplet state. Thus there is some probability that molecules from the excited singlet state will be transferred to the triplet state by a mechanism which is similar to the internal conversion. Unlike internal conversion, the transfer of molecules from the excited singlet state to the triplet state is forbidden classically as it involves a change of spin angular momentum. On the other hand based on quantum mechanics, there is a finite probability for the intersystem crossing to occur but it is very small as compared to the process which does not involve change of spin. In terms of rate process it may be mentioned that the reciprocal of the probability of per event is the time taken per event or lifetime of the process in question. It has been found that the probability of spin forbidden vibrational (intersystem crossing) process to occur is much lower (10^6 times) than the spin allowed vibrational crossing to take place. This suggests that mean lifetime of the spin forbidden process is much longer than the spin allowed process. In the last section we have found that the spin allowed vibrational transitions (vibrational relaxation and internal conversion) has the mean lifetime of 10^{-14} s. This means that the mean lifetime of the spin forbidden process (intersystem crossing) will be of the order of 10^{-8} s, which is of the similar order of magnitude as that of fluorescence lifetime. This suggests that although the intersystem crossing is too slow to compete with the fast internal conversion process but it has the lifetime which is comparable with that of fluorescence and can thus compete with fluorescence for the deactivation of the molecules present in the lowest excited singlet state.

It has been observed that aromatic hydrocarbons do undergo some degree of intersystem crossing from the lowest excited singlet state. The rate of this process is increased:

1. in the molecules having lone pair of electrons.
2. if heavy atoms are present in the molecule or in the solvent. The former is known as internal heavy atom effect and the latter as external heavy atom effect.
3. in transition metal ions

This is the major pathway (not always) for the deactivation of molecules (containing these substituents) if present in the first excited singlet state. In these kinds of molecules spin orbit coupling, (which consists of addition of spin and orbital angular momenta vectorially), is enhanced and thus the spin angular momentum of the molecule, per se, is not well defined. This partially removes the distinctiveness and forbiddenness of singlet triplet transition. Thus it has been observed that fluorescence is either not observed or very weak fluorescence is observed from the molecules containing heavy atoms (for

example iodine) or transition metal ion. Similarly in the molecules having $^1n\,\pi^*$ state as the lowest excited singlet state does not undergo fluorescence as the means of deactivation. In all these cases, excited molecules undergo intersystem crossing and end up in the triplet state.

As mentioned earlier, the difference in electronic energy between the singlet-triplet electronic states for the same electron orbital configuration can be nicely explained considering the Pauli's exclusion principle. This principle, based on quantum mechanics, states that in triplet state, when the two unpaired electrons are present in different orbital, experience the minimum repulsion. For better understanding the energy gap between the singlet and triplet states and its dependence on orbitals comprising the electronic configuration, one has to use quantum mechanics for the calculation of the energies of different orbitals. Broadly the energy of any state is given by the summation of the one electron energy (E) and the repulsion energy. The repulsion energy comprises of two terms. One term quantifies the repulsion due to Coulombic interactions (J) and the other term quantifies the repulsion because of exchange interactions (K). Both these quantities (J and K) have positive values. For example the energies of the ground and excited singlet and triplet states for the n, π^* configuration can be given as:

$$E(S_0) = 0 \quad \text{by definition} \tag{48}$$
$$E(S_1) = E(n, \pi^*) + J(n, \pi^*) + K(n, \pi^*) \tag{49}$$
$$E(T_1) = E(n, \pi^*) + J(n, \pi^*) - K(n, \pi^*) \tag{50}$$

The difference between the singlet and triplet states can be given by

$$\Delta E(\text{S-T}, n, \pi^*) = E(S_1) - E(T_1) = 2K(n, \pi^*) \tag{51}$$

It is clear from the above expression that the one electron energies and repulsion energy arising because of Coulombic interactions are the same for both the singlet and triplet states. The difference between the two states arises due to the repulsion energy arising because of exchange interactions. It increases the energy of the singlet state and decreases that of triplet state. The difference in the electronic energy between the singlet and triplet states arising from the $\pi\,\pi^*$ electronic configuration can also be written in similar manner.

$$\Delta E(\text{S-T}, \pi, \pi^*) = 2K(\pi, \pi^*) \tag{52}$$

Thus the separation between the singlet and triplet states depends on the magnitude of the term K (i.e. in quantum mechanical term the matrix element which determines the electronic energy of orbitals, configurations and states.). In qualitative sense this term is an integral which involves the overlap of the two orbitals involved in particular configuration. Knowing that n and π orbitals lie in orthogonal planes, their overlap will be minimum and thus the magnitude of K for n, π^* state will be small. On the other hand K for π, π^* state will be large as both these orbitals occupy more or less the same configuration space. In other words, the gap between the singlet-triplet states for the π, π^* configuration will be larger than that between n, π^* configuration. Singlet Triplet splitting for some molecules is given in Table 2. It is evident from Table 2 that the splitting between the singlet-triplet states in the hydrocarbons is very large and agrees with the experimental results that these systems possess the π, π^* states as the first singlet and first triplet. On the other hand in case of carbonyls where n, π^* are first singlet and triplet

states the energy gap is very small. In other words the intersystem crossing is very rapid in the carbonyl compounds as compared to that in hydrocarbons. This is consistent with the above statement that fluorescence is hardly observed from the $^1n, \pi^*$ state. If the lowest excited singlet state is of $^1n, \pi^*$ type, the lowest triplet state may be of $^3n, \pi^*$ type, as observed in case of benzaldehyde and acetophenone, but more often it may be of $^3\pi\ \pi^*$ type. It is due to the greater separation between $^1\pi, \pi$ and $^3\pi, \pi^*$ states as compared to that between $^1n, \pi^*$ and $^3n, \pi^*$ states. If the lowest excited singlet state is of $^1n, \pi^*$ type and lowest triplet state is of $^3\pi\ \pi^*$ type, intersystem crossing first populates the $^3n, \pi^*$ state, followed by rapid vibrational relaxation and the internal conversion to the $^3\pi, \pi^*$. This phenomenon is commonly observed in carbonyl compounds obtained from poly-condensed aromatic hydrocarbons, many benzaldehydes and acetophenones substituted with electron donating groups, and the N-heterocyclics having lowest triplet states of $^3\pi\ \pi^*$ type. The depopulation of the lowest triplet state to the ground state may occur by different pathways which will be discussed later.

Table 2: Singlet-Triplet Splitting

Molecule	Configuration ($S_1 - T_1$)	ΔE ($S_1 - T_1$) in kJ mol^{-1}
Ethylene	π, π^*	293
Benzene	π, π^*	167
Naphthalene	π, π^*	146
Anthracene	π, π^*	126
Formaldehyde	n, π^*	42
Acetone	n, π^*	29
Benzophenone	n, π^*	29

Radiative Processes: Similar to non-radiative processes, there are two radiative pathways also by which the excited molecules can be deactivated to the ground state.

Fluorescence

After the photo-excitation to the Franck-Condon state (unrelaxed state) the excited molecules come to the thermally relaxed state after undergoing vibrational and solvent relaxation (i.e. the zeroth vibrational level of the first excited singlet state). One of the processes followed by the excited molecule for deactivation to the ground state is by emitting radiation. *If the excited state has the same spin multiplicity as the ground state then light emitted during the transition is known as Fluorescence* (i.e. $\Delta S = 0$). In general both the states involved during fluorescence are singlet but both the states during fluorescence can be doublet or triplet as well.

The simplest example of fluorescence is given by the monatomic vapours at low pressure. Sodium atom in its ground electronic state ($^2S_{1/2}$) absorbs radiation to give $^2P_{1/2}$ and $^2P_{3/2}$ states. The atoms revert back to ground state with a mean lifetime of 10^{-8} s. In this case the exciting and emitting radiation has the same wavelength and this type of fluorescence is called "*resonance fluorescence*".

In case of molecules, as mentioned earlier (8.1), vibrational relaxation is very fast in solution phase. The molecule excited to state just after absorption of photon (known as

Franck-Condon excited state) loses excess vibrational energy to solvent molecules and relax to zero vibrational level of the first excited singlet state. This is followed by solvent interactions to get further stabilization of the excited state. The energy of the thermally excited relaxed state (combined effect of vibrational and solvent relaxation) is thus lower than that of the Franck-Condon state. In viscous solvents, solvent molecules take longer time to orient themselves around the excited fluorophore to a new equilibrium in the excited state. Thus the rate of solvent relaxation is slow as compared to the rate of fluorescence emission. Due to this the gap between Franck-Condon state and thermally relaxed state will be less as compared to that in less viscous solvents. Examples are already given earlier (8.1). The emission now occurs at a rate depending up on the environment and structure of the molecule. As in absorption, the molecules after emission return to the ground state vibrational levels which are different from which it started. Similar to absorption, the emission transition probabilities are different for different vibrational levels and the intensity of emission transitions in the spectra can again be represented by the height of the arrow (Figure 1). Subsequent to emission, thermal relaxation occurs in $\sim 10^{-12}$ s, with the molecules ultimately arriving in the lowest vibrational level (v = 0) of the ground state. Because vibrational relaxation processes in the excited state take place after the absorption of radiation, they are not reflected in the electronic absorption spectra. Similarly, because vibrational relaxation processes in the ground state occur after the emission of radiation they are also not reflected in the fluorescence spectra. This clearly suggests that fluorescence spectrum is always red shifted to the absorption spectrum. The red shift or displacement of the fluorescence spectrum to lower energy is manifested by **Stokes shift**, which is defined as the difference between the absorption and fluorescence band maxima expressed in wavenumber (i.e. $\bar{\upsilon}_{max}^{ab} - \bar{\upsilon}_{max}^{f}$). Stokes shift is a function of (i) vibrational relaxation, (ii) solvent relaxation and (iii) change in the geometry of the molecule on excitation.

In both the cases, (absorption and emission spectra) one transition is common and this is between the zeroth vibrational levels of both electronic states. This corresponds to the lowest energy transition in absorption spectrum and of highest energy in the emission spectrum. Further since all the absorption transitions are considered to start from the same lowest energy vibratonal level of the ground electronic state and terminate at different vibrational levels of the excited state (the non-relaxed or Franck-Condon state), the absorption spectra reflect vibrational structure of the excited state. On the other hand all the fluorescence transitions arise from the same vibrational level of the lowest excited singlet state and terminate in the different vibrational level of the ground state (the Franck-Condon ground state); the fluorescence spectrum reflects the vibrational structure of the ground state. If the Franck-Condon ground and the lowest excited singlet states have the same vibrational features (i.e. the gap between the successive vibrational levels are the same), the longest wavelength absorption and fluorescence spectra will be mirror image of each other. The absorption spectrum will be towards the left hand side and the fluorescence spectrum will be on the right hand side if the spectra are depicted in terms of wavelength scale on the same plot. In general the charge density at different positions of the molecule in the ground and excited states are different. This often leads to somewhat different vibrational structures of these states and thus the mirror image symmetry observed in the absorption and fluorescence spectra is not perfect.

Several absorption bands are observed from the ground state to different excited states of a molecule, but only one emission band is observed in the fluorescence spectrum even though the molecule is excited to higher excited state. This is due to the fact that the other processes like internal conversion and vibrational relaxation are very fast as compared to the lifetime of the first excited singlet state and thus the emission can not compete with these non-radiative processes from higher excited states. In other words *the fluorescence generally occurs from the lowest excited singlet state to the ground state*. This led to the formulation of two rules:

(i) *Kasha's rule*, i.e. in a complex (aromatic) molecule the emission occurs from the lowest excited state of a given multiplicity, i.e. from first excited singlet and triplet states. (ii) *Vavilov's law*, i.e. fluorescence quantum efficiency is independent of the excitation wavelength. Exceptions to these rules have been noticed but are very few. More than one emission bands are observed in the fluorescence spectrum but these are due to different species present in the system or formed from the excited molecule during their lifetimes. The fluorescence is also observed from the vibrational levels other than zero vibrational level of the first excited singlet state. This kind of emission is normally observed in the gaseous systems at low pressures. This is because under these conditions the mean free path is large and the inverse of the collisional deactivation rate of excess vibrational energy is comparable with the excited state lifetime. Parmenter[5] was the first to observe fluorescence emission from $v > 0$ of the first excited singlet state of fluorobenzene. Many other examples are there in literature. Azulene and its derivatives are other kind of molecules which violates Kasha's rule by emitting radiation from the second excited singlet state.

Since the fluorescence occurs generally from the first excited singlet state to the ground electronic state, the effects of substituents and size of the aromatic systems (i.e. extended conjugation) on the fluorescence band maximum is nearly similar to that on absorption spectrum. Extensive conjugation to aromatic systems introduces more π and π^* orbitals, thus decreasing the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Whereas the substituents (-OH, $-NH_2$, etc., excited state charge donors) or >C=O (excited state charge acceptor or vacant orbital donors) containing lone pairs of electrons increases the energy of bonding orbitals more that those of antibonding orbitals, thus again decreasing the gap between HOMO and LUMO. In both cases, similar to absorption spectrum, red shift is also observed in the fluorescence spectrum. For example, fluorescence band maximum observed in benzene, naphthalene, anthracene and tetracene, containing 1, 2, 3, and 4 rings, are at 262 nm, 314 nm, 379 nm and 480 nm respectively.

The fluorescence intensity observed at any one particular wavelength is related to the number of molecules populated in the excited state. It can be related to absorption intensity at that wavelength by using the Beer-Lambert's law. The intensity of radiation absorbed at any particular wavelength is given by equation (5):

$$I_a = I_0 - I = I_0 - I_0\, 10^{-\varepsilon C l} = I_0 (1 - 10^{-\varepsilon C l}) \qquad (5)$$

The fraction of light absorbed is

$$I_a / I_0 = 1 - 10^{-\varepsilon C l} \qquad (53)$$

However, if the fluorescence has a quantum yield Φ_f, the fraction of the absorbed light which appears as fluorescence (I_f / I_a)

$$\Phi_f = I_f / I_a \quad \text{or } I_f = I_a \Phi_f \tag{54}$$

$$I_f / I_o = \Phi_f (I_a / I_0) = \Phi_f (1 - 10^{-\varepsilon C l}) \tag{55}$$

Or in the arbitrary units, the intensity of light emitted is

$$I_f = \Phi_f I_0 (1 - 10^{-\varepsilon C l}) \tag{56}$$

If the absorptivity (ε C l) is very small, the term $10^{-\varepsilon C l}$ can be expanded as power series and taking only first term, the equation (56) reduces to

$$I_f = I_0 \Phi_f (1 - 1 + 2.303 \varepsilon C l) = 2.303 I_0 \Phi_f \varepsilon C l \tag{57}$$

It is thus clear that the fluorescence intensity at any wavelength on a molecular basis, depends up on the concentration and molar absorptivity of the absorbing species in the ground state and fluorescence quantum yield is a property of the fluorescing (excited) species.

Phosphorescence

Intersystem crossing is generally followed by vibrational relaxation to the zero vibrational level of triplet state, as observed in the first singlet state. The deactivation of molecule in the triplet state follows two routes. (i) Nonradiative process to the higher vibrational levels of the ground state, also known as intersystem crossing, as explained earlier (section 8.2.2). (ii) Similar to fluorescence, deactivation of the molecules in the triplet state to different vibrational level of the ground state also takes place by emitting radiation. Unlike fluorescence, *states involved in the emission process in this case are of different spin multiplicity*. Generally this emission is related to triplet → singlet but phosphorescence in general, can be related to emission between any two electronic states of different spin multiplicity, for example, doublet to singlet etc. Similar to fluorescence, phosphorescence also leads to different vibrational levels of the ground state. Thus the structure of the phosphorescence band represents the vibrational structure of the ground state. The gap between the peaks of the phosphorescence spectrum gives the vibrational frequencies of the phosphorescing molecules in their ground states and these frequencies match with the vibrational frequencies obtained with the help of infrared or Raman spectrum.

Similar to fluorescence spectrum, 0-0 band in phosphorescence represents the highest energy transition and other transitions are of lower energies and thus the phosphorescence spectrum is also red shaded. In the case of fluorescence spectrum, 0-0 transition (actually occurs at slightly lower frequency than the absorption band at 0 K) often coincides with the 0-0 transition of the absorption band, whereas in case of phosphorescence, 0-0 transition is red shifted to the 0-0 transition of the absorption band. This is because the triplet state always possesses lower energy as compared to the singlet state. As already explained (8.2.2), smaller magnitude of the triplet state energy as compared to that in the singlet state is due to smaller repulsive energy between the two unpaired electrons and this arises because of the exchange interactions. The same smaller repulsive energy also does not allow the intramolecular charge transfer interactions by the electron donor and acceptor substituents to take place in the triplet state to the same extent as observed in the

singlet state. Because of this stabilization of the triplet state by these groups is much less as compared to that noticed in the singlet state. In other words, the exocyclic groups do not extend the conjugation of the aromatic systems as efficiently as they do in case of first excited singlet state. Thus the shifting of phosphorescence band maximum towards lower energy (smaller frequency) by these groups is much smaller than that observed in the fluorescence and absorption spectrum (Table 3). For example, presence of –OH or –NH_2 group lowers the first singlet state of benzene by 1523 and 5787 cm^{-1}, whereas the presence of same groups on benzene decreases the triplet state energy of benzene by 886 and 2688 cm^{-1} only. Similar behaviour is also observed in case of naphthalene and anthracene when these kinds of subsituents are present on them. On the other hand in case of polycondensed aromatic systems the effect of increase in the number of rings in aromatic system on the phosphorescence spectrum is the same as observed in fluorescence or absorption spectrum. For example the 0-0 band in the phosphorescence spectra of benzene, naphthalene and anthracene are at $2.95x10^4 cm^{-1}$, $2.13x10^4$ cm^{-1} and $1.49x10^4$ cm^{-1} respectively, whereas that of fluorescence spectra of benzene, naphthalene and anthracene are $3.7x10^4$, $3.2x10^4$ and $2.67x10^4$ cm^{-1} respectively.

Table 3: Singlet and Triplet energies for aromatic hydrocarbons and some their derivatives

Compound	Origin of fluorescence (cm^{-1})	Origin of Phosphorescence (cm^{-1})
Benzene	37037	29498
Toluene	36697	28902
Aniline	31250	26810
Phenol	35714	28210
Anisole	35714	28210
Naphthalene	32050	21300
1-Methylnaphthalene	31746	21010
1-Aminonaphthalene	28570	18994
1-Hydroxynaphthalene	30770	20597
2-Chloronaphthalene	31056	21097
Anthracene	26700	14700
2-Methylanthracene	25320	14560
9-Methylanthracene	25800	14220
1,5-Dichloroanthracene	25600	14250

Theory and Interpretation of Fluorescence and Phosphorescence, R.S. Becker, Wiley Interscience, New York, 1969, pg. 138

As mentioned above phosphorescence involves a transition which is spin forbidden (i.e. low probability). Thus as compared to fluorescence, the phosphorescence is long lived (10^{-5} to several seconds). Similar to fluorescence the phosphorescence is also observed in the rigid molecules, like aromatic hydrocarbons, because these molecules have restricted degree of vibrational freedom. At room temperature even the occurrence of phosphorescence from the aromatic systems is rare, because of its long lived nature the other deactivation processes, like collisional deactivation by solvent molecules,

quenching by paramagnetic species, photochemical reactions, and energy transfer processes are more predominant. Thus phosphorescence is generally observed in the glassy state at liquid nitrogen temperature, in very viscous liquids where the collisional deactivation is too slow to deactivate the triplet state and in low pressure gases. Although the natural lifetime of triplet state is independent of temperature, the rates of the other processes mentioned below do vary with temperature and thus change its lifetime. The following factors are important in increasing the triplet population and thus intensity of phosphorescence.

(a) *Mixing of singlet and triplet states:* The mixing of two wave functions is dependent on the mixing coefficients and the mixing coefficients are inversely proportional to energy difference of the two states. Smaller the energy gap, greater will be population of the triplet states. From Table 2, it is evident that in the carbonyl group, the difference between S_1 and T_1 is only ~ 29 kJ mol^{-1} and thus very weak fluorescence is observed. In benzene, the difference is 167 kJ mol^{-1}, both fluorescence and phosphorescence are observed.

(b) *Heavy atom effect:* Presence of heavy atom in the molecule or system with orbital which can penetrate more deeply in the neighbour, increases the population of the triplet state. This is due to the interaction of spin and orbital angular momentum. The effect of heavy atom, present in the molecule and in the solvent, on the lifetimes and Φ_{Ph} / Φ_f is shown in Table 4. Triplet state lifetime decreases on replacing the hydrogen atom by fluorine to iodine in the naphthalene ring and with solvent in going from propyl chloride to propyl iodide, whereas the ratio of Φ_{Ph} / Φ_f increases from chloronaphthalene to iodonaphthalene.

(c) *Introduction of paramagnetic centre*: Paramagnetic species have spin angular momentum and an associated strong inhomogeneous magnetic field. This field is similar to that created by a high atomic number atom and increases spin-orbit coupling leading to an increase in absorption and emission between singlet and triplet states. For example when 9-anthroylacetone is coupled with Mn^{2+} ion, the forbidden transition $S_0 \rightarrow T_1$ (absorption) is enhanced. The introduction of oxygen at a pressure of 100 bar into solution of alkenes, alkynes and aromatic hydrocarbons induces the $S_0 \rightarrow T_1$ absorption and is useful in identifying the triplet state energy, although many other bands due to charge transfer complexes are also observed.

Table 4: Phosphorescence lifetimes of naphthalene and its derivatives in different solvents

Compound	τ (s) in A	τ (s) in B	τ (s) in C	τ (s) in D	Φ Ph / Φ_f
Naphthalene	2.5	0.52	0.14	0.075	0.09
1-Fluoronaphthalene	1.4	0.17	0.1	0.029	-
1-Chloronaphthalene	0.23	0.075	0.06	0.023	5.2
1-Bromonaphthalene	0.014	0.0073	0.0071	0.006	164
1-Iodonaphthalene	0.0023	0.001	0.001	0.001	1000

A = mixture of ethanol, isopentane and ether; B = propyl chloride; C = propyl bromide; D = propyl iodide.

S. P. McGlynn, M. J. Reynolds, G. W. Daigre and N. D. Christoouleous, J. Chem. Phys., 66 (1962) 2499; S. P. McGlynn, F. J. Smith and G. Cilento, Photochem. Photobiol., 3 (1964) 269.

Delayed Fluorescence

Besides phosphorescence a long lived high frequency emission is also observed occasionally in rigid and viscous media. The frequency of this emission is similar to that of fluorescence if the molecule undergoes fluorescence. The major difference is that the decay time of the former emission is similar to that of phosphorescence. This emission is known as **delayed fluorescence**. There are two ways by which this fluorescence can occur:

(a).*E-Type Delayed fluorescence:* This is produced by the thermal activation of a molecule from its triplet state. The intensity relative to that of triplet-singlet emission decreases exponentially with temperature and the activation energy is equal to the energy difference between the first singlet and first triplet state. The intensity is proportional to the first power of the rate of absorption of radiation. The lifetime is the same as that of the triplet state, observed from the solution under the similar conditions. The name E-type delayed fluorescence was given as this emission was first observed from *eosin* and is exhibited from the molecules where the gap between the first excited singlet and triplet states is not very large. The small energy gap allows the repopulation of the first excited singlet state from the first triplet state by reverse intersystem crossing.

*(*b). *P-Type Delayed fluorescence:* It is due to triplet-triplet annihilation as the two triplet molecules collide to form one molecule in the first singlet state and the other in the ground state. This kind of emission was first observed from *pyrene* molecule and thus known as P-type delayed fluorescence. The P-type delayed fluorescence can be observed even in molecules having substantial difference between the first singlet and first triplet states. In this case the total energy possessed by the colliding triplet particles is more than enough to excite one molecule in the first singlet state and the other deactivates to the ground state. The intensity relative to phosphorescence emission does not follow the exponential temperature law. The intensity of delayed fluorescence emission is

$$T_1 + T_1 \rightarrow S_1 + S_0 \qquad (58)$$

proportional to the square of the intensity of the exciting radiation as the two molecules are required to form one excited singlet state molecule. P-type delayed fluorescence is also called as biphotonic, because the absorption of two photons must be absorbed to produce on excited molecule. The lifetime of this emission is expected to be half of the lifetime of the triplet state under the similar conditions.

There are two other types of delayed fluorescence reported but are mainly either in solution phase with long lifetime or in rigid medium at low temperature. “Recombination delayed fluorescence” requires an ejection of electron as a first step and would be, therefore, expected to occur preferentially by exciting with high energy radiation. The second one is by “triplet excitation” and depends upon the absorption of second quantum of exciting light by triplet. This is applicable when the triplet state has exceptionally long lifetime, e.g. crystals or solids at low temperature.

Energy Transfer Reactions

When a molecule is excited to one of its electronic state, it possesses a large amount of energy. Besides the processes mentioned in sections 8.2 and 8.3 the excited state molecule may try to dispose of its energy to the other molecules. This process is called *energy transfer*. In general, the energy transfer reaction may be represented by equation (59)

$$A + D^* \rightarrow A^* + D \qquad (59)$$

where the asterisk represents an excited state molecule, A is an acceptor and D^* is donor.

Unlike intramolecular energy transfer (sections 8.2 and 8.3), exchange of energy between two different species (D and A) is not so restricted with regard to exact equivalence of internal energy between initial and final states. Excess of energy is distributed into the translational (kinetic) energy (or very rarely a deficiency supplied by the kinetic energy of collision). Ten different types of energy exchange can be considered according to different modes (e.g. electronic, vibrational, rotational, and translational) between which energy exchange can occur. In rare case the energy of the donor molecule matches with that of the acceptor molecule, known as exact energy resonance transfer. In most of the cases, the energy of the donor molecule is slightly smaller or slightly larger than the acceptor molecule. In the former case small amount of translational energy of the acceptor is used and in the latter case excess electronic energy of the donor is converted into the translational energy of the acceptor. In this section main attention will be given towards electronic-electronic energy exchange and it will be assumed that excess energy goes into other modes of excitation. Intermolecular energy transfer has become an interesting field as it has revealed many new photochemical reactions, elucidated the mechanism of number of photochemical reactions and much information has been obtained about the excited states which otherwise is not possible by spectroscopic methods (for example, direct population of triplet state from the ground singlet state). Photosynthesis in plants can occur only by energy transfer. There are many other reactions in radiation and photochemistry involving energy transfer.

There are two major theories regarding energy transfer reactions and these are discussed briefly in the following section.

Radiative Energy Transfer

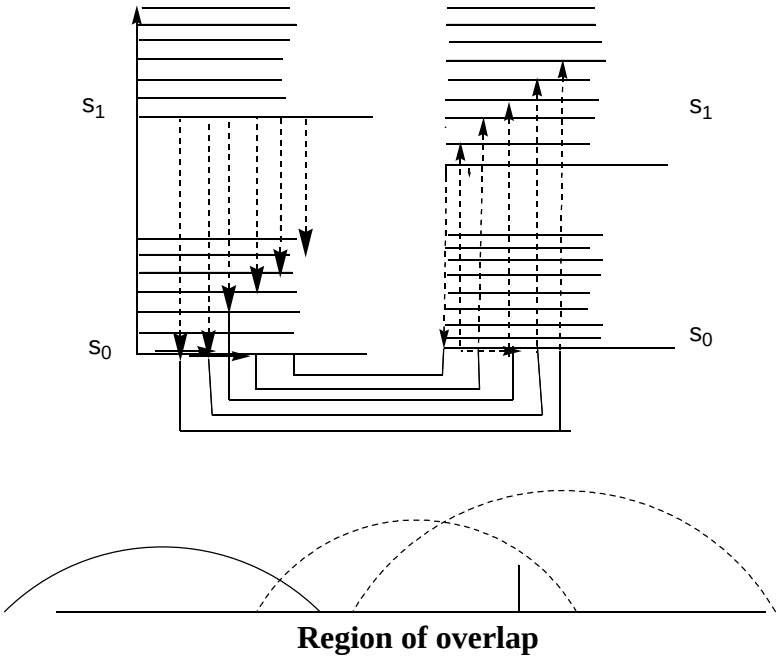
This process is also known as a trivial process and involves the following steps. This

$$D^* \rightarrow D + h\nu \qquad (60)$$

$$A + h\nu \rightarrow A^* \qquad (61)$$

process may be considered as two step process with photon emitted as the intermediate. In other words energies corresponding to that part of the emission spectrum of donor which overlap with the absorption spectrum of the acceptor can be transferred. Thus the efficiency of transfer depends on the quantum yield of the emission of the donor and molecular extinction coefficient of the absorbing system (a factor that appears in all transfer mechanism) and also on the size and shape of the sample. Since D^* will emit in all directions, the probability of radiative transfer increases with sample volume. The probability that the acceptor molecule may reabsorb radiation depends on the distance as

R^{-2}. This process can be characterized as being independent of viscosity since the donor and the acceptor molecules need not come in contact. This process can be depicted pictorially in Figure 5.



- - - - - - - - - - Absorption spectrum
……..Donor Emission spectrum
_____Donor absorption spectrum

Figure 5: Coupled transitions for donor-acceptor pair with electronic energy difference and relation between emission and acceptor spectra.

Non-radiative Transfer Process

Unlike the previous process, this process is a one step process. The de-energization of the donor and the excitation of the acceptor take place without the involvement of two systems and energy transfer is efficient if energies of the donor and acceptor are nearly equal. There are two ways by which this process can take place.

(i) *Long range Interactions*: Energy transfer can occur up to a separation of 5 to 10 nm which is much larger than the molecular diameters and thus independent of viscosity of the medium. The theory for this energy transfer has been developed mainly by Forster. Classically this process can be viewed as a coupling of two mechanical oscillators, tuning forks on the same base or two pendulums hanging from the same string. Here the two oscillating electric charges interact as dipoles. The interactions is strong if the dipole transition of D^* emitting and that of A, absorbing molecules are spin allowed.

$$A\ (\text{singlet}) + D^*\ (\text{singlet}) \rightarrow A^*\ (\text{singlet}) + D\ (\text{singlet}) \quad (62)$$

$$A\ (\text{triplet}) + D^*\ (\text{triplet}) \rightarrow A^*\ (\text{triplet}) + D\ (\text{triplet}) \quad (63)$$

Quantum mechanically this can be viewed as the interaction of two initial and final states, that is, $\psi (D^*) \psi (A)$ and $\psi (D) \psi (A^*)$. $\Psi (D)$ and $\psi (D^*)$ are the wave functions of the donor molecule, whereas $\psi (A)$ and $\psi (A^*)$ are those of acceptor molecule. When they couple together, they become degenerate. The time dependent perturbation theory shows that there is a finite probability of energy transfer from one state to the other. The dipole-dipole interactions depend on the inverse of third power of distance (r^{-3}) between the molecule and the probability of energy transfer on the inverse square of this interaction energy (r^{-6}). In other words, rate of energy transfer falls off to the sixth power of distance. Forster has derived an expression for the rate of energy transfer in terms of experimentally known quantities.

$$k (D^* \rightarrow A) = [(8.8x10^{-25} \kappa^2 \Phi (D))/\eta^4 \tau (D) R^6)] \int F_D (\bar{\upsilon}) \varepsilon (\bar{\upsilon}) d\bar{\upsilon} / \bar{\upsilon}^4 \qquad (64)$$

where η is the refractive index at that particular frequency, $\bar{\upsilon}$, wave number, $F_D (\bar{\upsilon})$ spectral distribution of donor emission in quanta normalized to unity. $\varepsilon_A (\bar{\upsilon})$ molar extinction coefficient of acceptor at the particular wavenumber ($\bar{\upsilon}$), κ is the orientation factor and for randomly distribution donors and acceptors κ is $(2/3)^{1/3}$, τ_D (s^{-1}) the radiative lifetime of the donor, Φ (D) is the fluorescence quantum yield of the donor molecule and R is the distance between the donor and acceptor molecules (cm).

The efficiency of this type of energy transfer is expressed usually in terms of "Critical radius R_0", the distance of separation of the donor and acceptor when this type of energy transfer is equal to $1/\tau$ (actual lifetime of the excited species), i.e.

$$R_0^6 = [8.8x10^{-25} \kappa \varphi (D)/ \eta^4] \int F_D (\bar{\upsilon}) \varepsilon (\bar{\upsilon}) d\bar{\upsilon}/ \bar{\upsilon}^4 \qquad (65)$$

Another mechanism depicting the long range energy transfer involves the exciton migration. Frenkal was the first to explain the spectral characteristics observed in certain crystals, solid solutions and some fluids and showed $1/R^3$ dependence. This mechanism involves an electron-hole pair, was looked upon as an entity that could move about the crystal as a result of interactions between lattice sites. This can be regarded as the electron excitation in an irradiated species as an exciton that is free to move over a considerable number of lattice sites. More detailed treatment is beyond the scope of this chapter. Table 5 gives the results which can be explained by this theory. The rate of intermolecular energy transfer between singlet-singlet is found to be constant with in experimental errors when studies were made in different solvents with five fold variation in viscosity. The agreement between the theory and experiment is fair.

Table 5: Calculated and experimental rate constants and critical distances.

Donor	Acceptor	k_{cal}, 10^9 $M^{-1} s^{-1}$	K_{exp}, 10^9 $M^{-1} s^{-1}$	R_0 (cal) Å	R_0 (exp) Å	H
Anthracene	Perylene	23.0	120.0	31	54	0.19
Perylene	Rubrene	13.0	130.0	38	65	0.89
9,10-dichloranthracene	Perylene	17.0	80.0	40	67	0.65
Anthracene	Rubrene	7.7	37.0	23	39	0.265
9,10-dichloroanthracene	Rubrene	8.5	31.0	32	49	0.65

W. Ware, J. Amer. Chem. Soc., 83 (1961) 4374.

Exchange Mechanism or Short-range Energy Transfer: This is also called as collisional transfer. This mechanism can be considered as a special case of chemical reaction where the chemical identity of the partners A and D does not change but the energy is transferred from one molecule to other. The transition state thus can be expected to be similar to that observed in the gas phase kinetic collision theory model, i.e. the energy transfer takes place if the molecules come close together and the distance is of the order of molecular collision diameter. If every collision leads to energy transfer then it should depend on the viscosity of the medium because viscosity limits the diffusion of excited state donor and acceptor molecule. The maximum bimolecular rate of energy transfer can be calculated from the simplified Debye equation. The expression is:

$$k_{diffusion} = 8\ R\ T/\ 3000\ \eta \qquad (66)$$

where R is a gas constant, η viscosity of the solvent in poise, T temperature in Kelvin.

Dexter has derived theoretical expression for this mechanism and has shown that spins of D^* and A need not to be equal to those of D and A^*. The spin allowed energy transfer reaction is

$$D^*(T) + A(S) \rightarrow D(S) + A^*(T) \qquad (67)$$

Table 6: Viscosities and diffusion controlled bimolecular rate constants at 20^0 C.

Solvent	Viscosity (0.001 η poise)	$k_{diffsuion}$ (M^{-1} s^{-1})
Hexane	3.26	$2.0x10^{10}$
Benzene	6.47	$1.0x10^{10}$
Cyclohexane	9.65	$6.9x10^{9}$
Water	10.05	$6.5x10^{9}$
Ethanol	11.94	$5.4x10^{9}$
Ethylene glycol	173.0	$3.8x10^{8}$
Glycerol	10,690.0	$6x10^{6}$

where D (T) and A(T) are triplet and D (S) and A (S) are singlet donor and acceptor molecules respectively. Wigner rules (known as *Wigner Spin Correlation Rules*) for this kind of energy transfer are more general and can be specified as follows. If the spins of the donor and acceptor are S_D and S_A, the total spin of the transition state can take magnitudes as $|S_D + S_A|$, $|S_D + S_A - 1|$,……$|S_D - S_A|$. It is then necessary to see whether the products, X and Y, can also give at least one of the same total spin magnitudes in the transition state. Table 7 shows multiplicities in the transition state that can arise from some multiplicities of two separated species. The following reaction illustrate this rule and gives rise to the possible excited state of the acceptor molecule

$$D^*(T) + A(T) \rightarrow D(S) + A^*(S) \qquad (68)$$
$$\rightarrow D(S) + A^*(T) \qquad (69)$$
$$\rightarrow D(S) + A^*(\text{quintet}) \qquad (70)$$

Experimental differentiation of these types of energy transfer can be accomplished by examining the concentration dependence of the energy transfer and some of the conclusions are listed in Table 8.

Table 7: Multiplicities of transition states for given multiplicities of two separated species.

Separated Species	Transition State
singlet + singlet	Singlet
singlet + doublet	doublet
singlet + triplet	triplet
doublet + doublet	singlet, triplet
doublet + triplet	doublet, quartet
triplet + triplet	singlet, triplet, quintet

Table 8: Characteristics of some energy transfer types

	Trivial Radiative Transfer	Long-range Radiationless transfer	Exchange Mechanism	Exciton Migration
Dependence of rate on increase of viscosity	None	Slightly decreased	Decreased	?
Donor lifetime	Unchanged	Decreased	Decreased	Decreased
Donor Emission Spectrum	Changed	Unchanged	Unchanged	Depends upon the magnitude of donor-donor interactions
Donor Absorption spectrum	Unchanged	Unchanged	Unchanged	Small change depending on the magnitude of donor-donor interactions
Dependency of efficiency on increasing volume	Increased	None	None	None

Photosensitized Reactions

Photosensitized phenomenon involves the reactions of the species which are different from those absorbing the radiations. Our interest lies in studying the reactions of the species which can not be excited directly. These reactions are shown to be of great significance in photobiology and also provide valuable insights in to photophysical processes.

Photosensitized reactions have attained great importance since the characteristics (energy, spin multiplicity, fluorescence and phosphorescence quantum yields etc.) of sensitizers are better understood. In photosensitized reactions, a foreign material is added whose main function is to absorb light and then excite other molecules by delivering the absorbed energy. The energy may be given either by resonance or by exchange mechanism and forming products of the acceptor molecule. In some cases the sensitizer decomposes into reactive fragments which either impart energy or react with other

molecules present in the system. The main advantage of this indirect method is that reactions which are not possible with direct radiation become feasible by using sensitizers. Reactions of triplet states of olefins, whose direct population to triplet state by absorption is highly improbable and intersystem crossing from singlet to triplet is also not efficient, can be brought about by photosensitization.

It is necessary to know the characteristics of both the sensitizer and the compound to be sensitized. The important factors for photosensitization are:

(a) absorption spectrum of the donor and acceptor molecules
(b) singlet and triplet energies of the donor and acceptor molecules
(c) the quantum yield of triplet formation of the sensitizer

As discussed in the section 8.4, the energy transfer is large if the absorption spectrum of acceptor and emission spectrum of donor overlaps maximum. Secondly, the energy transfer will be efficient if the excited state of the acceptor to be populated is of lower energy than that of the donor. Finally, high quantum yield of triplet formation of the sensitizer is favourable for photosensitization.

All the characteristics mentioned above are well satisfied by the carbonyl compounds and are used for organic photosynthesis. Engel and Monroes[6] have nicely reviewed the photosensitization reactions, giving singlet triplet energies of various compounds, quantum yields of fluorescence and phosphorescence, internal conversion and intersystem crossing and various types of reactions the compounds can undergo. Finally they have also discussed various types of complications which can arise.

Several examples of atom sensitized reactions can be considered. For example, dissociation of hydrogen needs 84.9 nm (1409 kJ mol^{-1}) which is the wavelength of continuum and present in vacuum UV region where as it needs only 435.1 kJ mol^{-1} (275 nm) to decompose into two hydrogen atoms.

$$H_2 + h\nu\ (\lambda \leq 84.9\ nm) \rightarrow H + H^* \qquad (71)$$

where H^* is electronically excited atom. But H_2 mixed with small amount of Hg vapours need only 468.6 kJ mol^{-1} (λ = 253.7 nm), the wavelength of radiation which excites Hg atom to its triplet state.

$$Hg\ (^1S_0) + h\nu\ (\lambda = 253.7\ nm) \rightarrow Hg\ (^3P_0) \qquad (72)$$

$$Hg\ (^3P_0) + H_2 \rightarrow Hg\ (^1S_0) + 2\ H\ (^2S_{1/2}) \qquad (73)$$

and 33.5 kJ of excess energy can go to translational degree of freedom. Similarly CH_4 is virtually transparent at $\lambda > 170$ nm. In the presence of mercury vapors, the mercury resonance line at 253.7 nm will dissociate it. The chemical reactions involved are (72) and followed by:

$$Hg\ (^3P_0) + CH_4 \rightarrow Hg\ (^1S_0) + CH_3. + H \qquad (74)$$

The energy of the excited mercury atom leads to dissociation of methane. *It may be emphasized here that energy transfer may lead to populate the electronically excited states differently from those which can be populated by direct absorption, as well as, photosensitized reactions may differ chemically from unsensitized photochemical reactions.* For example, the direct photolysis of CH_4 with radiation $\lambda < 144$ nm leads to the formation of molecular hydrogen and ethylene radical ($.CH_2$) in the primary process,

whereas in the photosensitized reaction (74), CH_4 decomposes to $.CH_3$ and hydrogen atom.

Ethyl pyruvate (EP, ethyl 2-oxopropanoate) decomposes to two molecules of acetaldehyde with quantum yield of 0.17 when excited with $\lambda = 313$ nm, whereas in presence of benzophenone and at $\lambda = 313$ nm, the similar decomposition reaction has the

$$CH_3COCOOC_2H_5 + h\nu \rightarrow 2\,CH_3CHO + CO \qquad (75)$$

quantum yield of 0.32. In the former case, EP is excited to the first excited singlet state, followed by intersystem crossing to triplet state from where it is decomposed, whereas in the latter case EP is directly produced in the triplet state via energy transfer from the triplet benzophenone. The above results suggest that: (1) population of triplet state of EP is different from different processes, leading to different quantum yield of decomposition and, (2) energy transfer from benzophenone (289 kJ mol^{-1}) to EP (272 kJ mol^{-1}) is energetically favourable. It has also been shown that decomposition of EP is negligible when 2-acetophenone (247 kJ mol^{-1}) was used as photosensitizer.
Cl_2O has a very weak absorption above 350 nm and its decomposition can be sensitized by Cl_2 and Br_2 in the region ≥ 350 nm. The quantum yield of direct and sensitized decomposition is the same in both cases. The reactions are:

$$Cl_2 \text{ (or } Br_2) + h\nu\ (\lambda > 350 \text{ nm}) \rightarrow 2\,Cl \text{ (or } 2\,Br) \qquad (76)$$
$$Cl \text{ (or } Br) + Cl_2O \rightarrow ClO + Cl_2 \text{ (or } BrCl) \qquad (77)$$

Similar reactions are also observed in the direct photolysis

$$Cl_2O + h\nu \rightarrow ClO + Cl \qquad (78)$$
$$Cl + Cl_2O \rightarrow ClO + Cl \qquad (79)$$

Finally, photosensitized reactions are so reproducible that they can be used for actinometery, for example, coloured uranyl ions absorb the radiation and energy is transferred to the oxalate ions which then decompose. The uranyl ions remain unchanged and can be used indefinitely as sensitizer.

Photosynthesis

The most commonly occurring photosensitized reaction in nature is the conversion of CO_2 and water to glucose and oxygen, by the green plants in the presence of sunlight.

$$6\,CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\,O_2 \qquad (80)$$
$$2\,H_2O + A \text{ (hydrogen acceptor)} + h\nu \rightarrow O_2 + AH_2 \qquad (81)$$

This phenomenon is known as *photosynthesis* and may also be looked as the natural reversal of cell metabolism. The reaction is highly endothermic (486.6 kJ mol^{-1}) and thus a very slow reaction. But the rate at which it occurs in nature automatically suggests that it must be sensitized by some other species present in the plants. These species are recognized to be *chloroplast* present in the plant cells. Each chloroplast contains species called *grana* which contains the green colored pigment *chlorophyll*, a sand-witched in layers between lipid and protein molecules. The chlorophyll molecule is a magnesium

complex of a highly conjugated heterocyclic system (Figure 6). The mechanism of this photosensitized reaction has been studied extensively and a review has been written by
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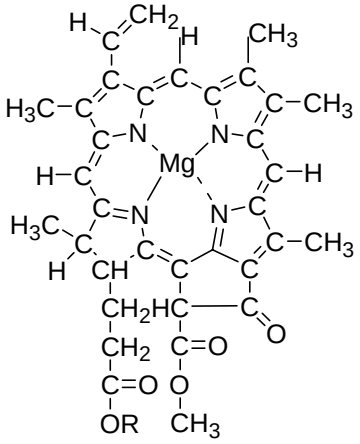


R = CH_3-C(CH_3)H-CH_2-(CH_2-CH_2-C(CH_3)H-CH_2)$_2$-CH_2-CH_2-C(CH_3)=CH-CH_2-

Figure 6: Structure of Chlorophyll.

Robinson[7, 8]. The total photosensitized reaction is quite complex. The activities in the photosynthetic unit can be divided into following distinct processes each seems to be more complicated than the step immediately preceding it. These are:

(a) absorption of light
(b) energy transfer to the active chlorophyll-a site
(c) electron transfer process producing chemically active reaction intermediate
(d) completion of CO_2 and water cycle.

Absorption takes place in two pigment systems individually, one absorbing in the far red (685 nm) and the other absorbing at shorter wavelength (300 nm). Since chlorophyll is a highly conjugated system so excitation and removal of electron is relatively easy. The first act of radiation is to excite the electron to high energy site. It has been found in laboratory that chlorophyll molecules looses the energy immediately after absorption as fluorescence but in plants it acts like a storage cell in the battery. It is due to the spatial arrangement of chlorophyll molecule and its orientation with respect to the lipids, cofactors and protein present closely.

Energy transfer to the active chlorophyll-a site, is so efficient and fast that photochemical energy arrives at the respective site immediately after absorption, even though it appears to occur over a large pigment molecule in the photosynthetic unit. At the photo-reactive site, oxidation-reduction involves a cytochrome, iron porphyrin quinone redox couple. The oxidized species then reacts with water to yield oxygen. The oxidizing agent is reproduced in the photosynthetic unit in a hydrogen transfer reaction. The second oxidant may be reproduced through the second pigment involved in the photochemical process. It is thought that the second photochemical pigment system produces a reactive site capable of producing an iron (III) cytochrome, reactive intermediate, capable of regenerating the necessary oxidant for the Hill reaction. The oxidation step, reaction in the laboratory can

be carried out with isolated chloroplasts and appropriate hydrogen acceptor. In general, quinones are used but other hydrogen acceptors are also used. The non-specificity of the hydrogen acceptors suggests that the conversion of water to oxygen within the cell is non-enzymatic.

$$2\,H_2O + \text{Quinone} + \text{sensitizer} + h\nu \rightarrow O_2 + 2\,\text{Hydroquinone} \qquad (82)$$

During the course of photosynthetic reactions, role of second pigment is also observed. This second pigment acts as a reducing agent and reduces one or other of the cellular pyridine nicotinamides, which may be nicotinamide adinine dinucleotide phosphate, NADP. A reduced pyridine nucleotide ($NADPH_2$) then participates in carbon dioxide reduction along with the phosporylating agent, adenosinetriphosphate (ATP) to produce a mole of ribulose diphosphate.

The role of light played in the photosynthesis of CO_2 to glucose is to produce energy rich ATP molecules and cofactor $NADPH_2$ as a reducing agent. After this, CO_2 undergoes many dark reactions along with energy rich ATP and $NADPH_2$ to from glucose. The complete mechanism has been given by Melvin Calvin and all the reactions are catalyzed by enzymes. Schematic diagram is given in Fig.7. Initially CO_2 is absorbed by ribulose, 1,5-diphosphate to give 3 phosphateglycerate. In the series of further many steps phosphateglycerate is converted into glucose by using ATP and $NADPH_2$. During same time the intermediate ribulose-1,5-diphosphate is regenerated from 3 glyceraldehyde phosphate via a number of reactions collectively known as pentose shunt.

Chemiluminescences

During the course of certain chemical reactions light is emitted. This emission of radiation is known as *Chemiluminescence*. The excitation is not thermal. Because emission characteristics of some species (CH, OH C_2 etc.) are also observed in flames, but the emission intensities observed in chemiluminescent reactions are generally higher than those expected from the flame temperature. The excitation of the molecules is due to energy released by the chemical reactions, also known as exothermicity of the reaction. Most common types of reactions are the recombination reactions and exchange reactions.

Recombination Reactions

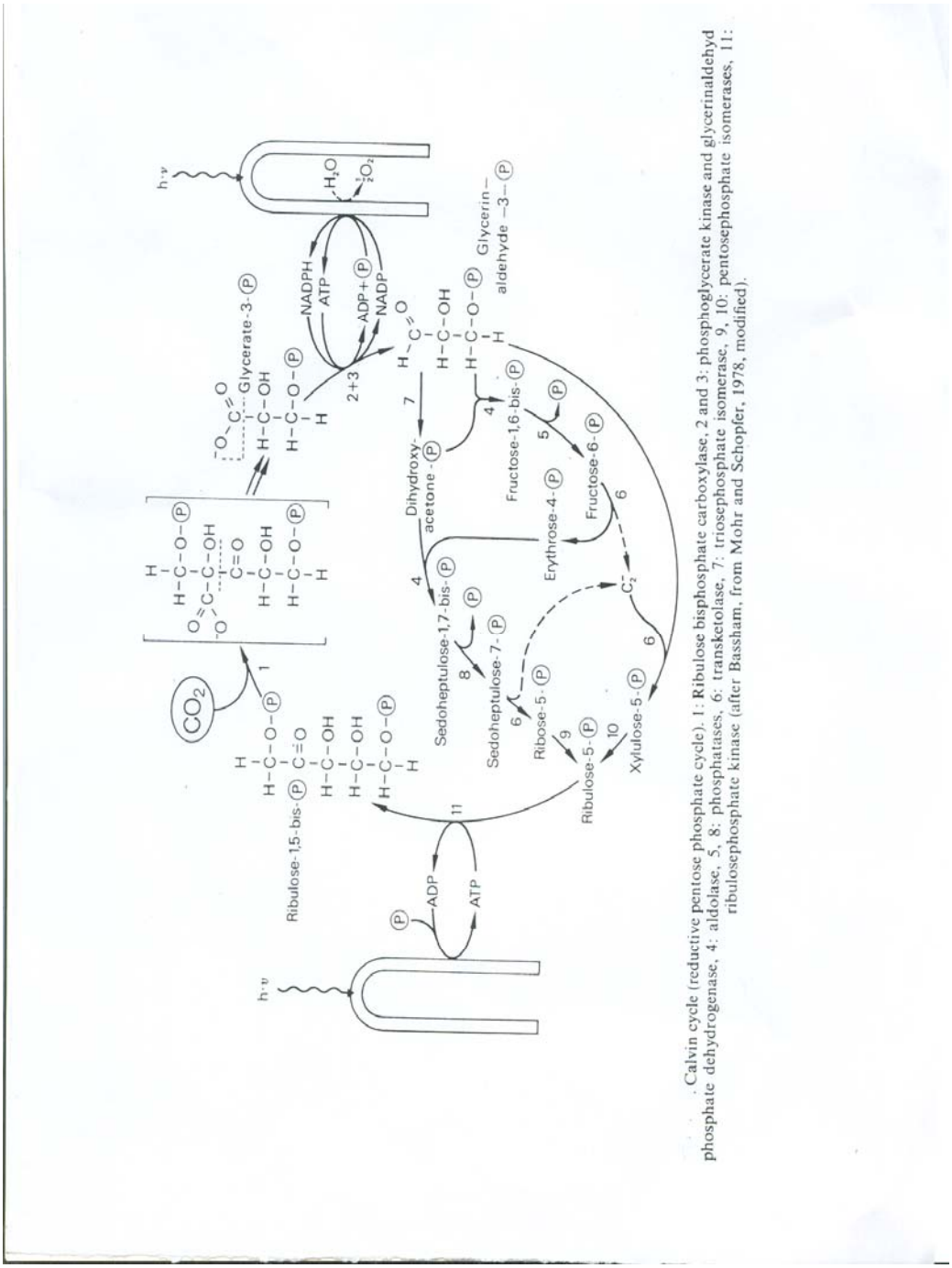
Two body recombination reactions do lead to the chemiluminescence but three body recombination reactions lead to more efficient and intense chemiluminescence. The third body 'M' stabilizes the newly formed species AB. The species involved mostly in these reactions are: atom-atom or atom-small molecules. If recombination and stabilization (or quenching) is the only processes the reaction scheme can be written as:

$$A + B + M \rightarrow AB^* + M \qquad k_1 \qquad (83)$$

$$AB^* \rightarrow AB + h\nu \qquad k_2 \qquad (84)$$

$$AB^* + M \rightarrow AB + M \qquad k_3 \qquad (85)$$

then the steady state treatment yields a value for the intensity of chemiluminescence, I_c,



. Calvin cycle (reductive pentose phosphate cycle). 1: Ribulose bisphosphate carboxylase, 2 and 3: phosphoglycerate kinase and glycerinaldehyd phosphate dehydrogenase, 4: aldolase, 5, 8: phosphatases, 6: transketolase, 7: triosephosphate isomerase, 9, 10: pentosephosphate isomerases, 11: ribulosephosphate kinase (after Bassham, from Mohr and Schopfer, 1978, modified).

$$I_c = \{k_1 k_2 [A] [B] [M]\}/\{k_2 + k_3[M]\} \qquad (86)$$

At moderate high pressure; $k_2 << k_3 [M]$, I_c is approximately independent of [M] and the reaction may appear to be second order. The emission intensity will however depend on the nature of M, since both k_1 and k_3 vary with chemical species.

Most of these gas-phase atom recombination chemiluminescence reactions have been carried out in flow system. In flow systems the atoms in high concentration (1 to 10%) are produced using an electric discharge. In general the atoms are produced in their

ground state and thus it is quite natural to expect the chemiluminescence from the atom recombination reactions from levels just below the dissociation threshold for normal (unexcited) fragments. However it is often found that the emission originates from an electronic state that does not correlate with the ground state of A and B (i.e. lie on the same potential energy curve or surface). It seems that emitting state is populated by radiationless transition from a state that does correlate with the normal species. In other words reaction (83) gives an oversimplified version of the excitation process. Several detailed mechanisms can be considered to give rise to overall third order kinetic behaviour. Since one of the states with which normal A and B correlate may be the ground state of AB, a considerable fraction of AB might be formed electronically unexcited and thus does not give rise to chemiluminescence

$$A + B + M \rightarrow AB + M \qquad k_1' \qquad (87)$$

There are also many gas phase chemiluminescence reactions in which the newly formed molecules are produced in electronically excited states and emit radiations. The following examples can illustrate the above points. Recombination of two ground state chlorine atoms ($^2P_{3/2}$) gives rise to a chlorine molecule in the $^3\pi_v$ excited state and emission takes place from this state as mentioned in the mechanism.

$$2\,Cl\,(^2P_{3/2}) + M \rightarrow Cl_2\,(^3\pi_{o,v}^{+}) + M \qquad k_1 \qquad (88)$$

$$Cl_2\,(^3\pi_{0,v}^{+}) + M \rightarrow 2\,Cl\,(^2P_{3/2}) + M \qquad k_2 \qquad (89)$$

$$Cl_2\,(^3\pi_{0,v}^{+}) + M \rightarrow Cl_2\,(^1\textstyle\sum^{+}_{g}) + M \qquad k_3 \qquad (90)$$

$$Cl_2\,(^3\pi_{0,v}^{+}) + M \rightarrow Cl_2\,(^1\textstyle\sum^{+}_{g}) + h\nu\ (\lambda > 500\ nm) \qquad k_4 \qquad (91)$$

and the intensity of emission is given by

$$I = \{ k_1 k_2 [M] [Cl]^2 \} / \{k_4 + k_3 [M]\} \qquad (92)$$

Similarly the recombination of bromine and chlorine atoms, nitric oxide and oxygen atoms etc. have also been found to emit in the respective region of the spectrum.

$$Br\,(^2P_{3/2}) + Cl\,(^2P_{3/2}) + M \rightarrow BrCl\,(^3\pi_{0,v}^{+}) + M \qquad (93)$$

$$BrCl\,(^3\pi_{0,v}^{+}) \rightarrow BrCl\,(^1\textstyle\sum^{+}) + h\nu \qquad (94)$$

$$O + NO + M \rightarrow NO_2^{*} + M \qquad (95)$$

$$NO_2^{*} \rightarrow NO_2 + h\nu \qquad (96)$$

The expression for the intensity emitted from NO_2^* is similar to the equation (92) and is proportional to [O] [NO] and to the nature of third body at ordinary pressures as predicted by the equation (92). At sufficient low pressures ($5x10^{-2}$ mm Hg) the intensity becomes proportional to [M] also. The example where chemiluminescence emission does not take place from the initially formed excited state is the recombination of N-atoms, i.e.

$$N\,(^4S) + N\,(^4S) + M \rightarrow N_2\,(^3\textstyle\sum_g^{+}) + M \qquad (97)$$

$$N_2\,(^3\textstyle\sum_g^{+}) + M \rightarrow N_2\,(^3\pi_g) + M \qquad (98)$$

$$N_2\,(^3\pi_g) \rightarrow N_2\,(^3\textstyle\sum_u^{-}) + h\nu \qquad (99)$$

Exchange Reactions

The second most important class of this type of reactions is the exchange reactions, having the general type:

$$A + BC \rightarrow AB^{v} + C \qquad (100)$$

The superscript on AB indicates that the product molecule AB is formed with a high degree of vibrational excitation in the newly formed bond. If the molecules are *infrared active* i.e. the molecule is having oscillating dipole moment finite, chemiluminescence emission is observed in the red or near infrared region of the spectrum. The other important point to be noted is that the vibrational excitation does not follow the Boltzmann distribution. The common example is the reactions of hydrogen atom with the halogens, i.e.

$$H + X_2 \rightarrow HX^{v} + X \qquad (101)$$

If $X_2 = Cl_2$, vibrational-rotational spectra has been observed for the transitions $\Delta v = 0$, 1, and 2. Under low pressure conditions, i.e. to avoid collisional deactivation, chemiluminescence is observed from $v = 6$. The main reason for studying these kinds of reactions was due to its application in theoretical kinetics. Computer simulations of reaction trajectories on the potential energy surface connecting reactants and products have been carried out to predict the vibrational and rotational excitation and these results have been compared with the experimental observations. Depending up on the nature of the reacting atom A and molecule BC, the amount of energy going in to the vibrational mode of the newly formed bond has been predicted. In the above reaction for $X_2 = Cl_2$, from the infrared emission it was found out that only 15% of the heat of reaction goes in to vibrational degree of freedom. Whereas in similar reactions of alkali metals with chlorine to form alkali metal chlorides, studied by molecular beam kinetics, about 90% of the exothermicity of the reaction is present in the internal degree of freedom. The difference between the above types of reactions is due to different kinds of potential energy surfaces involved in the above reactions. Similarly several four-atom reactions

$$A + BCD \rightarrow AB^{v} + CD \qquad (102)$$

also display chemiluminescence. For example reaction (102)

$$H + O_3 \rightarrow OH^{v} + O_2 \qquad (103)$$

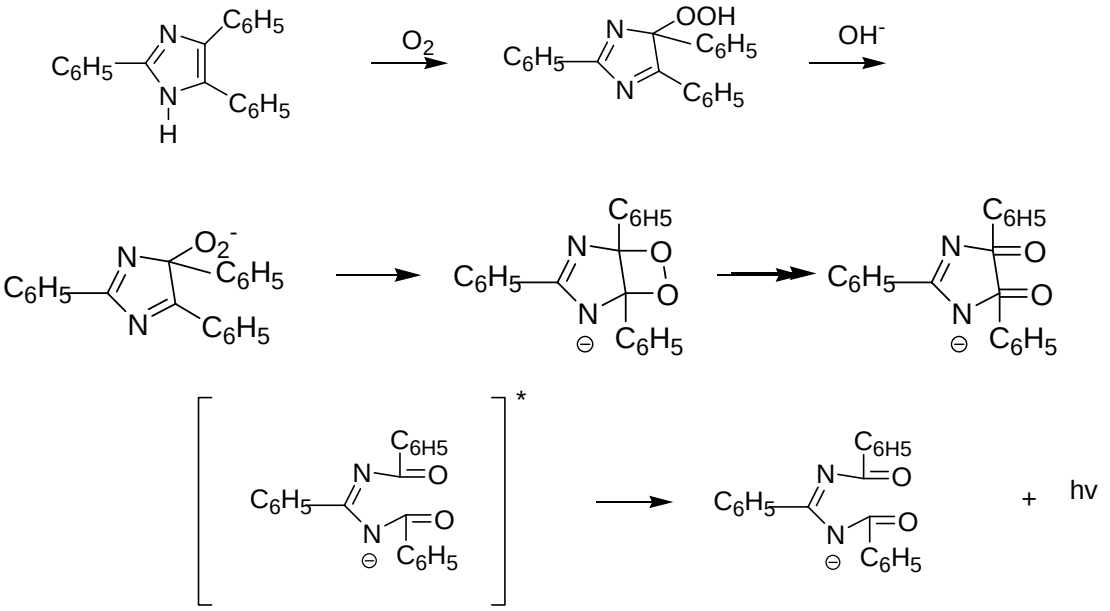
is a highly exothermic reaction (335 kJ mol^{-1}) and the emission observed from OH extends from the infrared to the long wavelength end of the visible spectrum and the bands are forbidden 'overtone' vibrational transitions ($\Delta v = 4$ or 5). These kinds of overtone bands are also observed in the glow of the night sky and reaction (103) is believed to be responsible for the OH excitation in the upper atmosphere.

Bio-luminescence

There are many transformations occurring in living organisms, fire fly crustaces etc., which are followed by the emission of radiation. The mechanism of this luminescence is

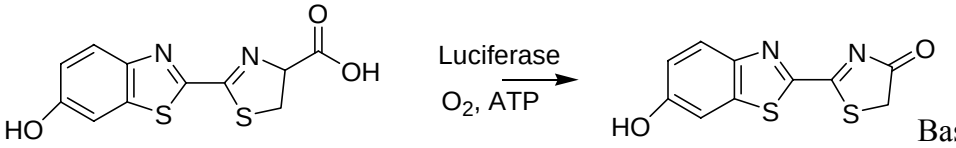
in general not properly understood but it is found that they involve oxidation of biological molecules before the light is emitted. These transformations have been tried in laboratory to understand these phenomena.

A laboratory reproducible system is 'Lophine'. Lophine, 2,4,5-triphenylimidazole, emits when treated with strong alkali in presence of oxygen. In this case the intermediates hydroperoxide, is separable and this emits upon treatment alone or thermally decomposed. The mechanism is:



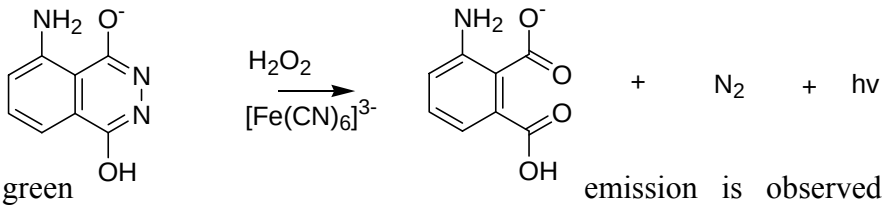
and the excited state decomposition is from excited singlet state. Similarly substituted imidazole, substituted phthalahydrazines also exhibit chemiluminescence and quantum yield of emission is found to increase with the presence of electron donating substituents. Peroxide formation, as with lophine, is probably important step in certain bacterial luminescence and is suggested that bioluminescence of *bacterium achromobacter fischeri* probably involves the peroxide formation. It is also generally observed that bioluminescence reactions involve the enzymatically catalyzed (luciferase) oxidation of certain compound called *Luciferin*. Firefly luciferin and substituted luciferins are prepared in the laboratory.

Chemiluminescence observed in the fire-fly systems is very efficient and the overall quantum yield for emission approaches unity. The substrate molecule luciferin is oxidized in the presence of the energy-rich phosphate ATP (adenosine triphosphate). The enzyme (luciferase) required in the fire-fly luminescence is Mg^{2+}, ATP and a source of O_2 (hydrogen peroxide is generally used). The initial step in the reaction of luciferin with the enzyme and ATP is to from inorganic phosphate. Enzymatic reaction of oxygen produces the excited species responsible for the light emission, the nature of which is still unknown, but the possible reaction is:



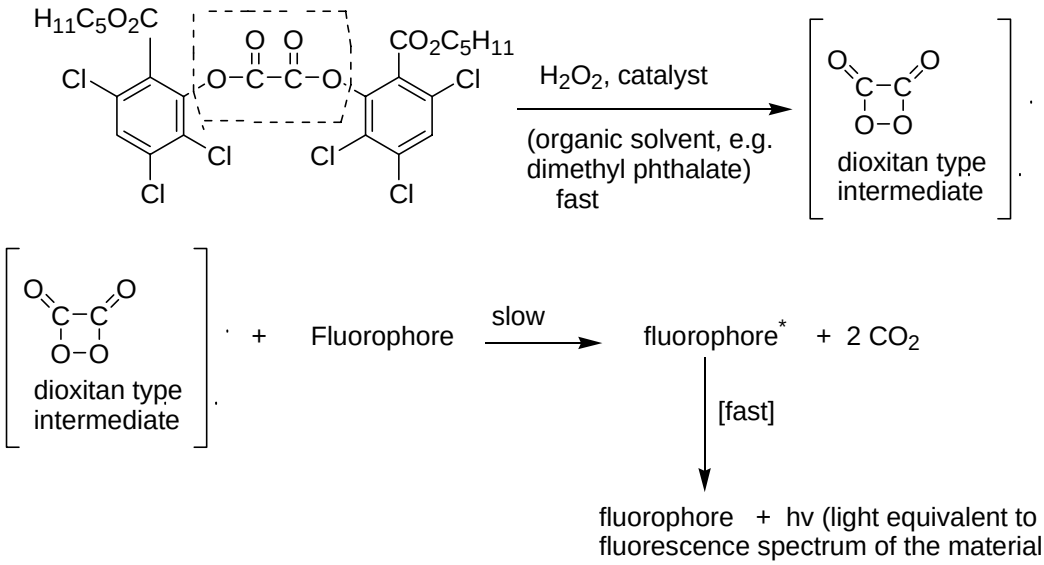
Based on the

above mechanism, many compounds have been synthesized in the laboratory to observe chemiluminescence. For example the oxidation of alkaline solutions of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione), usually by hydrogen peroxide, in the presence of $[Fe(CN)_6]^{3-}$ ion:



The blue green emission is observed from the excited aminophthalate ion. A narrow band at 634 nm is often emitted from the oxidation reactions those involve organic peroxides or hydroperoxide. A similar emission is also observed from the reaction of sodium hypochlorite and hydrogen peroxide. This emission band is observed from a collision complex (also known as excimer), formed from two excited oxygen molecules in $^1\Delta_g$ state. The reason for this emission is that transition $^1\Delta_g \rightarrow {}^3\sum^-g$ is highly forbidden for electrical dipole interactions (spin, parity and angular momentum forbidden), but a weak emission is observed as a result of magnetic dipole transition at $\lambda = 1269$ nm. The band at 634 nm is equivalent to twice the energy of $^1\Delta_g$ oxygen and is also called as *dimole emission.* If the fluorescent (also called fluorophore) substances (e.g. 9,10-disubstituted anthracene) are present in the oxidation systems, the characteristics fluorescence of these substances may be observed by intermolecular energy transfer from the energy rich products of the reactions.

The most efficient chemiluminescent systems, having practical utility, are based on esters of oxalic acid. Energy rich intermediates are formed by the catalytically decomposition of esters by hydrogen peroxide. The energy from the intermediate is transferred to the fluorophore present in the system and characteristic emission depending the nature of fluorophore, is observed from its excited state. Although the oxidation mechanism is very complex, leading to the formation of excited molecules of the parent substance, a typical example is given below. The starting molecule is the ester of CPPO (bis(carbopentoxy-3,5,6-trichlorophenyl) oxalate. Quantum yield of this reaction is quite (0.32) and the emission characteristics depends upon the nature of suitably selected fluorophore e.g. 9,10-diphenyl anthracene (blue), bis(phenyl ethyl)anthracene (green), rubrene (red),



tetrakis(dimethylamino)ethene (TKDE, very bright and long duration green), and commercial CYALUME.

Chemiluminescence has been found to be very useful in analytical chemistry. Both the oxalate and TKDE systems have found to be of great utility in emergency lighting systems, especially in situations where the absence of heat and flame may be vital. Life jacket markers using oxalate esters and ropes incorporating TKDE become illuminated when an evacuated covering is torn off. Potential artistic uses of chemiluminscence have been recognized and necklaces containing repackaged CYALUME are familiar sight. An improvement in the detectors (detecting as low as few photons per second) has led to its great utility in analysis. As standard biochemical assay for ATP uses nature's efficient chemiluminescent materials of fire-fly luciferin and luciferase, TKDE is sensitive indicator of oxygen and the oxalate esters may be used to detect picomole (10^{-12} mol) quantity of hydrogen peroxide.

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