

PHOTOCHEMISTRY

12.1 INTRODUCTION

There are so many reactions which occur due to absorption of light radiations by matter. For example reaction of carbon dioxide (CO_2) and water (H_2O) in the presence of chlorophyll is a photochemical reaction. The branch of chemistry which deals with study of kinetics of photochemical reactions, processes and their applications is called photochemistry. The vision process involves the absorption of photon by visual pigment rhodopsin. The chemical reactions occurring in atmosphere are photochemical reactions. For example formation and decomposition of ozone in stratosphere is a very important reaction for life on earth. This chapter deals with study of laws of photochemistry, kinetics of photochemical reactions, photochemical process like fluorescence and phosphorescence, chemiluminescence and lasers. The mechanisms involved in photosensitized reactions have been also described in this chapter.

12.2 PHOTOCHEMICAL AND THERMAL REACTIONS

The chemical reactions are results of collision of reactants. Each collision cannot cause a chemical reaction but a fraction of collision with proper orientation and sufficient energy causes a chemical reaction. The minimum energy needed to convert reactants into product is called activation energy. This energy can be provided by heating or irradiating reactions. Therefore chemical reactions can be classified as thermal and photochemical reaction. The basic differences between these reactions are given in table 12.1.

Table 12.1 Distinguishing properties between thermal and photochemical reactions

Thermal reactions	Photochemical reactions
These involve absorption or evolution of heat energy.	These chemical reactions evolve absorption of light energy.
These reactions may occur in the absence of light.	These reactions take place in the presence of light only.
Temperature significantly affects the rate of thermal reactions.	Temperature has very little effect on of photochemical reactions.

Thermal reactions	Photochemical reactions
These reactions are not affected by light intensity.	Light intensity significantly affect the rate of reaction.
The free energy change of thermal reaction is always negative.	Free energy of photochemical reaction may be negative or positive.
These reactions are accelerated by catalysts.	Some photochemical reactions involve photosensitizers instead of catalyst.
For example: Production of ammonia in Haber's process is an example of thermal process.	For example: A mixture of hydrogen and chlorine remain unreacted in the absence of light. This reaction takes place only in the presence of light.

12.3 LIGHT ABSORPTION AND BEER-LAMBERT'S LAW

When a solution or medium is irradiated with light, a part of it is absorbed. This absorbed light by the medium molecules causes the photochemical reaction. The absorption of monochromatic radiation by homogeneous solution or system is explained by two laws. Both these laws are valid for monochromatic radiations passing through transparent medium. First one is Lambert's law, which describes that absorbance is directly proportional to concentration of medium and is written as

$$A \propto c \quad (12.1)$$

Second one is Lambert's law which states that absorbance is directly proportional to path length (l) and can be written as

$$A \propto l \quad (12.2)$$

Combining the above two relations, we get

$$A \propto cl$$

$$A = \epsilon cl \quad (12.3)$$

Equation 12.3 represents Beer-Lambert's Law, where, ϵ is the constant of proportionality which is known as absorptivity, it is a measure of concentration of excited molecules. c is the concentration of the reactant specie in moles per liter and l is path length (in cm).

For a pure substance, absorbance is related to intensity as follows

$$A = -\log \frac{I_t}{I_o}$$

$$A = \log \frac{I_o}{I_t} \quad (12.4)$$

Where, I_o and I_t denote the intensity of the incident and transmitted light respectively.

Comparing equation (12.3) and (12.4), we get

$$\log \frac{I_0}{I_t} = \epsilon c l \quad (12.5)$$

For a particular substance the absorbance (A) of a solution at a specific wavelength remains constant as long as the product of the concentration and the path length is constant. But this is not always true because of the variation in molar extinction with the concentration of the solute. This may be due to the molecular association of the solute at high concentration, poor transmission of the solvent or fluorescence of the solute and ionization of the solute in the case of acids etc. Molar absorptivities of strongly absorbing compounds is very large (i.e. $\epsilon > 10,000$) and for weakly absorbing compounds its value is small (i.e. $\epsilon = 10$ to 100). Spectrophotometric technique is simple and useful in determining very low concentration of various components present in the reaction mixture.

Example 12.1

A solution of a compound having concentration 0.214 mM placed in a cell of path length 1 cm transmits 25.5 % of light of a particular wavelength. Calculate the molar absorption coefficient of the solute.

Solution As we know that from given data

$$\%T = 25.5$$

$$\text{Hence, } T = 0.255$$

It is known that transmittance is the ratio of intensity of transmitted light to the intensity of incident light so,

$$\frac{I_t}{I_0} = 0.255$$

$$\frac{I_0}{I_t} = \frac{1}{0.255} \Rightarrow 3.921$$

$$\log \left(\frac{I_0}{I_t} \right) = 3.921$$

$$A = 0.593$$

As we know that

$$A = \epsilon c l$$

By putting values in above equation we can get the value of absorption coefficient as follows

$$\epsilon = \frac{0.593}{(1)(0.214 \times 10^{-3})}$$

$$\epsilon = 2771.02 \text{ Lmol}^{-1}\text{cm}^{-1}$$

12.4 LAWS OF PHOTOCHEMISTRY

The basic laws of photochemistry are

1. Grothus-Drapper law
2. Stark-Einstein's law of photochemical equivalence

1. Grothus-Drapper law

This is known as 1st law of photochemistry and it can be stated as "only absorbed light can cause a chemical reaction". According to this law absorbed light may initiate reaction but it is not always true because absorbed light may re-emit in the form of fluorescence and phosphorescence. For a photochemical reaction it is necessary to absorb the light. So it is important to determine the intensity of light absorbed by a system. The intensity of absorbed light can be measured using Beer-Lambert law. According to this law absorption of light is expressed in terms of absorbance which is

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

Where, I_0 is the intensity of incident light and I_t is the intensity of transmitted light. The quantity A is associated with concentration of solution (c) and path length (l) according to Beer-Lambert law which can be stated mathematically as

$$A = \epsilon cl$$

Where, ϵ is called molar absorption coefficient. It is independent of concentration and path length. It is the characteristics of chromospheres.

By combining above equations, we get

$$\log \frac{I_0}{I_t} = \epsilon cl$$

$$\frac{I_0}{I_t} = 10^{\epsilon cl}$$

$$\frac{I_t}{I_0} = 10^{-\epsilon cl}$$

$$I_t = I_0 10^{-\epsilon cl}$$

(12.6)

Intensity of incident light can be expressed as a sum of intensity of absorbed light and that of transmitted light i.e.

$$I_0 = I_a + I_t$$

$$I_a = I_0 - I_t$$

(12.7)

By putting the value of I_t from equation (12.6) into equation (12.7), we get

$$I_a = I_0 - I_0 10^{-\epsilon cl}$$

$$I_a = I_0 (1 - 10^{-\epsilon c l})$$

According to Grothus-Draper law, only I_a is the cause of photochemical reaction.

2. Stark-Einstein law of photochemical equivalence

The quantitative aspects of photochemistry are explained by Johannes Stark and Albert Einstein in 1905 with the help of quantum theory of light by proposing a law. Stark-Einstein law is 2nd law of photochemistry which is also named as photochemical equivalence law. It is stated as "in a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the product". They studied that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. This process is explained with the help of example as shown in Fig. 12.1. A molecule A absorbs one photon and becomes activated to carry out a photochemical reaction. Then activated molecule (A^*) is converted into product (P).

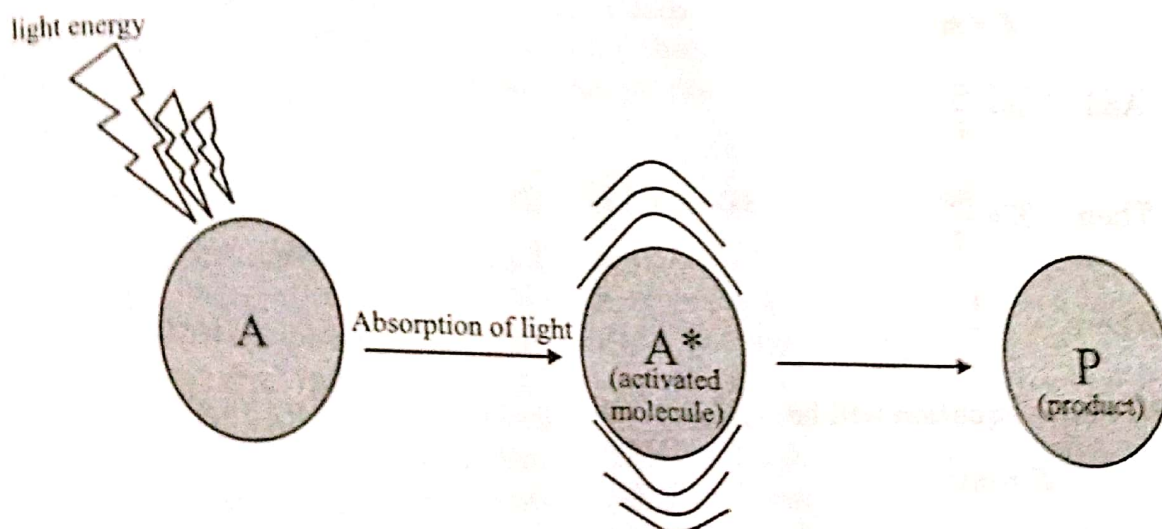


Fig. 12.1 Pictorial illustration of a photochemical reaction

When a photon is absorbed by a molecule, energy is transferred to a molecule. The amount of energy of a photon according to Planck's equation can be written as

$$E = \frac{hc}{\lambda} \quad (12.8)$$

Where, h is the Plank's constant (6.626×10^{-34} Js), c is the velocity of light in vacuum (3×10^8 ms⁻¹), ν is the frequency of light absorbed and λ is the wavelength of light.

In chemistry reactants or products are given in term of moles instead of molecules. Therefore, photons are also expressed in terms of moles. One mole of photons is known as an Einstein. The amount of energy transferred to reactants by an Einstein is given by the equation

$$E = N_A \frac{hc}{\lambda}$$

According to second law of photochemistry quantum yield should be equal to one. From above relation it is inferred that energy is inversely proportional to wavelength of radiation absorbed. It means that higher the wavelength, the smaller will be the energy per Einstein.

Example 12.2

Calculate the energy corresponding to the followings:

- (i) $\bar{\nu} = 3650 \text{ cm}^{-1} = 3.65 \times 10^5 \text{ m}^{-1}$
 (ii) $\lambda = 1.544 \text{ \AA}$
 (iii) $\nu = 5 \times 10^{15} \text{ Hz}$

Solution

We know that

$$E = h\nu$$

And $\nu = \frac{c}{\lambda}$

Then, $E = \frac{hc}{\lambda}$

Where, $\bar{\nu} = \frac{1}{\lambda}$

So, above equation will be

$$E = hc\bar{\nu}$$

(i) $E = hc\bar{\nu}$

By putting values in above equation we get

$$E = 6.62 \times 10^{-34} \times 2.9979 \times 10^8 \times 3.65 \times 10^5$$

$$E = 7.25 \times 10^{-20} \text{ J}$$

(ii) $E = \frac{hc}{\lambda}$

By putting values in above equation

$$E = \frac{6.62 \times 10^{-34} \times 2.9979 \times 10^8}{1.544 \times 10^{-10}}$$

$$E = 1.286 \times 10^{-15} \text{ J}$$

(iii) $E = h\nu$

By putting values in above equation we get

$$E = 6.62 \times 10^{-34} \times 5 \times 10^{15}$$

$$E = 3.313 \times 10^{-18} \text{ J}$$

12.5 QUANTUM YIELD

"The number of molecules reacted per photon of light absorbed is known as quantum yield". It is expressed as

$$\phi = \frac{\text{No. of molecules undergoing the process}}{\text{No. of quanta absorbed}}$$

It is observed that it is not necessary all photochemical reaction obeys Einstein's law. The number of molecules undergoing the process in the presence of light is found to be different from the number of quanta absorbed in given time.

The quantum yield is equal to one for a photochemical reaction which obeys the photochemical equivalence law in which one molecule is converted into product per quanta. If more than one molecule is decomposed by absorbing one quantum the quantum yield of that reaction is greater than one. Similarly, the quantum yield is less than one for a photochemical reaction when number of decompose molecules is less than one per quanta.

12.6 EXPERIMENTAL DETERMINATION OF QUANTUM YIELD

A photochemical reaction takes place by the absorption of light by reacting molecules. Thus, it is necessary to determine the intensity of absorbed light to study the rate of photochemical reaction. For this purpose a reaction mixture is irradiated with light of a selected wavelength. A light source is used to emit the radiations of suitable intensity. Tungsten filament or mercury vapor lamps are used as a light source. The light beam coming from the source passes through the lens which is used to select the radiations of one wavelength. After passing through lens monochromatic light enters into monochromator or filter. Then, light enters into the sample cell having sample mixture which is kept in a thermostat. The sample cell used is made up of glass or quartz which is suitable for the entrance or exit of light. Glass cells are usually used when visible region radiations are required. But below 3500 Å only quartz cells are used. Finally, transmitted light from sample cell strikes the detector where its intensity is determined. Mostly used detectors for the measurement of intensity of transmitted light are thermopile, photoelectric cell and actinometer. Thus, the intensity of light is measured first with the empty cell and then the cell filled with sample mixture. In this way, first reading gives the intensity of incident light (I_0) and second reading gives the intensity of transmitted light (I) from sample mixture. The difference between these readings ($I_0 - I$) gives the value of absorbed intensity by sample mixture. In this way it is possible to collect data on the rate of chemical reaction and light intensity, from which rate law and quantum yield can be determined. An experimental setup for determination of light intensity is shown in Fig. 12.2.

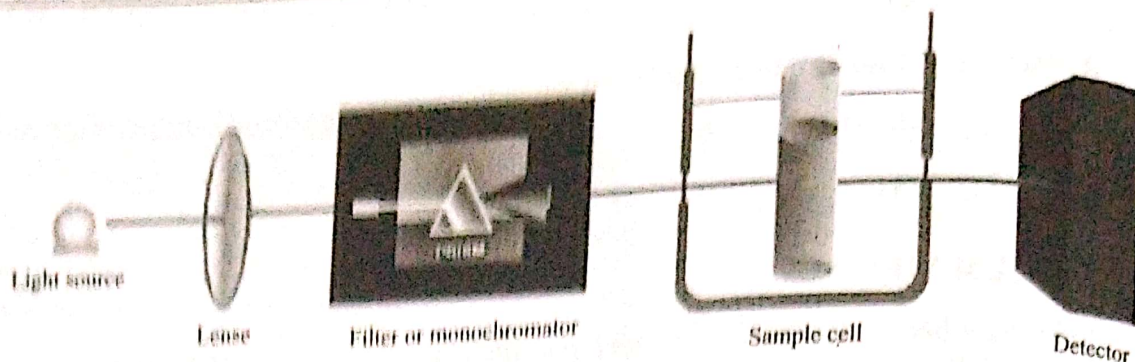


Fig. 12.2 Experimental setup for determination of absorbed intensity

12.7 PHOTOPHYSICAL PROCESSES

Light absorption by a system and relaxation of electronically excited species by various ways is called photophysical process because in such processes chemical change does not occur. Species absorbs light and moves into electronically excited state. This photophysical process is called excitation. System can lose this extra energy by different processes which are known as relaxation processes. These relaxation processes include radiative and non radiative relaxation processes. Internal conversion, intersystem crossing and vibrational relaxation are non radiative processes. Fluorescence and phosphorescence are radiative processes. All these photophysical processes can be explained on the basis of Jablonski diagrams as shown in Fig. 12.3. Alexander Jablonski, a Polish physicist who developed these diagrams to explain the kinetics of processes initiated by electronic transitions.

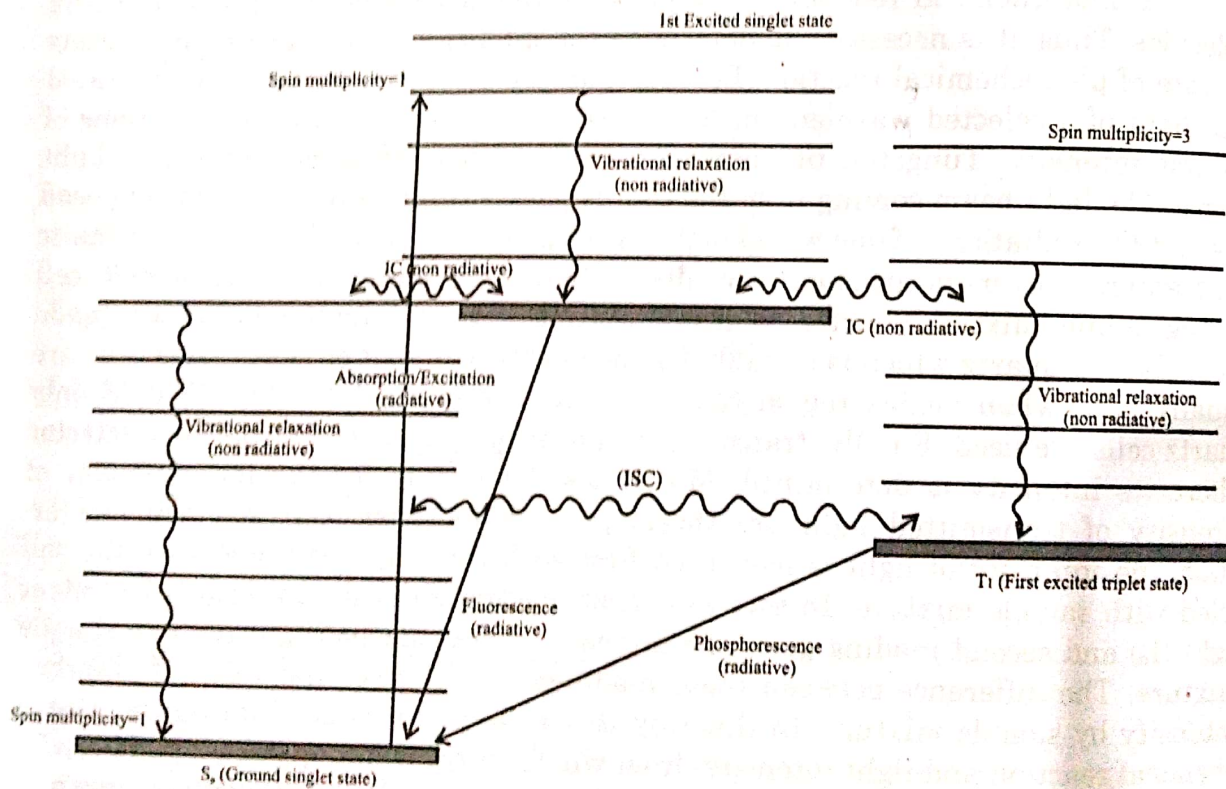


Fig. 12.3 Jablonski diagram indicating radiative (solid arrows) and non radiative (wavy arrows) processes.

In Fig. 12.3, ground singlet state is shown by S_0 where, spin multiplicity is equal to one and electrons are in paired form. The first excited singlet state is shown by S_1 where spin multiplicity is equal to one. The first excited triplet state is shown by T_1 where, spin multiplicity is equal to three and electrons are not in paired form. Each electronic state (S_0 , S_1 and T_1) has rotational and vibrational energy levels. But for simplicity only vibrational levels are shown in Fig. 12.3. The lowest vibrational level of each electronic state is shown by dark horizontal lines and higher vibrational levels are shown by lighter horizontal lines. The radiative and non radiative processes are shown by solid and wavy arrows respectively. The loss of excess electronic energy through emission of photon is called a radiative process and the loss of excess electronic energy without emission of photon is called non radiative relaxation process. We shall briefly describe these photophysical processes on the basis of Jablonski diagrams given in Fig. 12.3.

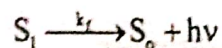
12.8 NON RADIATIVE RELAXATION PROCESSES

Vibrational relaxation (VR), internal conversion (IC) and intersystem crossing (ISC) are non radiative processes. The transition from higher vibrational level to lower vibrational level of an electronic state (S_0 , S_1 or T_1) without emission of light is called vibrational relaxation. The decay from the lowest vibrational level of S_1 to a high vibrational level of S_0 is referred to as internal conversion. Internal conversion schematically can be represented as $S_1 \rightarrow S_0$ and its rate will be equal to $k_{ic}[S_1]$ where, k_{ic} is the rate constant for internal conversion and $[S_1]$ is the concentration of species in first excited electronic state at any time t .

Intersystem crossing involves spin change. The transition from S_1 to T_1 or T_1 to S_0 is referred to as intersystem crossing. The rate of process $S_1 \xrightarrow{k_{isc}^s} T_1$ will be equal to $k_{isc}^s[S_1]$ where, k_{isc}^s is the 1st order rate constant for intersystem crossing for S_1 to T_1 transition. Similarly the rate of the process $T_1 \xrightarrow{k_{isc}^t} S_0$ will be to $k_{isc}^t[S_1]$ where k_{isc}^t is the 1st order rate constant for intersystem crossing for T_1 to S_0 transition.

12.9 RADIATIVE RELAXATION PROCESSES

Fluorescence and phosphorescence are radiative relaxation processes. Fluorescence is a radiative relaxation process in which photons are emitted as a result of transition from S_1 to S_0 without change in spin multiplicity. The process of fluorescence can be represented schematically in the following way



The rate of fluorescence process can be written as

$$v_f = k_f[S_1] \quad (12.10)$$

Where v_f is the rate of fluorescence, k_f is the 1st order rate constant for fluorescence and $[S_1]$ is the concentration of fluorescent material at electronically excited state S_1 at any time t . the units of k_f are s^{-1} .

Another radiative process is phosphorescence. It is relaxation process in which photons are emitted as a result of transition from first excited triplet state (T_1) to the ground state (S_0) with change in spin multiplicity. The process of

phosphorescence is slow as compared to that of fluorescence. Phosphorescence schematically can be written as



The rate of phosphorescence is

$$v_p = k_p [T_1] \tag{12.11}$$

Where v_p is the rate of phosphorescence, k_p is the 1st order rate constant for phosphorescence and $[T_1]$ is the concentration of species in first excited triplet state T_1 . The units of k_p are s^{-1} .

12.10 QUANTITATIVE ASPECTS OF FLUORESCENCE

For kinetic description of photophysical processes, Jablonski diagram can be modified to simplify the processes as shown in Fig. 12.4. The process of absorption, fluorescence, internal conversion, intersystem crossing and phosphorescence along with their respective rate constants are shown in Fig. 12.4.

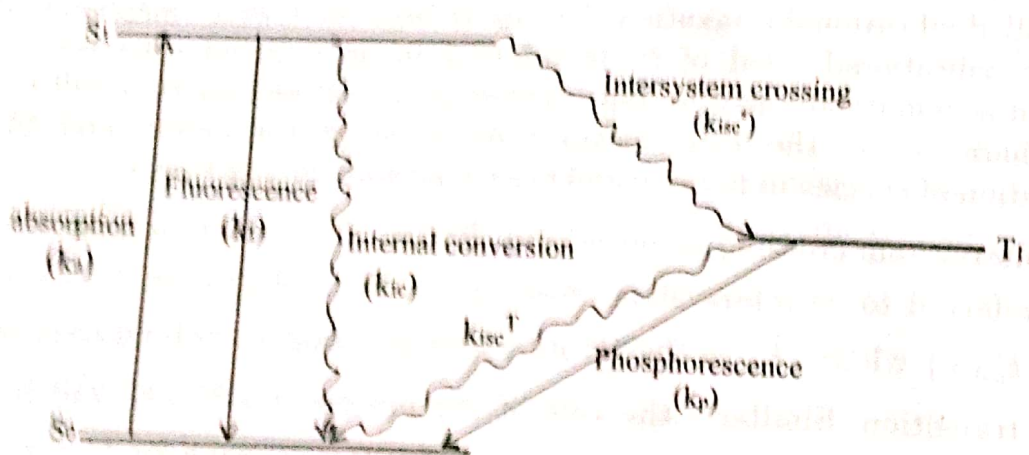


Fig. 12.4 kinetic description of photophysical processes i.e. radiative (solid arrows) and non radiative (wavy arrows)

Fig. 12.4 can be used to develop various expressions in the presence and absence of quencher.

12.10.1 Fluorescence life time in the absence of quencher

The rate of consumption of species in first excited singlet state (S_1) as a result of relaxation processes can be written as

$$\frac{d[S_1]}{dt} = -k_f[S_1] - k_{ic}[S_1] - k_{isc}^*[S_1]$$

$$\frac{d[S_1]}{dt} = -(k_f + k_{ic} + k_{isc}^*)[S_1]$$

By separating variables and integrating above equation, we get

$$\int \frac{d[S_1]}{[S_1]} = -(k_f + k_{ic} + k_{isc}^s) \int dt$$

$$\ln[S_1] = -(k_f + k_{ic} + k_{isc}^s)t + c \quad (12.12)$$

The value of constant of integration c can be obtained using initial conditions. i.e when $t = 0$, then $[S_1] = [S_1]_0$ by putting these values in equation (12.12), we get

$$\ln[S_1]_0 = c$$

By putting value of c in equation (12.12), we get

$$\ln[S_1] = -(k_f + k_{ic} + k_{isc}^s)t + \ln[S_1]_0$$

$$\ln[S_1] - \ln[S_1]_0 = -(k_f + k_{ic} + k_{isc}^s)t$$

$$\ln \frac{[S_1]}{[S_1]_0} = -(k_f + k_{ic} + k_{isc}^s)t$$

$$\frac{[S_1]}{[S_1]_0} = e^{-(k_f + k_{ic} + k_{isc}^s)t}$$

$$[S_1] = [S_1]_0 e^{-(k_f + k_{ic} + k_{isc}^s)t} \quad (12.13)$$

According to this expression, the value of concentration of species at first excited electronic state (S_1), decreases exponentially with time due to relaxation processes as shown in Fig. 12.5.

The fluorescence life time can be defined as "the time for which $[S_1]$ become $1/e$ times of initial concentration". Therefore,

When $[S_1] = \frac{[S_1]_0}{e}$ then $t = \tau_f^0$, so, equation (12.13) wi

$$\frac{[S_1]_0}{e} = [S_1]_0 e^{-(k_f + k_{ic} + k_{isc}^s)t}$$

$$e^{-1} = e^{-(k_f + k_{ic} + k_{isc}^s)\tau_f^0}$$

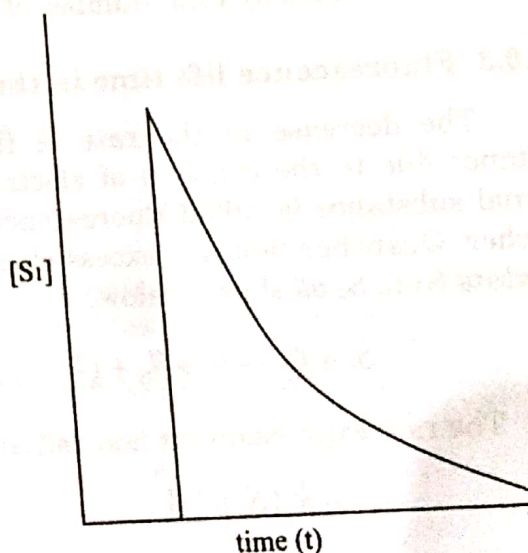


Fig. 12.5 Variation of concentration of specie at first excited singlet state with time

$$1 = (k_f + k_{ic} + k_{isc}^e) \tau_f^0$$

$$\tau_f^0 = \frac{1}{(k_f + k_{ic} + k_{isc}^e)} \quad (12.14)$$

This is the expression for fluorescence life time in terms of rate constants for fluorescence, internal conversion and intersystem crossing. Fluorescence life time decreases with increase of values of these rate constants.

12.10.2 Fluorescence quantum yield without quencher

The fluorescence quantum yield can be defined as ratio of rate constant for fluorescence to the sum of rate constants of all relaxation processes.

Mathematically, it can be written as

$$\phi_f^0 = \frac{k_f}{k_f + k_{ic} + k_{isc}^e} \quad (12.15)$$

So, fluorescence quantum yield depends upon the value of rate constants associated with fluorescence, internal conversion and intersystem crossing. It increases with increase of k_f and decreases with increase of k_{ic} and k_{isc}^e . It becomes maximum when sum of k_{ic} and k_{isc}^e is negligible as compared to k_f . Fluorescence quantum yield can also be defined as number of photons emitted as a result of fluorescence divided by total number of photons absorbed.

12.10.3 Fluorescence life time in the presence of quencher

The decrease in the rate of fluorescence in the presence of an external substance due to the collision of electronically excited molecules with molecules of external substance is called fluorescence quenching. The foreign substance is called quencher. Quencher removes excess electronic energy from molecules and converts it from state S_1 to S_0 as shown below.



The rate expression for non radiative quenching process can be written as

$$v_q = k_q [S_1] [Q]$$

Where, v_q is rate of quenching, k_q is bimolecular, second order rate constant for quenching process, $[Q]$ is the available concentration of quencher and $[S_1]$ is the concentration of species in first excited electronic state. The rate of decrease of concentration of species at first excited electronic state as a result of internal conversion, intersystem crossing, fluorescence and quenching process can be written as

as

$$\frac{d[S_1]}{dt} = -k_f[S_1] - k_{ic}[S_1] - k_{isc}^s[S_1] - k_q[S_1][Q]$$

$$\frac{d[S_1]}{dt} = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}[S_1]$$

By separating variables and integrating above equation

$$\int \frac{d[S_1]}{[S_1]} = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\} \int dt$$

$$\ln[S_1] = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t + c \quad (12.16)$$

We can determine the value of constant (c) by applying boundary conditions

When $t = 0$ then $[S_1] = [S_1]_0$ so, equation (12.16) will be

$$\ln[S_1]_0 = c$$

By putting this value of c in equation (12.16), we get

$$\ln[S_1] = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t + \ln[S_1]_0$$

$$\ln[S_1] - \ln[S_1]_0 = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t$$

$$\ln \frac{[S_1]}{[S_1]_0} = -\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t$$

$$\frac{[S_1]}{[S_1]_0} = e^{-\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t}$$

$$[S_1] = [S_1]_0 e^{-\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}t} \quad (12.17)$$

Hence, population at S_1 exponentially decreases with time more rapidly in the presence of quencher as compared to that in the absence of quencher.

Fluorescence life time expression can be derived using condition:

When, $[S_1] = \frac{[S_1]_0}{e}$ then $t = \tau_f$ So, equation (12.17) will be

$$\frac{[S_1]_0}{e} = [S_1]_0 e^{-\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}\tau_f}$$

$$e^{-1} = e^{-\{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}\tau_f}$$

$$1 = \{k_f + k_{ic} + k_{isc}^s + k_q[Q]\} \tau_f$$

Hence, fluorescence life time in the presence of quencher can be written as

$$\tau_f = \frac{1}{\{k_f + k_{ic} + k_{isc} + k_q[Q]\}} \quad (12.18)$$

So, value of fluorescence life time decreases with increase of quencher concentration.

12.10.4 Fluorescence quantum yield with quencher

According to definition of fluorescence quantum yield, the expression for it in the presence of quencher can be written as

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_q[Q]} \quad (12.19)$$

Hence, fluorescence quantum yield decreases by addition of quencher. The value of ϕ_f decreases with increase of concentration of quencher.

Example 12.3

Calculate the value of fluorescence quantum yield for $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^8$ s⁻¹ by assuming that rate constants for intersystem crossing and fluorescence quenching are small.

Solution

As we know that

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_q[Q]}$$

Since, k_{isc} and $k_q[Q]$ are negligible. So, above equation will be

$$\phi_f = \frac{k_f}{k_f + k_{ic}} \quad (i)$$

$$\tau_f = \frac{1}{k_f + k_{ic}}$$

$$1 \times 10^{-10} = \frac{1}{k_f + k_{ic}}$$

$$k_f + k_{ic} = \frac{1}{1 \times 10^{-10}}$$

$$k_f + k_{ic} = 1 \times 10^{10} \quad (ii)$$

By putting value of k_{ic} from given data in above equation we get

$$k_f + 5 \times 10^8 = 1 \times 10^{10}$$

$$k_f = 1 \times 10^{10} - 5 \times 10^8$$

$$k_f = 9.5 \times 10^9 \text{ s}^{-1} \quad \text{(iii)}$$

By putting values of $k_f + k_{ic}$ and k_f from equation (ii) and (iii) respectively into equation (i) we get the value of ϕ_f .

$$\phi_f = 9.5 \times 10^9 \times 1 \times 10^{-10}$$

$$\phi_f = 0.95$$

Example 12.4

If $k_{ic} = 1 \times 10^7 \text{ s}^{-1}$, $k_f = 2 \times 10^7 \text{ s}^{-1}$ and $k_{isc}^s = 1 \times 10^8 \text{ s}^{-1}$ calculate the fluorescence life time and fluorescence quantum yield in the absence of quencher.

Solution

As we know that

$$\tau_f^o = \frac{1}{(k_f + k_{ic} + k_{isc}^s)}$$

By putting values from data in above equation we get

$$\tau_f^o = \frac{1}{(2 \times 10^7) + (1 \times 10^7) + (1 \times 10^8)}$$

$$\tau_f^o = 7.69 \times 10^{-9} \text{ s}$$

$$\tau_f^o = 7.69 \text{ ns}$$

The formula of fluorescence quantum yield is given as

$$\phi_f^o = \frac{k_f}{k_f + k_{ic} + k_{isc}^s}$$

By putting values from data we can get

$$\phi_f^o = \frac{2 \times 10^7}{(2 \times 10^7) + (1 \times 10^7) + (1 \times 10^8)}$$

$$\phi_f^o = 0.1538$$

12.10.5 Stern-Volmer equation in terms of fluorescence life time
 A mathematical expression between fluorescence life time and quencher concentration can be presented which is known as Stern-Volmer equation.

Dividing equation (12.1) by (12.18), we get

$$\frac{\tau_f^0}{\tau_f} = \frac{1}{k_f + k_{ic} + k_{isc}^s} \times \frac{k_f + k_{ic} + k_{isc}^s + k_q[Q]}{1}$$

$$\frac{\tau_f^0}{\tau_f} = \frac{k_f + k_{ic} + k_{isc}^s}{k_f + k_{ic} + k_{isc}^s} \times \frac{k_q}{k_f + k_{ic} + k_{isc}^s} [Q]$$

$$\frac{\tau_f^0}{\tau_f} = 1 + k_q \tau_f^0 [Q]$$

$\frac{\tau_f^0}{\tau_f}$ versus $[Q]$ is a straight line equation with intercept form where intercept is equal to unity and slope of the plot is equal to $k_q \tau_f^0$. The value of k_q can be determined from the slope. This expression is called Stern-Volmer equation.

When $k_f \gg k_{ic} + k_{isc}^s$ then

$$\tau_f = \frac{1}{k_f + k_q[Q]}$$

$$\Rightarrow \frac{1}{\tau_f} = k_f + k_q[Q]$$

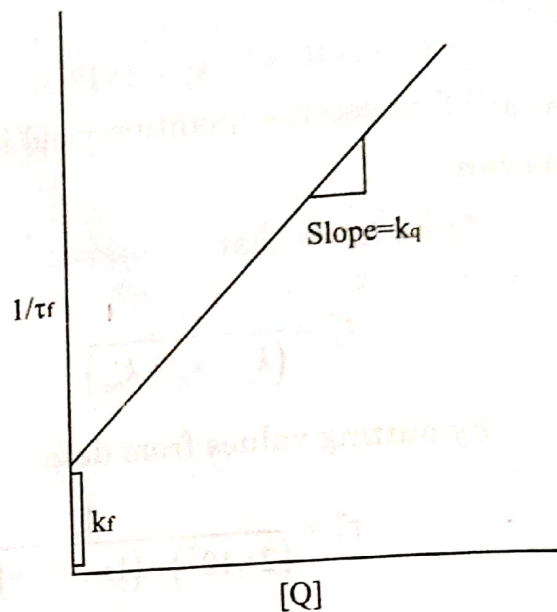


Fig. 12.6 Plot of $1/\tau_f$ versus $[Q]$

This is an equation of straight line as shown in Fig. 12.6.

1. Stern-volmer equation in terms of fluorescence quantum yield

Dividing equation (12.15) by (12.19), we get

$$\frac{\phi_f^0}{\phi_f} = \frac{k_f}{k_f + k_{ic} + k_{isc}^s} \times \frac{k_f + k_{ic} + k_{isc}^s + k_q[Q]}{k_f}$$

$$\frac{\phi_f^0}{\phi_f} = 1 + k_q \tau_f^0 [Q]$$

$\frac{I_f^0}{I_f}$ versus $[Q]$ is an equation of straight line with y intercept which is equal to one and slope is equal to $k_q \tau_f^0$.

2. Stern-Volmer equation in the form of fluorescence intensity

The net rate of formation of species at first excited electronic state S_1 as a result of absorption and relaxation in the presence of quencher can be written as

$$\frac{dS_1}{dt} = k_a[S_o] - k_f[S_1] - k_{ic}[S_1] - k_{isc}^s[S_1] - k_q[S_1][Q]$$

Using steady state approximation, we get

$$0 = k_a[S_o] - k_f[S_1] - k_{ic}[S_1] - k_{isc}^s[S_1] - k_q[S_1][Q]$$

$$k_a[S_o] = k_f[S_1] + k_{ic}[S_1] + k_{isc}^s[S_1] + k_q[S_1][Q]$$

$$k_a[S_o] = \{k_f + k_{ic} + k_{isc}^s + k_q[Q]\}[S_1]$$

Using equation (12.18), we get

$$\frac{[S_1]}{\tau_f} = k_a[S_o]$$

$$[S_1] = k_a[S_o]\tau_f \quad (12.20)$$

The fluorescence intensity is the rate of fluorescence which can be written as

$$I_f = k_f[S_1]$$

By putting value of $[S_1]$ from equation (12.20) into above equation we get

$$I_f = k_f k_a \tau_f [S_o] \quad (12.21)$$

Equation (12.21) is expression for fluorescence intensity in the presence of quencher in terms of rate constants for fluorescence and absorption process, fluorescence life time and concentration of fluorescent material in ground singlet state. The same expression in the absence of quencher can be written as

$$I_f^0 = k_f k_a \tau_f^0 [S_o] \quad (12.22)$$

Dividing equation (12.22) by equation (12.21), we get

$$\frac{I_f^0}{I_f} = \frac{k_f k_a \tau_f^0 [S_o]}{k_f k_a \tau_f [S_o]}$$

$$\frac{I_f^0}{I_f} = \frac{\tau_f^0}{\tau_f} \quad (12.23)$$

By putting values of τ_f^0 and τ_f from equation (12.14) and (12.18) respectively into equation (12.23), we get

$$\frac{I_f^0}{I_f} = \frac{1}{k_f + k_{ic} + k_{isc}^s} \cdot \frac{k_f + k_{ic} + k_{isc}^s + k_q [Q]}{1}$$

$$\frac{I_f^0}{I_f} = \frac{k_f + k_{ic} + k_{isc}^s}{k_f + k_{ic} + k_{isc}^s} + \frac{k_q}{k_f + k_{ic} + k_{isc}^s} [Q]$$

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f + k_{ic} + k_{isc}^s} [Q] \quad (12.24)$$

Using equation (12.14), we get

$$\frac{I_f^0}{I_f} = 1 + k_q \tau_f^0 [Q] \quad (12.25)$$

Equation (12.25) is an equation of straight line in intercept form and can be used for determination of k_q by plotting $\frac{I_f^0}{I_f}$ as a function of quencher concentration as shown in Fig. 12.7.

When $k_f \gg k_{ic} + k_{isc}$ then equation (12.24) can be written as

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f} [Q]$$

According to this expression $\frac{I_f^0}{I_f}$ as a linear function of concentration of quencher with intercept equal to one and slope equal to $\frac{k_q}{k_f}$.

Example 12.5

The Stern-volmer equation for fluorescence quenching is

$$\frac{\phi_f^0}{\phi_f} = 1 + \frac{k_q}{k_f + k_{ic} + k_{isc}^s} [Q]$$

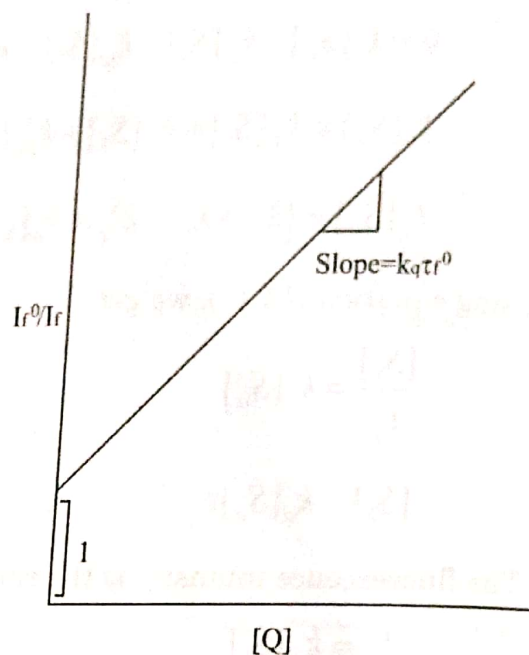


Fig. 12.7 Plot of I_f^0/I_f as a function of quencher concentration $[Q]$

Where, $\frac{k_q}{k_f + k_{ic} + k_{isc}^s}$ is called quenching constant and is denoted by k_{sv} .

Calculate the value of k_{sv} for the data

$$k_f = 2 \times 10^{-5} \text{ s}^{-1}, k_{ic} = 3 \times 10^{-4} \text{ s}^{-1}, k_{isc}^s = 4 \times 10^{-2} \text{ s}^{-1}, k_q = 4.10 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Solution

$$k_{sv} = \frac{k_q}{k_f + k_{ic} + k_{isc}^s}$$

By putting values in above equation we get

$$k_{sv} = \frac{4.10 \times 10^{11}}{(2 \times 10^{-5}) + (3 \times 10^{-4}) + (4 \times 10^{-2})}$$

$$k_{sv} = 1.7 \text{ Lmol}^{-1}$$

12.11 KINETIC ASPECTS OF PHOSPHORESCENCE

The process of phosphorescence includes the radiative transitions from triplet state to ground singlet state which is the lowest vibrational level as shown in Fig. 12.8.

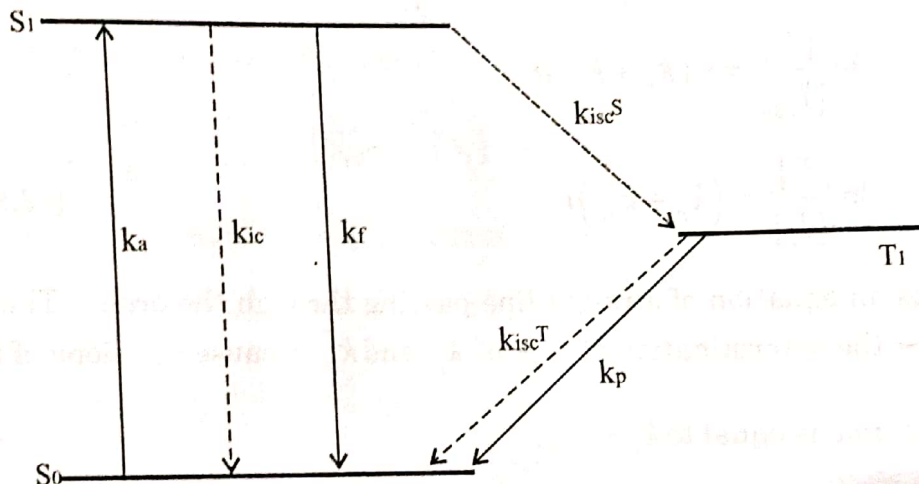
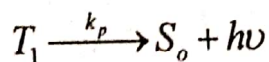


Fig. 12.8 Kinetic illustration of photophysical processes

Scheme of this process is



Rate of above reaction can be written as

$$v_p = k_p [T_1]$$

Where v_p is the rate of phosphorescence, k_p is the phosphorescence first rate constant having units s^{-1} .

Delay rate of $[T_1]$ is

$$\frac{d[T_1]}{dt} = -k_p[T_1] - k_{isc}^T[T_1]$$

$$\frac{d[T_1]}{dt} = -(k_p + k_{isc}^T)[T_1]$$

By separating variables and integrating above equation we get

$$\int \frac{d[T_1]}{[T_1]} = -(k_p + k_{isc}^T) \int dt$$

$$\ln[T_1] = -(k_p + k_{isc}^T)t + c$$

(12.26)

When $t = 0$ then $[T_1] = [T_1]_0$ so, equation (12.26) will be

$$\ln[T_1]_0 = c$$

By putting value of c in equation (12.26), we get

$$\ln[T_1] = -(k_p + k_{isc}^T)t + \ln[T_1]_0$$

$$\ln[T_1] - \ln[T_1]_0 = -(k_p + k_{isc}^T)t$$

$$\ln \frac{[T_1]}{[T_1]_0} = -(k_p + k_{isc}^T)t$$

$$\ln \frac{[T_1]_0}{[T_1]} = (k_p + k_{isc}^T)t$$

(12.27)

This is an equation of straight line passing through the origin. This equation can be used for the determination of sum of k_p and k_{isc}^T because the slope of the plot of

$\ln \frac{[T_1]_0}{[T_1]}$ versus time is equal to $k_p + k_{isc}^T$.

12.11.1 Relation of Phosphorescence Life Time

$$\ln \frac{[T_1]}{[T_1]_0} = -(k_p + k_{isc}^T)t$$

$$\frac{[T_1]}{[T_1]_0} = e^{-(k_p + k_{isc}^T)t}$$

$$[T_1] = [T_1]_0 e^{-(k_p + k_{isc}^T)t}$$

When $[T_1] = \frac{[T_1]_0}{e}$, then $t = \tau_p^0$. So

$$\frac{[T_1]_0}{e} = [T_1]_0 e^{-(k_p + k_{isc}^T)t_p^0}$$

$$e^{-1} = e^{-(k_p + k_{isc}^T)t_p^0}$$

$$1 = (k_p + k_{isc}^T) \tau_p^0$$

$$\tau_p^0 = \frac{1}{(k_p + k_{isc}^T)} \quad (12.28)$$

This is the phosphorescence life time in the absence of quencher.

12.11.2 Quantum Yield of Phosphorescence

$$\phi_p^0 = \frac{\text{Rate of phosphorescence emission}}{\text{Rate of absorption of radiation}}$$

$$\phi_p^0 = \frac{k_p [T_1]}{I_a} \quad (12.29)$$

Net rate of formation of $[S_1]$ is

$$\frac{d[S_1]}{dt} = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

By applying steady state approximation, we get

$$0 = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

$$I_a = (k_f + k_{ic} + k_{isc}^s)[S_1]$$

$$[S_1] = \frac{I_a}{k_f + k_{ic} + k_{isc}^s} \quad (12.30)$$

Similarly, net rate of formation of $[T_1]$ is

$$\frac{d[T_1]}{dt} = k_{isc}^s[S_1] - k_{isc}^T[T_1] - k_p[T_1]$$

By applying steady state approximation, we get

$$0 = k_{isc}^s[S_1] - k_{isc}^T[T_1] - k_p[T_1]$$

$$(k_p + k_{isc}^T)[T_1] = k_{isc}^s[S_1]$$

$$(k_p + k'_{isc})[T_1] = k^s_{isc}[S_1]$$

$$[T_1] = \frac{k^s_{isc}[S_1]}{(k_p + k'_{isc})} \quad (12.31)$$

By substituting value of $[S_1]$ from equation (12.30) into equation (12.31), we get

$$[T_1] = \frac{k^s_{isc}}{k_p + k'_{isc}} \cdot \frac{I_a}{k_f + k_{ic} + k^s_{isc}}$$

$$[T_1] = \frac{I_a k^s_{isc}}{(k_p + k'_{isc})(k_f + k_{ic} + k^s_{isc})}$$

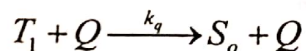
By putting the value of $[T_1]$ in equation (12.29), we get

$$\phi_p^o = \frac{k_p k^s_{isc}}{(k_p + k'_{isc})(k_f + k_{ic} + k^s_{isc})} \quad (12.32)$$

12.11.3 Phosphorescence Quenching

Deactivation by another molecule called quencher and the process is called quenching. Quenching provides a way for determination of rate constant of phosphorescence and rate constant for quenching.

12.11.4 Phosphorescence Life Time in the Presence of Quencher



Delay rate of $[T_1]$ is

$$\frac{d[T_1]}{dt} = -k_p[T_1] - k^T_{isc}[T_1] - k_q[Q][T_1]$$

$$\frac{d[T_1]}{dt} = -\{k_p + k^T_{isc} + k_q[Q]\}[T_1]$$

By separating variables and integrating above equation, we get

$$\int \frac{d[T_1]}{[T_1]} = -\{k_p + k^T_{isc} + k_q[Q]\} \int dt$$

$$\ln[T_1] = -\{k_p + k^T_{isc} + k_q[Q]\}t + c \quad (12.33)$$

When $t = 0$, then $[T_1] = [T_1]_0$ so, equation (12.33) will be

$$\ln[T_1]_0 = c$$

By putting value of ϵ in equation (12.33), we get

$$\ln[T_1] = -\{k_p + k_{isc}^T + k_q[Q]\}t + \ln[T_1]_0$$

$$\ln[T_1] - \ln[T_1]_0 = -\{k_p + k_{isc}^T + k_q[Q]\}t$$

$$\ln \frac{[T_1]}{[T_1]_0} = -\{k_p + k_{isc}^T + k_q[Q]\}t$$

$$\ln \frac{[T_1]_0}{[T_1]} = \{k_p + k_{isc}^T + k_q[Q]\}t$$

This is an equation of straight line passing through origin with slope equal to $k_p + k_{isc}^T + k_q[Q]$.

$$\frac{[T_1]}{[T_1]_0} = e^{-\{k_p + k_{isc}^T + k_q[Q]\}t}$$

$$[T_1] = [T_1]_0 e^{-\{k_p + k_{isc}^T + k_q[Q]\}t} \quad (12.34)$$

When $[T_1] = \frac{[T_1]_0}{e}$ then $t = \tau_p$, so, equation (12.34) will be

$$\frac{[T_1]_0}{e} = [T_1]_0 e^{-\{k_p + k_{isc}^T + k_q[Q]\}\tau_p}$$

$$e^{-1} = e^{-\{k_p + k_{isc}^T + k_q[Q]\}\tau_p}$$

$$1 = \{k_p + k_{isc}^T + k_q[Q]\}\tau_p$$

$$\tau_p = \frac{1}{k_p + k_{isc}^T + k_q[Q]} \quad (12.35)$$

This is the phosphorescence life time in the presence of quencher. With the increase of quencher concentration, phosphorescence time decreases.

12.11.5 Quantum Yield of Phosphorescence in the Presence of Quencher

$$\phi_p = \frac{\text{Rate of phosphorescence emission in the presence of quencher}}{\text{Rate of absorption}}$$

$$\phi_p = \frac{k_p[T_1]}{I_a} \quad (12.36)$$

Net rate of formation of $[S_1]$

$$\frac{d[S_1]}{dt} = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

By applying steady state approximation

$$0 = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

$$I_a = \{k_{ic} + k_f + k_{isc}^s\}[S_1]$$

$$[S_1] = \frac{I_a}{k_{ic} + k_f + k_{isc}^s} \quad (12.37)$$

Similarly, the net rate of formation of $[T_1]$ in the presence of quencher is

$$\frac{d[T_1]}{dt} = k_{isc}^s[S_1] - k_p[T_1] - k_{isc}^T[T_1] - k_q[Q][T_1]$$

By applying steady state approximation, we get

$$k_{isc}^s[S_1] = \{k_p + k_{isc}^T + k_q[Q]\}[T_1]$$

$$[T_1] = \frac{k_{isc}^s[S_1]}{k_p + k_{isc}^T + k_q[Q]}$$

By putting value of $[S_1]$ from equation (12.37) in above equation

$$[T_1] = \frac{k_{isc}^s}{k_p + k_{isc}^T + k_q[Q]} \cdot \frac{I_a}{k_{ic} + k_f + k_{isc}^s}$$

Putting value of $[T_1]$ in equation (12.36), we get

$$\phi_p = \frac{k_p}{I_a} \cdot \frac{k_{isc}^s}{k_p + k_{isc}^T + k_q[Q]} \cdot \frac{I_a}{k_{ic} + k_f + k_{isc}^s}$$

$$\phi_p = \frac{k_p k_{isc}^s}{(k_{ic} + k_f + k_{isc}^s)(k_p + k_{isc}^T + k_q[Q])} \quad (12.38)$$

Dividing equation (12.38) by (12.32), we get

$$\frac{\phi_p}{\phi_p^0} = \frac{k_p k_{isc}^s}{(k_{ic} + k_f + k_{isc}^s)(k_p + k_{isc}^T + k_q[Q])} \cdot \frac{(k_p + k_{isc}^T)(k_f + k_{ic} + k_{isc}^s)}{k_p k_{isc}^s}$$

$$\frac{\phi_p}{\phi_p^0} = \frac{k_p + k_{isc}^T}{k_p + k_{isc}^T + k_q[Q]}$$

$$\frac{\phi_p^0}{\phi_p} = \frac{k_p + k_{tr}^r + k_q[Q]}{k_p + k_{tr}^r}$$

$$\frac{\phi_p^0}{\phi_p} = 1 + \frac{k_q}{k_p + k_{tr}^r}[Q]$$

$$\frac{\phi_p^0}{\phi_p} = 1 + k_q \tau_p^0 [Q] \quad (12.39)$$

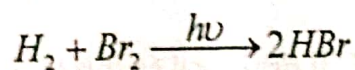
This equation is called Stern-Volmer equation for phosphorescence quenching. The rate of the intensity (I_p^0) of phosphorescence in the absence of quencher to the intensity (I_p) of phosphorescence in the presence of quencher is proportional to the ratio of the quantum yields so above equation can be written as

$$\frac{I_p^0}{I_p} = 1 + k_q \tau_p^0 [Q] \quad (12.40)$$

12.12 THE PHOTOCHEMICAL REACTION BETWEEN BROMINE AND HYDROGEN

The chemical reaction between hydrogen and bromine gives hydrogen bromide. The reaction can be initiated by heating or irradiation process. Mechanism of thermal reaction is described in chapter 5. In this section we shall discuss kinetics and mechanism of this reaction initiated by light absorption. Initiation step in photochemical reaction is different from that of the thermal reaction. Chain propagation and termination steps are same in both cases. In thermal reaction initiation step is thermal decomposition of bromine molecule into bromine radicals while in photochemical reaction the initiation step is dissociation of bromine molecule as a result of absorption of light of sufficiently short wavelength.

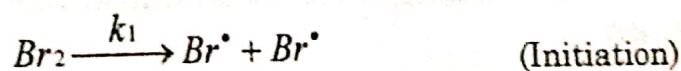
The overall reaction can be written as

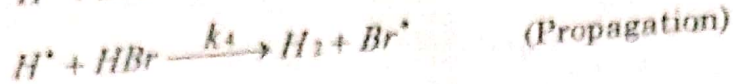


The experimental rate law expression for the above reaction was found to be

$$\frac{d[HBr]}{dt} = \frac{k[H_2]I^{\frac{1}{2}}}{1 + k' \frac{[HBr]}{[Br_2]}} \quad (12.41)$$

Where k and k' are constants and I is intensity of absorbed light (expressed in Einstein $\text{dm}^{-3}\text{s}^{-1}$). The mechanism of the above reaction is given below:





The rate of formation of HBr from the above mechanism can be written as

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}^\bullet][\text{H}_2] + k_3[\text{Br}_2][\text{H}^\bullet] - k_4[\text{H}^\bullet][\text{HBr}]$$

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}^\bullet][\text{H}_2] + \{k_3[\text{Br}_2] - k_4[\text{HBr}]\}[\text{H}^\bullet] \quad (12.42)$$

The concentration of Br^\bullet and H^\bullet can be determined using steady state approximation. From above mechanism rate of formation of bromine radical can be written as

$$\frac{d[\text{Br}^\bullet]}{dt} = 2I - k_2[\text{Br}^\bullet][\text{H}_2] + k_3[\text{H}^\bullet][\text{Br}_2] + k_4[\text{HBr}][\text{H}^\bullet] - 2k_5[\text{Br}^\bullet]^2$$

$$0 = 2I - k_2[\text{Br}^\bullet][\text{H}_2] + k_3[\text{Br}_2][\text{H}^\bullet] + k_4[\text{H}^\bullet][\text{HBr}] - 2k_5[\text{Br}^\bullet]^2$$

$$k_2[\text{Br}^\bullet][\text{H}_2] + 2k_5[\text{Br}^\bullet]^2 = 2I + k_3[\text{Br}_2][\text{H}^\bullet] + k_4[\text{H}^\bullet][\text{HBr}]$$

$$k_2[\text{Br}^\bullet][\text{H}_2] + 2k_5[\text{Br}^\bullet]^2 = 2I + \{k_3[\text{Br}_2] + k_4[\text{HBr}]\}[\text{H}^\bullet] \quad (12.43)$$

Two unknown quantities i.e. $[\text{H}^\bullet]$ and $[\text{Br}^\bullet]$ are still present in equation (12.43), so we cannot evaluate the value of one quantity without knowing the other.

Applying steady state approximation on rate of formation of hydrogen radical we can get the expression for concentration of hydrogen radical as

$$\frac{d[\text{H}^\bullet]}{dt} = k_2[\text{Br}^\bullet][\text{H}_2] - k_3[\text{H}^\bullet][\text{Br}_2] - k_4[\text{HBr}][\text{H}^\bullet]$$

$$0 = k_2[\text{Br}^\bullet][\text{H}_2] - \{k_3[\text{Br}_2] + k_4[\text{HBr}]\}[\text{H}^\bullet]$$

$$[\text{H}^\bullet]\{k_3[\text{Br}_2] + k_4[\text{HBr}]\} = k_2[\text{Br}^\bullet][\text{H}_2]$$

$$[\text{H}^\bullet] = \frac{k_2[\text{Br}^\bullet][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (12.44)$$

By putting the value of hydrogen radical concentration from equation (12.44) into equation (12.43) we get

$$k_2[Br^\bullet][H_2] + 2k_5[Br^\bullet]^2 = 2I + \{k_3[Br_2] + k_4[HBr]\} \frac{k_2[Br^\bullet][H_2]}{k_3[Br_2] + k_4[HBr]}$$

$$k_2[Br^\bullet][H_2] + 2k_5[Br^\bullet]^2 = 2I + k_2[Br^\bullet][H_2]$$

$$2k_5[Br^\bullet]^2 = 2I$$

$$k_5[Br^\bullet]^2 = I$$

$$[Br^\bullet]^2 = \frac{1}{k_5} I$$

$$[Br^\bullet] = \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}}$$

(12.45)

By putting the value of $[Br^\bullet]$ into the equation (12.44) from (12.45) we get

$$[H^\bullet] = \frac{k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2]}{k_3[Br_2] + k_4[HBr]} \quad (12.46)$$

By putting the value of $[Br^\bullet]$ and $[H^\bullet]$ from equation (12.45) and (12.46) into equation (12.42), we get expression for rate of formation of HBr in term of concentration of Br_2 , HBr, H_2 and intensity of the light absorbed.

$$\frac{d[HBr]}{dt} = k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2] + \{k_3[Br_2] - k_4[HBr]\} \frac{k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2]}{k_3[Br_2] + k_4[HBr]}$$

$$\frac{d[HBr]}{dt} = k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2] \left\{ 1 + \frac{k_3[Br_2] - k_4[HBr]}{k_3[Br_2] + k_4[HBr]} \right\}$$

$$\frac{d[HBr]}{dt} = k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2] \left\{ \frac{k_3[Br_2] + k_4[HBr] + k_3[Br_2] - k_4[HBr]}{k_3[Br_2] + k_4[HBr]} \right\}$$

$$\frac{d[HBr]}{dt} = \frac{k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2] 2k_3[Br_2]}{k_3[Br_2] + k_4[HBr]}$$

$$\frac{d[HBr]}{dt} = \frac{2k_2 \left(\frac{1}{k_5}\right)^{\frac{1}{2}} I^{\frac{1}{2}} [H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

$$\frac{d[HBr]}{dt} = \frac{kI^{\frac{1}{2}}[H_2]}{1 + k' \frac{[HBr]}{[Br_2]}} \quad (12.47)$$

Where,

$$k = 2k_2 \left(\frac{1}{k_5} \right)^{\frac{1}{2}}$$

And

$$k' = \frac{k_4}{k_3}$$

Expression (12.47) is same as given in equation (12.41).

12.13 THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE

The chemical reaction between hydrogen and chlorine in the presence of light produces hydrogen chloride with explosion. In 1930, Bodenstein and Hanger investigated the kinetics of this photochemical reaction. The rate law expression for the reaction on the basis of their experimental observation is given below

$$\frac{d[HCl]}{dt} = kI_a[H_2] \quad (12.48)$$

Where I_a is the rate of absorption of light in Einstein $\text{dm}^{-3}\text{s}^{-1}$. They proposed the following mechanism for the reaction



In the above mechanism, step (i) is initiation and it is a photochemical process. The chlorine radical produced in initiation step reacts with hydrogen molecule to produce HCl and hydrogen radical which reacts with chlorine molecule to generate HCl and chlorine radicals. The combination of chlorine molecule is a termination step. The above mechanism was suggested in the absence of impurities like oxygen for equimolar quantities of hydrogen and chlorine. The net rate of reaction in term of rate of formation of HCl according to above mechanism, can be written as

$$\frac{d[HCl]}{dt} = k_2[\text{Cl}^{\bullet}][\text{H}_2] + k_3[\text{Cl}_2][\text{H}^{\bullet}] \quad (12.49)$$

Hydrogen and chlorine radical concentration are two unknown quantities in the above expression and their value can be determined using steady state approximation.

Hence net rate of formation of chlorine radical is

$$\frac{d[Cl^*]}{dt} = 2I_a - k_2[Cl^*][H_2] + k_3[Cl_2][H^*] - k_4[Cl^*]$$

Applying steady state approximation

$$0 = 2I_a + k_3[Cl_2][H^*] - \{k_2[H_2] + k_4\}[Cl^*]$$

$$k_2[Cl^*][H_2] + k_4[Cl^*] = 2I_a + k_3[Cl_2][H^*] \quad (12.50)$$

Similarly net rate of formation of hydrogen radical is

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

$$0 = k_2[Cl^*][H_2] - k_3[Cl_2][H^*]$$

$$k_2[Cl^*][H_2] = k_3[Cl_2][H^*] \quad (12.51)$$

Subtracting equation (12.51) from equation (12.50), we get

$$k_4[Cl^*] = 2I_a$$

$$[Cl^*] = \frac{2I_a}{k_4} \quad (12.52)$$

By putting the value of $[Cl^*]$ from equation (12.52) into equation (12.51), we get

$$k_2 \left(\frac{2I_a}{k_4} \right) [H_2] = k_3 [Cl_2] [H^*]$$

$$[H^*] = \frac{k_2(2I_a)[H_2]}{k_3 k_4 [Cl_2]} \quad (12.53)$$

Equation (12.53) gives concentration of hydrogen radical in term of concentration of H_2 and Cl_2 and rate of absorption of light.

By putting the value of $[Cl^*]$ and $[H^*]$ from equation (12.52) and (12.53) respectively into equation (12.49), we get

$$\frac{d[HCl]}{dt} = k_2 \left(\frac{2I_a}{k_4} \right) [H_2] + k_3 [Cl_2] \frac{k_2(2I_a)[H_2]}{k_3 k_4 [Cl_2]}$$

$$\frac{d[HCl]}{dt} = k_3 \left(\frac{2I_a}{k_4} \right) [H_2] + k_2 \left(\frac{2I_a}{k_4} \right) [H_2]$$

$$\frac{d[HCl]}{dt} = 4k_2 \left(\frac{I_a}{k_4} \right) [H_2]$$

$$\frac{d[HCl]}{dt} = \left(\frac{4k_2}{k_4} \right) I_a [H_2]$$

$$\frac{d[HCl]}{dt} = k I_a [H_2]$$

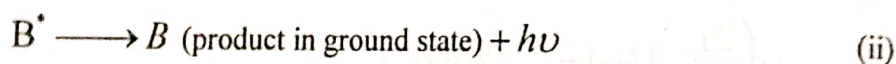
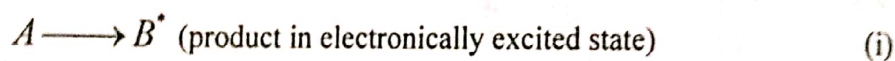
Where

$$k = \left(\frac{4k_2}{k_4} \right)$$

Hence rate of reaction depends upon rate of absorption of radiation and concentration of hydrogen. The above expression is similar as given in equation (12.48).

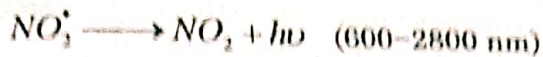
12.14 CHEMILUMINESCENCE

"The process of emission of cold visible light as a result of chemical reaction is called chemiluminescence". It is a reverse of photochemical reaction. In a photochemical reaction, reactant absorbs light and get excited then goes into product through activation by light absorption but in chemiluminescence, one of the product formed is in excited state. This product comes to ground state by emission of radiations. A general scheme for chemiluminescence is given below



In above scheme, reactant A is converted into product B in its excited state (B^*) and then B^* emits light ($h\nu$) to produce product B in its ground state. In this way chemical energy is converted into light energy. Some living organisms emit light and show phenomenon of chemiluminescence is known as bioluminescence. For example oxidation of protein, luciferin by atmospheric oxygen in the presence of enzyme luciferase produces cold lights which can be seen by naked eye. The chemiluminescence occurring in living organisms is called bioluminescence. In other words, bioluminescence is the emission of visible light as a result of a chemical reaction catalyzed by enzyme in living organisms. Chemical reaction between NO and O_3 generates NO_2 in its excited state and O_2 in its ground state. NO_2^* is converted into NO_2 by emission of light in the range of wavelength of 600-2800 nm as given below





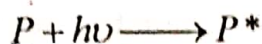
Chemiluminescence can be used as an analytical tool to determine the concentration of unknown substance because the rate of light output is directly related to amount of light emitted and accordingly proportional to the concentration of the luminescent material present. This technique is called luminometry.

12.15 PHOTSENSITIZED REACTION

There are some molecules which do not absorb light energy which is required for a chemical reaction of those molecules. They do not undergo a photochemical reaction. When a foreign substance is added in the reaction mixture, then these reactants can be converted into products in the presence of light. This foreign substance is called photosensitizer, these reactions are called photosensitized reactions and the process is called photosensitization.

Mechanism of Photosensitization

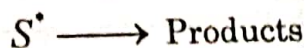
A photosensitizer absorbs light becomes excited and then pass on this energy to one of the reactants to activate it without itself taking part in the reaction. Hence, photosensitizer acts as an energy carrier. The role of photosensitizer in photosensitized reaction is similar to that of catalyst in thermal reactions. A general mechanism of a photosensitized reaction can be written as



In above scheme, P is the photosensitizer in ground state and P* is the photosensitizer in excited state.



Where S is the reactant in ground state and S* is the substrate or reactant in excited state.

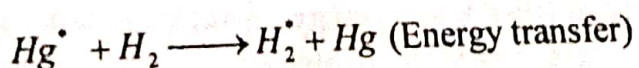
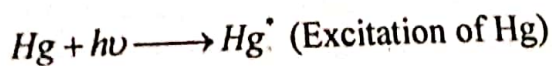


Examples of Photosensitized Reaction

1. H₂ gas undergoes dissociation in the presence of light when Hg vapors are present in the reaction mixture according to this scheme.



Mechanism of this reaction is



2. Chlorophyll acts as photosensitizer in photosynthesis of carbohydrates from a chemical reaction of CO_2 and H_2O in the presence of light as



12.16 LASERS

The term laser stands for "Light Amplification by Stimulated Emission of Radiation". Laser is a device which produces a highly intense, coherent, monochromatic and unidirectional beam of light.

Principle of Laser

Production of laser can be explained by understanding pumping, spontaneous emission and stimulated emission

(i) Pumping

First process is pumping. During pumping, electric discharge, intense radiations or electric current is passed through lasing medium. These agents cause excitation of electrons to electronic and vibrational energy levels of high energy. Thus excited states become more populated as compared to ground state by pumping as shown in Fig. 12.9 where E_x becomes populated as compared to ground states. Their life time is 10^{-13} - 10^{-15} seconds in excited states. So electrons jump to relatively stable excited states called metastable states E_x (life time = 10^{-3} seconds) by releasing undetectable amount of heat.

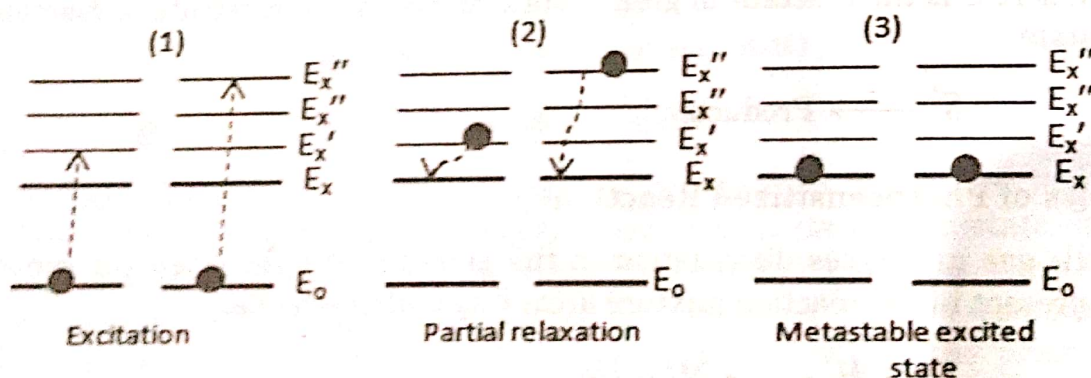


Fig. 12.9 Pumping or excitation

(ii) Spontaneous Emission

Some species in excited state may lose energy equal to $E_x - E_0$ by spontaneous emission. All excited molecules may not lose energy at same time. Moreover orientation of all excited molecules is not same also. So, spontaneous emission is a random process. Photons produced by spontaneous emission have phase difference and travel in different directions, thus they are termed incoherent (Fig. 12.10).

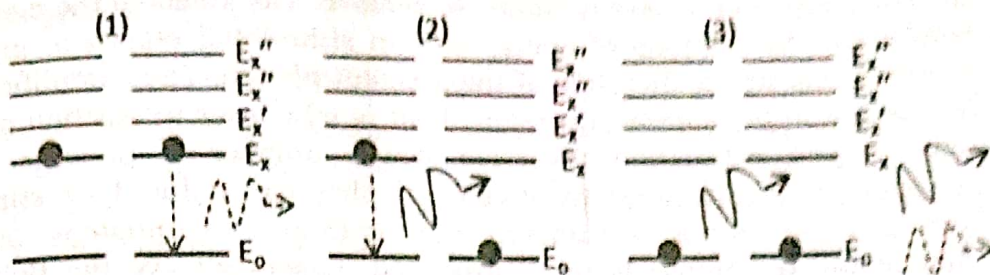


Fig. 12.10 Spontaneous emission

(iii) Stimulated Emission

Photons produced in previous step are struck up by other species in excited state. Photons induce them to lose energy immediately. Thus all atoms get de-excited and produce such photons of equal energy, same phase difference and travelling in similar orientations (Fig. 12.11). Photons produced by stimulated emission get multiplied within very small time and an intense laser beam is produced. Energy of colliding photons is almost equal to the energy of photons produced by stimulated emission.

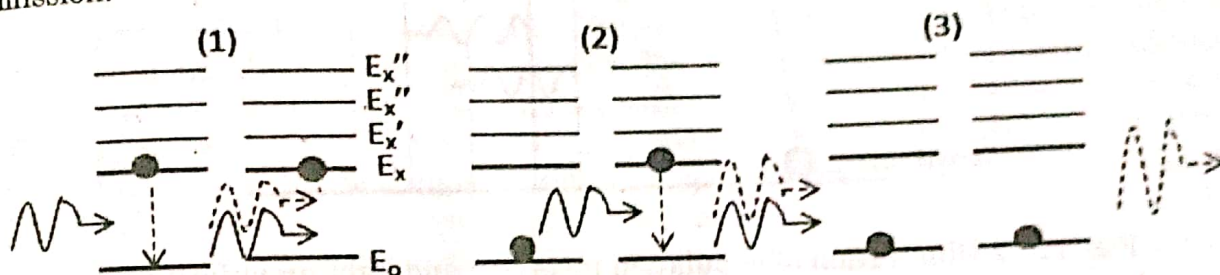


Fig. 12.11 Laser production or stimulated emission

Population Inversion and Light Amplification

In normal population more atoms will reside in the lower energy state than in the excited state. Whereas, a population inversion is that condition, in which higher energy state has a greater population than the lower energy state. Laser action depends on the inversion of the natural excess population in the lower state and then getting the excited state to emit all the excess energy at once. Let us consider three different states at which atoms can reside i.e. E_1 is the ground state, E_2 is the higher energy excited state also named as short lived state and E^* is the metastable state also named as long lived state as shown in Fig. 12.12. A metastable state is an excited state in which an excited electron is unusually stable and electrons spontaneously fall to lower state only after relatively longer time. The transition from or to this state is difficult as compared to other excited states. Hence, instead of direct excitation to metastable state, the electrons are excited to higher energy level. Then, electrons spontaneously fall to metastable state. The incident photons of energy (hf) are used to raise the atoms from the ground state to the excited state but the excited atoms do not decay back to ground state directly. Thus, excited atoms use alternative by decaying spontaneously to metastable state, the atoms reach metastable state much faster than they leave metastable state. This eventually leads to the situation that the metastable state contains more atoms than ground state this situation is known as population inversion. Once the population inversion has been

reached, the lasing action of a laser is simple to achieve. The atoms in the metastable state are bombarded by photons of energy (hf) in stimulated emission, giving an intense, coherent beam in the direction of the incident photon. Thus amplification of light is only possible in population inversion. That is why laser production principle is purely based upon population inversion where number of photons lost by absorption is smaller as compared to number of photons produced by stimulated emission. During amplification, one photon induces to give two photons, later two gives four and hence an intense beam is produced. Lasers involve the Boltzmann equation to calculate the populations of energy states.

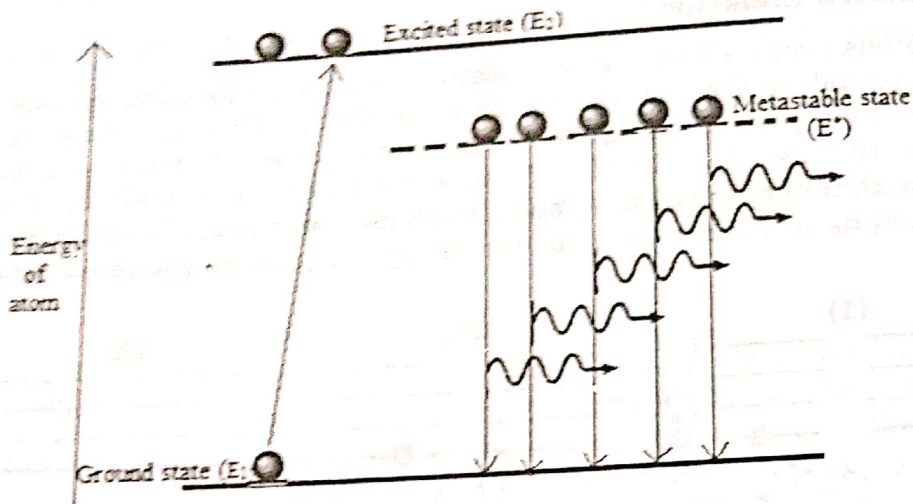


Fig. 12.12 Illustration of population inversion and light amplification

Three and Four Level Systems

Three and four level systems are used for production of laser shown in Fig. 12.13. Electrons jump from ground state E_0 to an excited state E_x by pumping. Later they move to a metastable state E_y by radiationless transition. From E_y , molecules jump to E_0 and produce laser. This occurs in three level systems where electrons move between three states. Four level system is little different. Here four states are involved. From excited state E_y , molecules jump to another state E_z by emission of photon and then immediately jump back to E_0 . Energy of E_z level is greater than that of E_0 . Four level systems produces more intense beam because here population inversion attains rapidly by input of small pumping energy.

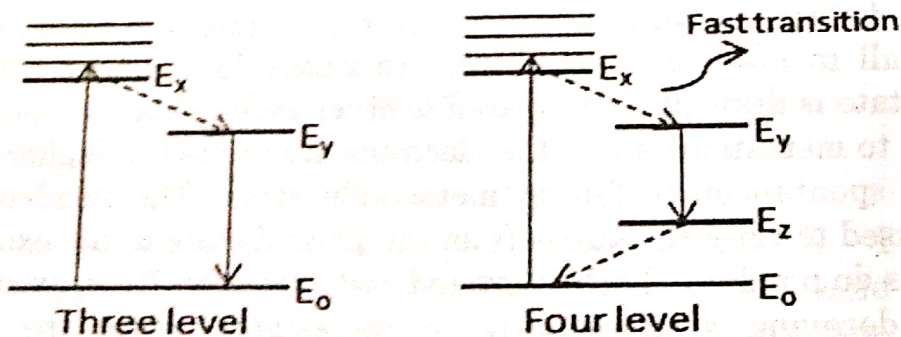


Fig. 12.13 Energy level diagrams of different laser systems

A laser is constructed from three major parts:

1. **An energy source:** The energy source is also referred to as pump or pump source. It provides energy to the gain medium to excite it. Electrical discharges, flash lamps, light from some other lasers, chemical reactions or even some explosive devices are used as an energy source depending upon the type of laser. For example He-Ne laser uses electrical discharge as energy source but Excimer laser uses a chemical reaction.
2. **Laser medium:** Laser medium is also known as gain medium. The gain medium is excited by the pump source to produce a population inversion, and photons takes place, leading to the phenomenon of optical gain, or amplification. Some dyes in organic solvents are used as a laser medium in liquid lasers. Gases like carbon dioxide, argon and krypton ore mixture of gases like Helium-Neon are used as gain medium in gas lasers.
3. **Optical resonator:** The optical resonator is also known as optical cavity. It consists of two parallel mirrors placed around the gain medium which provide feedback of the light. The mirrors are given optical coatings to optimize their reflective properties. Typically one mirror is a high reflector, and the other is a partial reflector called output coupler. The output coupler allows some of the light to leave the cavity to produce the laser output beam. Light from the medium, produced by spontaneous emission, is reflected by the mirrors back into the medium, where it may be amplified by stimulated emission. The light may reflect from the mirrors and thus pass through the laser medium many hundreds of times before exiting the optical cavity.

These principal parts of laser are shown in Fig. 12.14.

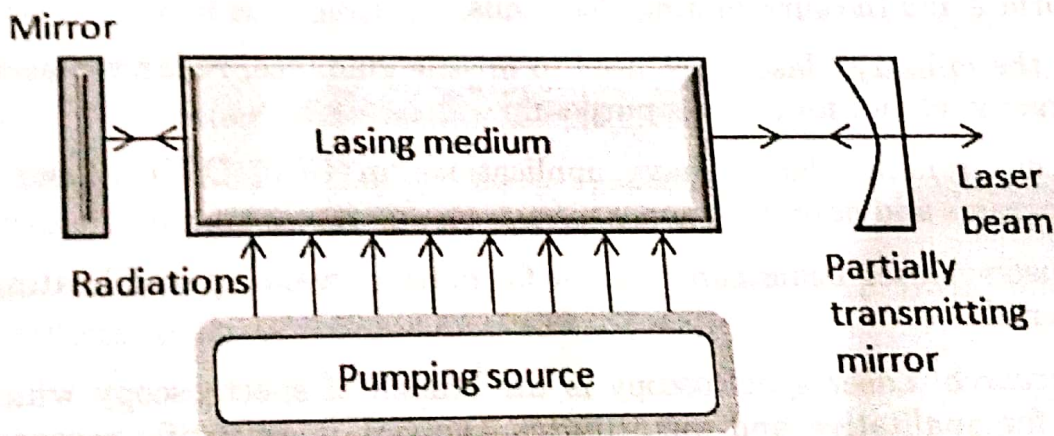


Fig. 12.14 A schematic diagram showing principal components of laser

Types of Lasers

Lasers can be classified according the following different schemes.

1. On the Basis of Active Media

- (a) **Gas lasers:** active medium used in gas lasers is gas. e. Examples of such ki of laser are He-Ne laser, CO₂ laser and N₂ laser.

- (b) Dye lasers: active medium used in these lasers is dye in liquid solvent or in solid.
- (c) Solid state lasers: In such kind of laser solid state material is used as an active medium. The semiconductor laser is an example of solid state laser.
- (d) Excimer lasers: In these lasers, chlorine or fluorine gas along with an inert gas is used as active medium.

2. On the Basis of Mode of Operation

- (a) Continuous wave lasers
- (b) Pulsed lasers

3. On the Basis of Number of Metastable Levels in Laser

- (a) 3 level lasers
- (b) 4 level lasers

Applications of Lasers

Lasers are used in various fields. Applications of lasers in some fields are given below

1. In medicine: lasers are used in surgical treatment, vision treatment, kidney stone treatment, dentistry, hair removal, skin treatment and tattoo removal. Laser beam can be used to remove ulcers in the stomach with very little loss of blood. Because of the burning action of lasers, the cut is also clotted and sealed immediately. The accumulation of red blood cells just under the skin of people appears in the form of red marks, called port wine stains. Laser surgery is done to remove these marks without damaging the outer skin surface and the surrounding blood cells.
2. In the military: lasers are used in missile guidance, radar replacement and target guidance for defense purpose.
3. In electronics: lasers have applications in CDs, DVDs, laser printers, holograms and barcode scanners.
4. Industry: laser beam can be used for cutting, welding and heating various materials.
5. In research: Laser spectroscopy is the branch of spectroscopy which can be used for qualitative and quantitative analysis in scientific research. Laser light scattering is used to characterize polymer and colloidal materials.
6. Environmental science: Lasers are used as environmental monitoring instruments for detection of various pollutants present in the atmosphere.