CHAPTER - 2

GENERAL CONCEPTS OF FLUORESCENCE

GENERAL ASPECTS OF LUMINESCENCE : -

Materials which are capable of emitting light mainly in the visible range, has been the subject of interest, to the scientists for many centuries, However, it was only in the Seventeenth century that Science came to the resuce of solving this mystery. Emission of light from liquid and / or solid thus became a topic of great interest. There is a wide variety of substances such as minerals, crystals and chemical substances that can emit the light. These materials capable o emitting light are termed as luminescent materials while the phenomenon is termed as luminescence.

According to Wiedemann [1] and Garlick [2] , luminescence is the phenomenon involving absorption of energy by a substance and its reemission in the visible or near visible region. Luminescence is, however, different than the thermal radiation. The phenomenon of luminescence doesn't follow kirchoffs law of absorption and emission; and on the basis of time delay, it also differs from physical processes like Raman effect and compton effect. In case of luminescence emission, this time delay is around or more than 10^{-9}S. While Raman and compton effects are completed in a time around 10^{-14}S. or less.

TYPES OF LUMINESCENCE : -

Luminescence from a substance does not occur spontaneously; but generally required energy to excite it. The excitation can be caused by ultraviolet light, X-rays or γ-rays. The excitation can deposit energy into the material which then subsequently is reemitted in the form of visible light. Various types of luminescence are often distinguished by the nature of the source of energy exciting the substance. If luminescence is produced by absorption of electromagnetic

radiation then it is known as photoluminescence. Cathodoluminescence is produced by energetic electrons or cathode rays. Electroluminescence is produced by an electric field applied to luminescent substances. Triboluminescence is the phenomenon where visible light is released during the grinding and pulverizing of the substance. Chemiluminescence utilizes the energy of a chemical reaction. Bioluminescence is the biological process and Sonoluminescence depends on the ultrosonics irradiation of materials.

The feature common to all types of luminescence are

1) Excitation of molecules to higher energy states by an excitation from a source.
2) De-excitation of excited molecules to ground states following radiative emission,

Some of more references in luminescence have been reviewed in books [3, 4, 5].

PHOTOLUMINESCENCE : FLUORESCENCE AND PHOSPHORESCENCE : -

When a luminescent material is excited by electromagnetic radiation, emission occurs only during the excitation in some materials while in other materials, emission occurs for considerably longer periods, even after the excitation has stopped.

In early experiments with phosphors (luminescent materials) depend on sunlight, as the source of excitation. The quality of phosphor was decided by the ability of material to show considerable luminescence even after the sample was transferred from sunlight into a dark place. This persisting ability of material was known as phosphorescence as studied by David Hercules and K. Mahesh, P.S.Weng, C.Furetta [6,7].

Definition of fluorescence was given, adopted and is now accepted as fluorescence being a short duration luminescence, typically the one in which light

emission persists to around 10^{-8}S. after the source of excitation has been cut off The emission that persist for longer period extending even to hours is known as phosphorescence.

A more meaningful distinction between fluorescence and phosphorescence is based on the dependence of luminescence decaytime in its absolute magnitude. Thus, if an emission due to spontaneous transition of a system from excited energy level E to ground energy level E_g (fig.2.1); then the luminescence will decay exponentially with decay time, determined by the probability of transition between these states. If this is an allowed electronic transition, then the photons, in the visible region of spectrum will be emitted.

The decay time will be in the range of 10^{-8}S. to 10^{-9}S. If the transition probability for the transition E----> E_g is of many orders low in magnitude having corresponding increase in the decay time. The transition probability in all cases is, however, an intrinsic characteristic of the luminescence center. The luminescence decays exponentially with time. The decay time is independent of the temperature in the range where luminescence efficiency remains high. All the above cases are properly characterized as fluorescence. When luminescence decay time depends on temperature and luminescence efficiency is high then the term phosphorescence is applied. On an atomic scale this situation can arise when an atom or molecule is somehow excited to an energy level E_m, energy level due to metastable state, from which it cannot return back to ground level by photon emission The transition of $E_m \rightarrow E_g$ has been completely forbidden, according to the selection rules. Let us suppose the system (Fig.2.1) can be raised by absorption of energy $\Delta E = E - E_m$ to an excited level E, such that the radiative transition $E \rightarrow E_g$ is an allowed one. Hence, if the energy $\Delta E_{absorption} = E - E_m$ is provided to the center, the energy $\Delta E_{emission} = E - E_g$ will be emitted. If ΔE absorbed can be provided by thermal means at room temperature, a continuous luminescence (phosphorescence) can

be observed even after the removal of excitation source. If the system is raised to a higher temperature, the energy $\Delta E_{absorption}$ will be provided at more rapid rate. The phosphorescence thus will be brighter and the decay time will be shorter due to faster depopulation of metastable state Via the path E_m + Heat→ $E^* \rightarrow E_g$ + Photon with lowering of temperature, there will be decrease in phosphorescence brightness and an increase in decay time. Thus, the important difference between fluorescence and phosphorescence is the temperature dependence and the decay time.

Depending on whether the transition to ground state is from lowest excited singlet energy level or triplet energy level, the fluorescence can be distinguished from phosphorescence. If the radiative transition occurs between lowest excited singlet state and singlet ground state, then the process is termed as fluorescence. For radiative transition between lowest excited triplet state and singlet ground state; the phosphorescence is observed. The radiative transition is allowed between two states of equal multiplicity. Therefore, there is no transition between singlet and triplet state.

In phosphorescence, radiative transition occurs between triplet and singlet ground states, which is not possible according to the selection rules. In facts, the atom from a triplet state is transferred to singlet state and then the transition takes place between singlet - singlet levels. So, in fluorescence the originating level for radiative transition is singlet while in phosphorescence it is triplet.

The schematic energy level diagram in (Fig.2.2) shows the principal pathways by which this transition occurs (Birks 1970) [8]. In most cases, molecules are raised from the ground state (S_0) to an excited singlet state (S_n) by absorption. The favoured path for deexcitation is one which minimizes the lifetime of the excited state. Almost all molecules drop quickly to the lowest level (S_1 or T_1) by

nonradiative process, so that the most commonly observed radiative transition are $S_1 \rightarrow S_0$ fluorescence and/or $T_1 \rightarrow S_0$ phosphorescence.

From the above discussion it is clear that for fluorescence, the multiplicities of the states are same while for phosphorescence, the multiplicities of the state are different.

If addition to the radiative processes discussed above, radiationless (also known as non-radiative) processes are possible. These processes are the result of conversion of an electronic energy into the vibrational energy. These can occur between excited state of the same or of different multiplicity. When a radiationless process occurs between the first excited singlet and lowest excited triplet it is known as intersystem crossing. In all other cases, the process is usually referred as internal conversion (Fig. 2.2.)

Excitation to any excited singlet state above the first one is normally followed by internal conversion so that the fluorescence or intersystem crossing occurs only from the first excited singlet state. Thus, individually fluorescence and phosphorescence will normally be the same in all respects, such as wavelength, shape, lifetime no matter which excited singlet state is initially occupied. Internal conversion from the first excited singlet state can occur, competing with and thereby quenching fluorescence and intersystem crossing (therefore also the phosphorescence). However, internal conversion from the first excited singlet is less likely than among the higher excited singlets and the complete quenching of fluorescence and phosphorescence is extremely rate Figure.2.2 shows as outline of the different processes [9].

ENVIRONMENTAL EFFECTS ON FLUORESCENCE : -

Environmental factors strongly influence the fluorescence of an organic molecule. The fluorescence of a substance is generally more affected by its environment than the absorption [10]. The life time of the excited state of a fluorescent molecule in a solution shows a large dependence on the solvent environment [11]. A large number of environmental effects are of importance. Few of these are the nature of solvent, pH, Heavy atoms, metal ions, oxygen, temperature etc.

EFFECT OF SOLVENTS : -

Electronic transitions occur at the rapid rates relative to the rates of internuclear motion in molecules. Hence, during an electronic transition of either absorption or emission, the nuclei remain essentially stationary (Frank-Condon principle). Accordingly, when a molecule in its ground state absorbs a photon it finds itself in a metastable excited state, in which the molecular geometry and solvent configuration are characteristics of the ground state. Solvent reorientation then occurs approximately 10^{-11} to 10^{-12}S. after excitation, producing an "equilibrium" excited state, in which the solvent configuration is optimal for the geometry and electron distribution of the molecule. Emission occurs from the equilibrium excited state. Solvent relaxation then occurs, forming the equilibrium ground state. Electronic excitation can produce drastic changes in both molecular geometry and electronic charge distribution, the energy difference between equilibrium and Frank-condon excited states can be quite large in some cases. Because solvent relaxation phenomena occur very rapidly. Such rapid phenomena are amenable to experimental observation. Some workers have studied solvent relaxation in detail [12,13]. Some results of these studies are mentioned below.

It is evident that the ground and excited states involved in absorption and fluorescence are 'different'. Accordingly there is no reason to expect precise correspondence between absorption and fluorescence solvent effects. Any single solution absorption or fluorescence spectrum involves either a ground or an excited state that is not even approximately in equilibrium with its solvent cage. Accordingly, great care must be exercised in the interpretation of " single" spectra, either absorption or emission [14,15].

In many polar molecules, the excited state is more polar than the ground state. Hence, an increase in the polarity of the solvent produces a greater stabilization of the excited state than that of the ground state, causing a shift in fluorescence towards longer wavelength (red shift). The magnitude of the shift depends on the specific nature of the solute - solvent interaction such as

1) Dipole - dipole interactions between solute and solvent, both being polar.
2) Interaction between polar solvent and non polar solute.
3) Interaction between non polar solvent and polar solute.
4) Interaction between solute and solvent when neither of them possess a permanent dipole.

The fluorescence spectrum will be influenced by one or more of these categories, the general effect is termed an " electrostatic solvent effect". The shift in non polar solvent and solute is caused by a dispersive interaction resulting from the fact that electronic transitions produce changes in the electron densities of solute molecules which results in red shift. The fluorescence intensities of aromatic compounds can be affected by electrostatic solvent effects. These effects are generally insignificant if both solute and solvent are non polar. For polar solute - solvent pairs, electrostatic intensity perturbations are minor, relative to those produced by specific short - range interaction such as complex formation, hydrogen bonding etc.

EFFECT OF HEAVY - ATOM SOLVENTS : -

Heavy atom substituents tend to reduce the fluorescence in aromatic molecules. Heavyatom solvents usually reduce the fluorescence yield and increases intersystem crossing [16] and $T_1^* \rightarrow S_0$ phosphorescence, but the effect on the latter is usually greater [17], so that the net effect is often an increase in the phosphorescence yield and decrease in fluorescence one.

The is some uncertainty regarding the actual processes responsible for external heavyatom effects. In the case of halogen containing perturbers [18,19], there is strong evidence that a 1:1 complex is formed between an excited state of the solute and the heavyatom species. The extent of spin - orbit coupling is much greater in this " exciplex" than in the unperturbed solute. The exciplexes appear to be strongly of a charge - transfer nature, and that excited - state complex formation is increasingly being recognized as a general fluorescence - quenching process. All heavyatom effects cannot be understood interms of exciplex formation. Some evidences have shown that heavyatoms occasionally decrease the rates for intersystem - crossing processes in organic molecules. These phenomena that categorize as " heavyatom effect" are complex and comprise several fundamentally different types of molecular interactions [20].

EFFECT OF pH : -

The fluorescence spectra of the most aromatic compounds containing acidic or basic functional groups are very sensitive to the pH and hydrogen bonding ability of the solvent. Most proton - transfer reactions in polar solvents are very fast. The large energy separation of the fluorescence spectra makes it easy to

determine the occurrence of acid - base reaction in the excited state. The step in reaction sequence can be explained as

1) Absorption of radiant energy to produce the excited molecule.
2) Deactivation of the excited molecule.
3) Radiationless deactivation of the excited molecule.

By measuring the relative fluorescence intensities for the neutral molecule and the anion, as a function of pH, it can be determined, that the excited state acidities for the aromatic compounds is about 3:1; that is, the excited singlet exhibits an acid strength which more than 10^6 times greater than that of ground state.

The knowledge of the equilibrium constants for excited state protolysis, alongwith knowledge of the relative fluorescence efficiencies of the two protic forms, can be of great importance in enhancing the sensitivity of fluorometric analysis of solutes, containing dissociable functional group [21,22].

Some compound classes, especially phenols, thiols and aromatic amines, become much stronger acids and excitation, whereas nitrogen and sulphur heterocyclics, carboxylic acids, aldehydes and ketones become much more basic.

The nature of excited - state acid - base chemistry in compounds containing more than one acidic or basic functional group is interesting. In the lowest - excited singlet state of this compound, the hydroxyl group greatly rises in acidity, and ester carbonyl greatly rises in basicity, relative to the ground state. Accordingly, during the life time of the excited state, and intramolecular acid - base equilibrium is established [23].

It has been shown that in the closely related intramolecular proton - transfer, equilibrium Is not established during the excited - singlet life - time [24].

There have been a number of fluorometric studies of bifunctional nitrogen heterocyclics and other compounds in which there are evidences for intramolecular proton transfers, but the problem becomes complicated by strong hydrogen - bonding interactions with the solvent

EFFECT OF HYDROGEN BONDING : -

Hydrogen bonding interaction of substituted aromatic molecules with the solvent or with other solutes can greatly affect the fluorescence behavior. The effect of hydrogen - bonding on the fluorescence of organic molecules have been reviewed in detail [25]. Formation of an excited - state hydrogen - bonded complex between the two, can occur by excitation of species already present in the ground state :

$$A - B \xrightarrow{h\nu} (A - B)^*$$

Alternatively, during the lifetime of an uncomplexed excited A^* molecule, hydrogen bonding with B can occur as

$$A \xrightarrow{h\nu} A^*, \; A^* + B \rightarrow (A - B)^*$$

In the former case, it Is obvious that both the absorption and fluorescence spectra of A will be affected by hydrogen bonding with B. However, when hydrogen bonding takes place, only after excitation, the fluorescence spectrum of A will be perturbed by the interaction. On careful comparison of the effect of B on the absorption and the fluorescence spectra of A, one can compute the relative abilities of A and A^* to hydrogen - bond with B.

In the solvents dimethysulphoxide, dioxane, acetonitrile it is found that, as enthalpy of formation of hydrogen bonds increases, fluorescence yield decreases for the solutions at room temperature [26].

Nitrogen heterocyclic like 5,hydroxyquinoline exhibits very inefficient $S_1^* \rightarrow T_1^*$ intersystem crossing in any solvent The influence of solvent on fluorescence yield for the compound is attributed to the increased $S_1^* \rightarrow S_0$ transition induced by hydrogen bonding with the solvent. Similar observations have been noted in other hydrogen- bonding systems [27,28]. Enhanced internal conversion affected by excited state hydrogen bonding, reduces the fluorescence yield. It was observed that hydrogen bonding of phenols with carboxylate anions causes total attenuation of phenol fluorescence. Formation of a hydrogen bonded complex between excited phenol and carboxylate can occur either before or after excitation of the phenol.

The influence of hydrogen bonding on the fluorescence of organic molecules is not limited to interaction with the solvent. The absorption spectra of 5-and 8- hydroxyquinoline are quite similar. But the fluorescence yield for 8-Hydroxyquinoline is found out to be large than that for 5-Hydroxyquinoline in the same solvent. The intramolecular and intermolecular hydrogen bonding in 8-Hydroxyquinoline may be the reason for observed reduction in fluorescence yield. Intramolecular and intermolecular hydrogen bonding affects the fluorescence, by increasing the rate constant for $S_1^* \rightarrow S_0$ transition. In a molecule, presence of intramolecular and intermolecular hydrogen bond with the phenolic hydroxyl, the fluorescence efficiency of a molecule should be maximum. Generally, effect of excited - state hydrogen bonding on the luminescence of nitrogen heterocyclics are dependent on whether the lowest excited singlet is (n , π^*) or (π, π^*). It is observed that the excited (π , π^*) singlet of nitrogen heterocyclics are much more strongly basic than the ground state. For a nitrogen heterocyclic, with a low - lying

(π , π^*) excited singlet, the frequencies of both absorption as well as fluorescence shifts to lower side as the hydrogen - bond formation ability of the solvent increases. In contrast, (n , π^*) excited singlet state of nitrogen heterocyclics are less basic than the ground state. Therefore, they are less susceptible to hydrogen - bonding interaction. Thus, energies of n $\rightarrow$ π^* absorption spectra increases with increasing hydrogen - bond - donor power of the solvent.

It is observed that aromatic carbonyl compounds and nitrogen heterocyclics fluoresce very weakly, or not at all in non polar, aprotic solvents. Their fluorescence yield increases sharply on the addition of hydrogen - bonding solvents. In such compounds, the lowest excited state is usually (n , π^*) in aprotic solvents, but the lowest (π , π^*) singlet often is not energetic than the (n , π^*) singlet. On increasing the "proticity " of the solvent, the (π , π^*) states shift to lower energies, relative to the ground state, while the energies of (n , π^*) singlets increase.

FLUORESCENCE IN ORGANIC MOLECULE :-

Many organic compounds fluoresce are phosphoresce, and these properties of organic compounds have been widely used in analysis.

The study of luminescence processes in organic molecules has also received attention from the physical chemist and physicist. Fluorescence is not a broadly useful method for determining molecular structure. However, it can be employed to obtain significant qualitative information concerning molecular structure. From the large number of known organic compounds, relatively few exhibits luminescence.

ALIPHATIC COMPOUNDS :-

Aliphatic compounds often do not absorb strongly, hence do not fluoresce strongly. From the aliphatic compounds which absorb strongly, a large number of aliphatic compounds absorb in short wavelength UV region. The strong absorption may lead to direct photodecomposition of the molecule, where absorbed energy is utilized to break one or more bonds. If direct photodecomposition does not occur for high energy UV absorption, a phenomena known as ' predissociation ' may take place [29].

Predissociation processes [30] are not completely understood, but they appear to provide important mechanism for the dissipation of excitation energy in saturated compounds.

The luminescence observed in aliphatic compounds originate from excited amines and hydroxyl radicals which are decomposed products of the original molecule. However, aliphatic aldehydes and ketones [32] do exhibit luminescence, originating from the molecule. Acetone shows visible luminescence in green region due to biacetyl formation, due to photochemical reaction of acetone [31]. For many aliphatic carbonyl compounds luminescence emission is usually a minor means of energy dissipation, such weak emission does not provide useful information. The luminescence studies for large time illustrate the facts : the absorber and emitter are not always the same molecular species. Even if the two species were identical, the emission does not necessarily result from a simple transition from excited state to ground state. Complexities arise in one of the following ways

1) The emission my vary with time.
2) The emission intensity may show unusual concentration dependence.
3) There may be an abnormally large displacement between the absorption and the emission maxima.

4) The quantum efficiency of emission may vary with wavelength.

In short, it may be concluded that a very small number of aliphatic compounds show fluorescence.

AROMATIC COMPOUNDS :-

As compared to aliphatic molecules,more number of aromatic compounds exhibits fluorescence. Benzene ring fluoresce in UV region but substitution of different groups in it, can make the compound to fluoresce. Certain functional group substituted in an aromatic ring exert definite, predictable influences upon both the energy and intensity of emission. These substituent effects are discussed briefly below

a) Alkyl Group:-

Generally, addition of alkyl groups of an aromatics nucleus has little influence upon the energy or intensity of emission, unless steric factors are involved. The number of aromatic compounds, substitution of methyl or ethyl groups causes substantial increase in the phosphorescence to fluorescence intensity ratio [33].

b) Halogens :-

Halogen - substituted aromatic substances, affects the fluorescence with diminished intensity; as the phosphorescence efficiency is increased. This is effect is termed as " intramolecular heavy - atom effect " [34]. Many ido - substituted aromatic compounds are subjected to predissociation or photodissociation in liquid solution, rendering the observation of any fluorescence even less probable. From the study of mechanism of the heavy - atom effect, it has been indicated that the

halogen substituent enhances the spin - orbit coupling mechanism of the aromatic hydrocarbon and in addition, introduces a new spin - orbit coupling process of its own [35].

A heavy - atom containing solvent is also quenches fluorescence of the solutes cause an increase in the rate constant for intersystem crossing, the mechanism is believed to be the charge transfer in nature [36,37]. It is proposed that a weak charge transfer complex is formed between the emitting and perturbing molecules, thereby facilitating intersystem crossing [38]. Also, it was proposed that the effect was caused by energetic collisions between the excited solute and perturbed molecules [39]. From these, it was concluded that the formation of weak charge - transfer complex is assumed to occur in both solvent quenching and the external heavy atom effect.

c) Nitro Group :-

Nitro - substituted aromatics may exhibit phosphorescence, but do not fluoresce. It appears that heavy atom effect and predissociation are both being involved in the quenching of fluorescence by nitro groups. Some dyes containing nitro groups, absorb at very long wavelengths, also emit fluorescence [40].

d) Hydroxyl and Amino Groups :-

These groups are mainly of interest due to the unusual acid - base dissociation properties of excited organic compounds.

Many other substituent groups such as carbonyl, ester etc. affects the fluorescence of parent compound. Sometimes substituent may change position and intensity of fluorescence peak or may quench the peak or may be a new peak being observed due to some of the effects.

FLUORESCENCE IN HETEROCYCLIC COMPOUNDS :-

Presence of hetroatom in benzene ring greatly affects the luminescence of aromatic compound, as most hetroatoms possess at least one ' lone pair ' of non - bonding electrons. Absorption of radiation results in n ----->π^* transition. This n---->π^* transition in hetrocyclic compounds is responsible for the differences between their luminescence properties and those of the aromatic compounds.

The presence of (n , π^*) excited state, in a hetrocycle, generally do not fluoresce. However, if the influence of lone pair on hetroatom can be negated, the hetrocycle molecule may fluoresces. Quinoline is non fluorescent in neutral aqueous solution, but fluoresce in acidic solution, due to protonation of the lone pair of electron on nitrogen atom [41].

The emission properties of compounds possessing low-lying (n , π^*) singlet states are sensitive to the nature of the solvent. The relative energy of excited (n,π^*) and (π , π^*) singlet state are functions of polarity and the hydrogen bonding [42] ability of the solvent. If solvent polarity is increased, (n , π^*) shifts towards lower energy [43]. However, if (n , π^*) and (π , π^*) states lie much closer in energy, the order of the states may interchange sufficiently for the polar solvents.

Fusion of benzene ring to a hetrocyclic nucleus causes a bathochromic shift and increases intensity of absorption. Thus, Acridine, Acridone and Carbazole exhibit visible fluorescence. Similarly, coumarin fluoresce in ultra- violet, but its hydroxy and amino derivatives fluoresce in the visible region.

Fluorescence of oxygen,sulphur, silicon and nitrogen heterocycles are investigated systematically, while heterocycles containing other elements viz. B,P,As,Se have not been investigated apparently. An oxygen heterocycle generally

do not appear to fluoresce unless it is fused to a benzene ring. Similarly,sulphur heterocycle fluoresce when it has been fused with benzene as stated earlier

Fluorene and its three heterocyclic analogues have also been investigated. As one carbon atom of fluorene is replace by oxygen, nitrogen and sulphur, the quantum yield of fluorescence decreases. It, therefore, appears that heterocycles containing heavier heteroatom are less prone to exhibit fluorescence.

It is known that oxygen heterocyclics generally do not fluoresce, but when fused with aromatic rings, they may fluoresce. The molecules like coumarin, which fluorescence, contain oxygen heterocyclic rings fused with benzene ring as in figure 2.3.

Luminescence in coumarin was studied by many workers. Mostly, the effect of different substituents in coumarin, on the fluorescence spectra was investigated. Jones Guilford [44] et al studied the fluorescence properties of coumarin for the charge transfer and twisted intra - molecular charge transfer. S.S. Rathi et al have explained the effect of solvent on the positions and intensity of emission spectra [45]. Guo Chu and Feng Yangbo [46] also studied the effect of solvent and substituent effects on intramolecular charge transfer of derivatives of 4 - Trifluoromethyl - 7 - amonicoumarin. Excited state dipole moment of 3 - Phenyl coumarin was calculated by R.Giri [47] et al. R.Giri [48] studied the effect of temperature upon the fluorescence emission of substituted coumarins Probable energy level scheme for 4, 7 - substituted coumarin was given by Shyam Singh and M.K. Machwe [49].

It has been concluded in studies that electron withdrawing substituent group lowers the energy difference between π and π^* orbital of the parent molecule, and electron donating substituent group enhances the energy difference between π and π^* orbitals.

FLUORESCENCE IN COUMARIN:-

Coumarin [50] has a very low fluorescence quantum yield, but its derivatives are highly fluorescent and have high quantum yield. The florescence of

large number of coumarin has been studied [50,51]. Extensive study of luminescence of different coumarins was made by several workers [52,53,54]. Fluorescence of coumarin has been employed for their detection in chromatography to detect the spot [55]. Fluorescence characteristics of 7,4 - substituted coumarin was studied by S.S.Rathi et al [56]. Fluorescence efficiency of coumarins depend on the nature and position of the substituents. Efficiency can also be changed by changing the surrounding media. Substituents which enhance electron mobility, increases the intensity [50]. It has been observed that electron attracting group at 3-position and electron repelling group at 7-position enhance the fluorescence intensity [31,32]. The study of fluorescence spectra of different coumarins in different solvents has been reported by many workers [53,54,56,59,60]. The effect of substituents on coumarin ring were studied by Giri et al [47], Shyam Singh and M.K.Machwe [49]. Temperature effect of fluorescence emission of substituted coumarins has been studied by Giri [48], leads to the conclusion that intramolecular quenching by substituent group plays an important role in deactivation process. Effect of solvent and substituent on fluorescence of coumarin was studied by Guo Chu and V.V.S. Murti et al [46,61].

LUMINESCENCE IN POLYMER : -

Many polymers exhibit photophysical and photochemical properties but there has been not much investigated on the fluorescence of polymers. Many workers have studied fluorescence in organic molecules in solid form and also when mixed in the solvents. It is believed [62] that photophysical properties of polymer resembles to those of small molecules of similar structure.

In decade, many polymers were undertaken to study the fluorescence observed in them. The fluorescence of the synthetic polymer e.g. in solid state has been examined [63,64,65,66] chiefly in connection with their performance in scintillation devices, in which polymer serves as energy donor. Yanari and Bovey [67] studied fluorescence

solution dynamics was explained by O.paulinus Nwammuo [69] Gau Chu and Yangbo [46] had studied solvent and substituent effects on intramolecular charge transfer (ICT).

First excimer fluorescence was observed by Forster and Kasper [70] in pyrene solution. Further studies lead to the conclusion that excimer fluorescence is characteristic of many aromatic chromophores [71,72]. Information on bond rotation rates was obtained in terms of excimers.

Fluorescence studies give knowledge of molecular motion in polymers. Information can be used to study the effect of chain stiffness and chain entanglement. Y. Bekbbes [73] et al studied the fluorescence properties of aromatic ether and their polymers and proposed a model for the molecular structure. Luminescence mechanism with the polaron model and lattice relaxation was discussed [74] by Cheng. Qing, Jin for explaining photoluminescence in polypropylene. In the present investigation, the effect of solvent polarity on luminescence in some of the polymers has been undertaken.

APPLICATIONS OF LUMINESCENCE : -

The various applications of luminescence are the fluorescent screens, paints, luminescent dyes for fibers, optical brightening agents, Scintillators, Lasers, Flaw detection, Analytical chemistry, Biology and Medicine, temperature indicators and dosimetry etc.

1) Fluorescent screens

The different luminescent materials under the exposure of ionizing radiations, display visible emission of different colours. If the screen in prepared

with luminescent materials, it can be used to give the visible image of an irradiated object. This property is used in T.V. screens, watch dials and luminescent lamps.

2) Paints

The unusual brightness of fluorescent paints is due to the presence of organic luminophores in them. The brilliancy observed in luminescent paints is due to the light reflected from painted surface and also the light due to luminescence. Enamels, decorative paints and printing inks belong to the category of luminescent paints and are by combining luminescent pigments and various binder. The different patents on the luminescent paints were reported [75,76,77].

3) Luminescent dyes for fibers

The rapid strides in the chemistry of polymer materials over the past several years have prompted to find solutions to the problems involved in the dyeing of fibers. Dyeing is generally done at high temperature and also, should stable to the process of dyeing. Different classes of colouring materials have been reported in the patents [78,79,80].

4) Optical brightening agents

The yellowness inherent in textile material was eliminated by optical brightening agents. Derivatives of stilbene [81,82], compounds with benzezole group [83,84] and derivatives of coumarin and carbostyryl [85,86] are the popular optical brightening agents. One of the coumarin derivatives is also used as brightner for photographic paper [87].

5) Organic scintillators

Luminescent materials capable of emitting light when exposed to ionizing radiation, allow the use of them as scintillators. Luminescent scintillators are usually in the form of single crystal or luminophore in organic solvent, or solid

solution in plastic single crystals of anthracene [88], stilbens [89] and tetracene [90] were reported for their use as scintillators. Liquid scintillators [91,92] are also reported with good efficiency. Plastic scintillators are more stable under varying temperature range than other organic scintillators. Reported plastic scintillators are polyvinylxylene, polymethyl styrene [93]. Plastic scintillators are widely employed in cosmic ray research, detection of short range particle, neutron detection and other applications [94].

6) Lasers

In recent years, lasers based on organic luminophores have been gaining in importance, their main advantage being the possibility of frequency tuning in a broad range of wavelengths.

7) Flaw detection

One of the major areas of application of organic luminophore is inspection of various materials for defects. Advances in aviation, rocketry, building of spacecrafts and many other machines operating under heavy duty conditions, impose increasingly stringent requirements on the strength of individual components and assemblies. It is, therefore, extremely necessary that the timely and reliable detection of all kinds of defects, including superficial one, arising in course manufacture and operation machines. It is known that surface microcracks tend to draw the wetting liquid by dint of intermolecular forces. This principle underlines luminescent dye penetrant testing used primarily for detecting surface cracks in the articles made of metals, alloys, glass etc. The physical aspects of this method have been discussed elsewhere [95]. Luminescence flaw detection technique is used to detect fine cracks in refractories, transverse defects, leaks through vessels etc.

8) Luminophores in Analytical chemistry

One of the practical application of luminophores is the fluorimetric determination of traces of inorganic substances present in metal alloys, soil, air, biological samples etc. [96,97]. The most frequently used technique of fluorescence analysis based on luminophores include fluorimetry. Different luminophores used for fluorimetric determination are Aminoxanthene dyes, Hydroxyxanthene dyes, Hydroxyanthroquione dyes. Fluorescent indicators are used to determine end point in titration.

9) Biology and medicine

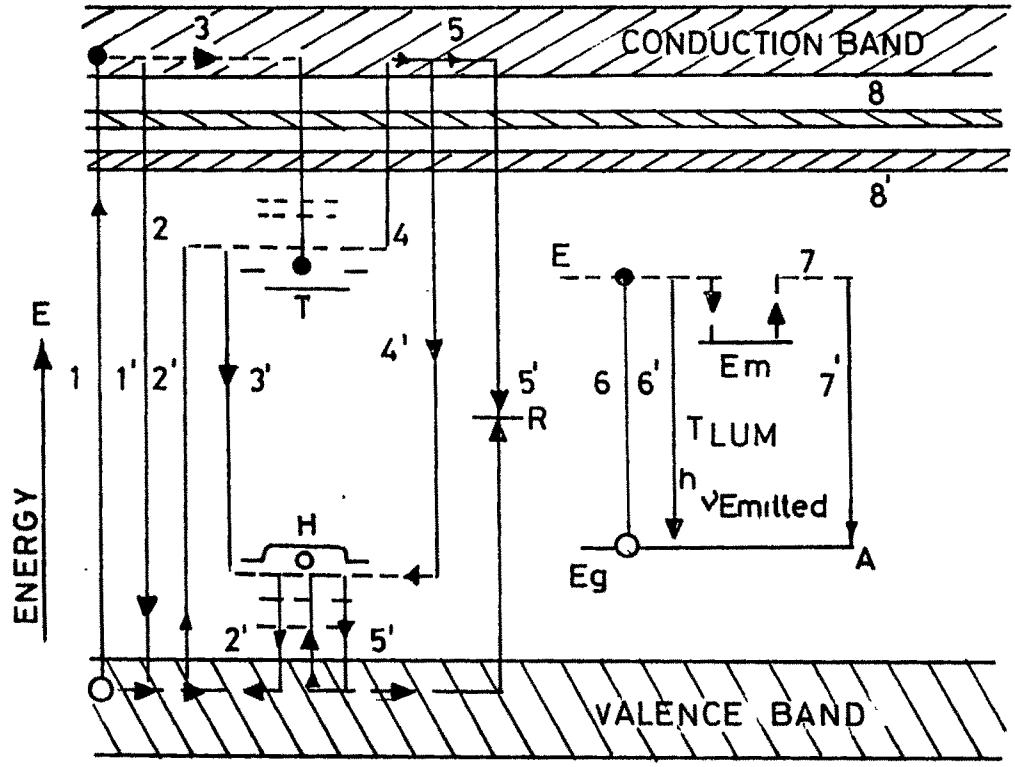
Luminescence is used to investigate structure of various biological molecules, bearing in mind, that the luminescence properties are extremely sensitive to structural changes and environment. This provides valuable information on the structure of complex biopolymers. Luminophores are also used to determine charge on the membrane surface, lipid phase velocity, membrane fluidity. Many pathological processes in the body are linked with structural rearrangement in biomembrane. To investigate the pathological process, fluorescent probes are found to be useful.

10) Temperature Indicator

Organic luminophores sensitive to temperature changes have found applications as temperature indicators. Reversible and irreversible indicators are widely used in modern technology. Reversible indicators permit timely detection of overheating in moving parts of various mechanisms and heating due to overloading of electrical equipment. Irreversible indicators used to sense the highest temperature inside complex mechanism during the operation. Solid solution of pyrene in polymethylmethacrylate, 1, 4 - distyryl benzene are used as luminescent temperature indicators

11) Dosimetry

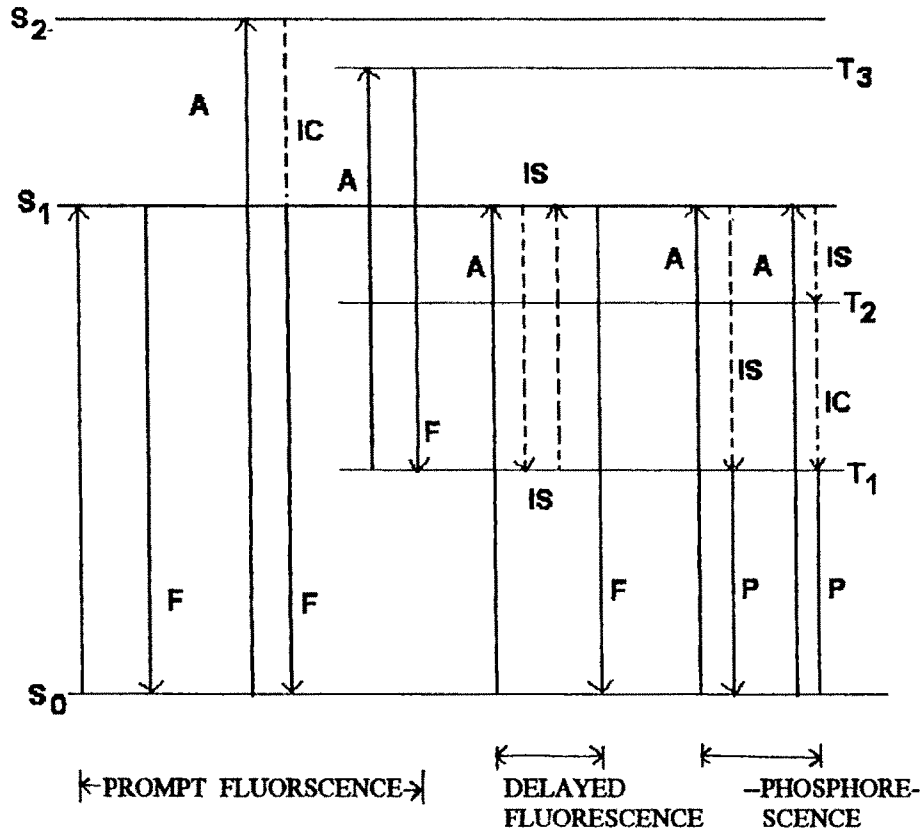
A great deal of interest has been displayed in the use of organic luminophores in the dosimetry of ionizing radiation by a method based on the relationship between the degree of damage substained by luminophores and radiation dose. The operation of dosimeter is based on the changes in luminescence properties under the effect of radiation. Advantages of fluorescent dosimeters are the small size and low cost, however, in it low thermal stability is the disadvantage.



●-ELECTRON, O-HOLE, T-ELECTRON TRAP, H-HOLE TRAP
Eg - GROUND STATE OF IMPURITY A, R - RECOMBINATION SITE
E - EXCITED STATE OF IMPURITY A, ------EXCITED STATE
Em - METASTABLE STATE OF IMPURITY A

1,1' ELECTRON HOLE RECOMBINATION IN THE VALENCE BAND.
2,2' RELEASED HOLE COMBINES WITH TRAPPED ELECTRON.
3,3' TRAPPED ELECTRON AND HOLE CENTRES INTERACT & ANNIHILATE.
4,4' RELEASED ELECTRON COMBINES WITH TRAPPED HOLE.
5,5' ELECTRON & HOLE COMBINE AT A RECOMBINATION SITE R.
6,6' EXCITED ELECTRON COMES BACK TO GROUND STATE.
7,7' RELEASED ELECTRON FROM META STABLE STATE Em FALLS BACK TO GROUND STATE Eg.
8,8' EXCITON BANDS.

FIG. 2-1 ENERGY LEVEL DIAGRAM SHOWING VARIOUS ELECTRONIC PROCESSES CONNECTED WITH EMISSION IN A CRYSTALLINE SOLID CONTAINING IMPURITIES AND RADIATION INDUCED TRAPS



S_0, S_1 : SINGLET LEVELS

T_1,T_2 : TRIPLET LEVELS

A : ABSORPTION ($10^{-18} - 10^{-15}$ S)

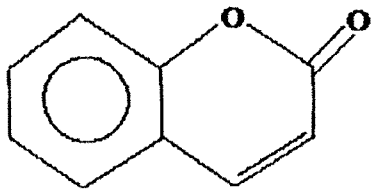
IC : INTERNAL CONVERSION (~ 10^{-12} S)

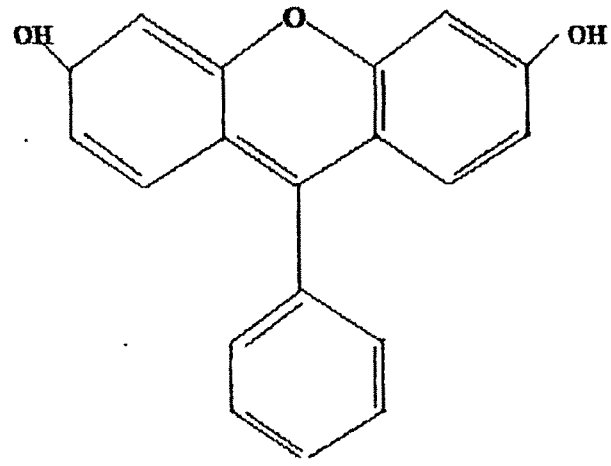
IS : INTERSYSTEM CROSSING (~10^{-9} S)

F : FLUORESCENCE (10^{-10} - 10^{-8} S)

P : PHOSPHORESCENCE (10^{-3} – 10 S)

FIGURE 2..2 PRINCIPAL RADIATIVE (⟶) AND NONRADIATIVE (⇢) TRANSITION CAUSING PHOTOLUMINESCENCE





COUMARIN **FLUORESCEIN**

FIGURE 2. 3

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