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Definition-“*Photochemistry is the branch of chemistry which deals with the interaction of light radiations with matter*”. It is mainly concerned with rates and mechanisms of reactions resulting from the exposure of reactants to light radiations. It is defined as the study of chemical effect produced by light radiations ranging from 2000 to 8000 Å wavelength. The photochemical reactions are induced by light radiation and are influenced by intensity of light radiations. On other hand the reactions which are caused by heat and in absence of light are called thermal or dark reactions. The thermal or dark reactions are influenced by temperature, concentration, presence of catalyst etc.

Nature of light: -

Light is a form of electromagnetic radiations. All electromagnetic radiations have wave characteristic and travels at the same speed of light but their wave length is different. The unit of wave length is nanometer i.e. $1 \text{ nm} = 10^{-9} \text{ m}$. γ - ray and X - rays have very small wave length i.e. less than 10^{-11} m . The visible light ranges from the violet region at about 380 nm to red region at 750 nm.

Interaction between light and matter: -

To understand matter, we have to make use of light and to understand light we must involve matter. Here the light is used as complete spectrum of electromagnetic radiation from radioactive to radio waves. We use X-rays to study the structure of molecule in their crystalline state and take the help of various spectroscopic methods, to understand the arrangement of atoms and molecules. On the other hand, if we want to study the nature of the light, we need matter. When light radiations fall on matter, it reflects, transmits, scatters or absorbs and thus allowing us to understand its behavior. A beam of light in a darkroom will not be visible to us, as it is scattered by dust particles floating in the air. A microscope is used to view particle, when incident light is scattered by it to the aperture of the object. All light measuring devices are based on interactions. In these interactions light behaves as a particle and in some other. Its behavior is like a wave.

Importance of Photochemistry: -

1. Preparation of very important products like cleaning solvents, insecticides, halogenated aromatic compounds by photo chlorination.
2. The important photochemical phenomenon like fluorescence and photo phosphorescence are used in fluorescence tube lights, X-rays, TV screens, and luminescent dials for watches.
3. The main application of photochemistry has been seen in the manufacturing of solar cells. Solar cells can be used as a source of fuel in the near future.
4. Flash photolysis and pulsed laser photolysis are widely used by scientist as new tools for the study of higher energy states.
5. Photochemistry plays very important role in the application of optical brightness as paints in advertisements.
6. Vita. D2 from ergo sterol isolated from certain yeasts, antioxidants, by photosulphonation, antiviral reagent like cubanes and synthesis of caprocalcium which is the monomer of nylon. These compounds are synthesized by using photochemistry.
7. There are certain chemicals which changes their colour, when exposed to suitable

radiations and restore their original colour when the irradiation source is cut off. These are known as photochromic materials.

Luminescence

Luminescence is most conveniently defined as the radiation emitted by a molecule, or an atom, after it had absorbed energy to go to an excited state. The main types of luminescence are consist of fluorescence and phosphorescence. The goal of this experiment is to investigate the properties of optical *excitations* in organic crystals and to understand the processes that lead to phosphorescence and fluorescence.

Nature of Electronic States

It is important to distinguish between the terms *electronic state* and *electronic orbital* when discussing the nature of electronic states. An *orbital* is defined as the volume element in which there is a high probability (99.9%) of finding an electron. It is calculated from a one-electron wave function and is assumed to be independent of all other electrons in the molecule. *Electronic states*, on the other hand, are concerned with the properties of all the electrons in all the orbitals. In other words, the wave function of an electronic state is a combination of the wave functions of each of the electrons in each of the orbitals of the molecule.

Another important distinction is that between excited electronic states and the transition state. Generally a transition state corresponds to a vibrationally excited ground state (*i.e.* ground state in a strained configuration), where as excited electronic states may contain no excess vibrational energy, but are still much higher in energy than the ground state. In fact a molecule in an excited state is best regarded as a completely new entity, only remotely related to the same molecule in the ground state. An excited state will have a completely different electron distribution from the ground state, a different geometry, and more than likely will undergo chemical reaction quite different from those of the ground state. Electronic states of organic molecules can be grouped into two broad categories, *singlet states* and *triplet states*. A *singlet state* is one in which all of the electrons in the molecule have their spins paired. *Triplet states* are those in which one set of electron spin have become unpaired. As will be seen later, triplet states and singlet states differ significantly in their properties as well as in their energies. A triplet state will always lie lower in energy than its corresponding singlet state.

The Nature of Absorption Processes

Figure 1 show a partial energy diagram for a photoluminescence system. One should note that each of the electronic states (ground or excited) has a number of vibrational levels superimposed on it. The vibrational levels arise because a molecule in a given electronic state may absorb small increments of energy corresponding to changes in vibrational

modes, although retaining the same electronic configuration. Another significant fact to be noted is the degree of overlap between the vibrational levels of excited states such as S_2 and S_1 . By convention the singlet states should be stacked in a column while the triplet states are stacked in another vertical column displaced to the right of the singlet column. One should also notice the overlap between the vibrational levels of the triplet state T_1 and its corresponding singlet state S_1 . The energy of a photon ($E = hc/\lambda$) required to produce a particular excited state is the difference in energy between that state and the ground state as shown in figure 1. Thus there is a range of wavelength that can lead to a transition between any two electronic states, which accounts for the fact that electronic absorption spectra generally occur as broad bands, rather than as single lines. As one might notice there is no arrow describing a transition from the ground state to the triplet state T_1 . These transitions are forbidden and thus highly improbable. A good rule of thumb is that singlet-triplet processes have a probability of about 10^{-6} that of a corresponding singlet-singlet or triplet-triplet processes.

Luminescence Processes

Luminescence processes can be interpreted only in terms of the excited state from which luminescence emission occurs and its relationship to the ground state of the molecule.

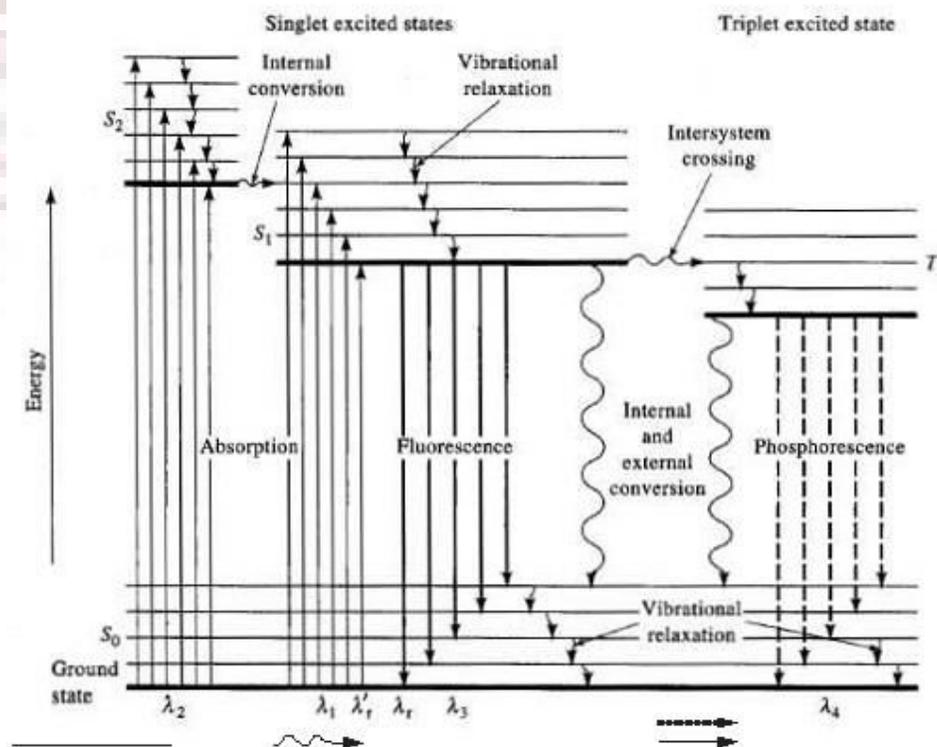


Figure 1: (Jablonski diagram)

Fluorescence

Once a molecule arrives at the lowest vibrational level of an excited singlet state, it can do a number of things, one of which is to return to the ground state by photon emission. This process is called *fluorescence*. The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-7} sec and therefore the decay time of fluorescence is of the same order of magnitude. If fluorescence is unperturbed by competing processes, the lifetime of fluorescence is the intrinsic lifetime of the excited singlet state.

The *quantum efficiency* of fluorescence is defined “as the fraction of molecules that will fluoresce” It should be noted that even though a quantum of radiation is emitted in fluorescence this quantum will be lower in energy on the average than the quantum absorbed by the molecule, due to vibrational relaxation (both after absorption and after emission). The change in photon energy causes a shift of the fluorescence spectrum to longer wavelength, relative to the absorption spectrum, this is referred to as the **Stokes Shift**. Therefore to summarize, the process of fluorescence consists of photon absorption by a molecule to go to an excited singlet state, relaxation from higher vibrational levels of that state to its lowest vibrational level, photon emission to a vibrationally excited level of the ground state, and again relaxation of the molecule to the lowest vibrational level of the ground state.

Internal Conversion

In addition to fluorescence one also encounters *radiationless* processes where molecules in an excited singlet state may return to the ground state without the emission of a photon, converting all the excitation energy into heat. The process called *internal conversion*, is not well understood and its efficiency is very difficult to measure. Generally internal conversion is an inefficient process and is probably only a small fraction of the total excitation energy in most molecules. This is particularly true in aromatic hydrocarbons, which we use in this experiment. So far the discussion was limited to the $S_0 \rightarrow S_1$ transitions, and the question might arise as to the nature of excited state processes if a molecule is excited to a higher singlet state such as S_2 . In such cases the molecule will undergo vibrational relaxation as discussed before. The fate of the molecule as it reaches the zeroth vibrational level of S_2 depends of the energy separation between the excited singlet states. Generally the separation between excited singlet states in an aromatic molecule is smaller than the energy separation between the lowest singlet state S_1 and the ground state S_0 . This means that the lowest vibrational level of S_2 will overlap with higher vibrational levels of the S_1 state, that do not involve extremely large difference in configuration from the zeroth vibrational level of the S_1 state. This situation gives rise to a high degree of coupling between the vibrational levels of the S_2 and S_1 states, which provides an extremely efficient path for crossing from the S_2 state to the S_1

state. In fact this process is so efficient that the molecule undergoes internal conversion from the S_2 state to the lowest vibrational level of the S_1 state in about the same time that it requires to convert from an excited vibrational level of the S_1 state to its zeroth vibrational level (*i.e.* 10^{-13} to 10^{-11} sec). Because of this situation one may formulate the following rule: a molecule may be considered to undergo internal conversion to the *lowest vibrational level of its lowest excited singlet state* in a time that is short, relative to photon emission, *regardless of the singlet state to which it was excited initially.*

Photoluminescence

Photoluminescence (abbreviated as **PL**) is light emission from any form of matter after the absorption of [photons](#) (electromagnetic radiation). It is one of many forms of [luminescence](#) (light emission) and is initiated by [photoexcitation](#) (excitation by photons), hence the prefix *photo-*. Following excitation various relaxation processes typically occur in which other photons are re-radiated. Time periods between absorption and emission may vary: ranging from short femtosecond-regime for emission involving free-carrier plasma in inorganic semiconductors up to milliseconds for phosphorescent processes in molecular systems; and under special circumstances delay of emission may even span to minutes or hours.

Phosphorescence and Intersystem Crossing

Although population of triplet states by direct absorption from the ground state is insignificant, a more efficient process exists for population of triplet states from the lowest excited singlet state in many molecules. This process is referred to as **intersystem crossing**, and is a spin-dependent internal conversion process. As singlet-triplet processes are generally less probable than singlet-singlet processes, one may be startled that a singlet-triplet process such as intersystem crossing can occur within the lifetime of an excited singlet state (10^{-8} sec). The mechanism for intersystem crossing involves vibrational coupling between the excited singlet state and a triplet state. Remembering that singlet-triplet processes are less probable than singlet-singlet processes by a factor of 10^{-5} to 10^{-6} , and that radiationless vibrational processes (such as internal conversion) occur in approximately 10^{-13} sec, the time required for a spin-forbidden vibrational process would be approximately 10^{-8} to 10^{-7} sec, which is the same order of magnitude as the lifetime of an excited singlet state. Therefore intersystem crossing can compete with fluorescence emission from the zeroth vibrational level of an excited singlet state but cannot compete with vibrational deactivation from higher vibrational level of a singlet state.

Once intersystem crossing has occurred the molecule undergoes the usual internal conversion process (10^{-13} to 10^{-11} sec) and falls to the zeroth vibrational level of the triplet state. Since the difference in energy between the zeroth vibrational level of the

triplet state and the zeroth vibrational level of the lowest excited singlet state is large compared to thermal energy, repopulation of a singlet state from a triplet state is highly improbable. There are two factors which tend to enhance a *radiationless* transition between the lowest triplet state and the ground state. First the energy difference between the triplet state and the ground state is smaller than the difference between the lowest singlet state and the ground state. This tends to enhance vibrational coupling between these two states, and therefore to enhance internal conversion. Second, and more important, the lifetime of a triplet state is much longer than that of an excited singlet state (about 10^{-4} to 10^4 sec) and therefore loss of excitation energy by collisional transfer is generally enhanced. In fact, this second process is so important that in solution at room temperature it is often the dominant pathway for the loss of triplet state excitation energy. If a molecule is placed in a rigid medium where collisional processes are minimized, a *radiative transition* between the lowest triplet state and the ground state is observed. This emission is called *phosphorescence*. As phosphorescence originates from the lowest triplet state, it will have a decay time approximately equal to the lifetime of the triplet state (ca. 10^{-4} to 10^4 sec). **Therefore phosphorescence is often characterized by an after glow which is not observed for fluorescence.**

Delayed Fluorescence

Delayed fluorescence is a non-collisional energy transfer process. This process has the fluorescence characteristic emission spectrum but a lifetime only a bit shorter than phosphorescence. Studies in a variety of aromatic hydrocarbons show that the intensity of delayed fluorescence is proportional to the square of the intensity of the exciting radiation and to the square of the phosphorescence intensity, indicating that it is a *biphotonic process* involving two triplet states. These data suggest the following mechanism for delayed fluorescence



The molecule in its ground state, S_0 , absorbs a photon and goes to the lowest excited singlet state, S^* . This, in turn, undergoes intersystem crossing to the triplet state T . The long life time of interaction between these triplet excitons and the molecules allows the these quasi particles to diffuse through the crystal and interact according to equation(3) producing an excited singlet state and a ground singlet state; the excited singlet state then emits its normal fluorescence as shown in (4). The process described above is referred to

as *P-type delayed fluorescence*. In this biphotonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence. However, if the crystal contains impurities the excitons are trapped by them with high probabilities due to favorable energy ratios. Doping with impurities has a negative influence on the intensities and lifetimes of the triplet excitons, The intensities can be reduced and the lifetimes shortened by orders of magnitude.

SELF-ASSESSMENT QUESTIONS (MCQs)

1. The transmittance of a $0.015 \text{ mol dm}^{-3}$ aqueous solution of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion was measured to be 0.84 at 600 nm through a cuvette of optical path length 1.0 mm. Determine the molar absorption coefficient.

- a) $9.0 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
- b) $6.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
- c) $5.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
- d) $50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

2. The absorbance of a solution of two laser dyes, cresyl violet and oxazine, was found to be 7.30×10^{-7} at a wavelength of 350 nm and 7.06×10^{-6} at a wavelength of 550 nm for a path length of 1.0 cm. Use the following data for the molar absorption coefficients of the dyes at these wavelengths to determine the concentration of cresyl violet in the solution.

	$\epsilon / (10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	
	350 nm	550 nm
Cresyl Violet	0.25	4.10
Oxazine	0.71	1.82

- a) $0.015 \text{ mol dm}^{-3}$
- b) $0.005 \text{ mol dm}^{-3}$
- c) $0.010 \text{ mol dm}^{-3}$
- d) $0.020 \text{ mol dm}^{-3}$

3. The longest wavelength absorption in the UV visible spectrum of acetone, CH_3COCH_3 , occurs at 335 nm. Predict the energy required to excite an electron from a lone pair orbital on the oxygen atom to an antibonding orbital centred on the carbonyl group.

- a) 3.70 eV
- b) 0.270 eV
- c) 2.99 eV
- d) 1.67 eV

4. The first ionization energy of nitric oxide, NO, is 9.27 eV. Calculate the velocity of the photoelectrons ejected when a sample of nitric oxide gas using radiation of energy 21.22 eV from a helium lamp source.

- a) $1.45 \times 10^6 \text{ m s}^{-1}$
- b) $6.36 \times 10^6 \text{ m s}^{-1}$
- c) $2.05 \times 10^6 \text{ m s}^{-1}$
- d) $1.09 \times 10^6 \text{ m s}^{-1}$

5. The first band in the photoelectron spectrum of hydrogen, H_2 , occurs close to 15.4 eV and consists of a progression of peaks separated by 285 eV corresponding to transitions to excited vibrational states of the H_2^+ ion. Calculate the wavenumber of the vibration of the lowest electronic state of the H_2^+ ion.

- a) 4400 cm^{-1} b) 2300 cm^{-1}
 c) 2850 cm^{-1} d) 1760 cm^{-1}

6. The second band in the photoelectron spectrum of oxygen, O_2 , at 17 eV corresponds to ionization to the excited $\text{A}^2\Pi_u$ state of the O_2^+ ion. The band consists of a long vibrational progression of peaks separated by approximately 900 cm^{-1} . The vibrational wavenumber of the ground $\text{X}^3\Sigma_g$ electronic state of a neutral oxygen molecule is 1580 cm^{-1} . Which of the following statements is consistent with the observed photoelectron spectrum?

- a) Ionization occurs from an antibonding orbital in O_2 .
 b) Ionization occurs from a bonding orbital in O_2 .
 c) Ionization occurs from a nonbonding orbital in O_2 .
 d) It is not possible to make any deductions about the nature of the ionization process.

7. When a solution of iodine, I_2 , molecules in tetrachlorometane solution is irradiated with radiation of wavelength 436 nm from a 50 W lamp source, the rate of production of iodine atoms by photodissociation when total absorption occurs is $1.45 \times 10^{20} \text{ s}^{-1}$. Calculate the quantum yield for photodissociation.

- a) 1.32 b) 0.83
 c) 0.66 d) 0.12

8. The quantum yield for the quenching of an excited fluorescing state was measured to be 0.34 with a lifetime of 4.1 ns. Calculate the lifetime of the state in the absence of a quencher.

- a) 6.2 ns b) 4.8 ns
 c) 3.4 ns d) 10.1 ns

9. The decay of photoexcited propanone in the presence of dicyanoethene in solution was investigated by measuring the fluorescence lifetime of the excited state for different concentrations of quencher. By constructing a Stern-Volmer plot of the following data, determine the rate constant for quenching.

$[\text{Q}] / \text{mmol dm}^{-3}$	5	10	15	20	25
$\tau_{\text{obs}}(\text{Q}) / \text{ns}$	1.91	1.85	1.79	1.74	1.69

- a) $3.5 \times 10^{-9} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ b) $1.7 \times 10^{-9} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
 c) $2.9 \times 10^{-9} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ d) $4.8 \times 10^{-9} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

10. Chlorophyll molecules act as both donors and acceptors in fluorescence resonance energy transfer. The fluorescence lifetime of chlorophyll molecules in a dilute solution of an organic solvent was found to be 1.2 ns. When chlorophyll molecules were instead embedded in a biopolymer, the fluorescence lifetime was measured to be 820 ps. Given that $R_0 = 5.6$ nm for chlorophyll molecules, estimate the separation between the donor-acceptor pairs in the polymer.

- a) 5.6 nm b) 6.3 nm
c) 8.9 nm d) 11.9 nm

