UNIT IV: PHOTOCHEMISTRY AND SPECTROSCOPY

Lecture Session 19: Photochemistry– Photochemical reactions with examples – difference between photochemical and thermal reaction

INTRODUCTION:

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions. The visible and UV radiations (2000-8000Ǻ wavelength) are mainly used in photochemical reactions.

Thermochemical reactions (dark reactions) are brought about by molecular collisions. These reactions are spontaneous and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy.

All ***photochemical reactions*** take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change. For example, in the combination of hydrogen and chlorine the first step is

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$$

The activated chlorine atoms ($Cl^{\cdot}$) then undergoes chemical reaction. It is evident from the above reaction that the second step can occur in absence of light.

Characteristics of photochemical reaction:

1. Photochemical reactions take place by absorption of light.
2. When a light composing number of colours are used, the photochemical reaction may not be initiated by all colours.
3. The free energy change (ΔG) of a photochemical reaction may be either negative or positive.

Differences between photochemical and thermal reactions:

Photochemical reactions	Thermochemical reactions
These involve the absorption of light.	These involve either absorption or evolution of heat.
Take place in presence of light.	Take place in dark or in presence of light.
They are independent of temperature.	They are dependent of temperature.
Rate of reactions is dependent on the intensity of the light absorbed.	Rate of reactions is not affected by the intensity of light.
The free energy change is negative or positive.	The free energy change is always negative.

Lecture Session 20: Laws of Photochemistry - Grotthus – Draper law, Stark–Einstein law and Beer-Lambert Law – Applications and Limitations, Problems

LAWS OF PHOTOCHEMISTRY:

Grotthus-Draper Law (or) The Principle of Photochemical Activation:

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change.

However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be re-emitted as heat or light or it remains unused.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon). When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Some important relations:

Photons ≡ quanta

One molecule absorbs ≡ one photon

One mole of a substance one mole of quanta (or)

Containing 6.023 x 10^{23} ≡ 6.023 x 10^{23} quanta of

(Avogadro number) light (or) one Einstein

Molecules absorbs

$$\text{One Einstein} = Nh\gamma$$

$$= Nhc/\lambda \ (\gamma = c / \lambda)$$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation

$$E = h\gamma = hc/\lambda$$ where, h – Planck's constant (6.625 x 10^{-34} Js)

c – velocity of light = 3.0 x 10^{8} ms^{-1};

λ – wavelength of light.

The energy of an Einstein E, is an Avogadro number (N) of photons. It is given as $E = Nhc/\lambda$ On substituting the values in the above equation it becomes

$$E= (6.023 \times 10^{23}) \times (6.625 \times 10^{-34}) \times (3 \times 10^{8})/ \lambda \text{ J mol}^{-1}$$

$$E = 0.1196/ \lambda \text{ J mol}^{-1} \text{ in SI units}$$

In CGS units: $c = 3 \times 10^{10}$ cm s^{-1}; $h = 6.625 \times 10^{-27}$ erg s^{-1}

$$E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/ \lambda \text{ erg mol}^{-1}$$

$$= 1.196 \times 10^{16}/ \lambda \text{ (in Å) erg mol}^{-1}$$

1 cal = 4.184×10^{7} ergs

$$E = 1.196 \times 10^{8}/4.184 \times 10^{7}/ \lambda \text{ cal mol}^{-1}$$

$$= 2.859/ \lambda \text{ cal mol}^{-1}$$

If l is expressed in Å, then $E = 2.859 \times 10^{8}/ \lambda \text{ (in Å) cal mol}^{-1}$

$$= 2.859 \times 10^{5}/ \lambda \text{ (in Å) kcal mol}^{-1}$$

LAMBERT's LAW

When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically, it may be stated as follows

$$- dI/I \,\alpha\, dl \quad \text{(or)} \quad -dI/I = kdl \quad \text{----------} \quad (1)$$

Where I = the intensity if incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating equation 1 and putting $I = I_0$ when $l = 0$, we get

$$\ln(I_0/I) = kl \quad \text{(or)} \quad I = I_0e^{-kl} \quad \text{----------} \quad (2)$$

BEER's LAW

The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0 e^{-kc} \qquad (3)$$

On combining both laws, we get $\log I_0/I = \varepsilon c l$ (4)

The equation 4 is termed as mathematical statement of Beer-Lambert‟s law. In the above equation ε = the molar absorption coefficient

$A = \log I_0/I$ is the absorbance (or) optical density (OD)

Limitations of Beer-Lambert's law : The law is not valid i) when non-monochromatic radiation is used, ii) if temperature changes during measurements, iii) the law is applicable only to dilute solutions.

Lecture Session 21: Quantum efficiency - Calculation of quantum yield - η Experimental determination- classification of reactions based on quantum yield with examples- Photo processes

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency „ϕ‟ is introduced.

Quantum yield is defined as "the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Ǻ; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

Number of einsteins absorbed = $q/(Nhc/\lambda) = q\lambda/Nhc$

Quantum yield $\phi = n/(q\lambda/Nhc) = nNhc/q\lambda$

In CGS units, $\phi = n/q \times [1.196 \times 10^{16} / \lambda \text{ (in Ǻ)}]$

High (or) Low Quantum Yield:

The quantum efficiency varies from zero to 10^6. If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield $\phi = 1$.

***High Quantum Yield*:** When two or more molecules are decomposed per photon, the quantum yield $\phi > 1$ and the reaction has a high quantum yield.

***Low Quantum Yield*:** When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfill the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.
2. The reactivity of the molecules should be temperature independent.
3. The molecules in the activated state should be largely unstable and decompose to form the products.

Causes (or) Reasons for high quantum yield:

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
2. Formation of intermediate products will act as a catalyst.
3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

Examples:

1. Decomposition of HI: In the primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

$HI + h\gamma \rightarrow H* + I*$ Primary reaction

$H* + HI \rightarrow H_2 + I*$ Secondary reaction

$I* + I* \rightarrow I_2$

Overall reaction : $2HI + h\gamma \rightarrow H_2 + I_2$

The overall reaction shows that the two HI are decomposed for one photon (hγ). Thus, the quantum yield (ϕ) = 2

2. Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon and discussed into two Cl atoms. This is followed by the secondary reaction as shown below:

$$Cl_2 + h\gamma \rightarrow 2Cl* \qquad \text{Primary reaction}$$

$$Cl* + H_2 \rightarrow HCl + H*$$

$$H* + Cl_2 \rightarrow HCl + Cl* \qquad \text{Secondary reaction}$$

The Cl atom consumed in step 2 is regenerated in step 3, this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

$$2Cl* \rightarrow Cl_2$$

Thus the quantum yield varies from 10^4 to 10^6.

***Causes (or) Reasons for low quantum yield*:**

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to anable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene

$$2C_{14}H_{10} + h\gamma \rightarrow C_{28}H_{20}$$

The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.

Classification of photochemical reaction based on quantum yield: Based on quantum yield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1, 2.

   Examples: a) Dissociation of HI & HBr;

   b) Combination of SO_2+Cl_2

   c) Ozonisation of O_2.

2. The reaction in which the quantum yield is less than 1.
   Eaxmples: a) Dissociation of NH_3, CH_3COCH_3& NO_2

   b) Transformation of maleic acid into fumaric acid.

3. The reaction in which the quantum yield is extremely high.
   Examples: a) Combination of $CO + Cl_2$
   b) Combination of $H_2 + Cl_2$.

Processes of photochemical reactions: The overall photochemical reaction consists of

***Primary reaction*.**

i. In the primary reaction, the quantum of light is absorbed by a molecule 'A' resulting in the formation of an excited molecule A*.

$$A + h\gamma \rightarrow A^*$$

Secondary reaction

ii. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.

$$A^* \rightarrow B$$

Lecture session 22: Jablonski Diagram – Internal conversion – Intersystem crossing – Florescence and phosphorescence.

Fluorescence and phosphorescence

Luminescence: emission of photons from electronically excited states of atoms, molecules and ions.

Fluorescence: a process in which a part of energy (UV, Visible) absorbed by a substance is released in the form of light as long as the stimulating radiation is continued.

Most molecules possess an even number of electrons and all the electrons are paired in ground state. The spin multiplicity of a state is given by 2S + 1, where S is the total electronic spin.

When the spins are paired (↑↓), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$$S = S_1 + S_2 = (1/2) - (1/2) = 0$$

$\therefore$ 2S + 1 = 1, ie., spin multiplicity is 1. The molecule is in the singlet ground state.

On absorption of a suitable energy, one of the paired electrons goes to a higher energy level. The spin orientation of the two electrons may be either

a) Parallel (↑↑), then $S = s_1 + s_2 = (1/2) + (1/2) = 1$, $\therefore 2S + 1 = 3$, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

Or

b) Anti-parallel (↑↓), then $S = s_1 + s_2 = (1/2) - (1/2) = 0$, $\therefore 2S + 1 = 1$, ie., spin multiplicity is 1. The molecule is in the singlet (S) excited state.

Since the electron can jump from the ground state to any of the higher electronic states depending upon the energy of the photon absorbed we get a series of

a) Singlet excited states ie., S_1, S_2, S_3, etc., (first singlet excited state, second singlet excited state, third singlet excited state, etc.) and
b) Triplet excited states ie., T_1, T_2, T_3, etc., (first triplet excited state, second triplet excited state, third triplet excited state, etc.).

Generally singlet excited state has higher energy than the corresponding triplet excited state. Thus, the energy sequence is as follows: $E_{S1} > E_{T1} > E_{S2} > E_{T2} > E_{S3} > E_{T3}$ and so on.

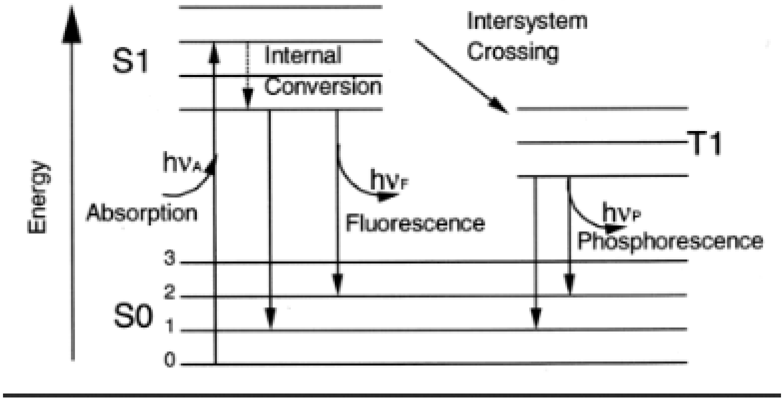
When a molecule absorbs light radiation, the electron may jump from S_0 to S_1, S_2 (or) S_3 singlet excited state depending upon the energy of the light radiation as shown in Jablonski diagram. For each singlet excited state there is a corresponding triplet excited state, ie.

$$S_1 \rightarrow T_1;\ S_2 \rightarrow T_2;\ S_3 \rightarrow T_3, \text{ etc.}$$

The molecule, whether it is in singlet or triplet excited state, is said to be activated. Thus,

$$A_0 + h\gamma \rightarrow A^*$$

where A0 – ground state molecule and A* - excited state molecule.



S0: fundamental electronic state
S0, S1, S2: singlet electronic states
T1, T2: triplet electronic states

Types of transitions: The activated molecules returns to the ground state by emitting its energy through the following general types of transitions.

1. **Non-radiative transitions** do not involve the emission of any radiations, so theses are also known as non-radiative or radiationless transitions. Non-radiative transitions involve the following two transitions.

a. Internal conversion (IC): These transitions involve the return of the activated molecule from the higher excited states to the first excited states, ie.

$S_3 \rightarrow S_1$; $S_2 \rightarrow S_1$ (or) $T_3 \rightarrow T_1$; $T_2 \rightarrow T_1$

The energy of the activated molecule is given out in the form of heat through molecular collisions. This process is called internal conversion (IC) and occurs in less than about 10^{-11} second.

b. Inter system crossing (ISC): The molecule may also lose energy by another process called inter system crossing (ISC). These transitions involve the return of the activated molecules from the states of different spins ie. Different multiplicity ie., $S_2 \rightarrow T_2$; $S_1 \rightarrow T_1$. These transitions are forbidden, occurs relatively at slow rates.

2. **Radiative transitions** involve the return of activated molecules from the singlet excited state S_1 and triplet state T_1 to the ground state S_0. These transitions are accompanied by the emission of radiations. Thus, radiative transitions involve the following two radiations.

   a. Fluorescence: The emission of radiation due to the transition from singlet excited state S_1 to ground state S_0 is called fluorescence ($S_1 \rightarrow S_0$). This transition is allowed transition and occurs in about 10^{-8} second.

   b. Phosphorescence: The emission of radiation due to the transition from the triplet excited state T_1 to the ground state S_0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition.

3. **Quenching of fluorescence**: The fluorescence may be quenched, when the excited molecule collides with a normal molecule before it fluoresces. During quenching, the energy of the excited molecule gets transferred to the molecule with which it collides. Quenching occurs in two ways.

   a. Internal quenching: Quenching may also occur, when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching.

   b. External quenching: Quenching may also occur from the addition of an external substance, which absorbs energy from the excited molecule. This phenomenon is called external quenching.

Lecture session 23: Difference between fluorescence and phosphorescence – Photosensitization – mechanism and examples quenching.

S.No	*Fluorescence*	*Phosphorescence*
1.	It is the absorption of energy by atoms or molecules followed by immediate emission of light or electromagnectic radiation	It is the absorption of energy by atoms or molecules followed by delayed emission of electromagnectic radiation.

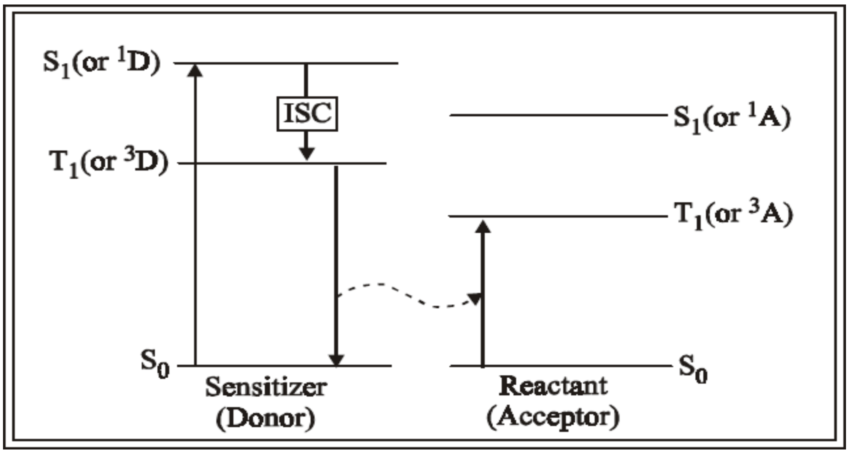
2.	The emission of radiation or light suddenly stops on removal of source of excitation	The emission of radiation remains for some time even after the removal of source of excitation
3.	In fluorescence, the excited atoms has comparatively short life time before its transition to low energy state	In phosphorescence, the excited atom has comparatively long life time before its transition to low energy state
4.	The time period or interval between the absorption and emission of energy is very short	The time period or interval between the absorption and emission of energy is comparatively long
5.	Absorption process occurs over short time interval and involves the transition from ground state to singlet excited state and do not change the direction of the spin	Phosphorescence involves the transition from the single ground energy state to excited triplet state and involving a change of spin state
6.	The emitted photon (light) has lower energy than the absorbed photon and emission occurs at a longer wavelength than the incident light	The emitted photon (light) has lower energy than the absorbed photon and emission occurs at a longer wavelength than the fluorescence
7.	In florescent materials, gives an ‘an immediate flash or afterglow’ on excitation	Phosphorescent materials appears to ‘glow in the dark’, because of slow emission of light over time
8.	**Examples of florescence:** Gemstones florescence, gypsum, talc, jelly fish, chlorophyll extract, vitamins etc	**Examples of phosphorescence:** Glow of clock dial or toys or bulbs after switching off the light in the room. The glow remains for some minutes or even hours in a dark room Phosphorescent materials in sign board illuminate during night.

Photosensitization

The foreign substance absorbs the radiation and transfers energy to the reactants is called a photosensitizer. This process is called photosensitization.

Eg: Atomic photosensitizers : Mercury, Cadmium, Zinc and

Molecular photosensitizers: Benzophenone, Sulphur dioxide.



The sequence of photosensitization and quenching may be represented as follows

$$D + h\nu \longrightarrow {}^{1}D$$

$$^{1}D \xrightarrow{ISC} {}^{3}D$$

$$^{3}D + A \longrightarrow D + {}^{3}A$$

$$^{3}A \longrightarrow \text{Products (photosensitization)}$$

$$^{3}D \longrightarrow \text{Products (quenching)}$$

Example: ***Dissociation of hydrogen molecule***

UV light does not dissociate H_2 molecule, because the molecule is unable to absorb the radiation.

But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here acts as photo sensitizer

$$Hg + hv \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow H_2^* + Hg$$

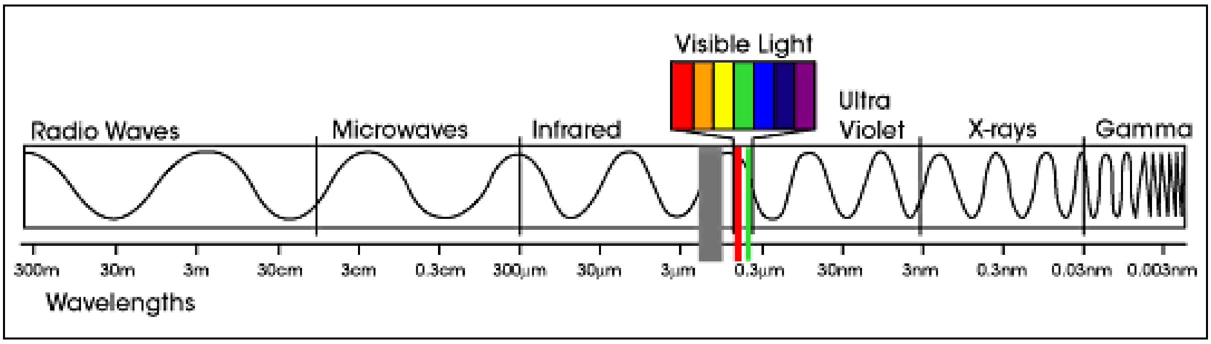
$$H_2^* \rightarrow 2H$$

Lecture session 24: Spectroscopy – Introduction Electromagnetic spectrum – Absorption of radiation – energy level diagram (Electronic, Vibrational, and rotational transitions) Types of spectra absorption and emission spectra.

Electromagnetic Spectrum

- EMR - a vast spectrum of frequencies and wavelengths.
- EMR spectrum includes the very energetic gamma-rays radiation with a wavelength range from 0.005 – 1.4 Å to radio waves (RW) in the wavelength range up to meters (exceedingly low energy).

- Region of interest - very limited range from 180-780 nm.
- This limited range covers both ultraviolet and visible radiation.
- Diagram below shows the typical EMR spectrum



Classification of Spectroscopic Methods

- Absorption
- Emission
- Scattering

Spectroscopic instruments dependent on any of the above mechanisms. They encompass common components.

Electromagnetic spectrum: The entire range over which electromagnetic radiation exists is known as electromagnetic spectrum.

Types of energy present in molecules:

1. Translational energy (Etrans) is concerned with the overall movement of the molecule along the three axes.

2. Rotational energy (Erot) involves the spinning of molecules about the axes passing through their centre of gravity.

3. Vibrational energy (Evib) is associated with vibrations within a molecule such as the stretching or the bending of bonds.

4. Electronic energy (Eelec) involves changes in the distribution of electrons by the excitation of electrons to higher levels by absorption of energy.

Now, if E is the energy of a molecule, it can expressed as

$$E = E_{trans} + E_{rot} + E_{vib} + E_{elec}$$

SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation with the matter. During the interaction the energy is absorbed or emitted by the matter. It is used to study theatomic and molecular structure of the substance.

Types of spectroscopy: Two types

1. ***Atomic spectroscopy*** deals with the interaction of the electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

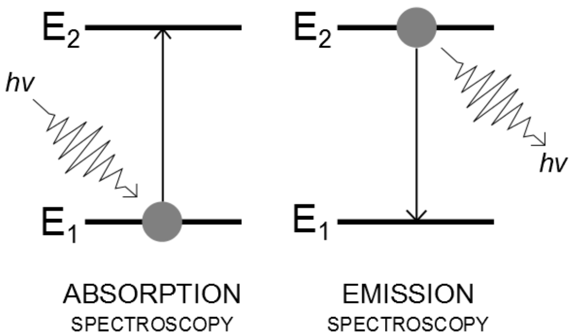
2. ***Molecular spectroscopy*** deals with the interaction of the electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

Difference between atomic spectroscopy and molecular spectroscopy

S. No.	***Atomic spectroscopy***	***Molecular spectroscopy***
1.	It is the study of interaction of electromagnetic radiation with atoms.	It is the study of interaction of electromagnetic radiation with molecules.
2.	The atoms absorb radiation and gets excited from the ground state electronic energy level to higher level.	This results in transition between rotational, vibrational and electronic energy levels.
3.	It is also called as line spectra or emission spectra.	It is also known as band spectra or absorption spectra.

Absorption spectrum: When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule absorbs photon of energy hγ and undergoes a transition from the lower energy level to the higher energy level. The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy (fig. 1).

The spectrum thus obtained is called the absorption spectrum.



Emission spectrum: If the molecule comes down from the excited state to the ground state with the emission of photon of energy, hγ, (fig. 2) the spectrum is called emission spectrum

Lecture session 25: UV-visible spectroscopy: Principles –electronic transition, Chromophore, Auxo Chrome, Red & Blue shift- instrumentation (Block diagram) – Applications

The absorption of UV-Visible radiation by a molecule leads to transition among the electronic energy levels of the molecule and therefore it is called as electronic spectroscopy. All organic compounds absorb UV light.

- The region between 200 – 400 nm is near UV region
- 400 – 800 nm is visible region
- Below 200 nm is far (or) vacuum UV region

Absorption bands appear rather than absorption lines because Vibrational and rotational effects are superimposed on the electronic transitions, so that an envelope of transitions arises

1. n→π* transition – shown by unsaturated molecule having hetero atoms like N, O, & S. It occurs at longer wavelength with low intensity. Eg. Aldehyde & ketone.

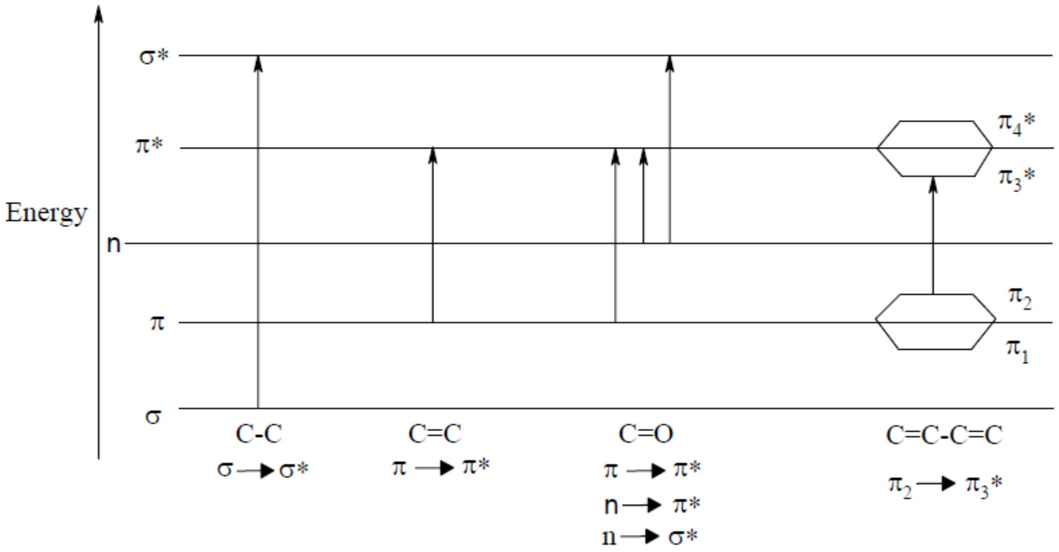
2. σ→σ* transition - occur in the compound in which all the electrons are involved in single bond and there are no lone pair of electrons. The energy required for this is very large (120 – 136 nm). Eg. Saturated hydrocarbons.

3. n→σ* transition – occur in the saturated compounds having lone pair of electrons. This occurs at longer wavelength (180 – 200 nm). Eg. Trimethylamine.

4. π→π* transition – occur in molecule having a π electron system. Eg. Ethylene.

Allowed transitions are σ→σ*, n→σ* and π→π*. These transitions give rise to strong absorption bands but the energy involved is higher than for n→π* transition. Forbidden transition is n→π*. It gives rise to band with low intensity.

Order of decreasing energy for the absorption is σ→σ* > n→σ* > π→π* > n→π*.



Relative energies of transitions

Characterization of UV - Visible spectra

- λ_{max} value is the wavelength at which absorption maximum occurs.
- ε- value : The extent of absorption for a given concentration (C) of a compound at any given wavelength is defined by molar absorptivity (or molar absorption coefficient) which is related to the height of the absorption band.

These two parameters depend on the concentration and the structure of the molecules and hence are regarded as characteristic properties of a molecule.

COLOUR and LIGHT ABSORPTION – THE CHROMOPHORE CONCEPT

CHROMOPHORE may be defined as any group which exhibits absorption of electromagnetic radiation in visible or UV region. Eg. Ethylenic, acetylenic, carboxylic acids, esters, etc.

Two types of chromophores are known

i) chromophores in which the group is having π electrons undergo π→π* transitions. Eg. Ethylene, acetylene, etc.
ii) chromophores having both *pi* electrons and n (non bonding) electrons undergo two types of transitions ie. π→π* and n→π*. Eg. Carbonyls, nitriles, azo compounds, nitro compounds, etc.

AUXOCHROME is a group which itself does not act as a chromophore but when attached to a chromophore it shifts the absorption maximum towards longer wavelength along with an increase in the intensity of absorption. Eg. -OH, -NH2, -OR, etc. For example, when the auxochrome $-NH_2$ is attached to benzene ring, it absorption changes from λ_{max} 255 nm (ε_{max} 203) to λ_{max} 280 nm (ε_{max} 1430).

CHANGE IN POSITION & INTENSITY OF ABSORPTION

1. **Bathochromic shift** (or) red shift involves the shift of absorption towards longer wavelength because of the presence of certain groups such as OH and NH_2 called auxochromes or by change of solvent.

2. **Hypsochromic shift** (or) blue shift involves the shift of absorption maximum towards shorter wavelength and may be caused by removal of conjugation or by change of solvent.

3. **Hyperchromic shift** involves an increase in the intensity of absorption and is usually brought out by introduction of an auxochrome. For example, when a methyl group is introduced in position 2 of pyridine ε_{max} increases from 2750 to 3560.

4. **Hypochromic shift** involves a decrease in intensity of absorption and is brought by groups which are able to distort the geometry of the molecule.

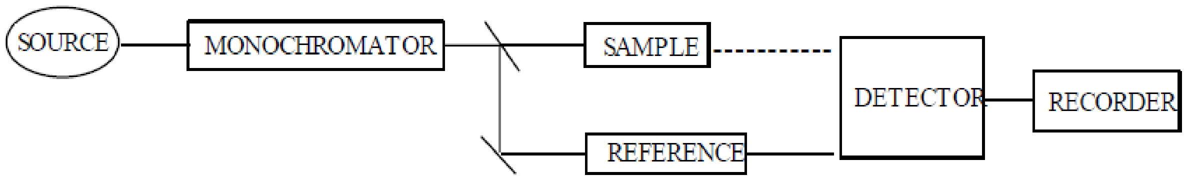
PRINCIPLE:

Visible and UV spectra arises from the transition of valence electrons within a molecule or ion from a lower electronic energy level (E_0) to higher electronic energy level (E_1). This transition occurs due to the absorption of UV or visible radiation by a molecule or ion.

The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons.

$$E_1 - E_0 = h\upsilon$$

INSTRUMENTATION



Block disgram – UV-visible spectrophotometer

The various components of UV-visible spectrometer are as follows.

1. **Radiation source:** The most commonly used radiation sources are hydrogen or deuterium lamps.

2. **Monochromator:** It is used to disperse the radiation according to the wavelength. The essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit. The dispersing element may be a prism or grating.

3. **Cells:** The cells (containing sample and reference for analysis) must transmit the light of the wavelength used. The most commonly used cells are made of quartz or fused silica.

4. **Detectors:** It converts the radiation, falling on which, into current. Commonly used detectors are Barrier layer cell, photomultiplier tube, and photocell.

5. **Recorder:** The signal from the detector is recorded by recorder pen.

WORKING:

The radiation from the source is allowed to pass through the monochromator which selects a narrow range of wavelength. A beam of radiation coming out from the monochromator is split into two equal beams. One-half of the beam is passed through the sample solution and the another half is passed through the solvent (reference). The instrument compares the intensity of the two beams.

If the compound absorbs light at a particular wavelength then the intensity of the sample beam (I) will be less than that of the reference beam (I_0). The instrument gives output graph which is a plot of wavelength vs absorbance. This graph is known as absorption spectrum.

Solvent effects:

The position and intensity of an absorption band may shift when the spectrum is recorded in different solvents. For changes to solvents of increased polarity the following pattern of shifts arise:

i) Conjugated dienes and aromatic hydrocarbons experience very little solvent shift.

ii) α, β - unsaturated carbonyl compounds show two different shifts: (a) the $\pi \rightarrow \pi^*$ band moves to longer wavelength (red shift) while (b) the $n \rightarrow \pi^*$ band moves to shorter wavelength (blue shift).

Effect of Conjugation and Auxochrome:

The conjugation of double bonds has a bathochromic shift (shift of an absorption band to a region of longer wavelength). Benzene, with its six *pi* electrons shows appreciable absorption in the near ultraviolet. The introduction of conjugated unsaturated side chain causes a shift to longer wavelengths (Bathochromic shift), eg. Stilbene $C_6H_5CH=CHC_6H_5$

The conjugation is destroyed by an introduction of a $-CH_2$ group in the unsaturated chain and causes a shift of the absorption band to shorter wavelengths

(-CH_2 group causes a hypsochromic shift), eg. $C_6H_5(CH=CH)_4C_6H_5$ is greenish yellow, but $C_6H_5CH_2(CH=CH)_4C_6H_5$ is colorless.

The -N=N- group also behaves similar to –CH=CH- group. For example, $CH_3N=NCH_3$ has an absorption band at 3450 Å, but $C_6H_5N=NC_6H_5$ absorbs strongly at 4450 Å. If one or two–CH2 groups are introduced, as in $C_6H_5CH_2N=NCH_2C_6H_5$ the absorption band appears at short wavelength region.

In the case of dyes, the intense colour is due to the presence of chromophore and auxochrome. Consider phenol in alkaline solution. The $C_6H_5O^-$ ion is colourless. The introduction of –NO_2 group in the para position, produces a yellow colour *p*-$NO_2C_6H_4O^-$ ion (-NO_2 group acts as auxochrome). The auxochromic groups are of two types:

(i) Basic or positive groups, such as –OH, -OR, -NR_2, -NHPh, -NH_2, etc. These are effective in acid solutions.
(ii) Acidic or negative groups, such as –NO_2, -NO, -CO, -CN, etc. These are effective in alkaline solutions.

Substitution in the ortho and para positions gives the greatest intensification of colour, but meta substitution has little or no influence.

APPLICATIONS:

1. Detection of impurities: The band due to impurities is very intense.
2. In quantitative analysis to determine the concentration of compound in solution by using Beer-Lambert’s law $A = \varepsilon cl$
3. Determination of dissociation energy of a molecule with great accuracy.
4. In identification of cis or trans isomers of a compound.
5. It can be used to study the kinetics of reaction.
6. Determination of structure of organic compounds.
7. It can be used to determine the percentages of various keto and enol form present in a tautomeric equilibrium.
8. Molecular weights of compounds can be measured.

Lecture session 26: IR spectroscopy: Principles – Fundamental modes of vibrations- Stretching, Bending - Instrumentation - (Block diagram) – Applications

INFRARED SPECTROSCOPY

IR spectroscopy provides useful information about the structure of molecule quickly over the other methods. When infrared light is passed through a sample of an organic compound, some of the frequencies are absorbed while other frequencies are transmitted through the sample. If we plot the percent absorbance or transmittance against frequency, the result is an infrared spectrum.

Principle: Infrared spectra is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels. So, IR spectroscopy is also known as vibrational spectroscopy.

Range of infrared radiation : IR = 650 – 4000cm^{-1}; Far IR = lower than 650cm^{-1};

Near IR = higher than 4000cm^{-1}

MOLECULAR VIBRATIONS:

At ordinary temperature, organic molecules are in a vibration state, each bond having its characteristic stretching and bending frequency and being capable of absorbing light of that frequency.

The stretching energy of a bond is greater than the bending energy and stretching absorption of a bond appear at higher frequencies in the IR spectrum than the bending absorption of the same bond.

Requisite for IR spectra

All type of molecules cannot interact with IR radiation. Only those molecules which exhibit change in dipole movement during a vibration can exhibit IR spectra. Example: Homonuclear diatomic molecules (H_2,O_2,N_2 or Cl_2) do not exhibit IR spectra.

MODES OF VIBARTIONS:

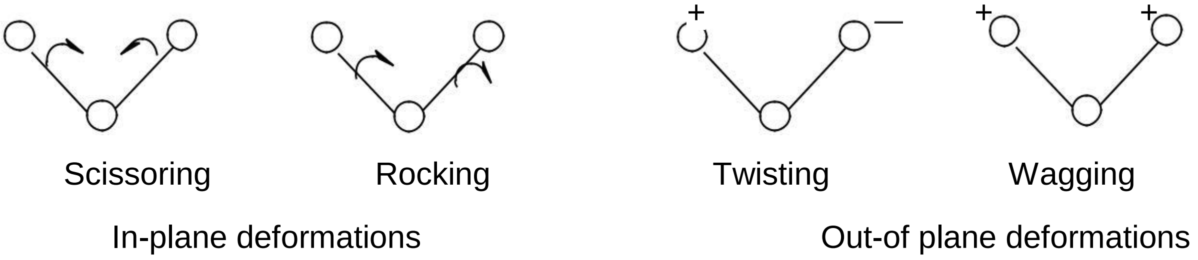
For a non-linear molecule with n atoms, the number of vibrational modes is (3n-6); eg. CH_4 possesses 9. For a linear molecules, the number of vibrational modes is (3n-5); eg. CO_2 possesses 4 modes of vibrations.

Stretching vibrations – the bond length increases or decreases

Bending vibrations – a change in bond angle. The bending vibration is also called as deformation vibration.

Stretching modes of vibrations

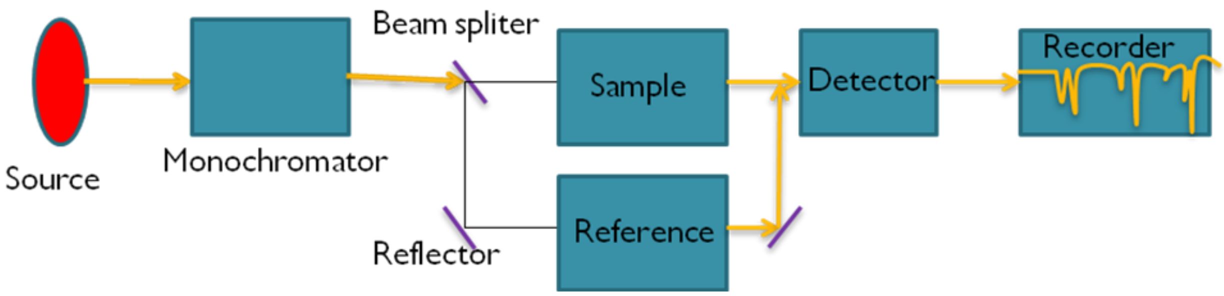
Symmetric Antisymmetric



Bending (deformation) vibrations

Only those molecules which exhibit change in dipole moment during a vibration can exhibit IR spectra. The vibrational frequency of a bond is expected to increase when the bond strength increases.

INSTRUMENTATION:



Block diagram of IR spectrophotometer

1. **Radiation source:** The main sources are a) Nichrome wire and b) Nernst glower. When they are heated nelectrically at 1000 to 18000C, they glow and produce IR radiation.
2. **Monochromator:** It selects the desired frequencies from the radiation source and reject the radiations of other frequencies. There are two types of monochromators : i) prism monochromator and ii) grating monochromator.
3. **Sample cells and sampling of substances:** The material containing the sample must be transparent to IR radiation.
   - For, solid sample – KBr pellet technique is used
   - Liquid sample – NaCl cell (or) Nujol is used (solvent can also be used).
4. **Detectors:** IR detectors convert thermal energy into electrical energy. Commonly used detectors are i) Photo conductivity cell; ii) Thermocouple; iii) Pyroelectric detectors.
5. **Recorder:** It records the signal coming out from the detector.

WORKING OF IR SPECTROPHOTOMETER:

The radiation emitted by the source is split into two identical beams having equal intensity.One of the beams passes through the sample and the other through the reference. The sample beam comes out from the sample cell is with less intensity compared to the reference beam. When the two beams recombine, they produce an oscillating signal which is measured by the detector and the signal is recorded by the recorder.

APPLICATIONS OF IR SPECTROSCOPY:

1. To identity the compounds and complexes.

2. To ascertain hydrogen bonding in a molecule (as the dilution is increased, the absorption band, due to intermolecular hydrogen bonding diminishes while that due to intramolecular hydrogen bonding remains unchanged).

3. In detecting impurities in a sample.

4. It provides valuable information of molecular symmetry, dipole moments, bond lengths, etc.

5. Distinguishing positional isomers of a compound.

6. It is useful for identifying isomers. Eg. *cis*-alkenes 970cm^{-1}; *trans*-alkenes 730 – 650cm^{-1}.

7. It may also be used for quantitative analysis of a mixture of compounds, in pollution detection, in milk analysis, etc.