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Subject Name: **Engineering Chemistry**

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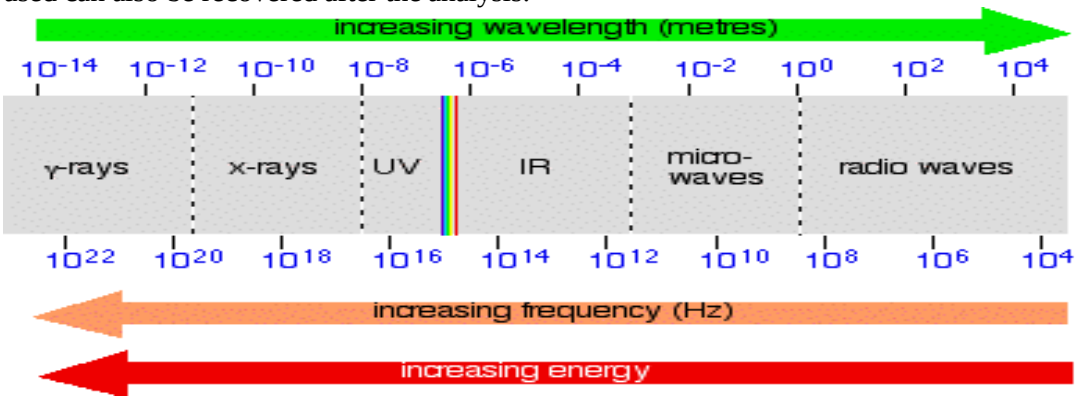
UV SPECTROSCOPY

INTRODUCTION

The spectroscopic methods have proved to be extensively useful for qualitative analysis identification and structural elucidation of organic compounds. Spectroscopic methods are advantageous over other methods because

(i) They are quick
(ii) They are sensitive
(iii) Information obtained by them is in the form of permanent record
(iv) The informations obtained by these methods are highly reliable
(v) Very small quantity of substance is required for the determination of spectra and even the quantity used can also be recovered after the analysis.



Origin of Electronic Spectra – Spectroscopy is the term applied for the branch of science which deals with the study of resolution of visible radiations into its component wave lengths. Now, the term is broadened and is applied to studies involving entire electromagnetic spectrum. Electromagnetic radiations consists of waves of energy and their parameters as:

(i) ***Wavelength*** **–** (8) It is the distance between two consecutive peaks or crests.
(ii) ***Wave Number*** **–** (V) It is the number of waves per cm.
(iii) ***Frequency*** **–** (V) It is the number of waves per second.

Different types of electronic spectra are – Emission Spectra, Absorption Spectra.

Emission spectra- when a substance is subjected to intense heat or to an electric discharge, its atoms & molecules absorb energy & get excited. These excited species, on returning to the ground state may emit radiation which on passing through a prism gives rise to a spectrum of atoms appears as bright lines on a dark back ground where as spectra of molecules appears as band, when white light is passed through a prism, we get a continuous spectrum of seven colours and sodium light gives a line spectrum [two-D-line] (yellow) of define wave length both are emission spectra.

Absorption spectra- when white light is passed through yellow sodium flame before reaching the prism, we get a continuous spectrum with two black lines in place of yellow lines obtained from sodium light. Here sodium flame has absorbed two wavelengths from white light which it itself emits. This is absorption spectrum.

During the absorption, some molecules falling in the path of incident beam colloid with photons of energy exactly equal to the difference in energy between the ground and excited states of the molecules. Thus a spectroscopic technique, qualitative or quantitative if it depends upon the measurement of an absorption spectrum is called absorption spectroscopy or molecular spectroscopy.

Principle- consider a molecule of a compound [X] have only two energy levels E_1 and E_2 the energy difference $\in E$ is determined as $\in E = E_2 - E_1 = h\nu$ or $hc/8$

Energy absorbed by each molecule is given by $\in E = N\ hc/8$

Where

h	=	Plank's constant = 6.63×10^{-34}
c	=	Velocity of electromagnetic radiations = 3×10^{8} ms^{-1}
N	=	6.02×10^{23} mol^{-1}

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8 = wavelength

The light of wavelength 8has photon of energy just equal to the energy difference between the two energy levels. In actual practice, molecules of compound have large number of energy levels and very small but definite amounts of energy is needed for transition between some of these while extremely large amounts of energy are involved between some other transitions. The following transitions are brought about by absorption of radiant energy by a molecule –

(i) ***Electronic Transition –*** Electrons are jumped to higher energy levels by the absorption of energy.

(ii) ***Vibrational Transition –*** Stretching, contracting and bending of covalent bond may occur due to absorption of energy.

(iii) ***Rotational Transition –*** Due to the absorption of radiant energy change in the rotational energy of the molecule takes place.

Bond	A	B
Bond Stretching	A	B
Contracting	A	B
Bending	A	B

Any wavelength of radiations absorbed by a molecule is determined by the changes in the electronic, Vibrational or rotational energy levels, permissible for it and its atoms.

(i) High-energy radiations as uv or visible are required to bring about electronic transition.

(ii) The low energy radiations as IR are required for Vibrational transitions.

(iii) The radiation of far infrared regions brings about rotational transitions.

ABSORBANCE

The intensity of absorption is related to the number of photons absorbed by the molecules usually some photons are absorbed by the molecules. The fraction of photon absorbed by the molecules at given frequency depends upon

(i) The nature of absorbing molecule.

(ii) The concentration of molecules. The higher the concentration the more molecules are present to absorb the photons.

(iii) The length of the path of the radiation through the material. The longer path, the larger number of molecules exposed and hence greater is the probability that a given photon will be absorbed.

Laws of Absorbance

(i) Lamberts Law – If a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of medium is proportional to the intensity of the incident light i.e. the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

$dI/I = -k\,dx.dI/I = -k\,dx$

dI = Change in transmitted light
I = Intensity of light
dx = Small thickness of medium
k = Proportionality constant

On integrating his equation between I = Io limits at x = 0 and I = I at x = L we get

(ii) Beers Law – The intensity of beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically.

It = $Io\ 0^{-k'c}$

According to Beers law, the absorbance at any particular wave length is directly proportional to the number of absorbing molecules. If the solution contains more than one type of absorbing species, the total absorbance will be the sum of the absorbance of all the species provided they do not interact chemically.

It = $Io\ 0^{-k'c}$
= $Io\ 0^{-0.47343\ k'c}$
= $Io\ 0^{-k'c}$ 3/-4 (Beer's Law)

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It = Intensity of Transmitted light
Io = Intensity of incident light
k = Proportionality constant
C = Concentration (Molar) of medium

(iii) Beer's Lambert's Law – Electronic spectra of organic compound are most frequently recorded in solution when a monochromatic light of intensity Io is passed through a solution of concentration C Molar, then intensity of Transmitted light It changes. The probability of absorption of r addition is determined by a mathematical expression given by Beer's lamberts law which expresses the relationship between amount of light absorbed and -

(i) Concentration of the solution
(ii) Length of the solution through which light passes

In I/Io = -K L or It = Io e^{-KL} --- (i) Lambert's Law
It = Io $e^{-K'C}$

From lambert's Law

In I/o = - Kcl
2.303 log I/Io = - Kcl

log Io/I= K / 2.303 cl = $\in$ cl = A

$\in$ = K/2.303 and is called molar absorptivity coefficient

From Beer's law

Log Io/I = A Absorbance
It = Io $e^{-K'C}$ = Io $10^{-K'C}$

By combining equation (i) and (ii) i.e. lambert's law and Beer's law.

It = Io .$10^{-\in cl}$
Where $\in$ = K/2.303
log Io/I = $\in$ cl
Where Io/I = A
A = $\in$x c x l or $\in$ = A/cl)
Io = Intensity of incident light
It or I = Intensity of transmitted light
C = Concentration of absorbing compound in moles per litre
L = Length of sample in cm
$\in$ = (Epsilon) is called molar absorptivity co-efficient
A = Absorbance of the solution
A = log Io/I or T = log I/Io or T = I/A

Where T is transmittance of the solution. The wavelength at which a molecule has highest absorption co-efficient [$\in$max] is designated as [λmax]. a spectrum may have several different maxima each with characteristic value of [$\in_{max}$].

INSTRUMENT USED FOR MEASUREMENT OF ABSORPTION

All chemicals interact with the electromagnetic radiations and due to this there occurs decrease in the intensity of radiant beam. This decrease in intensity is measured by absorption spectroscopic methods.

The various instruments used for measurement of absorption are:

(i) Colorimeter
(ii) Absorptionmeter
(iii) Spectro photometer

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(i) **Colorimeter –** It is concerned with the determination of concentration of substance by measurement of relative absorption of light with respect to known concentration of the substance [Absorption in visible region is employed].

(ii) **Absorptionmeter –** Includes instrument which are useful in other spectral region as well. This measures the ratio of some function of two, of radiant power or two electromagnetic beams.

(iii) **Spectrometer –** It is an absorption meter used for much narrower bands of wave lengths as produced by monochromator. They can be used in UV, Visible and IR region.

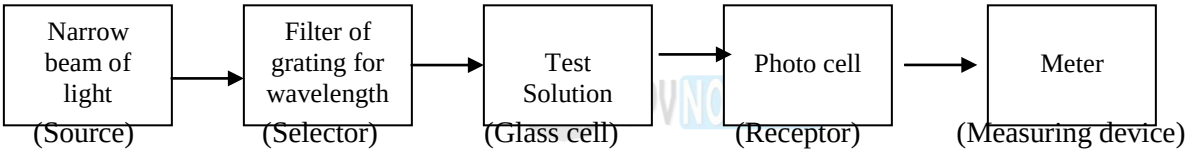
All these instruments have some common features like –

COLORIMETRIC ANALYSIS

The variation of color of the system with change in concentration is the basis of colorimetry. In colorimetry the concentration of a substance is determined by measurement of relative absorption of light with respect to a known concentration of a substance. In visual colorimetry, natural or artificial white light is generally used as a source of light and determinations are made by colorimeter because the method is convenient for the systems in which substances or their solutions are coloured. The eye is replaced by photoelectric cell and intensity of colour is easily measured by photoelectric colorimeter. If the substance is colourless then a suitable complexing agent is used to get a coloured complex (which absorb light in the visible region) for example for the estimation of cuprous ion, complexing agent ammonium hydroxide, is added to get blue coloured solution.

In a colorimeter, a narrow beam of light (of proper wavelength) passes through the solution under test towards a sensitive photocell. Usually colorimeters are provided with arrangements of filters or diffraction granting. Consequently it is possible to select the most appropriate wavelength by choosing a filter grating.

Signal Indicator



The current generated in the photocell is proportional to the amount of light transmitted by the solution. This depends upon depth of colour of substance under test. Thus current from photocell will be greatest when light transmitted is greatest. This occurs when coloured solution is dilute. The general meter is designed in such a way that it does not show the fraction of light transmitted but it shows the fraction of light absorbed. This is proportional to the concentration of the coloured substance in the test solution.

Thus colorimetric analysis is meant to compare under suitable conditions. The colour produced by a substance in unknown amount with the same colour produced by a known amount of material being determined.

ULTRAVIOLET SPECTROSCOPY

UV region of electromagnetic radiation lies between 200 – 400 nm and visible region lies between 400 – 800 nm. The UV region of the electromagnetic spectrum is subdivided into two spectral regions as follows –

(i) Near Ultraviolet 200 to 400 nm

(ii) Far Ultraviolet 10 to 200 nm
Or Vacuum Ultraviolet

Ultraviolet absorption spectra originates from transition of electron within a molecule or ion from lower electronic energy level to higher electronic energy level. When an electromagnetic radiation in ultraviolet region is made to pass through a compound containing multiple bonds, it is observed that a part of the incident radiation is usually absorbed which causes electronic excitation. The amount of radiation absorbed depends upon the structure of the compound as well as wavelength of the radiation. The energy of the radiation absorbed causes excitation of electron from lower energy level to higher energy level and the difference of energy is given by – E = hv. Thus the actual energy required depends upon the difference in energy between ground state (E_o) and the excited state (E_1) of the electron.

$$E_1 - E_o = hv$$

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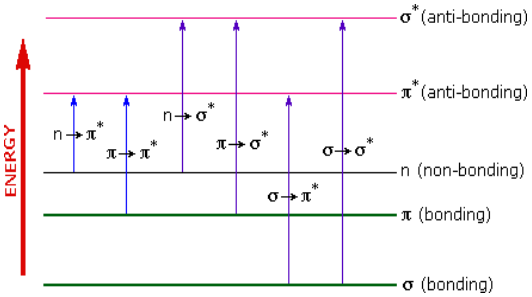
Electronic Transitions – When UV energy is in the form of quanta the absorption spectrum arising from single electronic transition is expected to consist of a single discrete line, but this does not happen because electronic absorption is super imposed upon Vibrational and rotational sub energy levels. Therefore, the spectra of simple molecules in the gaseous state contain narrow absorption peaks, where in each peak represents a transition from a particular combination of Vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. However, in case of polyatomic complex molecules, broad absorption bands are obtained due to coalescence of discrete bands.



When energy is absorbed by a molecule in the UV region, it brings about some changes in the electronic energy of the molecule resulting from transitions of valence electrons. The following three types of electrons are involved in organic molecules.

(i) ***π Electrons –*** The electrons which are forming double bonds are called relectrons. These are involved in unsaturated hydrocarbons like trienes and aromatic compounds. In unsaturated systems, π electrons predominantly determine the energy state of electron sheaths which are excited by the absorption of UV or visible light.

(ii) ***σ Electrons –*** The electrons which form single bonds are electrons according to molecular notation. They are involved in saturated bonds between 'C' and 'H' in paraffins such bonds are also known as 'S' bonds. The energy required to excite electrons in σ bond is very higher than the obtained by UV radiation hence electron do not absorb UV radiation and are not excited by UV radiations.

(iii) **η *Electrons –*** These are the unshared or non-bonded electrons and are not involved in the bonding between atoms in molecules. Examples – organic compounds containing N, O, or S, halogens. However η – electrons can be excited by UV radiation and hence compounds containing atoms like N, O, S, halogen compounds or unsaturated hydrocarbons may absorb UV radiations.

Representation in the electronic energy levels is as follows:

	Antibonding	σ*
Energy	Antibonding	π*
Level	non bonding	η
	Bonding	π
	Bonding	σ*

Electronic Energy Levels is Simple Organic Molecule

Energy absorbed in the UV region by complex organic molecules results in transitions of valency electrons in the molecules. These transitions are –

(a) η Transition – The general characteristics of $\eta \longrightarrow \pi^*$ bonds are (a) They have low intensity **(b)** They are shifted to shorter wave lengths by more polar solvents as well as electron donating groups. In the spectra of simple molecules $\eta \longrightarrow \pi^*$ transition requires the least energy and the corresponding bonds are of longer wave length. Such transitions are shown by unsaturated compounds which contain atoms like, N, O and S.

These show weaker bands in spectrum. In aldehydes and ketones the band due to $\eta \longrightarrow \pi^*$ transition generally occurs in the range 270-300 nm, while in case of carbonyl compounds, the bands are in the range 300 to 350 nm due to the $\eta \longrightarrow \pi^*$ transitions. This transition is between non-bonding orbital and

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antibonding orbital. In absorption of uV radiation, the nuclei along with electrons held together plays an important role in determining which wavelength of radiation will be absorbed. The nuclei determine the strength with which electrons are bound and influence the energy gaps between the excited and ground states.

(b) $\pi \longrightarrow \pi^*$ transition – These types of transitions are related to the transition of electron from bonding orbital to π an antibonding π^* Orbital. In unsaturated molecules, these transitions are possible. Alkenes absorb around 175 nm, alkynes absorb around 170 nm and carbonyl compounds absorb around 188 nm. For example the UV spectrum of ethylene exhibits an intense band at 174 nm and a weak band at 200 nm, both of these are due to $\pi \longrightarrow \pi^*$ transitions. According to selection rules only band at 174 nm represent an allowed transition. This can be represented as given in the figure. This is a transition between bonding orbitals and antibonding orbitals.

(c) $\eta \longrightarrow \sigma^*$ transition – The energy required for $\eta \longrightarrow \sigma^*$ transition is generally less than that required for $\sigma \longrightarrow \sigma^*$ transition and their corresponding absorption bands appear at longer wavelengths in the ultraviolet region (180 to 200 nm) saturated compounds with lone pair (non bonding) electrons undergo $\eta \longrightarrow \sigma^*$ transitions apart from $\sigma \longrightarrow \sigma^*$ transition. In case of saturated molecules which contain atoms having unshared pairs of electrons, $\eta \longrightarrow \sigma^*$ transition becomes be determined by commonly available spectrophotometers. For examples – alcohols and amines (containing –OH and $–NH_2$ groups) absorb between 175 to 200 nm.

(d) $\sigma \longrightarrow \sigma^*$ transition – Such transitions occur in case of saturated hydrocarbons which do not contain lone pairs of electrons. The energy required for this type of transitions is very large and absorption band occurs in (126 to 135 nm) for ultraviolet region. For example, methane has $_{max}$ at 1217 nm and ethane at 135 nm corresponds spectrophotometers which generally do not operate at wave lengths below 180 nm. Thus this is a transition between bonding orbital and antibonding orbital.

Concept of Chromophore and Auxochrome in the UV spectroscopy

Chromophore- Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or visible region (200-800 nm). Chromophores can be divided into two groups-
a) Chromophores which contain p electrons and which undergo pie to pie* transitions. Ethylenes and acetylenes are the example of such chromophores.
b) Chromophores which contain both p and nonbonding electrons. They undergo two types of transitions; pie to pie* and nonbonding to pie*. Carbonyl, nitriles, azo compounds, nitro compounds etc. are the example of such chromophores.

Auxochrome- An Auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the longer wavelength of the spectrum. –OH,-OR,-NH2,-NHR, -SH etc. are the examples of auxochromic groups.

Absorption and intensity shifts in the UV spectroscopy

There are four types of shifts observed in the UV spectroscopy-
a) Bathochromic effect- This type of shift is also known as red shift. Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents. The nonbonding to pie* transition of carbonyl compounds observes bathochromic or red shift.
b) Hypsochromic shift- This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength. Generally it is caused due to the removal of conjugation or by changing the polarity of the solvents.
c) Hyperchromic effect- Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.
d) Hypochromic effect- Hyperchromic effect is defined as the effect by virtue of intensity of absorption maximum decreases. Hyperchromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.

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INSTRUMENTATION OF UV SPECTROSCOPY

The instrumentation for UV spectroscopy i.e. UV spectrometer is made up of following important components.

(i) Source of Radiation
(ii) Monochromator
(iii) Beam splitter
(iv) Sample chamber
(v) Detector
(vi) Recorder

In UV spectrometer, a beam of light is split into two equal halves, one half of the beam called sample beam is directed through a transparent cell containing a solution of the compound being analyzed and one half (reference beam) is directed through an identical cell that contains only the solvent. The instrument is so designed that it can compare the intensities of the two beams at each wavelength of the region.

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-

Light Source- Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Monochromator- Monochromator generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Sample and reference cells- One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector- Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier- The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices- Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

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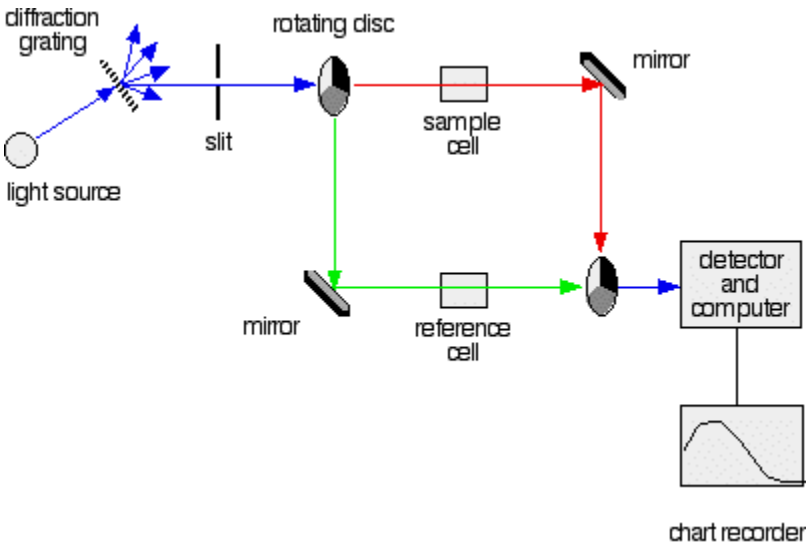

APPLICATION OF UV SPECTROSCOPY

(i) Qualitative Analysis – UV spectroscopy is used for characterization of aromatic compounds and conjugated olefins. Identification is done by comparing the UV absorption spectrum of the sample with the UV spectra of known compound for reference.

(ii) Detection of Impurities – Detection of impurities in organic compounds can also be done by UV spectroscopy. (a) If benzene is associated in small quantity with cyclohexane it can be detected by UV spectroscopy by the absorption band of benzene at 255 nm. (b) If impure adiponitrile or hexamethylene diamine is used for the preparation of nylon the product will be of poor quality. The impurities present with the raw materials can be detected by UV method. (c) Purification of organic compounds can be continued until the absorption bands characteristic of the impurities disappear in the spectrum.

(iii) Quantitative Analysis – UV spectroscopy is used for the quantitative analysis of compounds which absorb UV radiation. The determination is carried out on the basis of Beer Lamberts law according to which absorbance is determined by the formula

$$A = \log I_o / I = \log T = \in lc$$

Where I is molecular absorptivity co-efficient, L is length of the path or cell C is the concentration of solution.

(iv) Studying Kinetics of Chemical Reaction – UV spectroscopy can be used to steady the kinetics of chemical reactions by following the change in concentration of a product or a reactant with time during the reaction.

(v) Determination of Dissociation Constants of Weak Acids or Bases – UV spectroscopy can be used to determine the dissociation constants of acids or bases. The dissociation constant of an acid (HA) is determined by determining the ratio [HA]/[A] spectrometrically from the graph plotted between absorbance and wavelengths at different pH.

$$P\,Ka = pH + \log [HA] / [A]$$

(vi) Molecular Weight Determination – UV Spectroscopy is used in determination of molecular weight of the compound can be converted into a suitable derivative which shows an absorption band in its spectrum for example molecular weight of amine is determined by converting it into picrate. The concentration of amine picrate can be determined by using the formula -

$$C = \frac{\log(I_0 / I_1)}{\in_{max} xL}$$

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(vii) ***Study of Tautomeric Equillibria*** – UV spectroscopy can be used to determine the percentage of keto and enol forms present in compounds such as ethyl acethyl acetate by measuring the strength of the respective absorption bands.

(viii) ***Determination of Calcium in Blood Cerum*** – Calcium in blood can be indirectly determined by converting the calcium present in 1 ml of cerum as its oxalate, redissolving it into sulphuric acid and treating it with dilute ceric sulphate. The absorption of the excess ceric ion is measured at 315 nm. The amount of calcium in the blood cerum can thus be indirectly calculated.

(ix) ***Determination of Ozone in Environment*** – The ozone concentration present in (Smog.) smoke fog in environment can be calculated by measuring its absorption at 260 nm.

(x) ***Detection of functional groups***- UV spectroscopy is used to detect the presence or absence of chromophore in the compound. This is technique is not useful for the detection of chromophore in complex compounds. The absence of a band at a particular band can be seen as an evidence for the absence of a particular group. If the spectrum of a compound comes out to be transparent above 200 nm than it confirms the absence of – a) Conjugation b) A carbonyl group c) Benzene or aromatic compound d) Bromo or iodo atoms.

(xi) ***Identification of an unknown compound***- An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectrums coincide then it confirms the identification of the unknown substance.

(xii) ***Determination of configurations of geometrical isomers***- It is observed that cis-alkenes absorb at different wavelength than the trans-alkenes. The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances. The cis-isomer suffers distortion and absorbs at lower wavelength as compared to trans-isomer.

Lambert's and Beer'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 light."

Mathematically, the Lambert's law may be expressed as follows.

$$-dI / dt \ \alpha \ I$$

$$-dI / dt = KI \qquad \ldots\ldots\ldots (1)$$

Where I = intensity of incident light

t = thickness of the medium

K= proportionality constant

Beer's law may be stated as follows:

"Intensity of incident light decreases exponentially as the concentration of absorbing medium increases arithmetically."

The above sentence is very similar to Lambert's law. So,

$$I_t = I_0 \, e^{-k' c}$$

$$I_t = I_0 \, 10^{-0.4343 \, k' c}$$

$$I_t = I_0 \, 10^{K' c} \qquad \ldots\ldots\ldots (4)$$

Where k' and K'= proportionality constants

c = concentration

By combining equation (3) and (4), we get,

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$I_t = I_0 10^{-act}$

$I_0 / I_t = 10^{act}$

Where, K and K' = a or ε

c = concentration

t or b = thickness of the medium

$\log I_0 / I_t = \varepsilon bc$ . . . . . .(5)

Where ε = absorptivity, a constant dependent upon the λ of the incident radiation and nature of absorbing material. The value of ε will depend upon the method of expression of concentration.

The ratio I_0 / I_t is termed as transmittance T, and the ratio $\log I_0 / I_t$ is termed as absorbance A. formerly, absorbance was termed as optical density D or extinction coefficient E. the ratio I_0 / I_t is termed as opacity. Thus,

$A = \log I_0 / I_t$ . . . . . .(6)

From equation (5) and (6),

$A = \varepsilon bc$ . . . . . .(7)

Thus, absorbance is the product of absorptivity, optical path length and the concentration of the solution.

Limitations:

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at ***high concentrations (>0.01M)*** due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **fluoresecence or phosphorescence** of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

INTRODUCTION

Infrared spectroscopy is one of the most powerful analytical techniques, which provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of infrared radiation causes the various bands in a molecule to stretch and bend with respect to one another. After absorption of IR radiations, the molecules of chemical substance vibrate at different frequency of vibrations.

When infrared light is passed through the sample, the vibration and the rotational energies of the molecules are increased. Two types of fundamental vibrations are

(1) Stretching vibrations (2) Bending vibrations

(1) Stretching vibrations: In stretching vibrations the atoms move along the bond axis. As a result, the bond length increases or decreases but bond angle remains unchanged. There are two types of stretching vibrations:

(1) Symmetric stretching: In this type the atoms of the molecule move in the same direction.

(2) Asymmetric stretching: In this type the atoms of the molecule move in the opposite direction.

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(2) Bending or Deformation vibrations: Bending vibrations involves a change in the bond angle whereas the bond length remains unchanged.

There are two types of bending vibrations:

(A) In – plane bending vibrations:

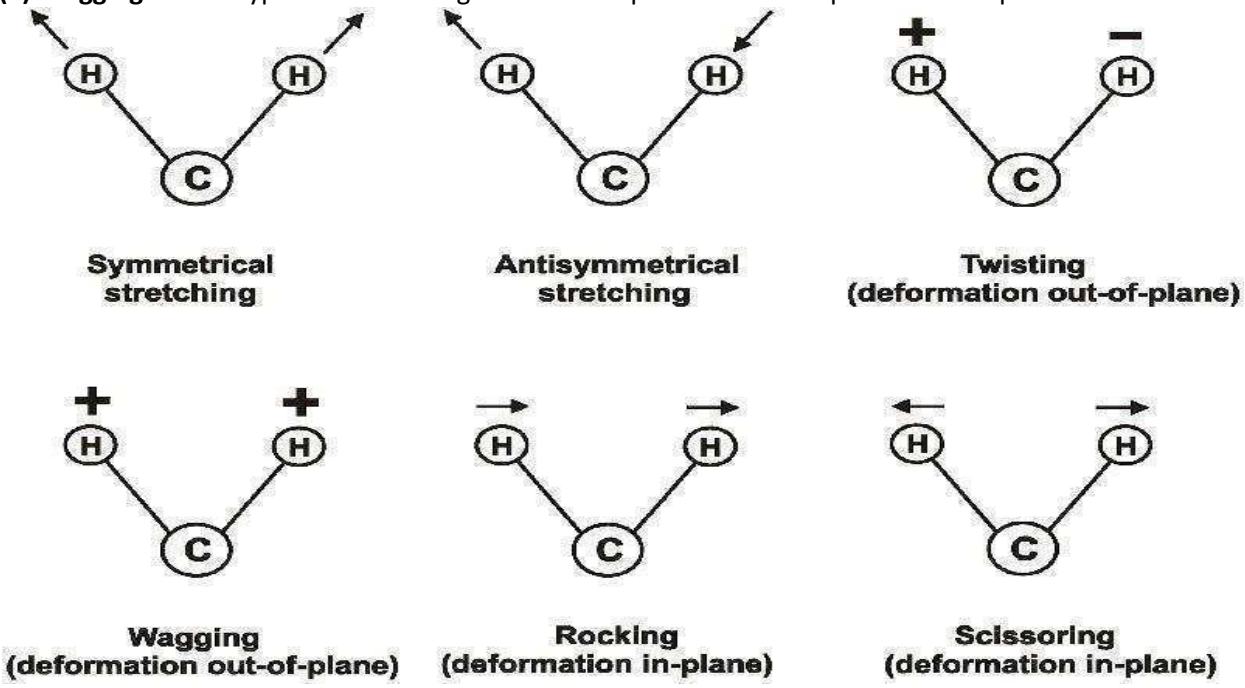
(i)Scissoring: In this type, the atoms move away and come close to each other in the same plane just like the blades of a scissor.

(ii) Rocking: In this type the movement of atoms takes place in the same direction.

(**B) Out-of-plane bending vibrations:**

(i) Twisting: In this type one atom moves up and the other moves down the plane with respect to the central atom.

(ii) Wagging: In this type two atoms together move up and below the plane with respect to the central atom.



The number of fundamental vibrational modes of a molecule can be calculated are as follows:

A nonlinear molecule containing N atoms has (3N-6) fundamental vibrational modes. For example water is a nonlinear triatomic molecule, therefore, vibrational degrees of freedom of water = (3N-6)= 3×3-6= 3

So, water is having three fundamental modes of vibration such as symmetrical stretching, asymmetrical stretching and bending vibrations. All the three vibrations are said to be IR active as there is a change in dipole moment during the vibration. So the IR spectrum of water exhibits three absorption bands.

Thus for a vibration to be IR active, there should be a change in dipole moment of the molecule. Homonuclear diatomic molecules like O_2, N_2 and H_2 have zero dipole moments and they are IR inactive.

A linear molecule containing N atoms has (3N-5) fundamental vibrational modes. For example CO_2 is a linear molecule. Therefore, vibrational degrees of freedom of CO_2 = (3N-5)= 3×3-5= 4

So, Carbon dioxide is having four fundamental modes of vibration such as symmetrical stretching, asymmetrical stretching in plane bending vibrations and out of plane bending vibrations.

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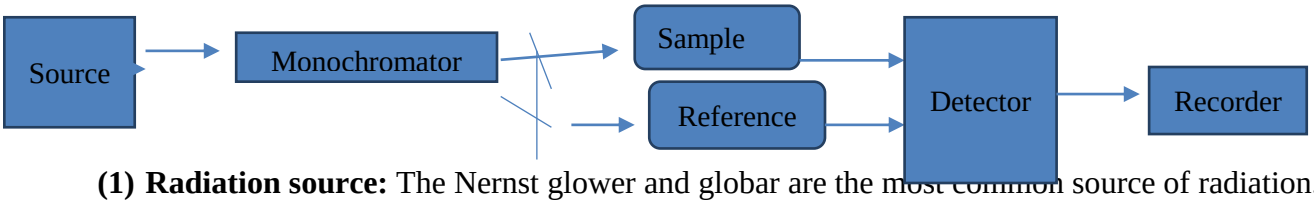
Instrumentation and working of IR spectrometer:

The essential components of an IR spectrometer are as follows:

(1) Radiation source (2) Monochromator (3) Sample holder (4) Detector



(1) Radiation source: The Nernst glower and globar are the most common source of radiation. The Nernst glower consists of a rod of hollow tube about 20 mm long and 1 mm in diameter made by sintering a mixture of oxides of zirconium, thorium and yttrium. Globar is a silicon carbide rod when heated electrically at 1200-2000^{o}C, it glows and produces IR radiations.

(2) Monochromator: The radiation source emits radiations of various frequencies. As the sample absorbs only at certain frequencies, it is therefore necessary to select desired frequencies from the radiation source. This has been achieved by monochromators. Prisms and gratings are commonly used for this purpose.

(3) Sample holder: The sample holder made up of sodium chloride or potassium bromide. It is used to contain sample solutions as well as reference solution because they are transparent to IR radiation.

(4) Detector: The detectors generally convert thermal radiation energy into electrical energy. Thermocouples and bolometer are generally used for this purpose.

Working of IR spectrometer: The radiation from source is passed through monochromator. Light reflected from the monochromator is diffracted to get the light of specific wavelength. The beam of radiation passed out to monochromator is split into two identical beams, out of which one passes through the reference solution and other through the sample solution. If the frequency of vibration of sample molecules falls within the range of the radiation, the molecule may absorb energy of this frequency from the light. Then the intensity of beam coming out of the sample solution is less than that of beam coming out of the reference solution. If I is the intensity of the sample solution and I_O that of the reference solution then I/I_O is called transmittance. A graph is recorded by the instrument which is plot of transmittance versus wave number.

Applications of IR spectroscopy

1. Identification of functional group and structure elucidation.
2. Identification of substances.
3. Studying the progress of the reaction.
4. Detection of impurities.
5. Quantitative analysis

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