



Bansilal Ramnath Agarwal Charitable Trust's

VISHWAKARMA INSTITUTE OF INFORMATION TECHNOLOGY

Department of Engineering & Applied Sciences

F.Y.B.Tech

Course Material (A brief reference version for students)

Course: Engineering Chemistry (2020 pattern)

Academic year 20-21

Unit 3: Instrumental Methods of analysis

Disclaimer: *These notes are for internal circulation and are not meant for commercial use. These notes are meant to provide guidelines and outline of the unit. They are not necessarily complete answers to examination questions. Students must refer reference/text books, write lecture notes for producing expected answer in examination. Charts/diagrams must be drawn whenever necessary.*

Unit 3 – Instrumental Methods of analysis

Objective: To study instrumental methods of qualitative and quantitative analysis of chemical substances

Content: pH metry- introduction, pH metric titration, Conductometry – introduction, Conductometric titration

Spectroscopy - Fundamentals of spectroscopy,

a) Ultraviolet (UV)-Visible spectroscopy- Principle of UV-Visible spectroscopy, Beer- Lambert's law, Types of electronic transitions, Terms related to UV – Visible spectroscopy, Instrumentation of UV – Visible spectroscopy, Applications of UV- Visible spectroscopy

Infrared (IR) spectroscopy –Principle of IR spectra, requirements of IR absorption, Calculation of vibrational frequency, Modes of vibration, Factors influencing IR spectra, Instrumentation of IR spectroscopy, Applications of IR spectroscopy

3.1 pH metry:

Introduction:

pH scale indicates the degree of acidity or alkalinity of solution. The term pH was introduced by Sorenseno who defined it as $\text{pH} = -\log [\text{H}^+]$. pH is efficiently measured by using pH meter. pH meter uses glass electrode as indicator electrode whereas standard calomel electrode(SCE) or silver chloride electrode as standard reference electrode. The cell is represented as



Glass electrode:

A glass electrode is a type of ion selective electrode. It is made up of doped glass membrane which is sensitive for hydrogen ions. **Potential developed** across glass electrode (ion selective electrode) is as follows:

1) Ion selective electrode: In this electrode, a suitable non porous membrane separates two solutions, containing similar ions of different concentrations and act as electrochemical membrane. Potential is developed on either sides of membrane E1 or E2

Potential experienced by membrane is termed as boundary potential (E_b)

$$E_b = E_2 - E_1$$

ISE responds to particular ion, in presence of many other ions in the solution. Potential developed is a function of concentration of specific ion in the solution ignoring the other ions totally



2) Glass electrode: Typical glass electrode used for measuring pH of the solution, consist of a thin glass bulb having high electrical conductivity. The bulb contains 0.1 M HCl sealed with silver-silver chloride electrode or platinum electrode. When glass is in contact with the solution, potential is developed between glass surface and the solution. The value of potential is a function of H^+ ion concentration of the solution.

Potential developed is given by $E_G = E_G^0 - 0.0591 \log [\text{H}^+]$
 $= E_G^0 + 0.0591 \text{ pH}$

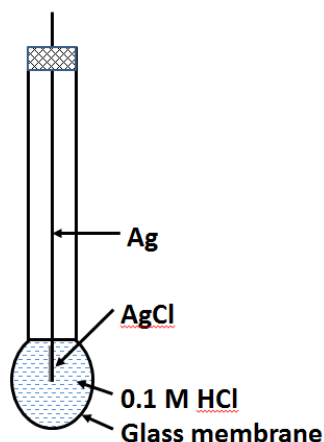
Where E_G is potential of electrode and E_G^0 is constant for given glass electrode.

Composition of glass electrode:

Special glass of low melting point and high electrical conductivity. Na_2O (22%), CaO (6%) & SiO_2 (72%)

Glass electrode representation: Glass electrode is represented as





3) Combined glass electrode: Modern pH electrode is a combined glass electrode which combines both glass and reference electrode (calomel electrode).

4) Advantages of glass electrode:

- i) It may be used in presence of strong oxidizing and reducing solutions.
- ii) It can be used for solutions having pH 2 to 10.
- iii) It is simple to operate
- iv) It can detect and estimate H^+ ions in presence of other types of ions

5) Disadvantages of glass electrode:

- i) The glass bulb is very fragile and has to be used with great care.
- ii) As glass membrane has a high electrical resistance, ordinary potentiometer can not be used, electronic potentiometer are used
- iii) it can not be used for solutions of fluoride ions

3.1.1 pH metric titration (acid verses base titration):

i) Electrode system: pH meter is an electronic instrument used for measuring pH of the liquid. It uses glass electrode in combination with reference electrode (usually calomel electrode). Now a days combined glass electrode (a combination of glass electrode and calomel electrode together) is available in market.

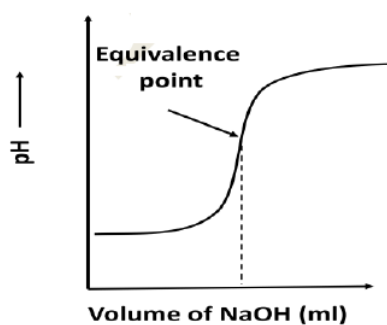
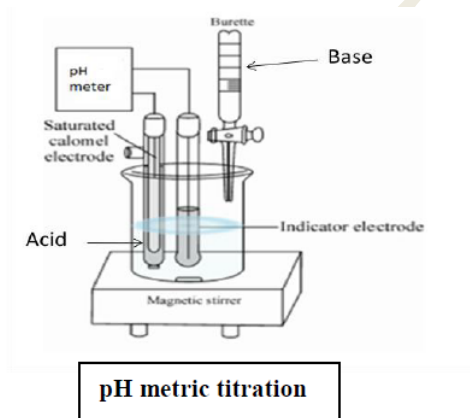
ii) Standardisation: As, the glass electrode does not give a precise, reproducible emf over longer period of time, for precise work, the pH meter should be standardised before actual use. It is done by using buffer solutions of pH 7, 4 and 9. For standardization, glass electrode is first dipped in buffer of pH 7. It is expected that display of pH meter should read pH = 7. If it is not so, then, asymmetric potential knob of pH meter is adjusted in such a way that the display shows pH = 7. Then the glass electrode is dipped in buffer solution of pH = 4 or pH = 9. The slope knob is then adjusted to read as pH = 4 or pH = 9.

pH meter

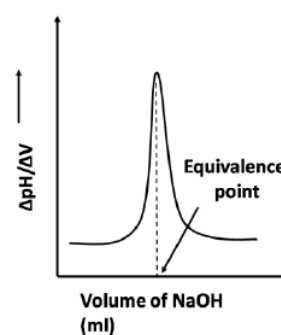


iii) Measurement: A known volume of acid to be titrated is taken in the beaker kept on magnetic stirrer. Combined glass electrode connected to pH meter is dipped in it after standardization. pH of the solution is noted after every addition of base from burette into beaker.

iv) Graphs: Titration curve is plotted with pH Vs volume of base added. The equivalence point occurs on the titration curve in the region where there is sharp change in pH with small change in volume. A more sensitive method is a plot of $\Delta\text{pH}/\Delta V$ against volume of base added. It gives maxima that indicate equivalence point.



Graph 1: pH verses volume of base



3.2 Conductometry

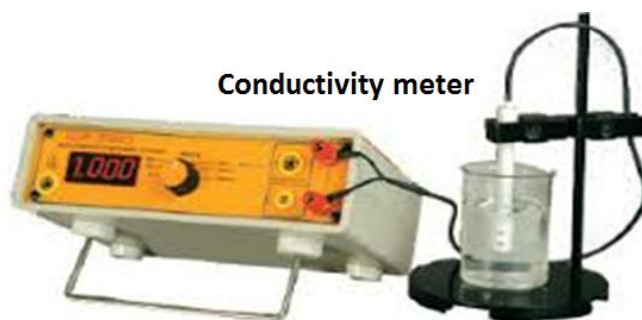
Introduction

Conductometry is the measurement of the electrical conductivity of a solution. The conductance is defined as the current flow through the conductor. Conductometry has notable application in analytical

chemistry, where conductometric titration is a standard technique. In usual analytical chemistry practice, the term conductometry is used as a synonym of conductometric titration, Conductometry is often applied to determine the total conductance of a solution or to analyze the end point of titrations that include ions. The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of the ions is mainly depended on the concentration of the ions.

3.2.1 Conductometric titration

Conductometric titration is a method in which volumetric analysis is done on the basis of change in conductance of the solution, at equivalence point during titration. During titration not only number of free ions but the type of ions may also change. As the conductivity depends on number of free ions, charge on free ions and the mobility of free ions, conductivity of solution changes during titration.

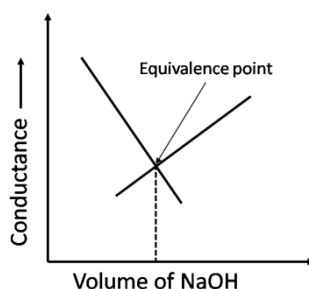


3.2.2 Types of conductometric titration:

(i) Titration of strong acid against strong base:

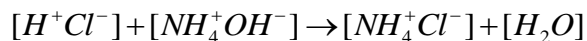
Consider titration of HCl with NaOH. $[H^+ + Cl^-] + [Na^+ + OH^-] \rightarrow [Na^+ + Cl^-] + H_2O$

At the beginning, the acid solution has a high conductivity due to high mobility of hydrogen ions. When NaOH is added to HCl, smaller size highly mobile hydrogen ions are replaced by comparatively bigger, less mobile sodium ions. This decreases conductivity rapidly. The solution at neutralization i.e. at equivalence point will have only sodium and chloride ions which have minimum conductivity. If more NaOH is added, then conductivity increases owing to the increase in conductivity of OH^- ions. A graph of conductivity is plotted against volume of sodium hydroxide. The point of intersection of two lines gives equivalence point.



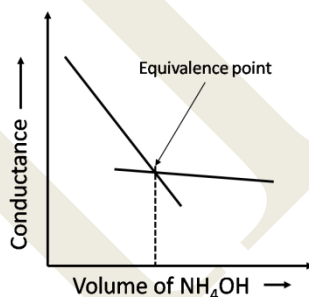
(ii) Titration of strong acid against weak base:

Consider titration of HCl (strong acid) with NH_4OH (weak base).



HCl is taken in beaker and NH_4OH is added from burette. Initial conductivity of solution is high because of strong acid HCl dissociates completely into ions. As ammonium hydroxide is added from burette, conductivity decreases because of replacement of fast moving H^+ ions with slow moving NH_4^+ ions. Addition of NH_4OH after end point, does not change conductance much as

NH_4OH is weak electrolyte and has a very small conductivity as compared to its salt.

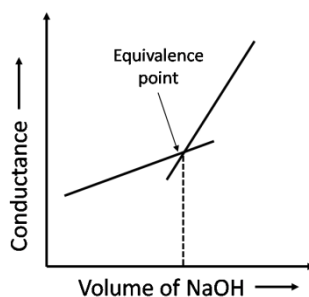


(iii) Titration of weak acid against strong base:

Consider titration of CH_3COOH (weak acid) with NaOH (strong base)



Acetic acid is taken in beaker and sodium hydroxide is taken in burette. Initial conductivity is less because acetic acid is a weak acid and dissociates less into its ions. After addition of NaOH from burette, conductivity increases due to formation of salt which dissociates more into its ions. When neutralization of acid is complete, further addition of NaOH produce excess of OH^- ions causing rapid increase of conductance.

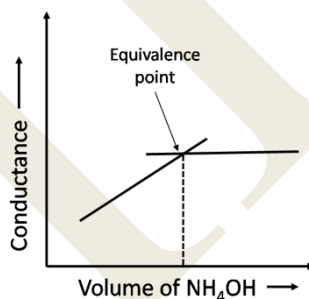


(iv) Titration of weak base against weak acid:

Consider titration of CH_3COOH (weak acid) with NH_4OH (weak base).

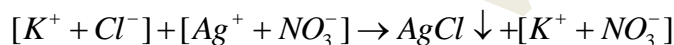


Acetic acid is taken in beaker and ammonium hydroxide is taken in burette. Initial conductivity is less because acetic acid is a weak acid and dissociates less into its ions. After addition of ammonium hydroxide from burette, conductivity increases due to formation of salt which dissociates more into its ions. After the neutralization of acid, further addition of ammonium hydroxide does not cause much change in conductance.

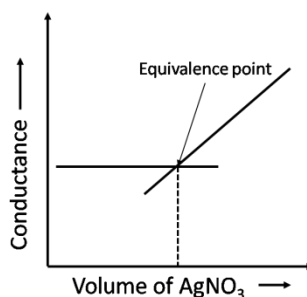


Precipitation titration:

Consider titration of potassium chloride solution with silver nitrate solution.



When $AgNO_3$ is added from burette to the beaker containing KCl , $AgCl$ gets precipitated. K^+ ions remain unchanged whereas Cl^- ions are replaced by free NO_3^- ions. The mobility of Cl^- and NO_3^- ions are practically same. As a result conductance of KCl solution will not change with the addition of $AgNO_3$. When equivalence point is reached, further addition of $AgNO_3$ to the solution add free Ag^+ and NO_3^- ions causing a sharp rise in conductivity.



3.3 Spectroscopy:

Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiation with matter. Spectroscopy is one of the powerful tools available for the study of atomic and molecular structure and is used in analysis of wide range of samples

3.3.1 Fundamentals of spectroscopy:

Spectroscopy

It deals with interaction of electromagnetic radiation with matter.

Due to these interactions, energy is absorbed or emitted by the matter. Measurement of radiation frequency is done experimentally to give change in energy involved.

Spectroscopy means measurement of spectrum of a sample containing atoms or molecules.

Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).

The study of spectroscopy can be carried out under the following heads:

1. Atomic spectroscopy: This spectroscopy is concerned with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state called ground state
2. Molecular spectroscopy: This spectroscopy deals with the interaction of electromagnetic radiation with molecules. This results in transitions between rotational and vibrational energy levels in addition to electronic transitions

The most important atomic and molecular transitions related to the successive regions are

X- ray	K and L shell electrons
Far ultra violet	Middle shell electrons
Near ultraviolet	Valency electrons
Visible	
Near and mid infra red	Molecular vibrations
Far infra red	Molecular rotations and low lying vibrations
Microwave	Molecular rotations

Defn.: Spectroscopy is the analysis of the electromagnetic radiation absorbed or emitted by atoms or molecules.

3.3.2 Types of spectroscopy

a) **Absorption spectroscopy:** results when molecule undergoes change in energy from lower energy to higher energy with the absorption of photon of energy $h\nu$, if $h\nu$ is equal to energy difference ΔE .

In absorption spectroscopy, a beam of polychromatic light falls on a sample. Part of light is absorbed by the sample and remaining part is transmitted. The intensity of transmitted light coming from sample is measured at different wavelengths by suitable photo detector. This information is presented as a graph of intensity of absorbed radiation. Spectrum of sample consist of number of absorption bands with different intensity.

b) **Emission spectroscopy:** results when molecule falls from higher energy to lower energy with emission of photon of energy $h\nu$.

In this technique, sample is subjected to intense source of energy like electrical arc. As a result, sample is vaporized and electrons in the sample are excited to higher energy state. When these electrons come back to ground state energy level, they emit radiation. These radiations are analysed by spectrophotometer to generate spectrum that gives information about atoms present in the sample.

3.3.3 Electromagnetic radiations and electromagnetic spectra:

- 1) **Electromagnetic radiations:** it is a form of energy that is transmitted through space with high velocity. Each electromagnetic radiation is characterized by wavelength (λ), wave number (cm^{-1}) and frequency (ν). The energy associated with electromagnetic radiation is given by $E = hc/\lambda$ or $E = h\nu$.

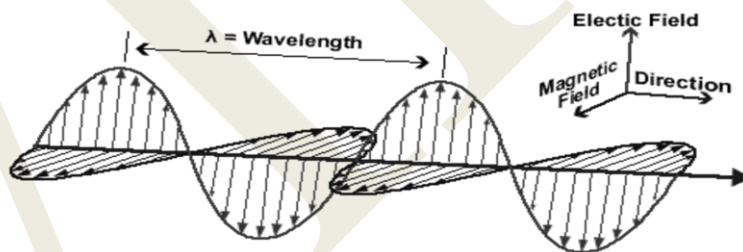
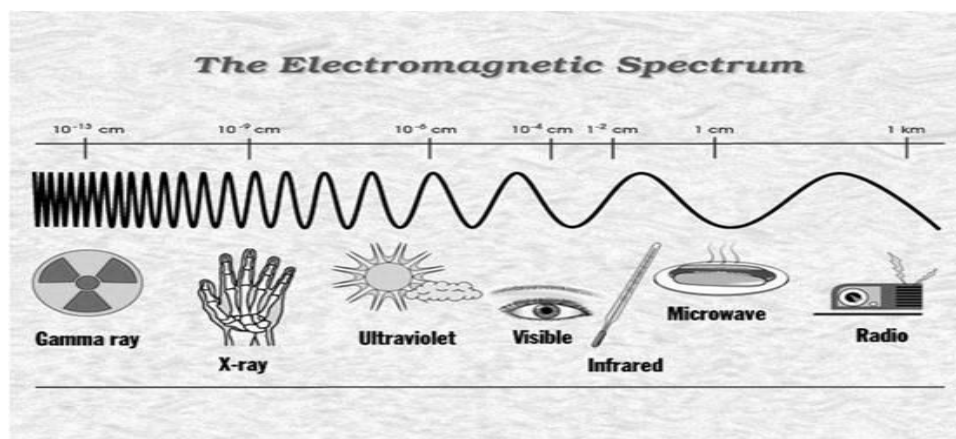


Fig: Electromagnetic radiation

- 2) **Electromagnetic spectra:** The entire range of electromagnetic radiations starting from gamma rays, X rays to microwaves and radio waves are covered in electromagnetic spectra. It shows the range of electromagnetic radiations with different wavelengths hence associated with different energies. As wavelength goes on increasing, energy associated goes on decreasing.



3.3.4 Molecular spectroscopy:

1) Molecular spectroscopy: It deals with the interaction of electromagnetic radiation with molecules. These interactions result in rotational, vibrational and electronic transitions of energy levels. Total internal energy of molecule is given by

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

- i) **Rotational energy** - This type of energy is associated with overall rotation of the molecule with the atoms considered as fixed point masses.
- ii) **Vibrational energy** – This type of energy is associated with the oscillation of atoms of molecule which are considered as point masses about equilibrium position. When molecule absorbs energy, the increase in vibration motion of molecule is usually accompanied by increased rotation of the same molecule. This combination provides the basis for IR absorption spectroscopy.
- iii) **Electronic energy** - This type of energy is associated with the motion of electrons considering nuclei of atoms of a molecule as fixed point, to move from the ground state to excited state.
- iv) **Relation between these energies can be shown as:**

$$E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$$

2) Molecular absorption of electromagnetic radiation: When molecules absorb electromagnetic radiation, it gets excited from ground state energy level to excited state. When it returns to ground state, it gives bands that are characteristic of that molecule, known as molecular spectra.

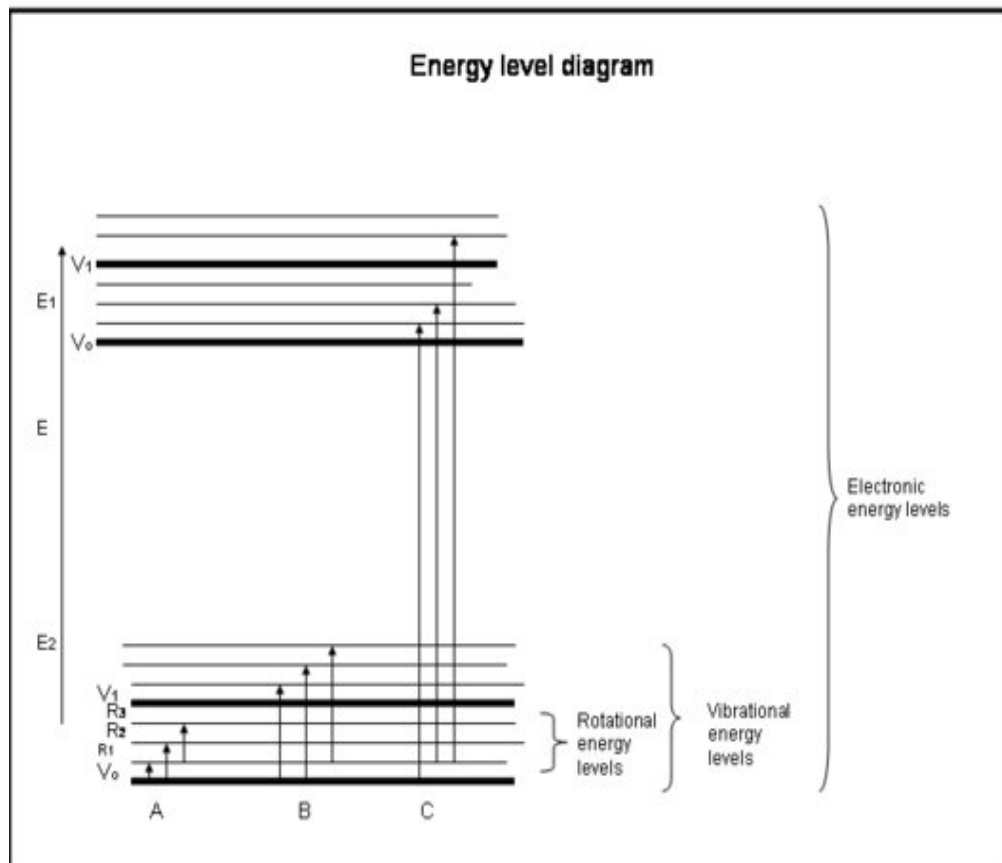
Total energy states of molecule include electronic, vibrational and rotational levels. All energy components are quantized.

Rotational energy levels of a molecule are very closely spaced. Little energy is required for rotational energy transitions which occur in microwave region. Rotational absorption spectra is in the form of single lines.

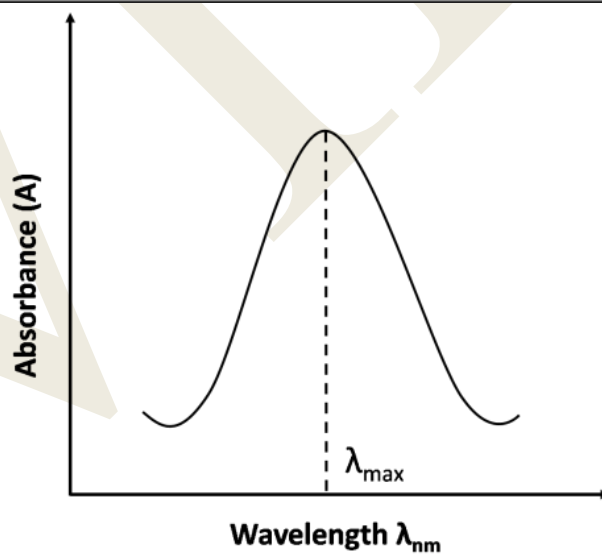
Vibrational energy levels are placed further apart. Vibrational energy transitions require more energetic photons than rotational transitions. These transitions occur in infrared region. **Vibrational transitions are accompanied by rotational transitions.** Thus, a typical vibrational absorption spectra consist of complex bands instead of single lines.

When molecules absorb photons in UV Visible regions, electronic transitions take place from ground state to excited state. **Electronic transitions are accompanied by vibrational**

and rotational transitions. These transitions result into molecular spectrum involving band of wavelength rather than a single line, therefore, broad absorption spectra is observed. The value at which maximum absorption takes place is called λ_{max} value.



**UV – Visible
absorption spectra**



3.4 UV – Visible spectroscopy:

UV- Visible absorption spectroscopy is powerful tool for structural determination and quantitative analysis.

3.4.1 Principle of UV- Visible spectroscopy:

i) UV and visible radiations are more energetic radiations. Absorption of these radiations by any substance brings about electronic excitations. These excitations are accompanied by vibrational and rotational changes that result in spectrum. As a result, bands in UV –visible spectrum are relatively broad. Electronic excitation responsible for absorption in UV – Visible region can be mostly $\pi \longrightarrow \pi^*, n \longrightarrow \sigma^*, n \longrightarrow \pi^*$ transitions.

ii) Quantitative analysis using UV – Visible spectrophotometer can be done according to Beer's law. According to Beer's law, the absorbance of monochromatic light from UV – Visible region by substance is directly proportional to concentration of substance in solution, for constant path length.

3.4.2 Laws of absorbance of radiation:

i) **Lamberts law:** When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to path length.

Let intensity of incident radiation = I

Rate of decrease in intensity of incident radiation with thickness dx of the medium will be

$$\frac{-dI}{dx}$$

$$\frac{-dI}{dx} \propto I \quad \therefore KI = \frac{-dI}{dx} \quad (K \text{ is proportionality constant})$$

$$\therefore \frac{dI}{I} = -K \cdot dx$$

On integrating equation between the limits $I = I_0$ at $x = 0$ and $I = I_t$ at $x = x$ (length of solution)

$$\therefore \int_{I_0}^{I_t} \frac{dI}{I} = \int_0^x -K \cdot dx$$

$$\ln \frac{I_t}{I_0} = -Kx \quad I_t = I_0 \cdot e^{-Kx}$$

- ii) **Beers law:** When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to concentration.

Let intensity of incident radiation = I

Rate of decrease in intensity of incident radiation with concentration dC of the medium will be $\frac{-dI}{dC}$

$$\frac{-dI}{dC} \propto I \quad \therefore KI = \frac{-dI}{dC} \text{ (K is proportionality constant)}$$

$$\therefore \frac{dI}{I} = -K \cdot dC$$

On integrating equation between the limits I = I₀ at C = 0 and I = I_t at C = C

$$\therefore \int_{I_0}^{I_t} \frac{dI}{I} = \int_0^C -K \cdot dC$$

$$\ln \frac{I_t}{I_0} = -KC \quad I_t = I_0 \cdot e^{-KC}$$

- iii) **Combined law (Beer – Lambert's law):**

$$\ln \frac{I_t}{I_0} = -K \cdot x \cdot C$$

$$2.303 \log \frac{I_t}{I_0} = -K \cdot x \cdot C$$

$$\log \frac{I_t}{I_0} = -\frac{K}{2.303} \cdot x \cdot C$$

$$\log \frac{I_0}{I_t} = \frac{K}{2.303} \cdot x \cdot C$$

$$\frac{K}{2.303} = \epsilon$$

ϵ = absorption coefficient

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

$$A = \epsilon \cdot C \cdot x$$

$$T = \log \frac{I_t}{I_0} = \text{transmittance}$$

$$A = -\log T$$

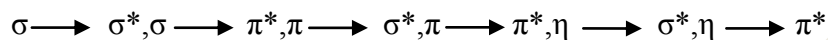
3.4.3 Electronic transitions:

When energy is absorbed by a molecule in UV Visible region, it brings changes in electronic energy of molecule because of transition of valence electrons.

3 types of electrons are involved in organic molecule:

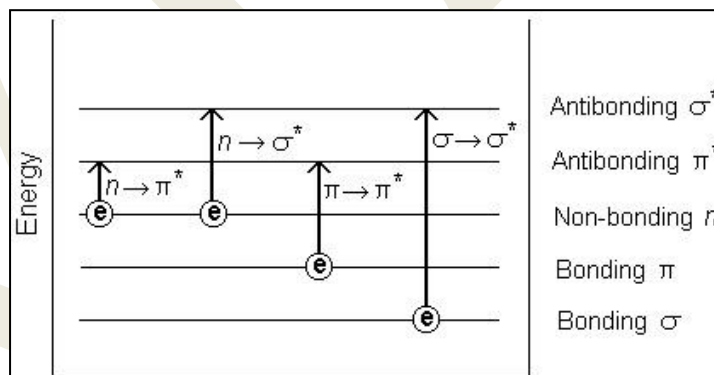
- σ electrons:** electrons forming single bonds are called σ electrons. These are involved in forming bonds in saturated hydrocarbon such as C-H bonds
- π electrons:** electrons involved in forming double bonds are called as π electrons. These are involved in forming bonds in unsaturated hydrocarbon.
- η electrons:** these are non bonded or lone pair of electrons and are not involved in bonding between atoms in molecules

When energy is absorbed in UV Visible region, **possible electronic transitions** are:



Out of these, $\sigma \longrightarrow \pi^*, \pi \longrightarrow \sigma^*$ are considered as **forbidden** transitions.

- $\sigma \rightarrow \sigma^*$:** These transitions are observed in saturated hydrocarbons. Energy required for these transitions is very large. Absorption band occur in the far UV region (126-135nm). For e.g. methane has λ_{\max} at 121.9nm, ethane at 135 nm.
- $\pi \longrightarrow \pi^*$:** These transitions are involved in transition of electrons from bonding π to antibonding π^* orbital. These transitions occur in molecules having π electron system such as alkenes and alkynes. For e.g. ethylene shows intense band at 174nm and weak band at 200nm due to π to π^* transition. λ_{\max} value increases with increase in conjugation.
- $\eta \longrightarrow \sigma^*$:** Saturated hydrocarbons with lone pair of electrons/non bonding electrons undergoes these transitions. The energy required is less than that of σ to σ^* transitions. Corresponding absorption bands appear near UV region (180-200nm) For e.g. aliphatic alcohols, alkyl halides show such transitions.
- $\eta \longrightarrow \pi^*$:** These type of transitions are shown by unsaturated molecules which contain atoms such as oxygen, sulphur, nitrogen. Absorption band of aldehydes and ketones usually occur in the range of 270-300nm.



3.4.4 Terms related to UV Visible spectroscopy:

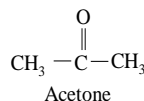
- Chromophore:** is a functional group containing multiple bonds capable of absorbing radiation in UV-visible region. e.g. C=O, C=C, N=O, C=N etc.
While interpreting UV –visible spectroscopy, following points are to be considered.

a) Non conjugated alkenes show an intense absorption below 200 nm therefore inaccessible to UV spectrophotometer.

e.g. λ_{max} for ethylene ($\text{CH}_2=\text{CH}_2$) is 171 nm.

b) Non –conjugated carbonyl group give a weak absorption in the region 200- 300nm.

e.g. Acetone has $\lambda_{\text{max}} = 279$ nm



c) When double bonds are conjugated in a compound, λ_{max} is shifted to longer wavelength.

e.g. 1,5 – Hexadiene : $\lambda_{\text{max}} = 178$ nm (non conjugated system)

2,4 – Hexadiene : $\lambda_{\text{max}} = 227$ nm (conjugated system)

Absorptions of Organic Molecules

Alkanes:

- Saturated molecules that lack lone pairs
- Only transitions possible are $\sigma \rightarrow \sigma^*$
- high energy; absorb UV radiation at very short wavelengths
- not accessible using UV spectroscopy

Alcohols, Ethers, Amines, & Sulfur Compounds:

- Saturated molecules with lone pairs of electrons
- Important transitions are $n \rightarrow \sigma^*$
- high energy, most often at wavelengths shorter than 200 nm
- alcohols and amines: 175 – 200 nm
- thiols and sulfides: 200 – 220 nm

Alkenes & Alkynes:

- Important transitions are $\pi \rightarrow \pi^*$
- high energy, but impacted by substitution
- simple alkenes: 175 nm
- simple alkynes: 170 nm

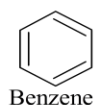
Carbonyls:

- Important transitions are $\pi \rightarrow \pi^*$ (188 nm)
- $n \rightarrow \pi^*$: also possible (280 – 290 nm)
- sensitive to substitution

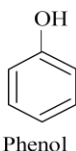
ii) **Auxochrome:** is a saturated functional group which does not absorb radiation in UV range but when attached to chromophore changes both wavelength & intensity of absorption.

e.g. $-\text{OH}$, $-\text{NH}_2$, $-\text{Cl}$.

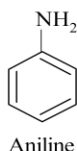
It causes shift in absorption to longer wavelength. It is a group, which extends the conjugation of chromophore by sharing of non bonding electrons.



$$\lambda_{\max} = 255 \text{ nm}$$

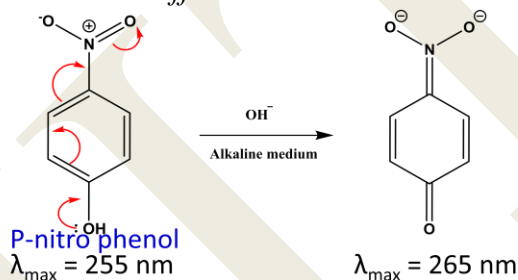


$$\lambda_{\max} = 270 \text{ nm}$$

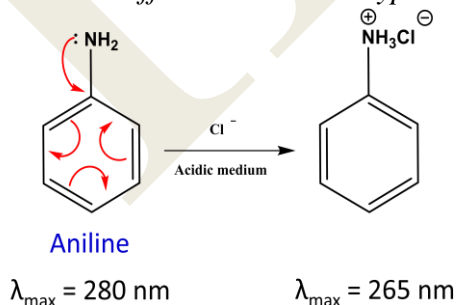


$$\lambda_{\max} = 280 \text{ nm}$$

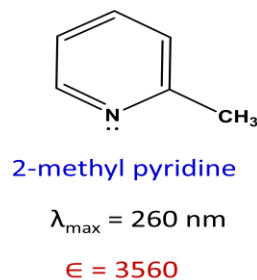
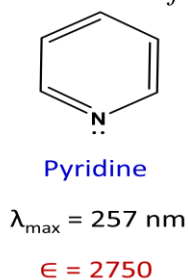
- iii) **Bathochromic shift/Red shift:** The shift of absorption maxima (λ_{\max}) to a longer wavelength due to substitution or solvent effect is known as bathochromic shift or red shift.



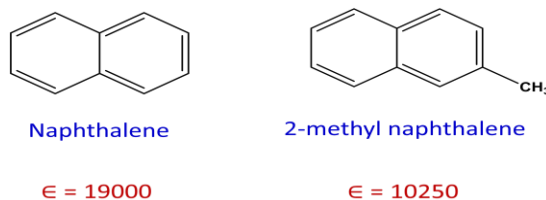
- iv) **Hypsochromic shift/Blue shift:** The shift of absorption maxima (λ_{\max}) to a shorter wavelength due to substitution or solvent effect is known as hypsochromic shift or blue shift.



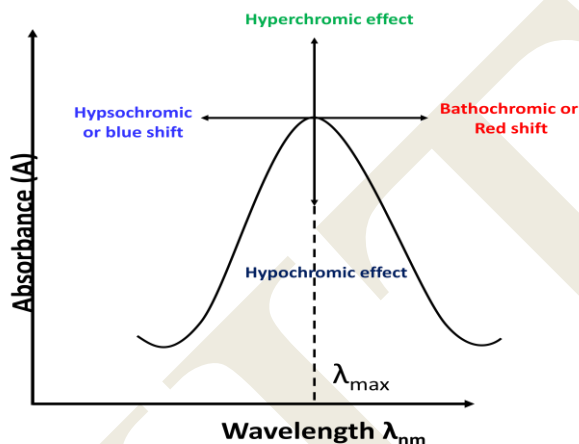
- v) **Hyperchromic shift:** An increase in intensity of absorption maxima is called hyperchromic shift. It is observed due to introduction of auxochrome.



- vi) **Hypochromic shift:** Decrease in intensity of absorption maxima is called hypochromic shift. It occurs due to introduction of groups that distort the original geometry of the molecule



These shifts and effects on the absorption can be shown as



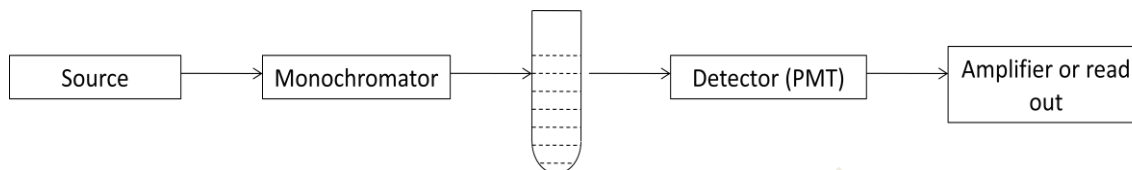
3.4.5 Instrumentation of UV Visible Spectroscopy

Various components of UV Visible spectroscopy and their **functions** are as follows

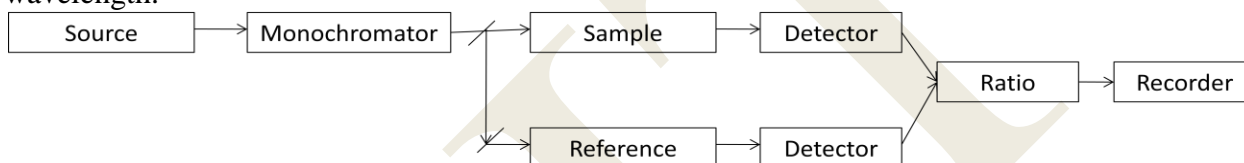
- i) **Radiation source:** It gives a source of continuous electromagnetic radiation in the required region. Tungsten filament lamp is most commonly used for visible radiations (Wavelength range 400 to 750nm). Hydrogen discharge lamps are used for UV radiations (Wavelength range 200 to 400nm)
- ii) **Monochromators:** Radiation source provides polychromatic light which is passed through monochromator. Monochromators disperse radiation according to wavelength. Dispersing element may be prism or grating. Position of dispersing element is adjusted to vary wavelength passing through exit slit. Thus it helps to give monochromatic light.
- iii) **Sample holder:** Sample holders are used to hold sample solution and reference solution. They are constructed of the material which does not absorb radiation in the UV Visible region. Optically matched fused glass cells are used for visible spectroscopy whereas **Corex glass or quartz cells** are used for UV spectroscopy. (Glass absorbs radiations of wavelength less than 350 nm hence not used for UV spectroscopy but can be used for visible spectroscopy)
- iv) **Detectors:** A detector is a transducer that converts electromagnetic radiation into an electron flow and consequently into current or voltage in readout circuit. Phototubes, photomultiplier tubes, photovoltaic cells etc. are used for the purpose.

- v) **Amplifiers and readout:** signal received from the detector is amplified and read on recorder.

Single beam spectrophotometer: In this, a sample is examined to determine the amount of radiation absorbed at a given wavelength. The results are compared with a reference obtained in a separate measurement.

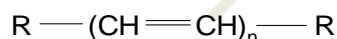


Double beam spectrophotometer: In double beam instrument, a monochromatic beam of radiation is split into two components of equal radiant power. One beam is passed through sample and other through reference solution. The two beams, one from sample and other from reference are focused on detector. The output is connected to amplifier and is transmitted further to a recorder. Absorbance or transmittance of the sample is recorded as a function of wavelength.



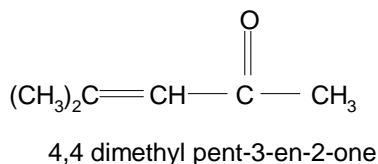
3.4.6 Applications of UV Visible spectroscopy:

- i) **Detection of functional group:** The technique is applied to detect presence or absence of chromophore, the absence of absorption band at particular wavelength may be regarded as an evidence for the absence of functional group. If spectrum is transparent above 200 nm it shows absence of conjugation, carbonyl group, benzene or other aromatic compound, Bromo or Iodo group
- ii) **Extent of conjugation:** Can be employed for polyenes i.e.

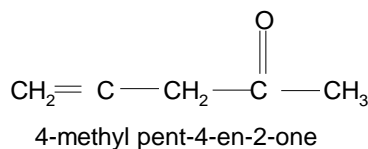


Increase in conjugation shifts absorption to longer wavelength.

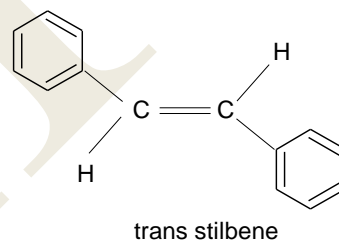
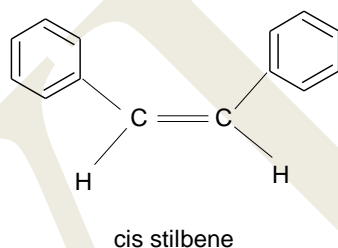
- iii) **Distinguish between conjugated and non-conjugated double bonds:** The technique helps in distinguishing a conjugated compound from a non conjugated compound.
 - 1) Conjugated system (peak appear at longer wavelength)



- 2) Non conjugated system (peak appear at shorter wavelength)

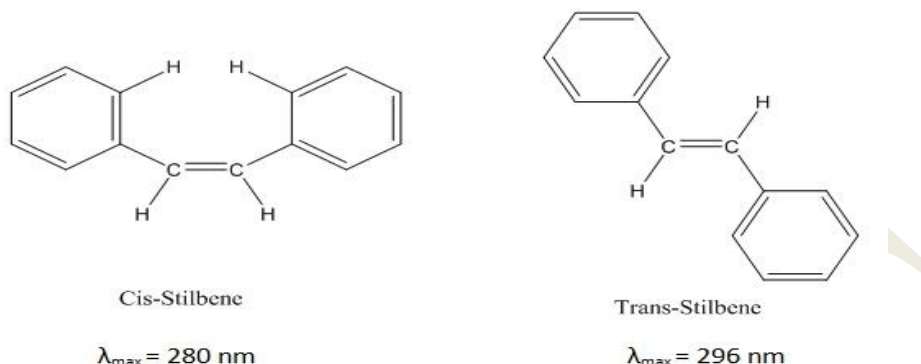


- iv) **Identification of an unknown compound:** It is useful in identifying chemical substances by comparing spectra of unknown samples with that of standard substance
- v) **Examination of polynuclear hydrocarbons:** Benzene and other polynuclear hydrocarbons have characteristic spectra of their own which can be compared with spectra of known polynuclear compounds.
- vi) **Quantitative estimation of solute in solution:** It is useful in determining very low concentration of solutions which cannot be determined by volumetric or gravimetric method
- vii) **Detection of impurities:** It is used in detection of impurities. Impurities may give different peak position other than standard
- viii) **Study of kinetics of reaction:** It is useful in studying kinetics of the reactions by following change in concentration of reactants and product with time during reaction
- ix) **Determination of configuration of molecules:** The technique is useful in distinguishing two geometrical isomers. This distinction is possible when one of the isomers is forced to be non coplanar by steric hindrance. For e.g. cis – Stilbene has $\lambda_{\text{max}} = 274 \text{ nm}$ whereas trans-Stilbene has $\lambda_{\text{max}} = 294 \text{ nm}$



Illustrative examples:

1) Trans stilbene absorbs at higher wavelength than its cis isomer.



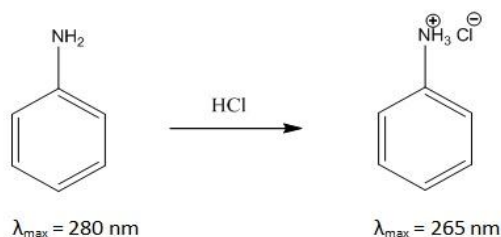
In the pair of geometrical isomers the cis isomer absorbs at lower (shorter) wavelength than a trans isomer due to two reasons

- In cis isomer there is steric hindrance due to bulky phenyl groups and this disturbs the planarity of molecule, thereby inhibiting resonance (delocalization).
- The length of chromophore decreases. More energy is required for $\pi \rightarrow \pi^*$ excitation and hence absorption towards a shorter wavelength occurs.

In case of trans isomer, the absorption takes place at longer wavelength due to two reasons

- In trans isomer, the molecule is planar as there is no steric hindrance
- The length of chromophore increases (extension of conjugation). This situation demands less energy for $\pi \rightarrow \pi^*$ excitation, hence absorption towards longer wavelength occurs.

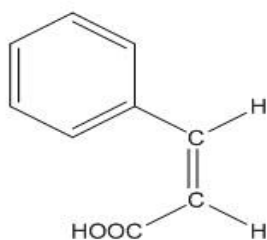
2) The absorption band at 280 nm in aniline is disappeared upon addition of hydrochloric acid



a) Aniline shows peak in UV-Visible spectra at 280 nm. Lone pair of electrons on nitrogen is in conjugation with benzene ring, increasing conjugation of benzene. As conjugation increases, energy required for $\pi \rightarrow \pi^*$ transition decreases, hence absorption takes place at 280 nm.

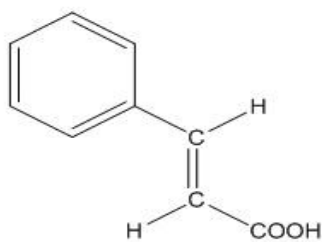
b) Upon adding of HCl, amine group gets converted into its salt. Lone pair of electron on nitrogen is now not available for conjugation. As there is decrease in conjugation, there is increase in energy required for $\pi \rightarrow \pi^*$ transition, hence absorption takes place at 265 nm (lower wavelength). Hence peak at 280 nm disappears and new peak appears at 265 nm (Hypsochromic shift).

3) Trans cinnamic acid shows absorption at longer wavelength than cis cinnamic acid.



Cis-Cinnamic acid

$\lambda_{\text{max}} = 268 \text{ nm}$



Trans-Cinnamic acid

$\lambda_{\text{max}} = 272 \text{ nm}$

Due to greater crowding in cis - form (both bulky groups are on same side), the geometry of alkene chromophore is distorted and departure from coplanarity results. Thus $\pi \rightarrow \pi^*$ transition in cis-cinnamic acid takes place at lower wavelength.

4) Which of the following shows higher absorption wavelength?



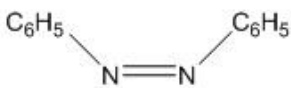
(1)



(2)

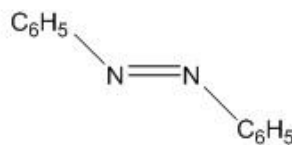
(2) absorbs longer than (1). In (2), there is extension of conjugation due to the additional double bond. Hence energy required for $\pi \rightarrow \pi^*$ transition is lower. Thus absorption wavelength is higher.

5) Which of the following shows higher absorption wavelength?



azobenzen

(1)



(2)

(2) absorbs higher than (1).

In (1), steric hindrance restricts the conjugation, distorting planarity, hence less absorption wavelength.

In (2), no steric hindrance, structure is planar, thus absorption takes place at higher wavelength.

3.5 Infrared spectroscopy:

Introduction:

UV and Visible spectrum provides information about the structure of molecules that contain double bond or triple bond or two or more conjugated double bonds. IR spectrum provides information about functional groups of molecule and also useful for identification of molecule. IR spectrum is obtained by exposing molecules of compound to electromagnetic radiation of IR region.

3.5.1 Principle of IR spectra:

A molecule is not rigid. Atoms and molecule continuously rotate, vibrate and move from one point to other. The atoms in the molecule vibrate in many different ways and each vibration requires different energy i.e. molecule has number of vibrational energy levels each of which is quantized. If molecule absorbs IR radiation, it gets excited to higher vibrational energy level. The type of IR wavelength absorbed by the molecule depends on the type of atoms and chemical bonds in the molecule, In IR spectrum, position of peak is specified in terms of frequency (ν) or wavelength(λ) or wave number ($\bar{\nu}$) of IR radiation absorbed.

Parts of IR spectrum:

The electromagnetic radiations having wavelength range 0.78 to 200 μ or wave number range 12800 to 50 cm^{-1} are called infrared radiations.

The infrared region is further divided into three regions:

Near Infrared region	Infrared region		Far Infrared region
	Functional group region	Finger Print region	
12800 to 4000 cm^{-1}	4000 to 667 cm^{-1}		667 to 50 cm^{-1}

IR spectroscopy is not only useful in elucidation of structure of organic compounds but also useful in quantitative determinations.

The technique is based upon a simple fact that a chemical substance shows selective absorption in the infrared region. After absorption of IR radiations, the molecules of chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands, called IR absorption spectra. Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in chemical substance.

The region between 4000 - 1250 cm^{-1} is called as **functional group region** whereas from 1250-909 cm^{-1} is called as **fingerprint region**. Absorption bands in this region are very complex and characteristic for a particular organic molecule. 909 to 667 cm^{-1} is characteristic region for aromatic compound.

Band positions in infrared spectrum may be expressed conveniently by wave number $\bar{\nu}$, whose unit is cm^{-1} . The relation between wave number $\bar{\nu}$, wavelength λ and frequency ν is as follows

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

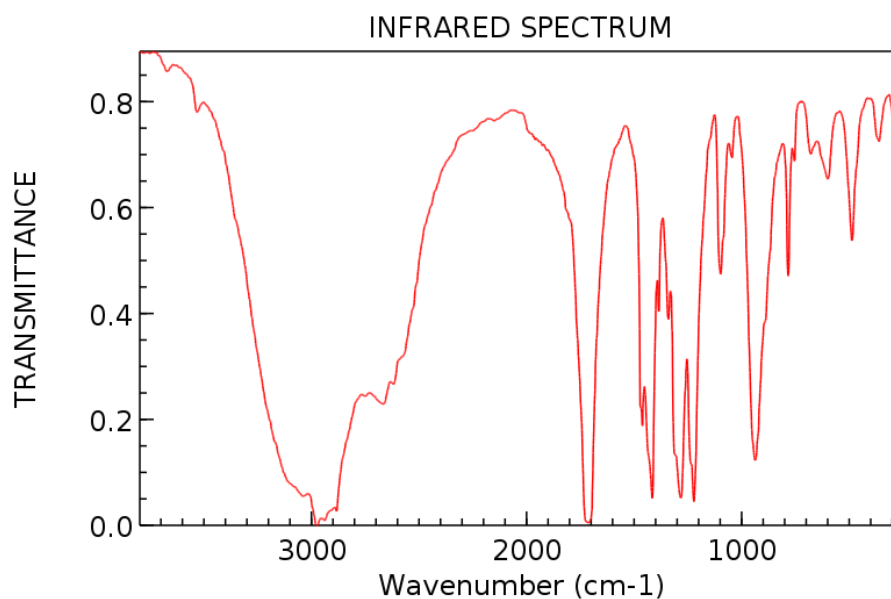
$$\text{or } \bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

where 'c' is velocity of light.

3.5.2 Infrared spectra:

Spectra is generally a graphical representation of % Transmittance on Y- axis and wavenumber or wavelength on X- axis.

Band intensities are expressed in % Transmittance.



3.5.3 Requirements of IR absorption/conditions for absorption of IR radiation:

For a molecule to absorb IR radiations, it has to fulfill following requirements-

- 1) **Correct wavelength of radiation:** A molecule absorbs radiation only when the natural frequency of vibration of some part of a molecule (i.e. atom or group of atoms present in molecule) is the same as the frequency of incident radiation.

When frequency of vibration of a bond and frequency of IR radiation used for excitation match perfectly then only IR energy is absorbed.

For e.g. natural frequency of vibration of HCl molecule is about $8.7 \times 10^{13} \text{ sec}^{-1}$ (2890 cm^{-1})

When IR radiation is permitted to pass through a sample of HCl and the transmitted radiation is analysed by the IR spectrophotometer, it is observed that part of radiation which has a frequency of $8.7 \times 10^{13} \text{ sec}^{-1}$ (2890 cm^{-1}) has been absorbed by HCl molecule whereas the remaining frequencies of the radiations are transmitted. Thus, the frequency $8.7 \times 10^{13} \text{ sec}^{-1}$ is characteristic of HCl molecule.

After absorbing the correct wavelength of radiation, the molecule vibrates at an increased amplitude. This occurs at the expense of the energy of IR radiation which has been absorbed.

- 2) **Electric Dipole:** This is another condition for a molecule to absorb IR radiation. A molecule can only absorb IR radiation when its absorption causes a change in its electric dipole (dipole moment).

Only those vibrations which result in change in dipole moment, absorb IR radiation. Such vibrations are said to be IR active.

A molecule is said to have electric dipole when there is a slight positive and a slight negative electric charge on its component atoms. When the molecule having electric dipole

is kept in the electric field (molecule kept in the beam of IR radiation), the field will exert forces on the electric charges in the molecules. Opposite charges will experience forces in opposite directions. This tends to decrease separation. As the electric field of the IR radiation is changing its polarity periodically, it means that the spacing between charged atoms (electric dipoles) of the molecule also changes periodically.

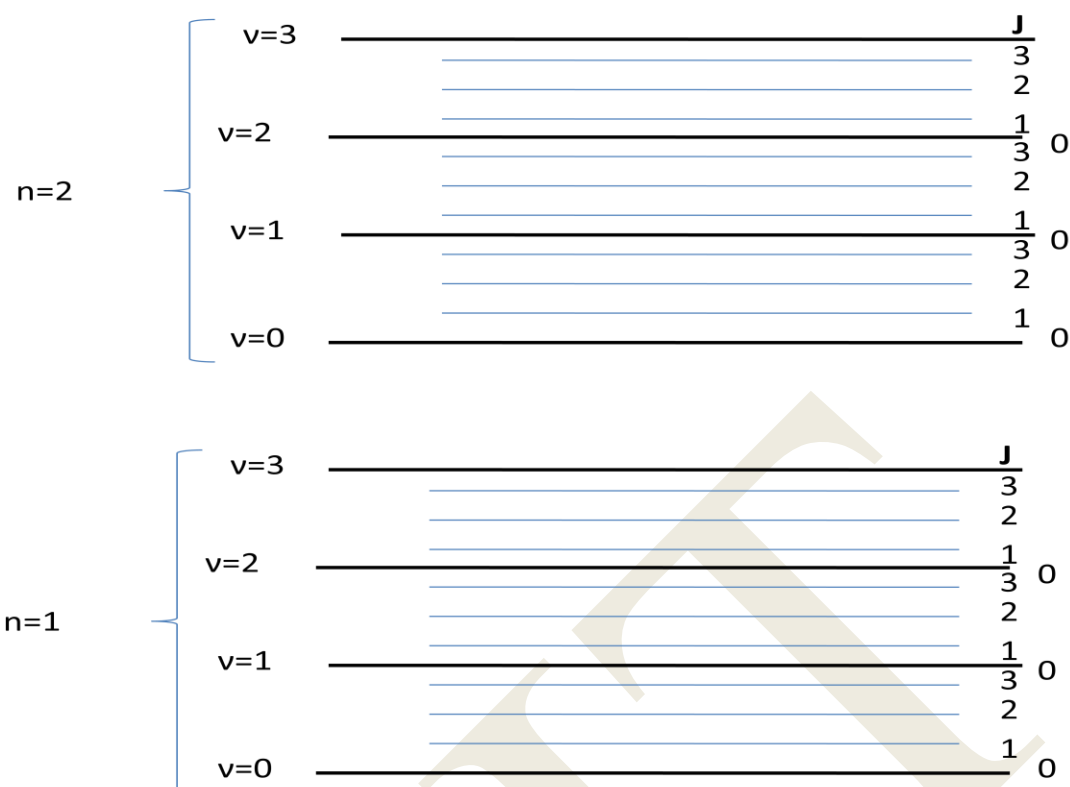
When these charged atoms vibrate, they absorb IR radiation from the radiation source. If the rate of vibration at charged atoms in a molecule is fast, the absorption of radiation is intense, thus, IR spectrum will have intense absorption bands. On the other hand, when the rate of vibration of charged atoms in a molecule is slow, there will be weak bands of IR spectra.

Symmetrical diatomic molecules like O_2 , N_2 do not possess electrical dipole. They can not be excited by infra red radiation and thus do not give rise to IR spectra. Such molecules are IR inactive.

Further, no change in dipole moment is produced by the carbon- carbon double bond stretching of the symmetrical molecule like ethylene. Since there is no change in dipole moment, the bond does not absorb infrared radiation. On the other hand, substitution of a bromine for a hydrogen atom to form bromoethylene destroys the symmetry around the double bond. The stretching of double bond now generates a significant changes in dipole moment and strong absorbance in infrared is observed.

3.5.4 Origin of Infrared spectra:

Consider diatomic molecule AB. Such molecule consists of two nuclei corresponding to atoms A and B and their corresponding electrons. These electrons contained in atoms can exist in number of energy levels. When excited, i.e. when energy is absorbed, the transition of electrons occurs from low energy level to higher energy level. On returning to low energy level, it emits spectral lines of frequency determined by the difference in two energy levels



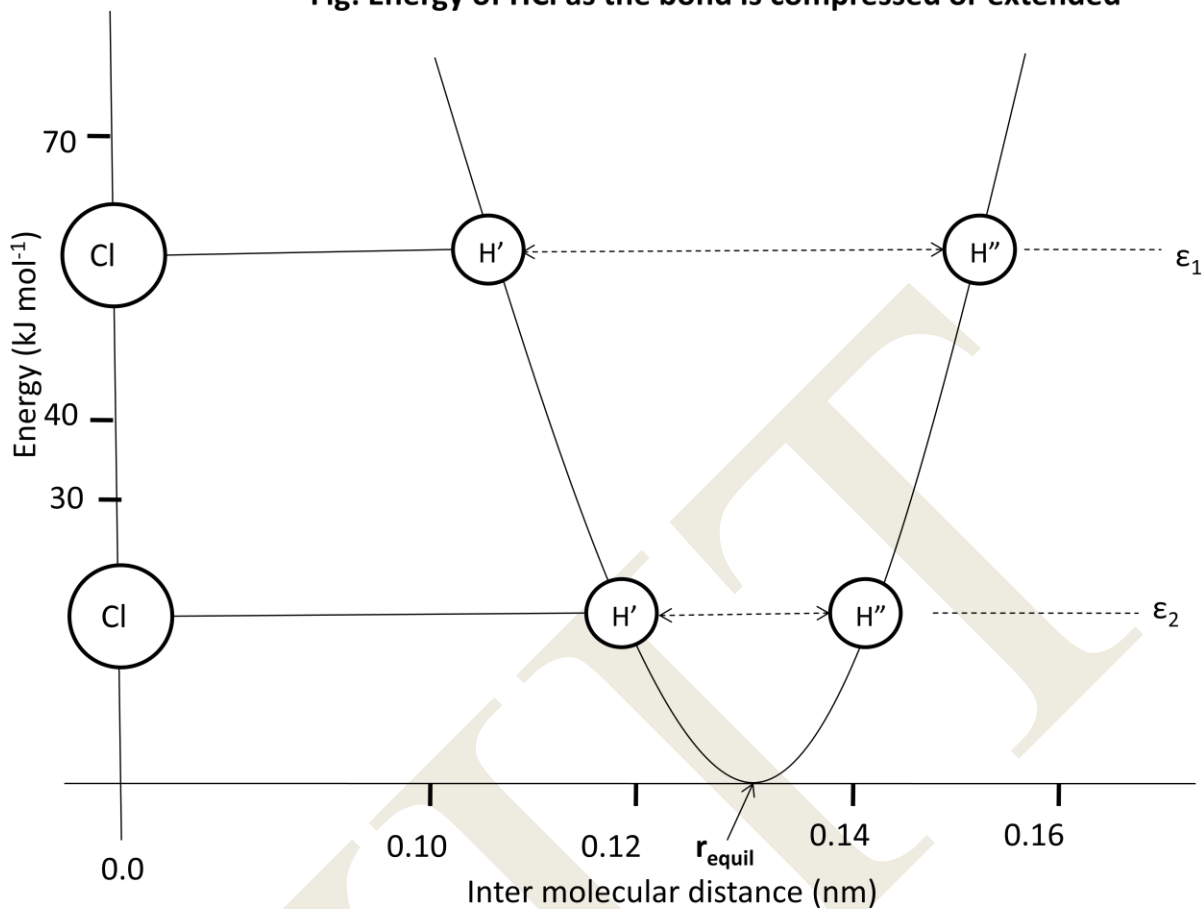
Energy required for exciting emission will be least for rotation and higher for vibrational and still greater for electronic transitions. Thus, if the excitation energy is kept so small as to produce only transition from one rotational quantum level to another within vibrational level, the emission spectra observed would correspond to changes in rotational quantum numbers. Such type of spectra is called **rotational spectrum**. Since energy involved is small, these spectra are found in the **far infra red**.

If the energy required for excitation is still higher and sufficiently large to cause transition from one vibrational quantum to another within given electronic level, emissions are observed corresponding to the change in vibrational quantum numbers. Change in vibrational level involves change in rotational levels, resulting in spectrum known as **vibrational rotational spectrum**. Since energies involved are still higher such type of spectra are found in the **near infrared region**.

3.5.5 Vibration of diatomic molecule:

Consider a diatomic molecule. On one hand there is a repulsion between the positively charged nuclei of both atoms and between their negative electron clouds whereas on the other hand there is attraction between the nucleus of one atom and electrons of other. The two atoms settle at a mean inter nuclear distance such that these forces are just balanced and the total energy of whole system is minimum. Squeezing the atoms more closely together will cause the repulsive forces to rise rapidly, while pulling them apart is resisted by the attractive force. Any attempt to distort bond length requires input of energy. At the minimum energy, the inter nuclear distance is referred as equilibrium distance r_{equil} or more simply as bond length.

Fig: Energy of HCl as the bond is compressed or extended



The compression and extension of bond may be linked to the behavior of spring, and we may extend the analogy by assuming that the bond, like a spring, obeys Hooke's law.

$$f = -k(r - r_{equil})$$

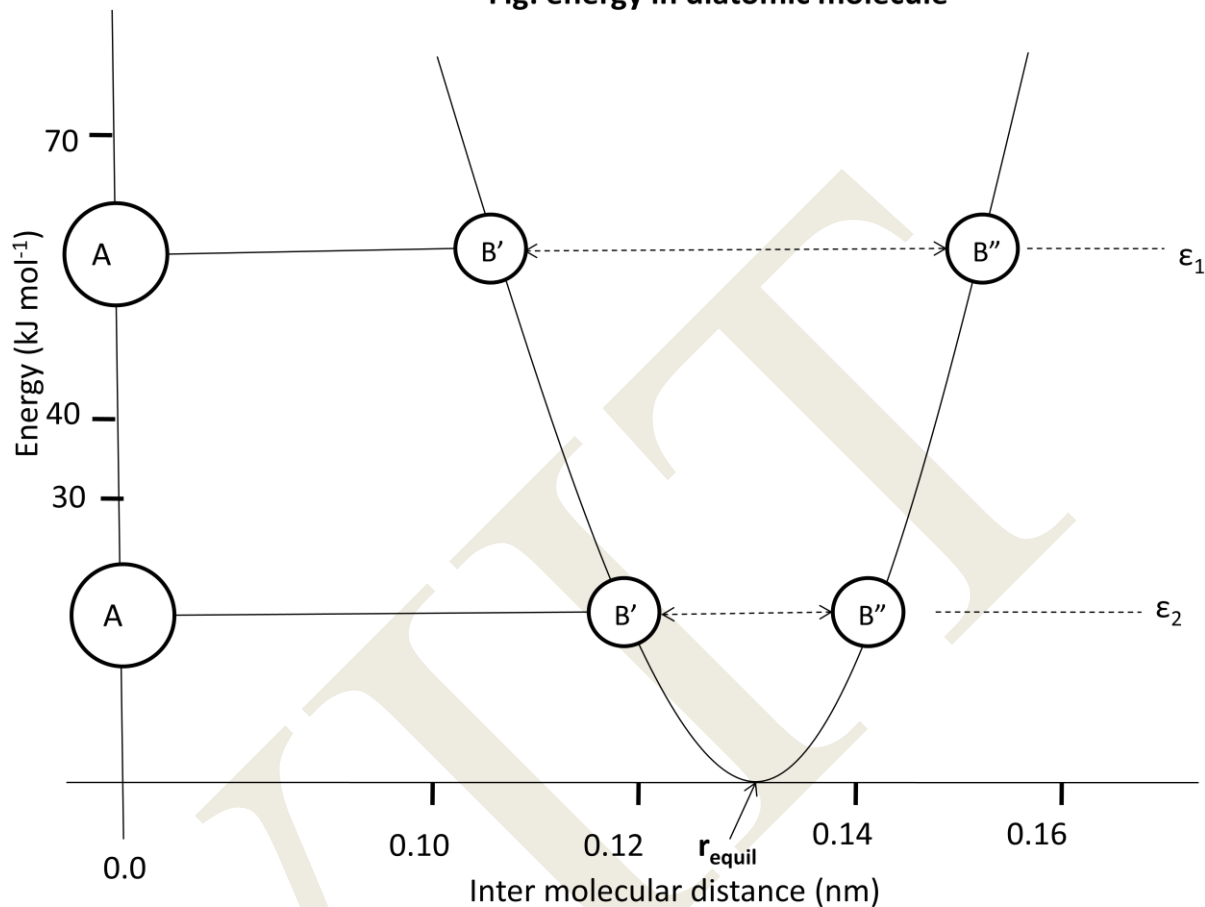
Where 'f' is the restoring force, 'k' is force constant, and 'r' is inter nuclear distance. In this case the energy curve is parabolic and the value of energy is given by (by applying Hooke's law)

$$E = \frac{1}{2}k(r - r_{equil})^2$$

The model of a vibrating diatomic molecule is considered as so called simple harmonic oscillator model.

3.5.6 Calculation of vibrational frequency:

Fig: energy in diatomic molecule



Whenever molecule is vibrating, it will experience path along B'--- r_{equil} ---B'' i.e. compression - ----equilibrium -----extension. As the energy is increased the higher oscillation occurs. Number of oscillations will remain same per unit time i.e. vibrational frequency remain constant but the oscillations will be vigorous.

Consider ω_{osc} = vibrational frequency or oscillation frequency. Classically it is shown by

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{in Hz}$$

k = frequency constant

μ = reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{where } m_1 \text{ and } m_2 \text{ are masses of atoms}$$

To convert oscillation frequencies into wave number, divide by 'C' where 'C' is velocity of light ($\bar{\nu} = \frac{\nu}{c}$)

$$\bar{\omega}_{\text{osc}} = \frac{\omega_{\text{osc}}}{c} = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} \quad \text{in cm}^{-1}$$

(a) Frequency of vibration is directly proportional to force constant (k) i.e. bond energy. Thus stronger bonds will have higher frequency of vibration.

(b) Frequency of vibration is inversely proportional to reduced masses of atoms.

Relation between force constant, frequency and bond length: As the bond order increases, the force constant increases hence frequency increases while bond length decreases. Thus, frequency of C-C single bond is less than that of double bond which in turn is less than triple bond.

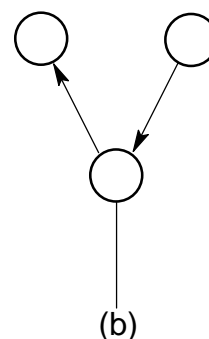
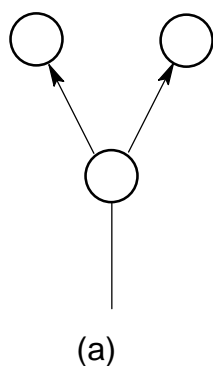
3.5.7 Modes of vibration:

Since IR spectrum is concerned with the vibrational modes, it will be pertinent to know how many modes of vibrations are possible in molecules. For nonlinear molecule containing 'N' atoms, there are '3N' degrees of freedom, of which, 3 are rotational, 3 are translational and remaining (3N-6) are vibrational. These vibrations involve transition of molecule from lower energy level (V_0) to higher vibrational level (V_1). These (V_0 to V_1) are called as fundamental modes of vibration. For linear molecules fundamental modes of vibrations will be (3N-5).

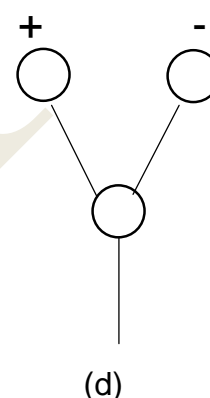
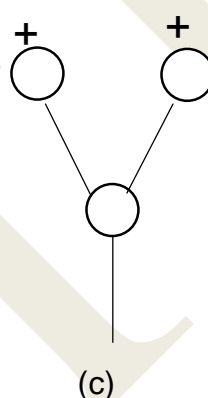
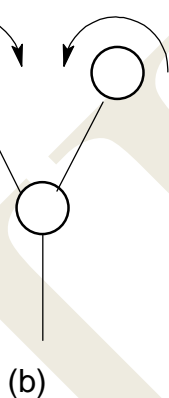
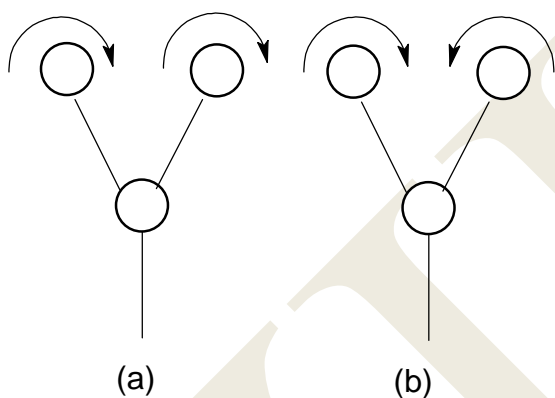
Molecule	N	Geometry of the molecule	Fundamental modes of vibration
NO	2	Linear	1
CO ₂	3	Linear	4
H ₂ O	3	Non- linear	3
NH ₃	4	Non- linear	6
CH ₄	5	Non- linear	9
C ₆ H ₆	12	Non- linear	30

There are 2 kinds of fundamental vibrations (i) stretching vibrations (ii) Bending vibrations

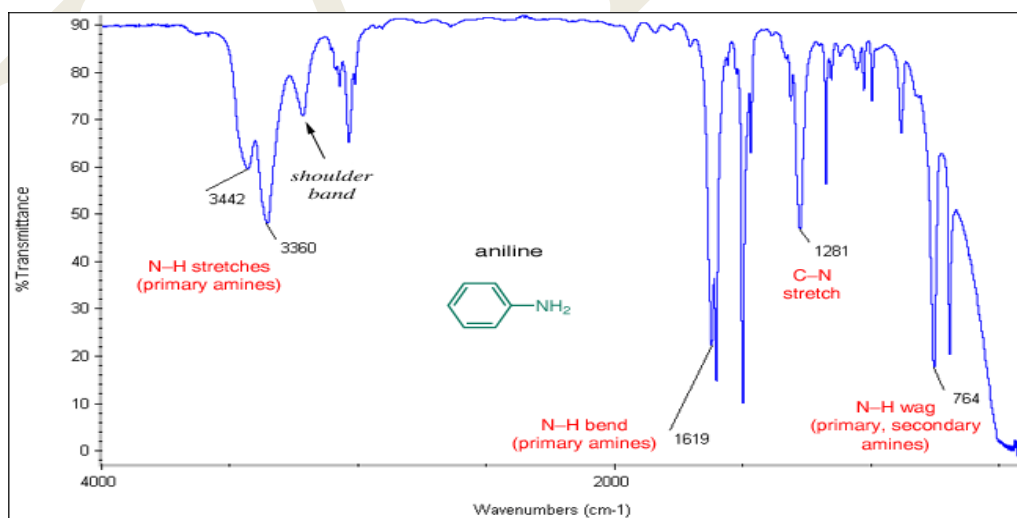
- (i) **Stretching vibrations:** The distance between the two atoms (i.e. bond length) increases or decreases but atoms remain in the same plane. These modes of vibrations are further divided into (a) Symmetrical stretching vibrations and (b) Asymmetrical stretching vibrations

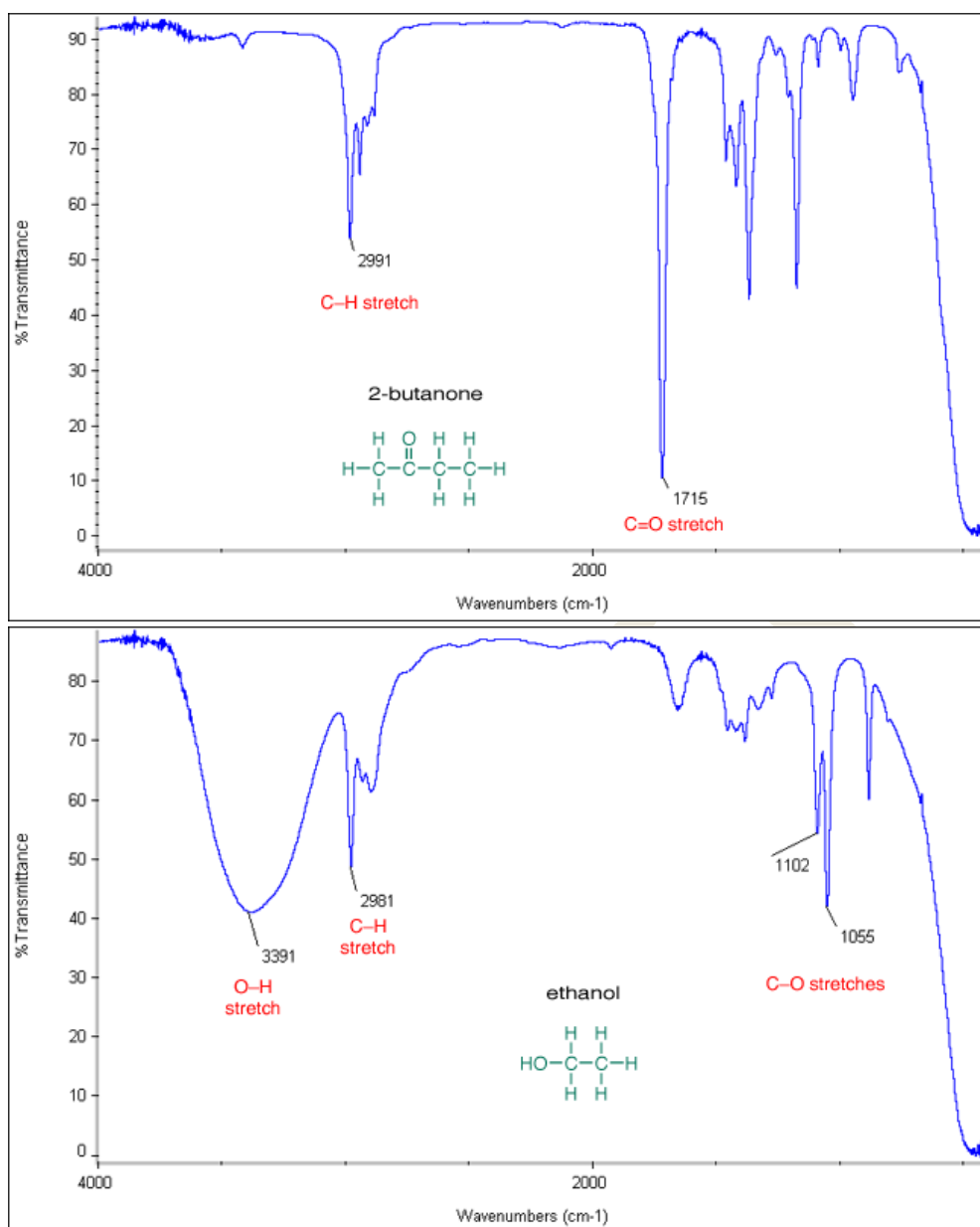


(ii) **Bending vibrations:** The position of the atoms changes relatively to the original bond axis. These modes are further divided into 4 types, (a) Rocking (b) Scissoring (c) Wagging and (d) Twisting. Scissoring and Rocking are in- plane whereas Wagging and Twisting are out-of -plane



Representative IR spectra:





3.5.8 Factors influencing IR absorption:

It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. This is due to the fact that vibrations of each group is influenced by the structure of the molecules in the immediate neighborhood of the bond. The value of absorption frequency is shifted since the force constant of a bond changes with its electronic structure. Frequency shifts also takes place on working with same substance in different states (solid, liquid, vapour state)

Following are some factors responsible for shifting the vibrational frequencies:

i) **Fermi Resonance and Dipole moment:** In IR spectrum, absorption bands are spread over a wide range of frequencies. It may happen that the energy of an overtone level coincides with fundamental mode of different vibration. A type of resonance occurs as in case of coupled pendulums. This type of resonance is called “Fermi Resonance” in which a molecule transfers its energy from fundamental to overtone and back again. For a particular vibration to result in IR absorption energy, the vibration must cause a change in dipole moment. In a symmetrical molecule due to its symmetry, the vibration does not cause any appreciable change in dipole moment and the IR band is said to be inactive. For e.g. CO_2 is linear and 4 fundamental modes of vibrations are expected for it. Out of these, symmetrical stretching vibrations are IR inactive since it produces no change in dipole moment of the molecule.

ii) **Inductive effect:** The introduction of electron donating groups such as alkyl group cause (+I) effect which results in the lengthening or weakening of bond and hence force constant is lowered and wave number of absorption decreases. (+I) effect decreases double bond character of carbonyl group. As single bond character increases, frequency decreases.

Consider the frequencies of absorption of the following compounds

Acetaldehyde $\text{CH}_3\text{-CHO}$ 1745 cm^{-1}

Acetone CH_3COCH_3 1715 cm^{-1}

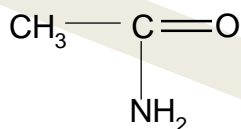
Aldehydes absorption is at higher frequency than ketone. In ketones, there are 2 ‘R’ groups showing +I effect whereas in aldehyde, there is only one ‘R’ group. Carbonyl group in aldehyde has more double bond character so frequency is higher.

Electron withdrawing atom or group causes (-I) effect. e.g. Cl. This results in increase in bond order, force constant and hence frequency of absorption.

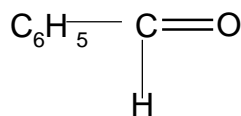
Acetone CH_3COCH_3 1715 cm^{-1}

Chloroacetone $\text{CH}_3\text{COCH}_2\text{Cl}$ 1725 cm^{-1}

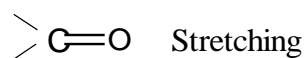
iii) **Resonance (Mesomorphic effect):** Mesomorphic effect causes lengthening or weakening of a bond which lowers the frequency of absorption



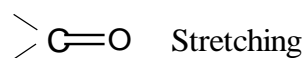
Acetamide



Benzaldehyde



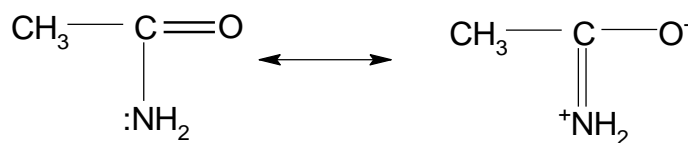
1660 cm^{-1}



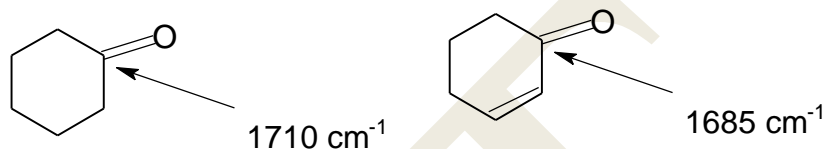
1745 cm^{-1}



Here band due to stretching in acetamide appears at lower frequency due to participation of lone pair of electrons of ‘N’ in resonance

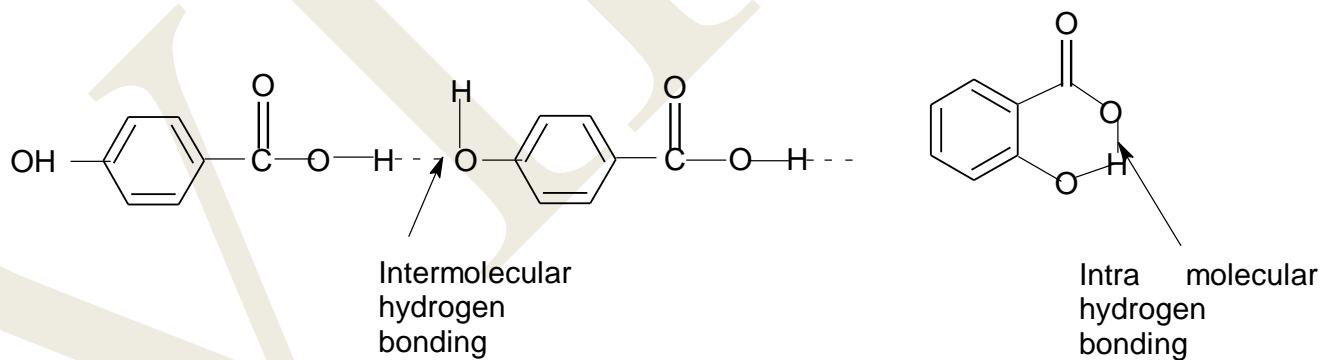


When the carbonyl group is conjugated to a carbon- carbon double bond, there is electron donating resonance effect, which decreases the double bond character of carbonyl group, this decreases the stretching frequency of carbonyl group. Electron donating (+R) group decreases stretching frequency and electron withdrawing (-R) group increases stretching frequency of carbonyl group.



Hydrogen bonding: Carboxylic acids, alcohols, phenols, amines, amides show strong hydrogen bonding effect. Hydrogen bonding increases the O-H bond length so bond strength decreases. Thus, hydrogen bonding lowers the frequency. Stronger the hydrogen bonding, greater is the absorption shift towards lower frequency. Generally, intermolecular hydrogen bonds give rise to broad bands whereas band arising from intra-molecular hydrogen bonds are sharp and well defined.

e.g. Aliphatic -OH free 3650 cm^{-1}
 Aliphatic -OH hydrogen bonded 3350 cm^{-1}



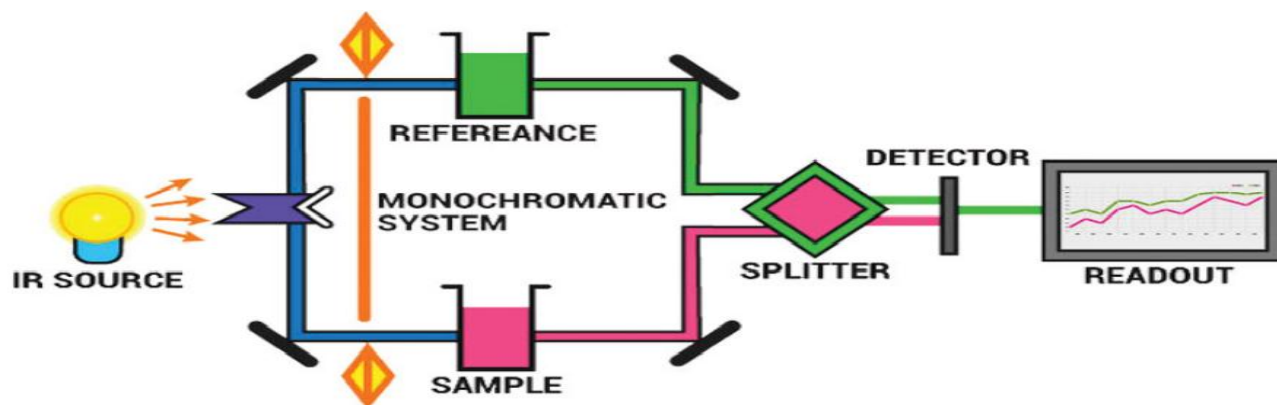
Effect of dilution:

Intermolecular H- bonds depends upon concentrations. On dilution, the intensities of intermolecular H-bonds decrease due to intervening solvent molecules and finally disappear. Intramolecular hydrogen bonds are independent of concentration. Thus, to distinguish intermolecular and intramolecular H-bonding, the spectra of are scanned at two different concentrations.

3.5.9 Instrumentation of IR Spectroscopy

The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference and the sample

respectively. Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.



The main parts of IR spectrometer are as follows:

- i) Radiation source
- ii) Sample cells and sampling of substances
- iii) Monochromators
- iv) Detectors
- v) Recorder

i) IR radiation sources

IR instruments require a source of radiant energy which emit IR radiation which must be steady, intense enough for detection and extend over the desired wavelength.

Various sources of IR radiations are as follows.

Nernst glower
Incandescent lamp
Mercury arc
Tungsten lamp
Glober source
Nichrome wire

ii) Sample cells and sampling of substances

IR spectroscopy has been used for the characterization of solid, liquid or gas samples.

- a) Solid – Various techniques are used for preparing solid samples such as pressed pellet technique, solid run in solution, solid films, mull technique etc.
- b) Liquid – Samples can be held using a liquid sample cell made of alkali halides. Aqueous solvents cannot be used as they will dissolve alkali halides. Only organic solvents like chloroform can be used.
- c) Gas– Sampling of gas is similar to the sampling of liquids.

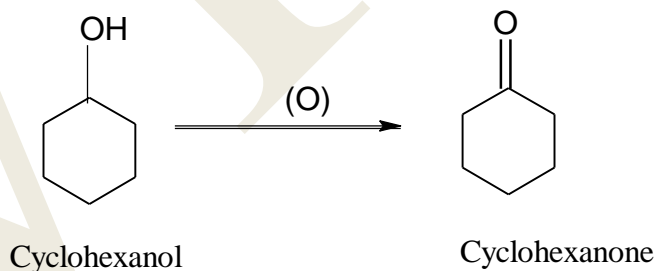
iii) Monochromators

Filters are made up of Lithium Fluoride and Diffraction gratings are made up of alkali halides.

Detectors like thermocouples, Bolometers, thermistors, Golay cell, and pyro-electric detectors are used.

Recorders are used to record the IR spectrum.

2) **Study of course of reaction(Kinetics of a chemical reaction):** A comparison between IR spectra of reactants and products can help to determine the course of a reaction



3) Hydrogen bonding: IR spectroscopy gives information regarding the hydrogen bonding. Bands due to hydrogen bonding appears at lower frequency

Aliphatic -OH hydrogen bonded 3350 cm⁻¹

4) Distinction between intermolecular and intra molecular hydrogen bonding

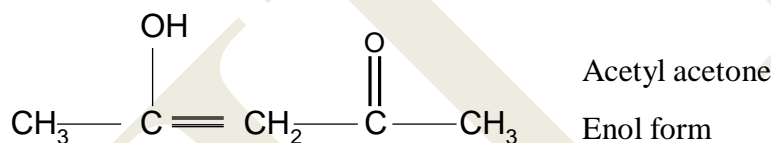
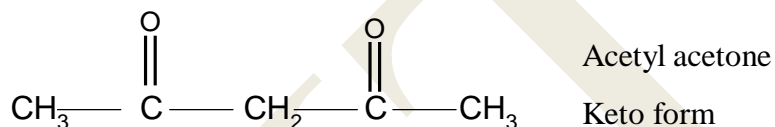
IR spectroscopy can also distinguish between intermolecular and intra molecular hydrogen bonding as in case of phenols, alcohols, salicylic acid etc.

This is done by taking series of IR spectra of a compound at different dilutions. As dilution increases the absorption band due to inter molecular hydrogen bonding disappears while that of intra molecular hydrogen bonding remain unchanged

5) Detection of impurities: IR spectra of impure sample will show extra absorption bands. By comparing with IR spectra of pure compound, presence of impurity can be detected. e.g. presence of cyclohexanone in cyclohexanol can be detected by presence of carbonyl absorption band.

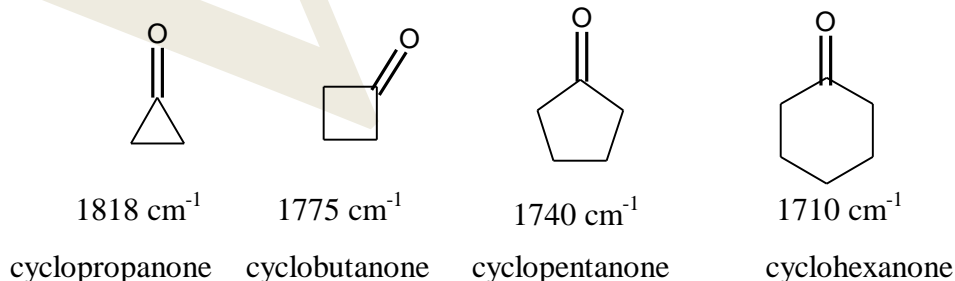
6) Study of isomerism:

Keto enol tautomerism can be studied by IR spectra. IR spectra shows characteristic absorption of carbonyl group along with a broad -O-H and C=C stretching frequencies for enol form



Geometrical isomers: Geometry and symmetry of molecule influences frequency and intensity of vibration

7) Determination of size of ring ketones: Ring strains in cyclic ketones shifts the carbonyl group stretching frequency to higher wavelength value. Angle strain in rings causes carbonyl group to have more electron density and stiffer bonds. This enables us to differentiate the ring ketones



Miscellaneous applications:

1) Identifying atmospheric pollution: quality and quantity of pollutants can be identified by IR spectroscopy. Water pollutants can be identified

- 2) Measurement of ethanol in breath can be detected easily by IR spectroscopy by device called as intoximeter
- 3) Measurements of paints and varnishes: Paints and varnishes are measured by reflectance method, where sample is irradiated by IR and reflected light is introduced into IR instrument. This technique is used to identify the paint on appliances or automobiles without destroying the surface. It can also be used in identifying and examining old paintings and artifacts. From this information, fake 'masterpieces' can be identified
- 4) In industry, IR is used to determine impurity in raw material to ensure good product

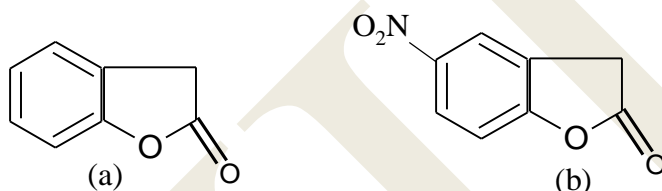
3.5.11 Important Infrared Absorption Frequencies

Sr.No.	Frequency Region cm^{-1}	Type of vibration	Functional group
1	3640-3610	O-H stretch, free hydroxyl	Alcohols, phenols
2	3500-3200	O-H stretch, H-bonded	Alcohols, phenols
3	3400-3250	N-H stretch	Primary, secondary amines, amides
4	3300-2500	O-H stretch	Carboxylic acids
5	3330-3270	$\text{-C}\equiv\text{C-H}$, C-H stretch	Alkynes (terminal)
6	3100-3000	C-H stretch	Aromatics
7	3100-3000	$=\text{C-H}$ stretch	Alkenes
8	3000-2850	C-H stretch	Alkanes
9	2830-2695	H-C=O, C-H stretch	Aldehydes
10	2260-2210	$\text{C}\equiv\text{N}$ stretch	Cyanides/nitriles
11	2260-2100	$\text{-C}\equiv\text{C-}$ stretch	Alkynes
12	1760-1665	C=O stretch	Carbonyls (general)
13	1760-1690	C=O stretch	Carboxylic acid
14	1750-1735	C=O stretch	Esters, saturated aliphatic
15	1740-1720	C=O stretch	Aldehydes, saturated, aliphatic
16	1730-1715	C=O stretch	α,β -unsaturated esters
17	1715	C=O stretch	Ketones, saturated aliphatic
18	1710-1665	C=O stretch	α,β -unsaturated aldehydes, ketones
19	1680-1640	-C=C- stretch	Alkenes
20	1650-1580	N-H bend	Primary amines
21	1600-1585	C-C stretch (in ring)	aromatic
22	1550-1475	N-O asymmetric stretch	Nitro compounds
23	1500-1400	C-C stretch (in ring)	Aromatic
24	1470-1450	C-H bend	Alkanes

25	1370-1350	C-H rock	Alkanes
26	1360-1290	N-O symmetric stretch	Nitro compound
27	1335-1250	C-N stretch	Aromatic amines
28	1320-1000	C-O stretch	Alcohols, carboxylic acids, esters, ethers
29	1300-1150	C-H wag(-CH ₂ X)	Alkyl halides
30	1250-1020	C-N stretch	Aliphatic amines
31	1000-650	=C-H bend	Alkenes
32	950-910	O-H bend	Carboxylic acids
33	910-665	N-H wag	Primary, secondary amines
34	900-675	C-H (out of plane)	Aromatic
35	850-550	C-Cl stretch	Alkyl halides
36	725-720	C-H rock	Alkanes
37	700-610	-C \equiv C-H:C-H bend	Alkynes
38	690-515	C-Br stretch	Alkyl halides

Illustrative examples:

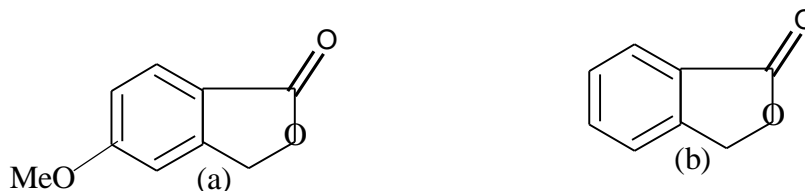
- 1) Which of the following will absorb at higher frequency? Justify.



(b) will absorb at higher frequency than (a)

In case of (b) electron withdrawing nitro group is present at para position with respect to ring oxygen atom. The electron pair on this ring oxygen atom is pulled towards the nitro group. The polarization of carbonyl group is thus inhibited. Therefore C=O has more double bond character. The bond length is consequently decreased in turn bond strength is increased increasing force constant, obviously raising absorption frequency. In case of (a), the ring oxygen is attached to phenyl ring. The phenyl ring has electron withdrawing effect to limited extent.

- 2) Which of the following will absorb at higher frequency? Justify.



(b) will absorb at higher frequency than (a)

In case of (a), the C=O group is in conjugation with aromatic ring having electron donating methoxy group at para position. The carbonyl group is easily polarized increasing C-O bond length, consequently bond strength is decreased. Hence force constant is decreased. Hence drop in absorption frequency.

3) How will you distinguish by using IR spectra

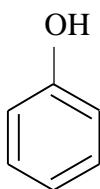
(a) $\text{CH}_3\text{CH}_2\text{OH}$

(b) $\text{CH}_3\text{CH}_2\text{CHO}$

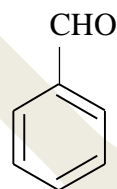
(a) Shows stretching frequency at $3640\text{--}3610\text{ cm}^{-1}$ due to O-H stretching

(b) Shows stretching frequency due to aldehyde in the region $1740\text{--}1720\text{ cm}^{-1}$. The presence of aldehyde is confirmed by occurrence of additional two bands at 2830 and 2695 cm^{-1} due to C-H stretching

4) How will you distinguish by using IR spectra



(a)



(b)

(a) Shows stretching frequency of O-H at $3500\text{--}3200\text{ cm}^{-1}$

(b) Shows carbonyl stretching frequency at $1710\text{--}1665\text{ cm}^{-1}$, additionally at $2830\text{--}2695\text{ cm}^{-1}$ for C-H stretch of aldehyde

5) Calculate approximate frequency of the C-H stretching from the following data $k=500\text{Nm}^{-1}$, Mass of carbon atom = 20×10^{-24} , Mass of hydrogen atom = 1.6×10^{-24}

According to Hook's law,

ω_{osc} = vibrational frequency or oscillation frequency.

$$\omega_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{in Hz}$$

k = frequency constant

μ = reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{where } m_1 \text{ and } m_2 \text{ are masses of atoms}$$

$$k = \text{frequency constant} = 500\text{Nm}^{-1} = 5 \times 10^5 \text{g/s}^2 \quad (1\text{N} = 10^3 \text{g/s}^2)$$

$$\omega_{\text{osc}} = \frac{1}{2 \times 3.14} \sqrt{\frac{(5 \times 10^5)(20 + 1.6)10^{-24}}{(20 \times 10^{-24})(1.6 \times 10^{-24})}}$$

$$\omega_{\text{osc}} = 9.3 \times 10^{13} \text{ Hz}$$

6) Calculate possible number of fundamental vibrations in CO₂, CH₄, NO, C₂H₆

Since CO₂ and NO are linear, fundamental modes of vibration = 3N-5

fundamental modes of vibration of CO₂ = 3x3-5=4

fundamental modes of vibration of NO = 3x2-5=1

CH₄, and C₂H₆ are non linear , fundamental modes of vibrations = 3N-6

fundamental modes of vibrations of CH₄ = 3x5-6 = 9

fundamental modes of vibrations of C₂H₆ = 3x8-6=18