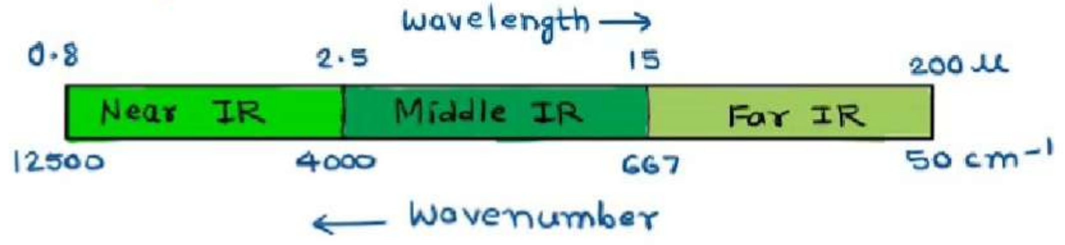
→ Infrared spectroscopy :→

- All the inorganic and organic compounds containing covalent bonds absorb electromagnetic radiations in the infrared region.
- Infrared spectroscopy gives information about molecular vibrations which is used to determine molecular structure.
- Infrared spectroscopy is simplest, most rapid and most reliable method for detecting functional groups. It can also provide information on structure, symmetry, purity, hydrogen bonding, structural and geometrical isomers.

→ Units and range of IR-radiations :→

- The position of an absorption in the IR spectrum is expressed in terms of wavenumber ($\bar{\nu}$), i.e. no. of waves per centimeter (cm^{-1}).
- This unit reflects directly the energy of radiation, i.e. higher the wavenumber higher the energy of absorption.
- The IR region of electromagnetic radiations is divided in three regions-



- The most important region for an organic chemistry is 2.5 μ to 15 μ (667 to 4000 cm^{-1}) in which molecular vibrations can be detected and measured in an infrared spectrum and in a Raman spectrum.

- Principle of IR spectroscopy :→

- Each molecule contains electronic, vibrational and rotational energy levels. Each electronic level is associated with set of vibrational levels having less energy separation and each Vibrational level is associated with set of rotational levels having less energy separation.

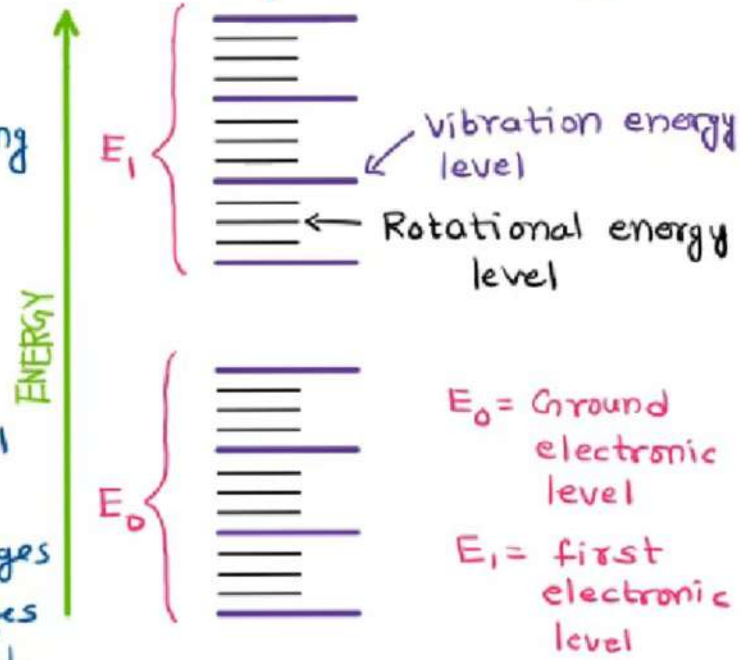
- when a molecule absorbs radiation, its energy increase in proportion to the energy of the photon absorbed according to the relation.

$$\boxed{E = h\nu = \frac{hc}{\lambda}}$$

here h = planck's constant
ν = frequency
c = Velocity of light
λ = wavelength of light

- The molecule may gain electronic, vibrational or rotational energy on absorption of radiation.

- Changes in electronic energy level involve larger quanta, changes in vibrational energylevel require smaller quanta and changes in rotation level require lesser quanta than vibrational level.



- The IR radiation has smaller energy and hence can not cause electronic transitions but can cause transitions b/w vibrational and rotational energy levels of molecule.
- The absorption in IR region occurs due to excitation of molecules from lower to higher vibrational level. since each vibrational level is associated with set of rotational levels, the IR spectra maybe considered as vibrational - rotational spectra.
- Each non rigid bond has a characterstics streching and bending frequency. At room temp, majority of molecule of a sample will be in the lowest vibrational level ($v=0$) i.e. ground state.
- on irradiation with IR radiation some of the molecule get excited from lowest to next higher vibrational energy level ($v=1$) i.e. first excited state.
- The characteristic frequency of vibration of the bond remains the same in the excited state but amplitude increases.
- Because of increased amplitude on oscillating, dipole moment is set up in molecule.
- This dipole moment interact with IR radiations and cause absorption of energy.
- In this process, only a specific frequency of IR radiation get absorbed. due to this molecule will show a specific number of peaks in the IR region.

→ Hooke's law – Calculation of vibrational frequencies or wavenumbers :→

- A spring set into simple harmonic motion obey Hooke's law which states that the restoring force (F) is proportional to degree of displacement (x) and acts in a direction opposite to that of displacement i.e

$$F \propto x$$

$$\text{or} \quad \boxed{F = Kx}$$

here K = proportionality constant and is called force constant of spring.

- Force constant is a measure of the strength of the spring or is a measure of the binding force b/w the atoms in case of bonds in a molecule.
- The frequency of stretching vibration of any bond can be calculated using Hooke's law, according to which

$$\boxed{\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}} \quad \text{—①}$$

here $\bar{\nu}$ = wavenumber (cm^{-1}) of the stretching vibrations

c = velocity of light = 3×10^{10} cm/s

K = Force constant (Bond strength) in dynes/cm

μ = Reduced mass = $\frac{M_1 M_2}{M_1 + M_2}$

- Here M_1 and M_2 are masses of atoms in grams forming the bond which undergoes vibration.
- If m_1 and m_2 are the atomic masses of the atoms forming the bond in amu and 6.02×10^{23} is the avogadro's number, then

1gm is equivalent to Avogadro No. 6.02×10^{23} AMU

$$M_1 = \frac{m_1}{6.02 \times 10^{23}}\,g \qquad \text{and} \qquad M_2 = \frac{m_2}{6.02 \times 10^{23}}\,g$$

Therefore $$\mu = \frac{m_1 m_2}{(m_1+m_2)(6.02\times10^{23})}$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

$$M_1 = m_1/2 \;\&\; M_2 = m_2/2$$

$$\mu = \frac{\frac{m_1}{2} \times \frac{m_2}{2}}{\frac{m_1}{2} + \frac{m_2}{2}} = \frac{\frac{m_1 m_2}{4}}{\frac{(m_1+m_2)}{2}} = \frac{m_1 m_2}{(m_1+m_2)2}$$

putting the value of μ in eq. ① we get

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\frac{m_1 m_2}{(m_1+m_2)(6.02\times10^{23})}}} \quad \text{or} \quad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K \times (6.02\times10^{23})}{\frac{m_1 m_2}{(m_1+m_2)}}}$$

or $$\bar{\nu} = \frac{7.76\times10^{11}}{2\pi c}\sqrt{\frac{K}{\mu}} \quad — ② \qquad \because \mu = \frac{m_1 m_2}{(m_1+m_2)}$$

on putting values of π and c in eq. ② we get

$$\bar{\nu} = \frac{7.76\times10^{11}\times7}{2\times22\times3\times10^{10}}\sqrt{\frac{K}{\mu}} \quad \text{or} \quad \boxed{\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}} \quad — ③$$

- The frequency (ν) can be calculated by the following eq.

we know that

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

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

Example:- Calculate the wave number and frequency of stretching vibration for A-B bond given atomic weight of A = 12 and B = 2 amu and force constant = 5×10^5 dyne/cm

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{12 \times 2}{12+2} = \frac{24}{14} = 1.714$$

Value of $K = 5 \times 10^5$ dyne/cm

on putting value of μ an K in Hooke's eq. ③

$$\bar{\nu} = 4.12 \sqrt{\frac{5 \times 10^5}{1.714}}$$

$$\bar{\nu} = 2225 \text{ cm}^{-1}$$

Frequency $\nu = \bar{\nu} c$

$$\nu = 2225 \times 3 \times 10^{10}$$

$$= 6.675 \times 10^{13} \text{ Hz}$$

→ Molecular vibrations – Types of fundamental Vibrations :→

- A molecule may be regarded as a non-rigid system of balls (atom) of different sizes joined together by a weightless springs (bond).
- When molecule absorbs infrared radiations, it shows two types of fundamental vibrations–

Ⓐ Stretching vibrations Ⓑ Bending vibrations.

Ⓐ Stretching vibrations :→

- Stretching is described as rhythmical movement of bonded atoms along the bond axis in such a manner that the interatomic distance increasing (stretching) or decreases (contraction).
- During stretching vibrations, the distance between two atoms increases or decreases but the atoms remain in the same bond axis.
- As more energy is required to stretch than to bend a spring, stretching vibrations require higher energy and occur at higher frequency.

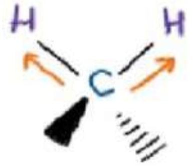
– Types of stretching vibrations :→

- They are of two types

(i) Symmetrical stretching vibrations (ii) Asymmetrical stretching vibrations

(i) symmetrical Stretching:→

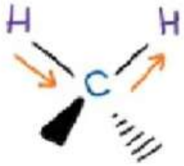
- In this stretching mode, both the atoms move in and out simultaneously. i.e. all the bonds are stretched or contracted simultaneously.
- It is denoted by ν_{sym}



Symmetric C-H stretching vibration ($-CH_2$ group)
(ν_{sym} C-H ; 2853 cm^{-1})

(ii) Asymmetrical stretching:→

- In this stretching mode, one atom moves in while other moves out. i.e. one bond is being stretched while the other one is being contracted.
- it is denoted by ν_{asym}
- Asymmetrical vibrations occurs at higher energy than symmetric vibrations and hence appear at higher wavenumber.



Asymmetric C-H stretching vibration ($-CH_2$ group)
(ν_{asym} C-H ; 2926 cm^{-1})

Ⓑ Bending vibrations (deformations):→

- In bending vibrations, the distance between the atoms remains constant but the position of the atoms changes relative to original bond axis.
- Bending vibrations require lower energy and occur at lower frequency than stretching vibrations.
- Types of bending vibrations:→

(i) In-plane bending vibrations (ii) out-of-plane bending vibrations

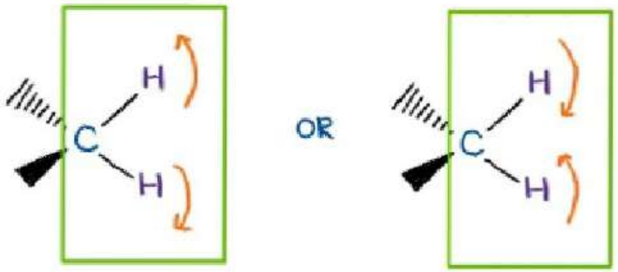
(i) In-plane bending vibrations:→

- In this bending mode, the atoms of the molecule remain in the same plane as the nodal plane of the system due to which it is called In-plane bending vibrations.

- They are of two types-

ⓐ In-plane scissoring deformation :→

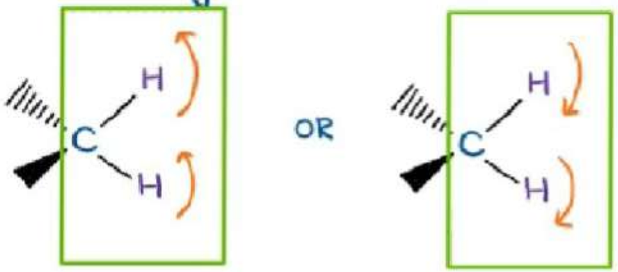
- In this mode, both the atoms move in opposite direction. i.e. the atoms move like the two blades of scissors.



Scissoring vibrations
(δ_{C-H} ; ~ 1450 cm^{-1})
($-CH_2$ group)

ⓑ In-plane rocking deformation :→

- In this mode, both the atoms move in the same direction. i.e both move simultaneously clockwise and then anticlockwise.

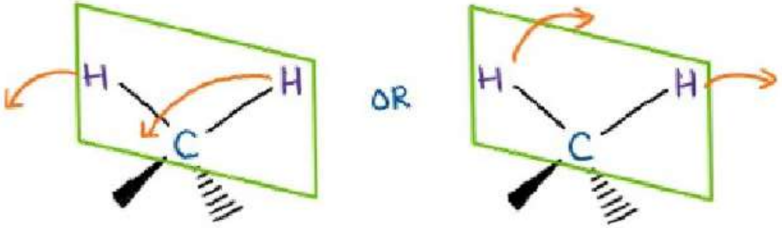


Rocking vibrations
(ρ_{C-H} ; ~720 cm^{-1})
($-CH_2$ group)

(ii) out-of-plane bending vibrations:→ when the atoms bend out of the nodal plane of the system, the bending mode is called out-of-plane bending.

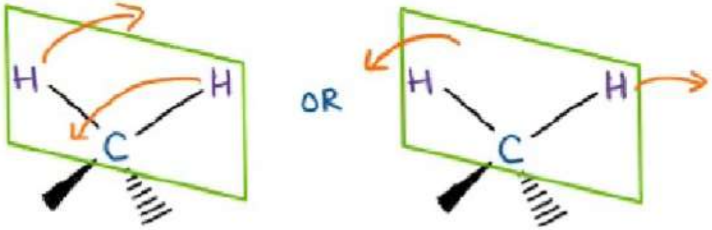
- They are of two types-

ⓐ out-of-plane wagging deformation:→ In this mode, both atoms move simultaneously up and down out of the plane of the molecule with respect to central atom.



Wagging ($\sim 1250\ cm^{-1}$)
($-CH_2$ group)

ⓑ out-of-plane twisting deformation:→ In this mode, one atom move up and the other moves down relative to the plane of the molecule with respect to central atom.



Twisting ($\sim 1250\ cm^{-1}$)
($-CH_2$ group)

→ Selection Rule :→

- The selection rules determine whether a particular vibration would be infrared active or not.
- In general, all those transitions which are non-centrosymmtric (does not contain centre of symmtry) are IR active because only during such transitions (vibrations) there will be a change in the dipole moment and absorption of energy in IR region will take place.
- During the absorption of energy the molecule can change its 'v' value (vibrational quantum number) and its 'J' value (rotational quantum number)
- For IR spectroscopy

  $\Delta v = \pm 1$ and

  $\Delta J = \pm 1$ i.e. only those transitions will be IR active for which both Δv and ΔJ are equal to ± 1

→ Mutual Exclusion Principle : →

- This rule determine weather a particular vibration would be IR active or Raman active.
- IR and Raman spectra tend to be complementary because of their different selection rules for activity.
- In IR spectroscopy, the energy absorption occurs due to interaction between the radiation and dipole moment change of the molecule.
- In Raman spectroscopy, the enegy absorption occurs due to interaction between the radiation and polarizability of the molecule.
- According to this rule —

For all molecules with a centre of symmetry, all vibrations are centrosymmetric (i.e. symmtrical about the centre of symmetry of the molecule) are Raman active but IR inactive and those vibrations with are not centrosymmetric are raman inactive but IR active.

→ Position of Absorption bands :→

- According to Hooke's law, the frequency of a stretching vibration i.e. the position of absorption band is depend on two factors -

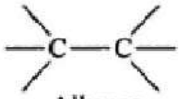
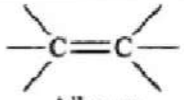
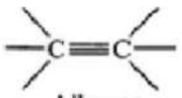
① Force constant, i.e., strength of a bond.

② Reduced mass, i.e. masses of the atom forming the bond.

① Force constant - Strength of a bond :→

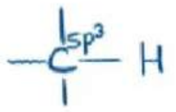
strength of a bond $\propto$ stretching frequency

- The force constant for single, double and triple bond are -

Hydrocarbon series	Force constant (dynes/cm)	Bond order	Bond length (pm)	Stretching frequency (cm^{-1})
 Alkanes	5×10^5	1	154	1300–800
 Alkenes	10×10^5	2	133	1700–1600
 Alkynes	15×10^5	3	120	2300–2100

- Further hybridisation also affects the force constant (k) of bond or strength of bond.

bond strength	$sp^3 < sp^2 < sp$
s - character	25% 33·3% 50%
Electronegativity	$sp^3 < sp^2 < sp$



$-\overset{|}{\underset{|}{C}}\overset{sp^3}{-}H$

2960 - 2870 cm^{-1}

$=\overset{|}{C}\overset{sp^2}{-}H$

3080 cm^{-1}

$\equiv\overset{sp}{C}-H$

3300 cm^{-1}

② Reduced masses of the bonded atoms :→

$$\text{Reduced mass of the system} \propto \frac{1}{\text{stretching frequency}}$$

- i.e. bond between atom of lower masses will vibrate at higher frequency than the bonds having heavier atoms.
- This effect is highly significat when one of the atoms forming single bond is hydrogen atom such as C-H , O-H, N-H etc.

Example :-

C - H bond
3032 cm^{-1}

C - D bond
2225 cm^{-1}

- In such cases bond strength is same but mass of D is more than H.

- For prediction of actual treds, both force constant and reduced mass must be considered together.

$$\begin{array}{ccccccc} C-H & < & N-H & < & O-H & < & F-H \\ 3032\,cm^{-1} & & 3300\,cm^{-1} & & 3570\,cm^{-1} & & 4138\,cm^{-1} \end{array}$$

- There is one more factor i.e. type of molecular vibration which affect the position of absorption bands in the IR spectrum.
- $\bar{\nu}_{stretching} > \bar{\nu}_{bending}$
- $\bar{\nu}_{assy} > \bar{\nu}_{sym}$

Example:- for $-CH_2-$ group.

- symmetric stretching $2853\ cm^{-1}$
- Asymmetric stretching $2962\ cm^{-1}$

- different bending vibrations of $-CH_2-$ group occurs at different positions.

$\bar{\nu}_{scissoring} = 1450\ cm^{-}$ $\bar{\nu}_{wagging} = \bar{\nu}_{twisting} = 1250\ cm^{-1}$

$\bar{\nu}_{rocking} = 720\ cm^{-1}$

-Factors affecting vibrational frequencies :→

- The calculated vibrational frequency of an absorption band using Hooke's law is always not equal to experimental value. This variation is due to following factors -

① Electronic effect ② Hydrogen bonding

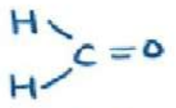
① Electronic effect :→

- Both inductive effect and resonance effect work together to affect C=O & C=C stretching frequencies.
- Somtimes I effect is more than R effect and vice versa.
- The absorption band is shifted to higher or lower frequency depending upon the fact whether the force constant is decreased or increased by such electronic factors.

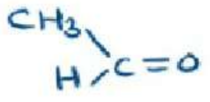
Case I - Inductive effect :→

(1) The C=O bond lenth increases with increase in number of electron - donating alkyl groups (due to +I effect) and hence the absorption shifts to lower wave number.

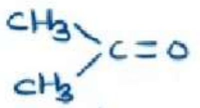
e.g.



Foraldehyde
1740 cm^{-1}



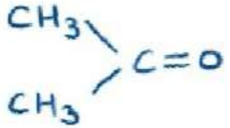
Acetaldehyde
1725 cm^{-1}



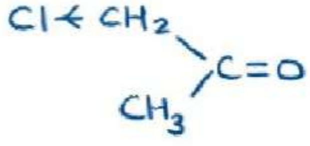
Acetone
1715 cm^{-1}

(ii) The C=O bond lenth decrease with increase in number of electron-withdrawing groups (due to −I effect) and hence the absorption shifts to higher wave number.

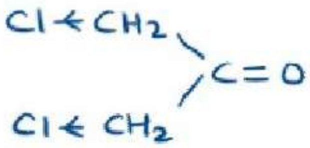
e.g.



Acetone
1715 cm^{-1}



chloroacetone
1725 cm^{-1}

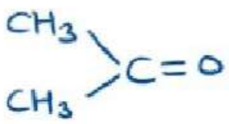


dichloroacetone
1740 cm^{-1}

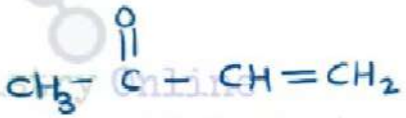
Case-II- Resonance effect:-

As the force constant decreases with an increase in the conjugation (R-effect) hence absorption shifts to lower wavenumber by approx. 25-45 cm^{-1}

e.g.

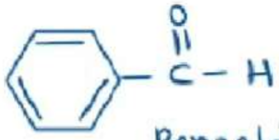


Acetone
1715 cm^{-1}

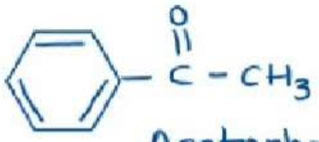


$CH_3-\overset{O}{\overset{\|}{C}}-CH=CH_2$

Methyl vinyl ketone
1690 cm^{-1}



Benzaldehyde
1700 cm^{-1}



Acetophenone
1690 cm^{-1}

② Hydrogen bonding :→

- In IR spectra of alcohols, phenols, carboxylic acids and amines, the absorption band due to O–H and N–H stretching vibrations are shifted to lower wavenumber.
- This is due to H-bonding because the H-bonding increases the bond length thereby decreasing the force constant.
- Some important generalisations about the effect of H-bonding on IR-spectra are–

(i) stronger the H-bond, larger is the downward shift in absorption frequency.

(ii) Broader bands indicate intermolecular H-bonding while sharp and well defined bands indicate intramolecular H-bonding.

(iii) Intermolecular H-bonding causes more downward shift than intramolecular H-bonding

(iv) For Intermolecular H-bonding, ~~the~~ intensity is conc^n dependent which decreas on dilution, but the intensity of intramolecular H-bonding is conc^n independent i.e. remain uneffected on dilution.

Example – In very dilute solution carboxylic acid exist as monomer (no H-bonding)

free $C=O$ group = 1760 cm^{-1} free $O-H$ group = 3600 cm^{-1}

– In conc^n sol. or solid stata Carboxylic acid exis as dimer (H-bonding)

$C=O$ group = 1710 cm^{-1} $O-H$ group 3400-2500 cm^{-1}

→ Intensity of Absorption band :→

- The intensity of absorption band in the IR-spectroscopy is not measured with the same accuracy as in UV-spectroscopy.
- In the case of IR-spectroscopy, it is usually sufficient to know that a band is strong, weak or of variable intensity.
- For this purpose the most intense peak is assigned a relative intesity of 100%. (base peak) while the intensity of other peaks is assigned as

Very strong (intesity of 80% of that of the base peak)
Strong (80% – 60%)
medium (60 – 50%)
Weak (50-30%)
Very weak (<30%)

– Factors affecting intensity of peaks (absorption bands):-

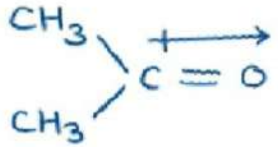
① Magnitude of change in dipole moment :→

- The intensity of any fundamental absorption depends upon the difference between the dipole moment of the molecule in the ground state and the vibrationally excited state.

change in dipole moment ∝ intensity of peak

- If there is no change in dipole moment during a vibration, then it will be IR inactive.

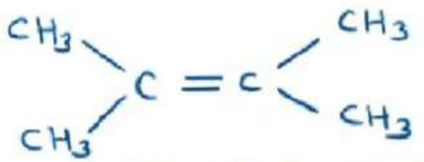
Example :-



Acetone

($\mu > 0$)

1715 cm-1



2,3-Dimethyl-2-butene

($\mu = 0$)

(No IR absorption for C=C stretching)

- C=O stretching produces a substantial change in dipole moment than C=C stretching. Due to this intensity of C=O stretching is always much higher than that of C=C stretching and hence the band of C=O stretching is strong.

② concentration of the sample:→

Larger the no. of absorbing molecule in sample ∝ Intensity of absorption band.

③ Number of absorbing group in a molecule:→

Larger the no. of absorbing groups in a molecule ∝ Intensity of absorption band.

e.g. Nonane (C_9H_{20}) has large no. of C-H bonds than butane (C_4H_{10}). So it will show a stronger absorption band for C-H stretching.

④ Fermi resonance :→

- When a fundamental absorption undergoes Fermi resonance with an overtone, the intensity of the fundamental peak is decreases while that of the overtone increases.

✱ some important terms:→

ⓐ **overtone :→** An overtone is the simple multiple of a given fundamental frequency or wavenumer which appears at twice, three times etc. of the wavenumber.

e.g.

fundumental vibration for C=O streching = 1700 cm^{-1}

first overtone will appear at = 3400 cm^{-1} (twice times)

ⓑ Fermi resonance :→

- Fermi resonance is the mechanical coupling b/w fundamental and overtone or combination bands.

ⓒ Combination band :→

- Those absorption bands, which appears as sum of the wavenumbers of two fundamental vibrations are called combination band. $\bar{\nu}_{comb} = \bar{\nu}_1 + \bar{\nu}_2$

ⓓ difference band :→

- Those absorption bands which appears as difference of the wavenumbers of two fundamental vibration are called diffence band. $\bar{\nu}_{diff} = \bar{\nu}_1 - \bar{\nu}_2$

→ Regions of IR spectrum:→

- The entire IR spectrum can be divided into the following two regions -

① Group frequency region ② Fingerprint region

① Group frequency region or Functional group region:→

- The region of the IR spectrum from 4000 - 1400 cm^{-1} exhibits absorption bands assignable to almost all function groups and hence it is called group frequency region or functional group region.
- This part of the IR spectrum mostly contains absorption due to stretching vibration and is more useful diagnostically.

② Fingerprint region :→

- This region of IR spectrum extends from 1400-900 cm^{-1} and contains many combination and difference bands apart from some fundamental stretching and bending vibrations.
- It is very difficult to analyse all the bands appearing in this region but a peak by peak comparision of the IR spectra of two different compounds is an excellent tool to establish their identity. That is why this region is called as finger print region.

- Identity of IR spectra of two compounds is much more characteristics than comparision of their physical parameters.
- Different compounds having the same functional group absorb similarly in the functional group region (above 1400 cm^{-1}) but there will be significant difference in their absorption pattern in the fingerprint region.
- It is not possible to interpret each and every band in the IR spectra. But for indentifying the functional group using IR spectra the Knowlege of the regions of absorption bands due to various functional groups is necessary.
- The characteristic frequencies of various functional groups are given in table.

Type of vibration	Class of compound	Range of absorption		Intensity
		nm	cm^{-1}	
C—H (*stretch*)	(*a*) Alkanes	3.38–3.51	2962–2853	*s*
	(*b*) Alkenes	3.22–3.32	3100–3010	*s*
	(*c*) Aromatics	3.17–3.27	3150–3050	*s*
	(*d*) Alkynes	3.03 approx.	3300 approx.	*s*
	(*e*) Aldehydes	3.45–3.55	2900–2820	*w*
	(*two bands*)	3.60–3.70	2775–2720	*w*
C═C (*stretch*)	(*a*) Alkenes	5.59–6.25	1680–1600	*m*, *w*
	(*b*) Aromatics	6.25–6.90	1600–1450	*m*, *w*
C≡C (*stretch*)	Alkynes	4.42–4.76	2260–2100	*s*
C═O (*stretch*)	(*a*) Aldehydes	5.75–5.81	1740–1720	*s*
	(*b*) Ketones	5.90–5.86	1725–1705	s
	(*c*) Carboxylic Acids	5.90–5.88	1725–1700	*s*
	(*d*) Esters	5.71–5.78	1750–1730	*s*
	(*e*) Amides	5.95–6.13	1680–1630	
	(*f*) Anhydrides	5.40–5.55	1850–1800	*s*
	(*two bands*)	5.58–5.74	1790–1740	*s*
	(*g*) Acid chlorides	~5.57	~1795	*s*

O—H (*stretch*)	Alcohols, phenols (*dilute solutions*)	2.74–2.78	3650–3590	sharp (‘*free*’ OH)
	Alcohols, phenols (*hydrogen bonded*)	2.81–3.12	3550–3200	broad, *s* (*bonded* OH)
	Carboxylic acids (*Several weak bands in dilute solution*)		2700–2500	
N—H (*stretch*)	1° Amines, amides (*free, two bands*)	~2.86	~3300	*m*
	1° Amines, amides (*hydrogen bonded, two bands*)	~2.94	~3400	*m*
	2° Amines, amides (*free, one band*)	3.80–4.02	3500–3310	*m*
	2° Amines (hydrogen bonded, one band), Amides (Several bands)	3.0–3.20	3320–4140	*m*
C≡N (stretch)	Nitriles	4.42–4.46	2260–2220	*m*
Nitro (N—O) (stretch)	Two bands			
	(*a*) Asymmetric	6.37–6.67	1570–1500	*s*
	(*b*) Symmetric	7.30–7.70	1370–1300	*s*

→ Characteristic absorption of various functional groups :→

① Alkanes :-

- Alkanes show most characteristic absorption due to C-H stretching and bending vibrations as discussed below-

(i) C-H stretching vibrations :→

ⓐ $-CH_3$ group (1° carbon atom) → Two bands

$$\nu_{asym} = 2962 \text{ cm}^{-1}$$

$$\nu_{sym} = 2872 \text{ cm}^{-1}$$

ⓑ $>CH_2$ group (2° carbon atom) → Two bands

$$\nu_{asym} = 2926 \text{ cm}^{-1}$$

$$\nu_{sym} = 2853 \text{ cm}^{-1}$$

ⓒ $\rightarrow CH$ group (3° Carbon atom) → one weak band = 2890 - 2850 cm^{-1}

(ii) C-H in-plane bending vibration :→

- CH_3 shows two bands $\nu_{asym} = 1375\ cm^{-1}$

  $\nu_{sym} = 1450\ cm^{-1}$

> CH_2 shows medium band in 1480-1460 cm^{-1}

② Cycloalkanes :→

- The IR spectrum of cycloalkanes are almost similar to those of alkanes. They also show C-H stretching and C-H bending vibrations.

(i) C-H Stretching vibrations :→

- The band due to $-CH_2-$ group lie in the same region as that of alkanes.
- In case of strained cycloalkanes such as cyclopropane the band appears in the range 3100 to 2940 cm^{-1} region.

(ii) C-H in-plane bending vibrations :→

- for $-CH_2-$, scissoring appears in 1470-1440 cm^{-1}

(iii) C-C stretching vibrations :→

- C-C stretching vibration appears as weak bands in 1200 to 800 cm^{-1} region and hence has no significant diagnostic value.

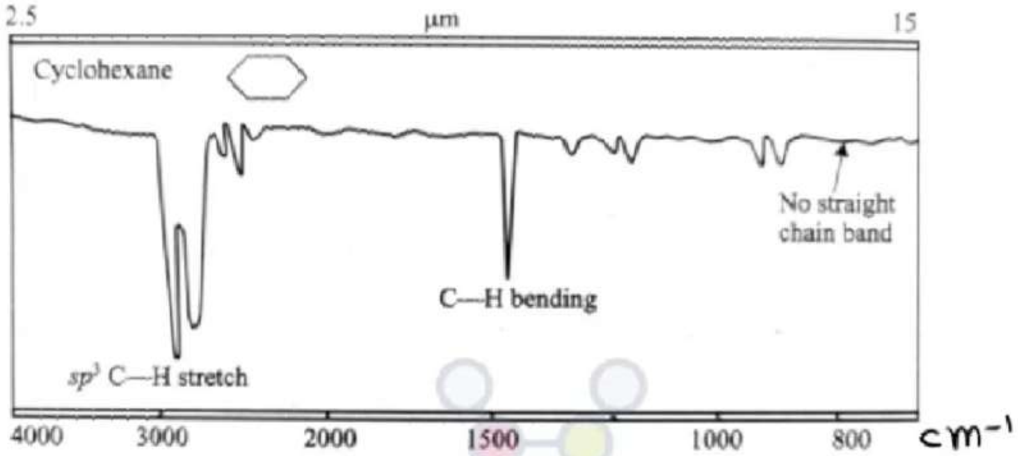


fig:- IR spectrum of cyclohexane

③ Alkenes:→

(i) C=C stretching vibrations:→

- C=C stretching vibrations appears in 1680-1620 cm⁻¹ region.
- The position of band depends on the extent of substitution.
- conjugation lowers the frequency, with increase in intensity.
- The absorption due to $\nu_{C=C}$ becomes inactive in symmetrical trans and tetrasubstitued alkenes (symmetrically substituted)

(ii) =C-H stretching vibrations:→

- Appears in the range of 3095 - 3070 cm⁻¹

(iii) In-plane C-H bending vibration :→

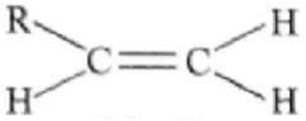
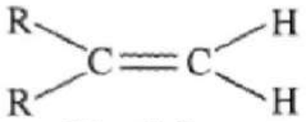
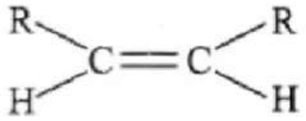
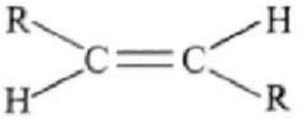
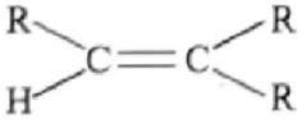
$=CH_2$ scissoring near 1420 cm^{-1}

$=CH_2$ rocking near 1075 cm^{-1}

- A weak band near 1300 cm^{-1} may be due to C-H rocking vibration of vinyl, trans and trisubstitued double bonds.

(iv) Out-of-plane C-H bending vibration :→

- Wagging vibration occurs in the range 1000-680 cm^{-1}
- The exact position of the bands depends upon the substitution pattern of the double bond and its configuration across double bond.
- The position of different types of alkenes (olefins) are given in table:-

Types of olefins	Modes of vibration	Position (cm^{-1}) and intensity of band
 Vinyl	*trans*-CH wagging CH_2 wagging (*Two bands*)	1000–985 (*s*) 920–905 (*s*)
 Vinylidine	CH_2 wagging	900–880 (*s*)
 *cis*-Disubstituted	*cis*-CH wagging	975–960 (*m*)
 *trans*-Disubstituted	*trans*-CH wagging	~690(*s*)
 *Tri*-substituted	CH wagging	870–790 (*s-m*)

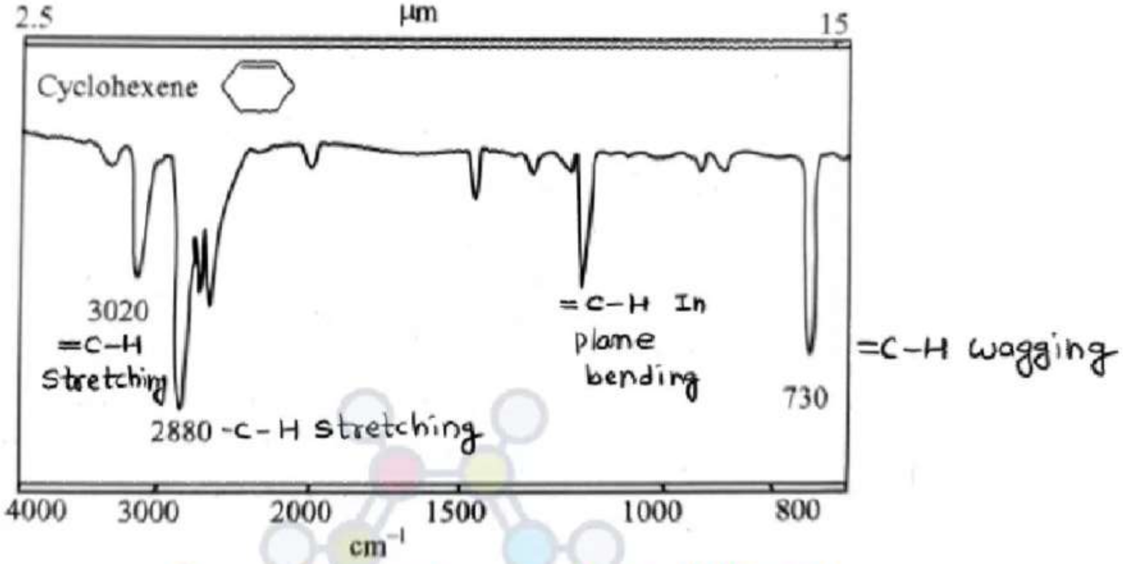


fig:- IR spectrum of cyclohexene

④ Alkynes:→

(i) C-H stretching:→

- Appears at near 3300 cm^{-1}

- The sharpness of this band prevents its confusion with other absorption in this region (e.g. N-H, O-H and C=O overtones)

(ii) ≡C-H out-of-plane bending:→

- Appears as a strong and broad band near 680-610 cm^{-1}

(iii) C≡C stretching:→

- simple alkyens = 2250-2150 cm^{-1} Terminal alkynes = 2140-2100 cm^{-1}

- Non terminal alkynes shows near 2260 - 2190 cm^{-1}
- This absorption may be completely absent in the spectra of acetylene and symmetrical alkynes.
- The IR spectrum of 1-hexyne is shown in fig.

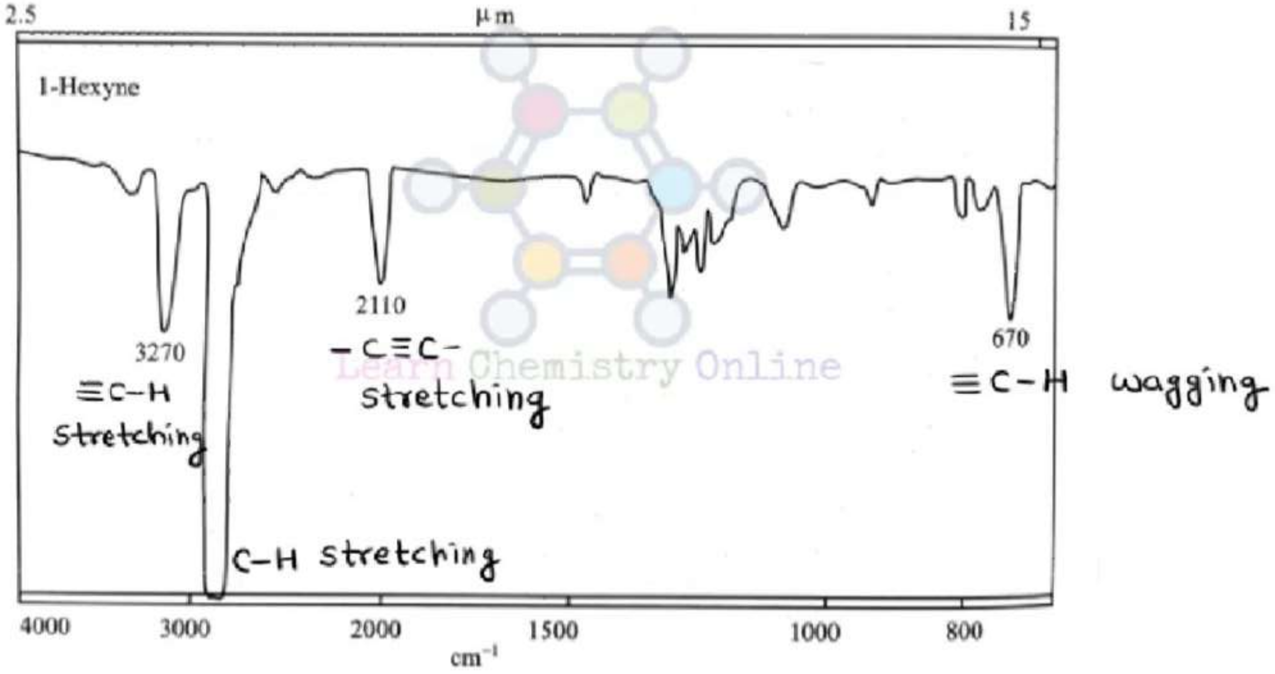


fig:- IR spectrum of 1-hexyne

→ characteristic Absorption of various functional groups :→

① Aromatic compounds :→

- Aromatic compounds show the following five modes of vibrations :-

(i) Aromatic C–H stretching vibrations :→

- Aromatic hydrocarbons show a weak absorption band in the 3040 - 3010 cm^{-1} region.

(ii) C=C stretching vibrations :→

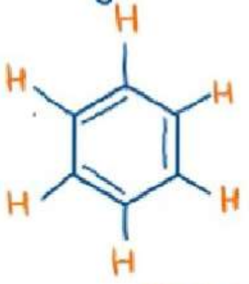
- Four characteristic bands due to C=C stretching vibrations are expected in 1600 to 1450 cm^{-1} region.
- The position of these bands are 1600 cm^{-1}, 1580 cm^{-1} (as a shoulder on 1600 cm^{-1} band) 1500 cm^{-1} and 1450 cm^{-1}.
- Two of three bands are sufficient enough to establish that the given compound is aromatic.
- Absence of these four peaks indicates that the compound is not aromatic.

(iii) In-plane C–H bending vibrations :→

- These vibrations occurs in 1300–1000 cm^{-1} region with medium- weak intensity.
- These vibrations are rare useful because they overlap with stronger absorptions occurs in this region (C–C stretching vibrations).

(iv) out-of-plane C-H bending vibrations :-

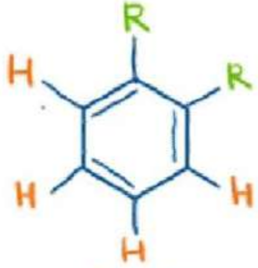
- These vibrations are occur in the region 900-690 cm^{-1}.
- These bands are quite useful in determining the substitution pattern.
- The number and position of these bands due to C-H out-of-plane bending vibrations alongwith the assignment of substitution pattern are illustrated below-


671 cm^{-1} (six adjacent hydrogens)

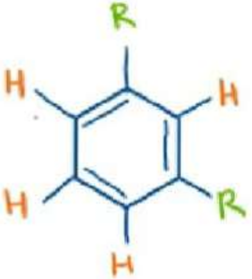
Benzene


770-730 cm^{-1} (five adjacent hydrogens)

monosubstitued benzene


770 - 735 cm^{-1} (Four adjacent hydrogens)

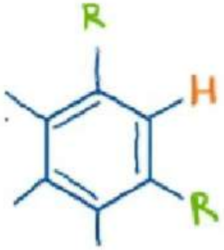
o - disubstitued benzene


795-770 cm^{-1} (Three adjacent hydrogens)

- m-disubstituted benzene
- Vicinal trisubstituted benzene


850 - 795 cm^{-1} (Two adjacent hydrogens)

- p-disubstituted benzene
- unsymmtrical tri, symmtric-tetra, unsymmtrical-tetra and pentasubstitued benzene


890 - 835 cm^{-1} (lone Hydrogen)

(V) Overtones and combination bands:→

- Many weak overtone and combination bands appears between 2000 – 1667 cm^{-1}!
- The relative number and shape of these bands are useful in knowing the substitution pattern on the rings.

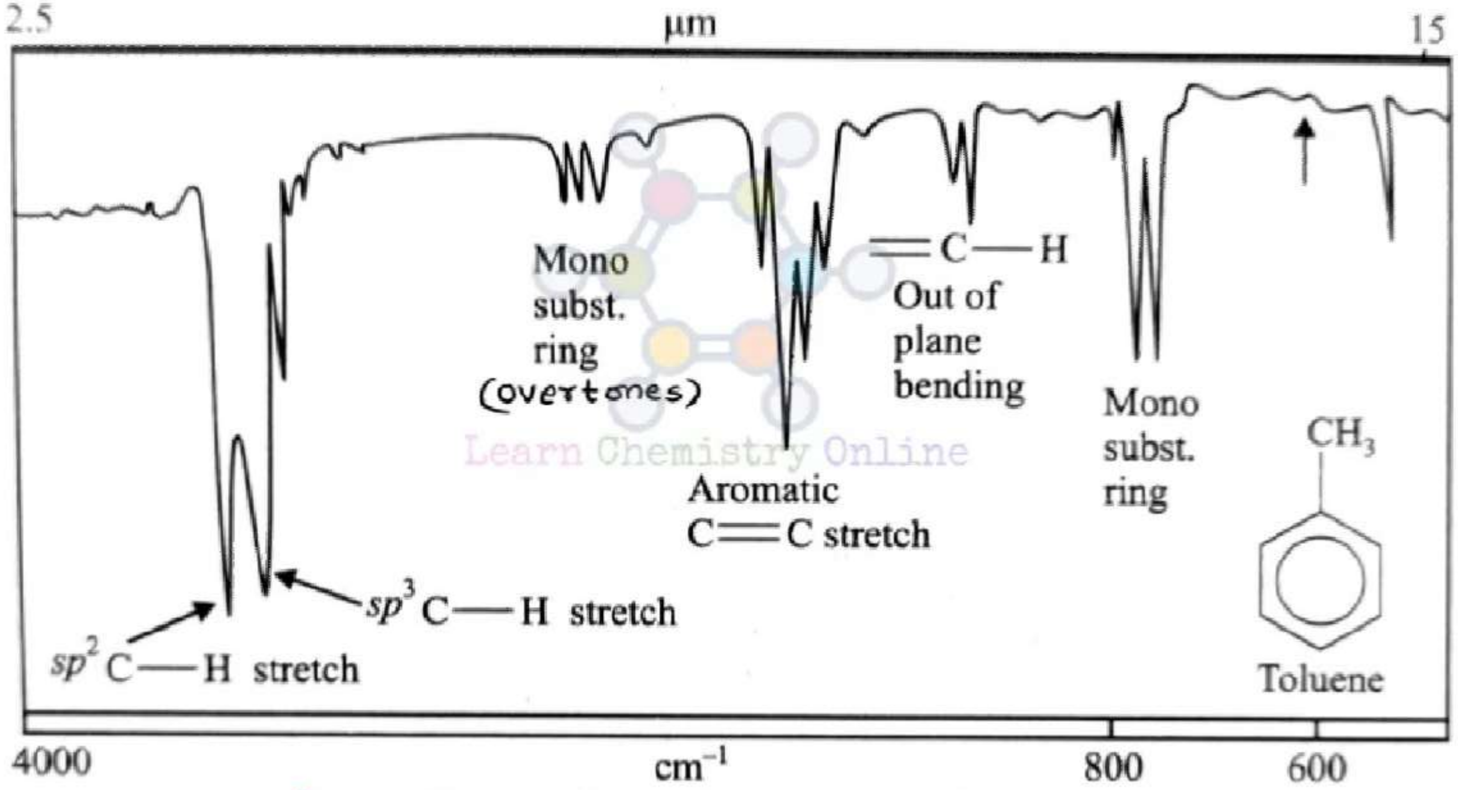


fig:- IR spectra of Toluene in KBr pellet.

→ Characteristics absorption of various functional groups:→

① Alcohols and phenols:→

- The IR spectra of alcohols and phenols show the following characteristic absorptions due to different modes of vibrations of O-H and C-O bonds:

ⓐ O-H stretching vibrations:→

- These compounds show a strong and broad absorption band in the 3400-3300 cm^{-1} region.
- The position of this band depends upon the extent of hydrogen bonding.

$$\text{Extent of H-bonding} \propto \frac{1}{\text{wavenumber}}$$

for alcohols and phenol free O-H group = 3650-3600 cm^{-1}

for intermolecular H-bonded O-H group = 3400-3200 cm^{-1}

ⓑ In-plane O-H bending vibrations:→

- These vibrations appear in the region of 1420-1260 cm^{-1}
- This band is, however, not very useful since it overlaps with the C-H bending vibration of the methyl group (1375 cm^{-1})

ⓒ out-of-plane bending vibrations:→

- These vibrations appears in 770-650 cm^{-1} region.

ⓓ C-O stretching vibrations:→

- These vibrations appears in 1260-1000 cm^{-1} region.
- This band is used to differentiate 1°, 2°, 3° alcohols and phenols.

1° alcohols = 1050 cm^{-1}
2° alcohols = 1100 cm^{-1}
3° alcohols = 1150 cm^{-1}
Phenols = 1220 cm^{-1}

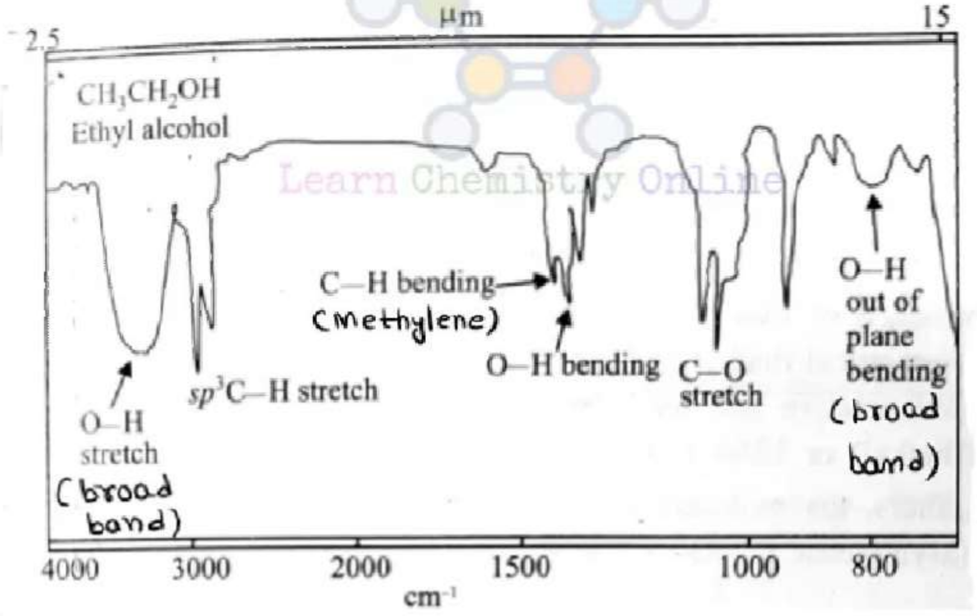


fig:- IR spectrum of Ethylalcohol

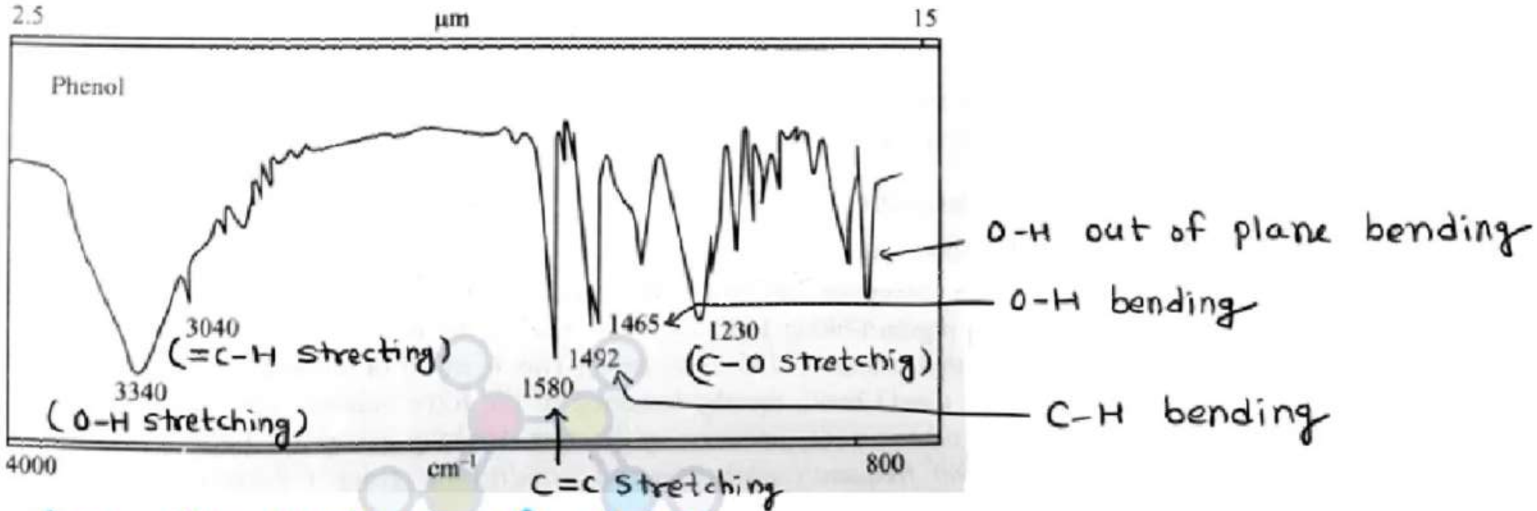


fig:- IR spectrum of phenol

) Ethers :→

- The most important bands due to strong C-O-C stretching absorption are found in the IR spectra of ethers in the range 1300-1000 cm^{-1}.

The band in this region is also observed for other oxy compounds such as alcohols, aldehydes, ketones, carboxylic acid. Therefore, the presence of ether is confirmed only if the oxy-compounds show no absorption band in the hydroxy (3650-3200 cm^{-1}) or carbony region (1870-1650 cm^{-1}) region.

Antisymmetric C–O–C stretching in dialkyl ether = 1130-1050 cm^{-1}
Antisymmetric C–O–C stretching in diaryl ether = 1250-1150 cm^{-1}
symmetrical stretching is infrared inactive (non polar)
In alkyl aryl ether → Asymmetric appears at = 1270-1230 cm^{-1}
symmetric appears at = 1120-1030 cm^{-1}

③ Ketones:→

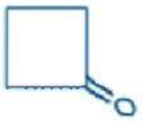
- Ketones show following absorptions-

ⓐ C=O stretching:→

- Generally appears as a strong band in the region 1730-1645 cm^{-1}
- unconjugated acyclic dialkyl ketone absorbs at ~1720 cm^{-1}.
- conjugation of C=O group with an arylgroup or α,β-double bond shits the C=O stretching to lower frequency by about 20-30 cm^{-1}!
- For cycloalkanones, C=O stretching band shift to higher frequency with decrease in the ring size. This is due to increase in angle strain which in turn increases the s-character of the C=O bond.

1715 cm^{-1}

1745 cm^{-1}



1780 cm^{-1}

1815 cm^{-1}

ⓑ Ketones show weak absorption in the region 1300 - 1100 cm^{-1} due to $C-\underset{\overset{\|}{O}}{C}-C$ stretching and bending vibrations which may consist of multiple bonds.

④ Aldehydes:-

ⓐ C=O stretching:→

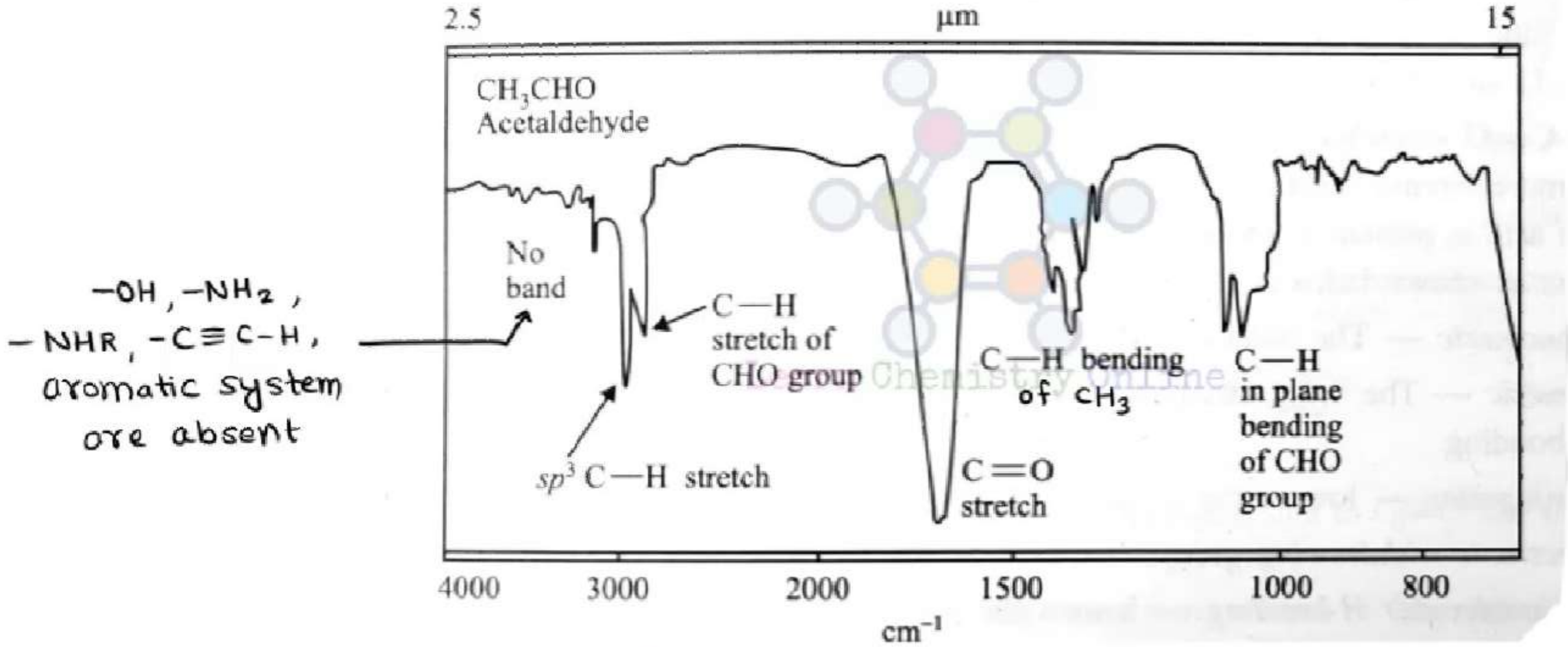
- Generally appears as a strong band in the region 1740 - 1690 cm^{-1}.
- The presence of +I group shifts the absorption to lower frequency while -I group shift the band to higher frequency.

ⓑ C-H stretching and in-plane C-H bending vibrations:→

- Generally appears as weak intensity doublet in the region 2860 - 2800 cm^{-1} and 2760 - 2700 cm^{-1}.
- The band 2760-2700 cm^{-1} is more reliable as the band near 2860 - 2800 cm^{-1} overlaps with the band due to C-H stretching. The double is due to fermi resonance.

ⓒ C-H out-of-plane bending :->

- Band appears as weak band in the region from 975-780 cm⁻¹!



$-OH$, $-NH_2$, $-NHR$, $-C\equiv C-H$, aromatic system are absent

fig:- IR spectrum of Acetaldehyde

→ Characteristic absorption of various functional groups:→

① Carboxylic acids:→

- These compounds show following characteristic absorption frequencies-

ⓐ O-H stretching vibration:→

- As alcohols, carboxylic acid also exhibit hydrogen bonding and occurs as dimer.
- In vapour phase (free -OH) = 3520 cm^{-1} (sharp, medium or weak band)
- In condensed phase (solid or pure liquid phase) =
  - → hydrogen bonded -OH = 3400 - 2400 cm^{-1}
  - → This band overlaps the C-H stretching bands (3100-2800cm^{-1}) and shows distinctive shoulders b/w 2600 - 2500 cm^{-1} region.
  - → These distinctive shoulders are observed in carboxylic acid dimer and are due to overtones and coupling between O-H bending and C-O stretching.

ⓑ -C=O stretching vibrations:→

- These vibrations appear as a broad and more intense than that of aldehyde and ketones.

- Position of band is depend on the following factors.

(i) Monomeric → 1760 cm^{-1}

(ii) Dimeric → 1720 - 1700 cm^{-1} (lower frequency due to H- bonding)

(iii) Conjugation → 1710 - 1680 cm^{-1}

(iv) -I group → increase the frequency by 20-30 cm^{-1}

(v) Intra molecular H-bond → lower the frequency

(vi) Halogenation at α - carbon increases the absorption frequency.

Ⓒ In-plane O-H bending and C-O stretching vibrations:→

- Monomeric
  O-H bending = 1380 - 1280 cm^{-1}
  C-O stretching = 1180 - 1082 cm^{-1}

- Dimer
  O-H bending = 1420 cm^{-1} (weak band)
  C-O stretching = 1300 cm^{-1} (Intense band)

ⓓ out-of-plane O-H bending vibrations:→

- bonded -OH group of dimer = 930 cm^{-1}

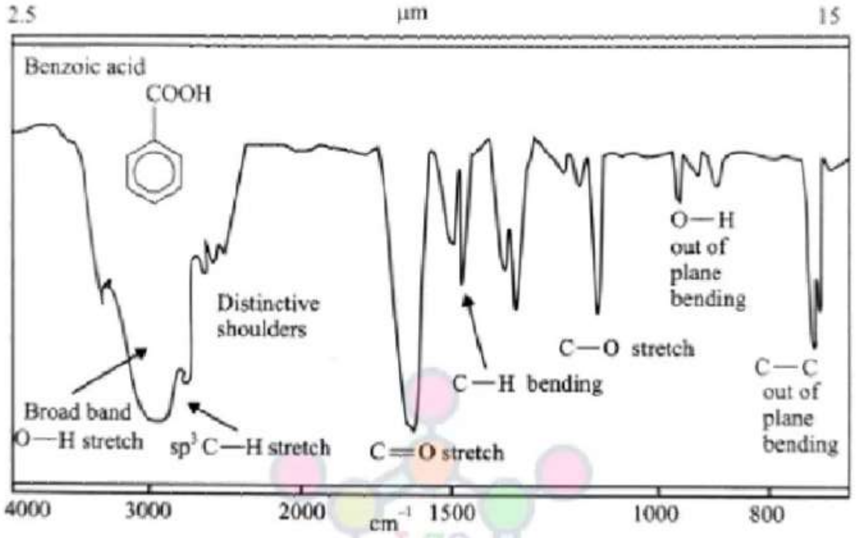


fig:- IR spectrum of benzoic acid

② Esters:→

- Esters are characterised by appearance of strong absorption bands due to C=O and C—O stretching vibrations.

ⓐ C=O stretching vibrations:→

- unconjugated esters show a band in the range 1750-1735 cm^{-1} (higher than ketone and aldehyde).
- This is due to -I effect of ester oxygen which raise the force constant of C=O bond.

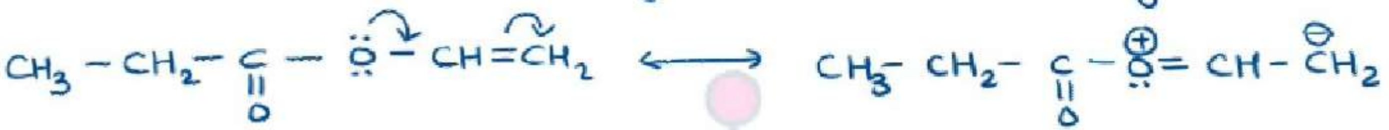
$R-\underset{\underset{O}{\|}}{C} \leftarrow O-R'$

- Effect of conjugation:

(i) conjugation in R lowers the frequency of $C=O$ stretching vibrations.

$$-C=C-C=O \longleftrightarrow -\overset{+}{C}-C=C-\overset{\ominus}{O}$$

(ii) conjugation in R' raises the frequency of $C=O$ stretching vibrations.

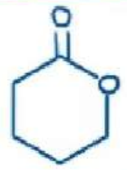


$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\ddot{O}-CH=CH_2 \longleftrightarrow CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\overset{\oplus}{O}=CH-\overset{\ominus}{C}H_2$$

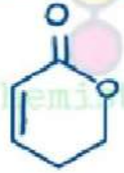
- Similar phenomenon of conjugation also occurs in cyclic esters.

- $C=O$ stretching frequency increases with decrease in ring size.

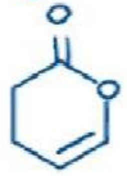
Ring size effect — α,β-conjugation — conjugation with oxygen



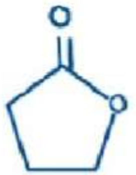
1735 cm⁻¹



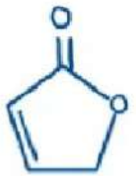
1720 cm⁻¹



1760 cm⁻¹



1770 cm⁻¹



1750 cm⁻¹

1800 cm⁻¹

ⓑ C–O stretching :→

- Alkyl alkanoates → 1300-1100 cm⁻¹ (strong)
- vinyl esters → 1300-1150 cm⁻¹ (strong)
- Aryl esters → 1150-1100 cm⁻¹

③ Acid anhydrides :→

- Acid anhydrides show the following two absorptions-

ⓐ C=O stretching vibrations :→

  - Asymmetric C=O stretching = 1830-1800 cm⁻¹ →

  - Symmetric C=O stretching = 1775-1740 cm⁻¹ →

- Conjugation with α,β-double bond or aryl group shift the absorption to lower frequency.
- Ring strain shifts the absorption to higher frequency.

ⓑ C-O stretching vibrations :→

- strong band is appear in the region 1300-900 cm⁻¹
- unconjugated straight chain anhydrides = 1050-1040 cm⁻¹
- cyclic anhydrides = 950-900 cm⁻¹ and 1300-1180 cm⁻¹

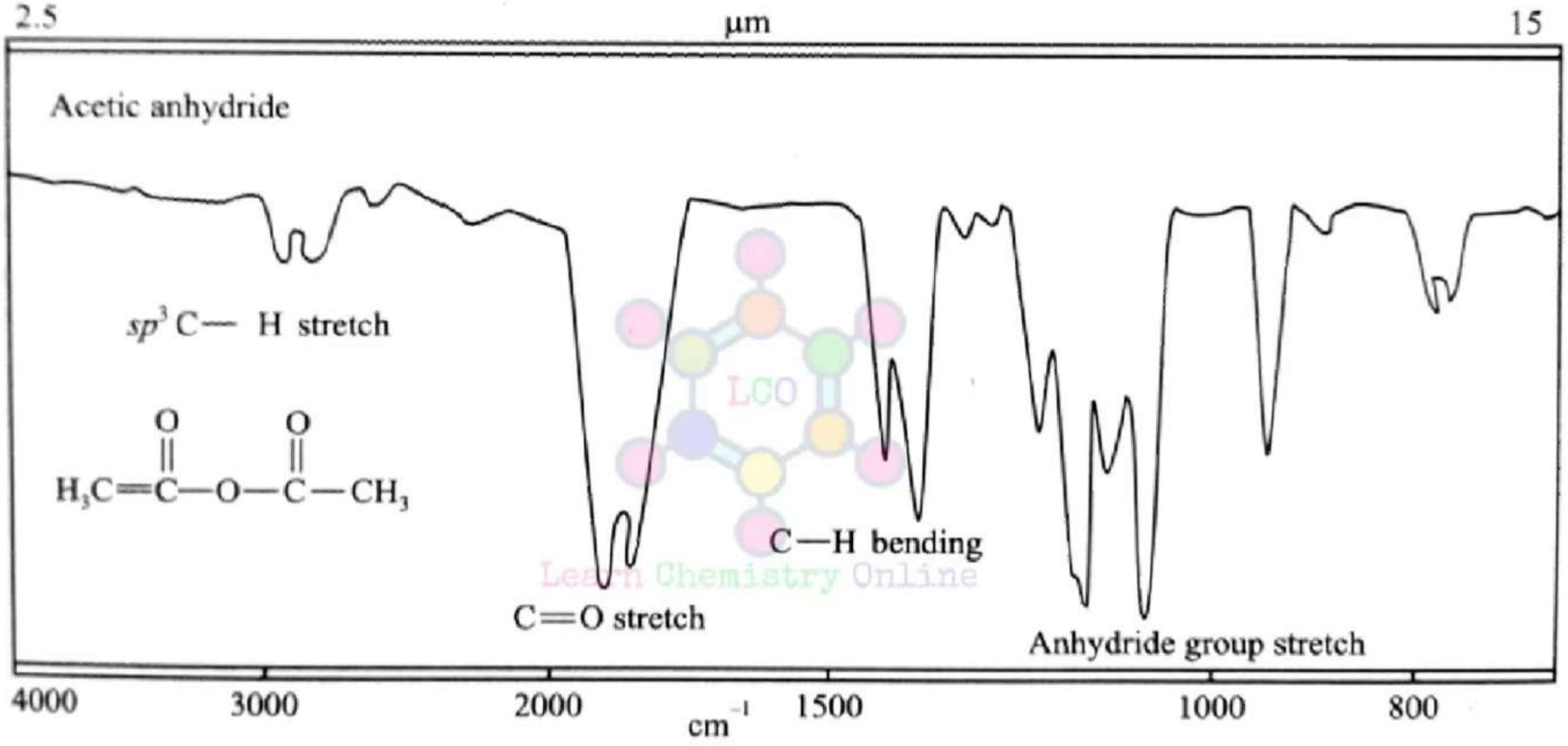


fig:- IR spectrum of Acetic anhydride

→ Characteristic absorption of various functional groups :→

① Acid halides :→

- C=O stretching → 1810 - 1770 cm^{-1} (higher frequency due to - I effect of chlorine)
- C-Cl stretching → 875 cm^{-1}
- In aromatic acid chlorides, a shoulder is appears on the lower wave number side of the carbonyl bond and it is due to fermiresonance b/w C-O stretching band and first overtone of C-Cl stretching.

② Amides :-

ⓐ N-H stretching vibrations :→

- Primary amides → dilute solution (free N-H) = 3500 - 3400 cm^{-1}
  Solid state (H-bonded) = 3350 - 3180 cm^{-1}

- Secondary amides → dilute solution (free N-H) = near 3450 cm^{-1} (trans configuration)
  solid state (H-bonded) = 3330 - 3100 cm^{-1} (cis and trans confi.)

- Tertiary amides → due to absence of H-atom atom, do not show any N-H stretching band.

ⓑ C=O stretching and N-H in-plane bending vibrations :→

- Primary amides. → solid state (doublet) (C=O) → 1655 – 1630 cm^{-1}
  dilute solution (C=O) → 1690 - 1670 cm^{-1}
  dilute solution (N-H bending) → 1620 - 1615 cm^{-1}
- Secondary amides → C=O stretching → 1680 - 1640 cm^{-1}
- Tertiary amides → C=O stretching → 1690 - 1650 cm^{-1}

ⓒ C-N-H vibrations :→ (N-H in plane bending and C-N stretching vibrations)

- Primary amides (C-N stretching) → 1400 cm^{-1}
- Trans secondary amides → 1550 cm^{-1} (strong band) } due C-N-H vibrations
  1250 cm^{-1} (weak band) }

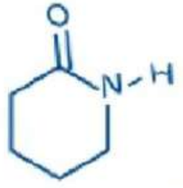
ⓓ O-C-N bending vibrations :→

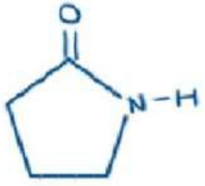
- appears near 650 cm^{-1}

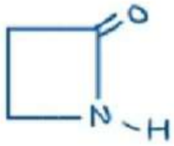
ⓔ N-H out-of-plane bending vibrations :→

- Primary and secondary amides show broad and medium intensity band at 700 cm^{-1} due to N-H wagging vibrations.

- C=O stretching vibration frequency increases with decrease in ring size of cyclic amides


~ 1660 cm⁻¹


~1705 cm⁻¹


~1745 cm⁻¹

③ Amines:→

- Amines show four types of absorption bands:-

ⓐ N-H stretching vibrations:→

- Primary amines → Symmetric stretching = 3450-3220 cm⁻¹
  Asymmetric stretching = 3550 - 3330 cm⁻¹
  Aliphatic 1° amine = 3400 - 3300 cm⁻¹ and 3330 - 3250 cm⁻¹
  Aromatic 1° amine = 3500 - 3400 cm⁻¹
- Secondary amines → 3500 - 3300 cm⁻¹
- Tertiary amines → do not show any N-H vibration because no H-atom is attached to N-atom.

ⓑ N-H in-plane bending:→

- Primary amines → 1650-1580 cm^{-1}
- Aromatic secondary amines → 1515 cm^{-1} (Very weak intensity for aliphatic secondary amines which is not easily detectable)

ⓒ C-N stretching vibrations:→

- Primary and secondary aliphatic amines = 1250-1020 cm^{-1}
- Aryl amines → 1360 - 1250 cm^{-}

ⓓ N-H out-of-plane bending:→

- Aliphatic primary amines → 909-666 cm^{-1} (strong broad band)
- Aliphatic secondary amines → 750-700 cm^{-1} (strong band)
- Amine salts → N-H stretching vibrations → 3000-2200 cm^{-1}
  N-H bending vibrations → 1610-1500 cm^{-1}

④ Nitriles:→

- $C\equiv N$ stretching vibrations appear in the range 2260-2220 cm^{-1}
- conjugation with α,β-double bond or aryl groups lower the frequency of absorption.

⑤ Nitro compounds:→

ⓐ NO_2 stretching vibrations:→

- Asymmetric N–O stretching → 1565–1510 cm^{-1}
- symmetric N–O stretching → 1380–1300 cm^{-1}
- Aliphatic compounds:- 1550–1380 cm^{-1}
- Aromatic compounds:- 1530–1350 cm^{-1} (frequency lowers due to conjugation)

ⓑ C–N stretching and C–N–O bending:→

- C–N stretching vibrations → near 870 cm^{-1}
- C–N–O bending vibrations → near 610 cm^{-1}

→ Interpretation of an IR spectrum:→

- For interpretation of an IR spectrum of an unknown compound, the following points should be considered

ⓐ Always start analysing the spectrum from highest frequency region as most of the functional groups absorb above 1400 cm^{-1} i.e. functional group region.

ⓑ The figerprint region (below 1400 cm^{-1}) is used for conformation of identity of the compound.

ⓒ It is neither necessary nor possible to interpret each and every absorption band.

ⓓ A negative evidence is much more conclusive. i.e. absence of a characterstic band due to a particular functional group confirms the absence of that functional group.

- General Guidelines:→

- For a systematic analysis of an IR spectrum for determining the presence or absence of functional groups, the following guidelines should be followed -

Step 1 :- Check the presence or absence of carbonyl group :→

- The $C=O$ group is appears as strong band in the region 1820-1640 cm^{-1}

ⓐ $C=O$ group is present :-

- check for the presence of complemetary bands to identify the functional groups having $C=O$ moiety.

(i) Acids :-

- check the presence of $-OH$ group in the region 3400-2500 cm^{-1} with shoulder peaks b/w 2600-2500 cm^{-1} (Strong band)
- If $-OH$ also present then unknown compound is carboxylic acid $(-\underset{\underset{O}{\|}}{C}- + -OH)$

(ii) Amides :→

- check the presence of $-NH_2$ group in the region 3400-3200 cm^{-1} (medium and sharp band)
- If $-NH_2$ group is present then unknown compound is amide $(-\underset{\underset{O}{\|}}{C}- + -NH_2)$
- Two bands indicate a primary amides while multiple band indicate secondary amides.

(iii) Esters :→

- Check the presence of $C-O$ group in the region 3400-3200 cm^{-1} (strong band)
- If $C-O$ group is present then unknown compound is ester $(-\underset{\underset{O}{\|}}{C} + -O-)$

(IV) Anhydrides:→

- Two absorption bands near 1810-1760 cm^{-1}

(V) Aldehydes:→

- check the presence to C-H band in the region 2820-2720 cm^{-1} (two weak bands)
- doublet is due fermi resonance i.e. coupling between C-H stretching and first overtone of C-H in-plane bending vibration. The latter band is diagnostic.
- If C-H is present then unknown compound is aldehyde $(-\underset{\underset{O}{\|}}{C}-+-H)$

(Vi) Ketones:→

- if all the above functional groups (i to v) are absent, the unknown compound is ketone.

(b) C=O group is absent:→

(i) Alcohols and phenols:→

- check the presence of O-H group in the region 3400-3200 cm^{-1} (broad band)
- Check the presence of C-O near 1300-1000 cm^{-1}
- If both absorptions are seen, then unknown compound is an alcohol or a phenol.

(ii) Amines:→

- check for medium absorption near 3400 cm^{-1} (N-H stretching)
- If these bands are present then unknown compound is amine.
- Primary amine → 2 bands
- Secondary amine → 1 band
- Tertiary amine → No band

(iii) Ethers:→

- Check for C-O stretching vibrations near 1300-1000 cm^{-1} region with the absence of O-H stretching near 3400 cm^{-1}
- If this is so, unknown is ether

(iv) Double bonds or aromatic ring:→

- check for C=C group near 1650 cm^{-1} region
- check for medium to strong band near 1600-1450 cm^{-1} region [four bands 1600 cm^{-1}, 1580 cm^{-1} (shoulder on 1600), 1500 cm^{-1} and 1450 cm^{-1}] Two of three bands in this region confirms the aromatic nature of unknown.

(v) Triple bonds :→

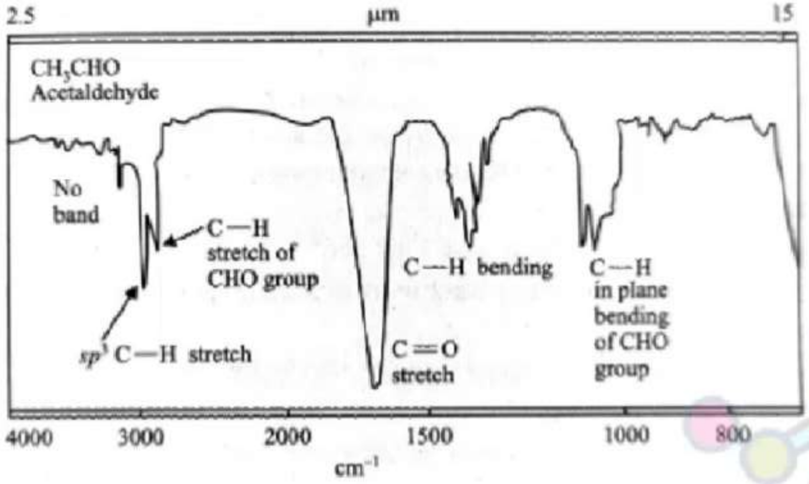
- check for medium and sharp absorption band near 2250 cm^{-1}. if present, the unknown has a $-C\equiv N$ group.
- check for weak and sharp absorption band near 2150 cm^{-1}. if present, the unknown has a acetylenic linkage. $(-C\equiv C)$
- check for strong absorption bands near 3300 cm^{-1} alongwith weak band at 2150 cm^{-1} if present, the unknown is a terminal alkyne $(-C\equiv C-H)$

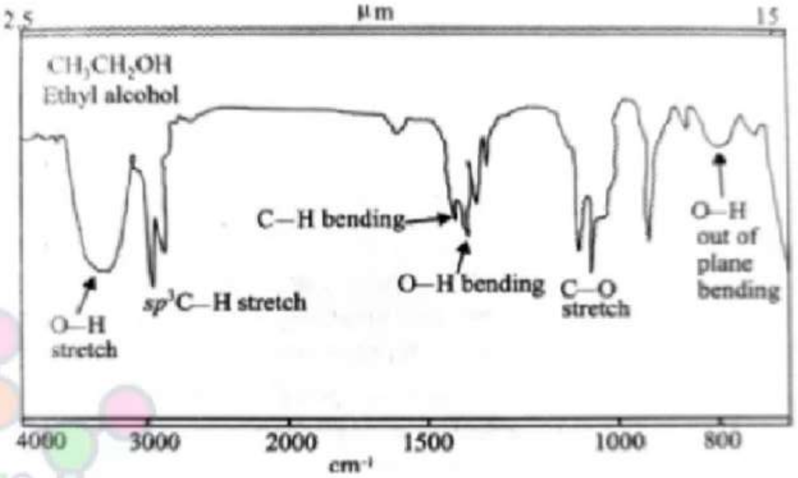
(vi) Nitro group :→

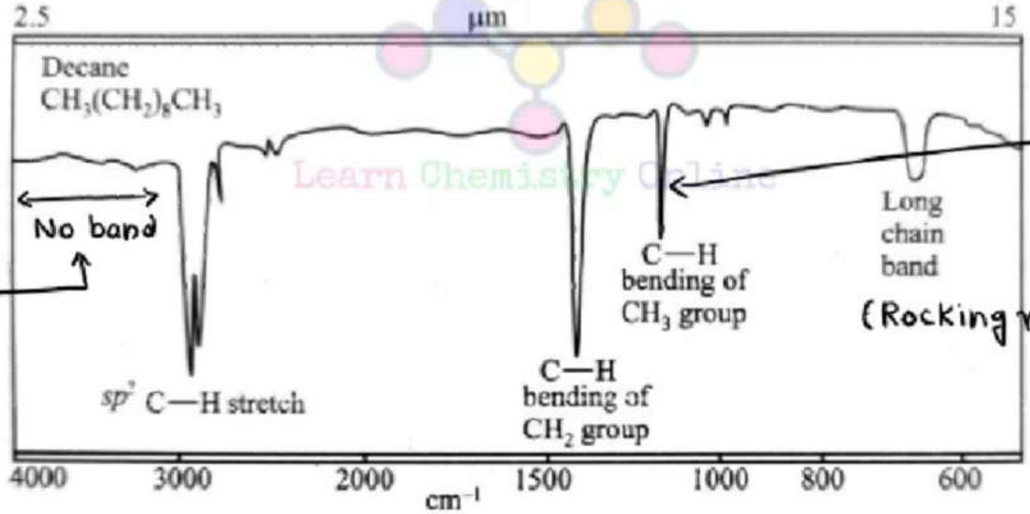
- check for two strong absorption bands at 1600-1500 cm^{-1} and 1390-1300 cm^{-1}.
- If both are present, the unknown has nitro group.

(vii) Hydrocarbon :→

- If all the above classes of compounds are absent and there are major absorption bands near 3000 cm^{-1} (C-H stretching) alongwith 1460 and 1375 cm^{-1} (bending vibration), the unknown compound is hydrocarbon.







Excludes the presence of $-OH$, $-NH_2$ $-NHR$, $H-C\equiv C-R$, $-C=C-$, aromatic system etc.

sharp band indicates the absence of isopropyl and t-butyl group

(Rocking mode)

→ Measurement of IR spectrum :→

- For the measurement of IR spectrum, infrared spectrophotometer is used.
- Modern double-beam infrared spectrophotometer consist of following componanents:-

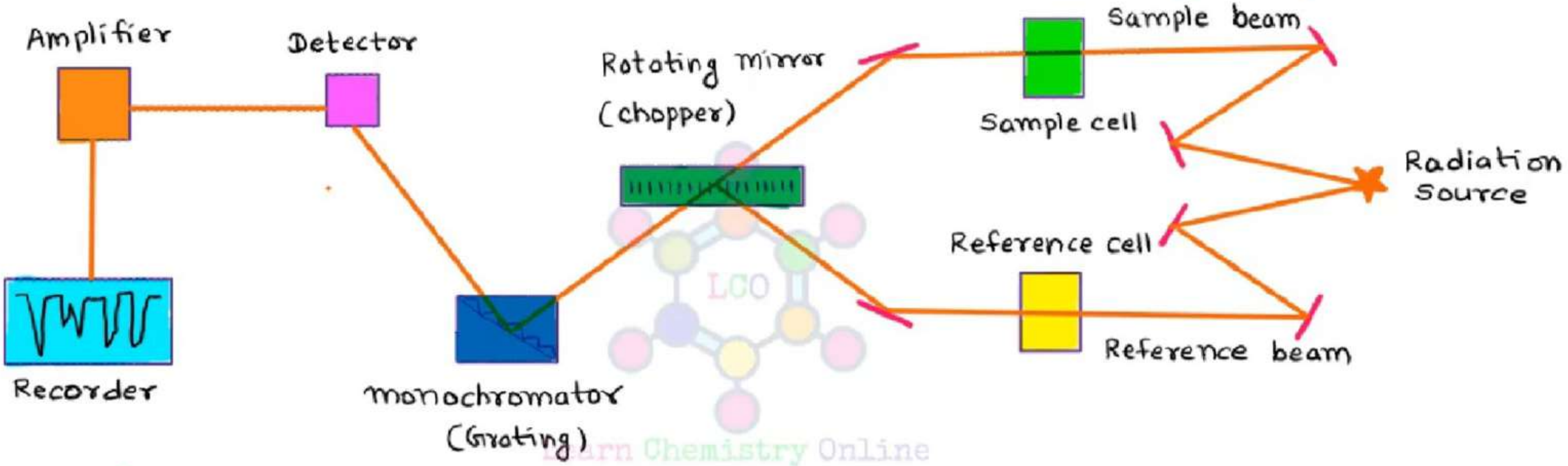


fig:- Block diagram of a double beam IR spectrophotometer

(i) Radiation source :→

- The source of radiation is a small ceremic rod, heated electrically in the range 1100 – 1800°C and is made of either silicon carbide (Globar) or Nernst glower (a high resistance, brittle element composed of mixture of sintered oxides of zirconium, thorium and cerium held together by a binding material.

- The radiation is divided into two beams, one beam passes through sample whereas other passes through reference cell.
- The reference and the sample beams are then passed alternatively into a monochromator at very short intervals by means of a rotating mirror called chopper.

(ii) Sample cell and sample preparation :-

- The cell are made up of rock salt (NaCl) or potassium bromide. (Glass and quartz cells are unsuitable as these materials themselves absorb IR radiation).
- One disadvantage of using NaCl is that it is hygroscopic and require protection from moisture. This can be done by heating it above room temp.
- Sample solution is prepared by dissolving it in suitable minimum absorbing solvent such as $CHCl_3$, CCl_4, CS_2 etc and examined as liquid film. The reference beam is passed through the solvent selected.
- If sample is not sufficiently soluble in these solvents, a nujol mull or a KBr pellet is obtained by pressing the sample in a hydraulic press with KBr.
- Nujol → white mineral oil (heavy paraffin oil so it is chemically inert)
- mull → a very thick suspension.

(iii) Monochromator :→

- Optical prism or gratings are used as monochromator.
- In high resolution rating instruments, a filter is used to reject unwanted radiations.

(iv) Detector, amplifier and recorder :→

- Detector usually made of a sensitive thermocouple.
- This thermocouple sense radiation as heat and converted into electric current. The magnitude of current is proportional to the intensity of radiation falling on the thermocouple.
- The signal from detector is amplifed electronically.
- The signal from amplifier is recorded by recorder.

→ Applications of IR spectroscopy:→

1. Identification of an organic compound:-

- The fingerprint region of IR spectrum of an organic compound, is very useful for establishing its identity.
- Two different compounds containing the same functional group may have similar bands in functional group region but their spectra differ significantly in the fingerprint region.

2. Structure determination:-

- Structure of an unknown compound can be establised by using IR spectroscopy.
- Here negative evidence is more conclusive than the positive evidence, i.e. absence of the peak means absence of the functional group.

3. Detection of Impurities:-

- IR spectroscopy is used for the detection of impurities in a compound by comparison of its IR spectrum with that of the pure sample.
- Sometimes bands due to impurities are less intense, therefore small amounts of inpurities remain undetected.

4. Study of progress of reaction:-

- Progress of a organic reaction can be studied by examining the IR spectra of small amount of mixture (aliquots) withdrawn time to time.

5. Distinction between inter and intramolecular hydrogen bonding:-

- If the IR frequency changed on dilution then hydrogen bonding is intermolecular.
- If the IR frequency not affected on dilution then hydrogen bonding is intramolecular.

6. Keto-enol tautomerism:-

- The keto and enol forms exist as tautomeric mixture. Keto and enol forms show characteristics absorption in the IR region.
- In addition to the expected C=O stretching frequency, a broad absorption band due to O-H stretching and band due to C=C stretching vibrations are observed.

7. Geometrical isomers:-

- Geometrical isomers can be identified on the basis of the change in their dipole moment during absorption. cis-isomer have some dipole moment while trans-isomer havo zero dipole moment.
- cis-isomer shows C=C stretching vibration and in trans-isomer C=C stretching vibrations are symmetry forbidden.