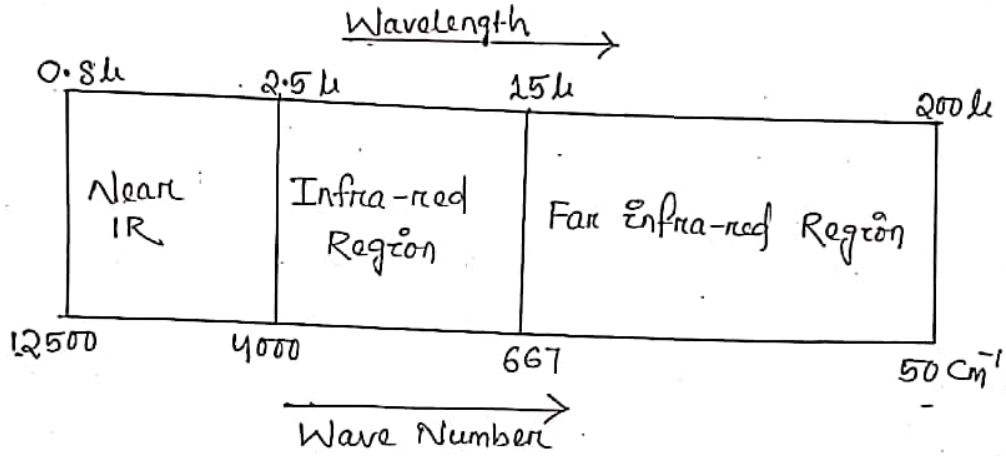
INFRA-RED SPECTROSCOPY

Infrared spectrum is an important record which give sufficient information about the structure of a compound.

→ The absorption of an IR-radiation causes various band in a molecule to stretch or bend w.r.t. one another.

→ The region from 0.8 μ – 2.5 μ is called near IR-region and that from 15 μ – 200 μ is called far IR-region.



Basic Principle Of IR-Spectroscopy :

The absorption of IR-radiation causes an excitation of molecule from a lower to the higher vibrational level.

→ Each vibrational level associated with closely packed rotational levels. So, IR spectra are also called vibrational rotational spectra.

→ All bonds in a molecule are not capable of absorbing IR radiation but these bands which absorb IR radiation which are accompanied by a change in dipole moment.

→ The vibrational transitions which are accompanied by a change in dipole moment are called IR-active transition. and these are responsible for absorption of energy in IR region.

EX :-
Vibrational transition of C=O, N-H, O-H etc. are accompanied by a charge in dipole moment this energy absorb strongly in the IR-region.

→ Since, the absorption in IR region are quantised, a molecule of organic compound will show no. of peaks in IR region.

Theory Of Molecular Vibration

When radiations of frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place.

→ Discrete lines are formed at the absorption is quantised in the spectrum due to molecular rotation.

→ When more energetic radiation in the range between $10^4 - 10^2$ cm^{-1} are absorbed by the molecule, molecular vibration takes place i.e. a single vibrational energy change is accompanied by a large no. of rotational energy changes.

→ Thus, in this region both vibrational bands appear.

→ The change in vibrational-rotational level depends upon :

(i) Mass of the atom present in the molecule
(ii) Strength of the bonds.
(iii) The arrangement of atoms within the molecule.

→ It has been found that, no new compounds except the enantiomers can have similar IR spectra.

→ When IR light is passed through the sample, two types of vibrations are found.

i.e (1) Stretching Vibration
(2) Bending Vibration

① Stretching :-

In this type of vibration, the distance between two atoms increases or decreases but the atoms remain on the same bond axis.

Types of Stretching Vibration:

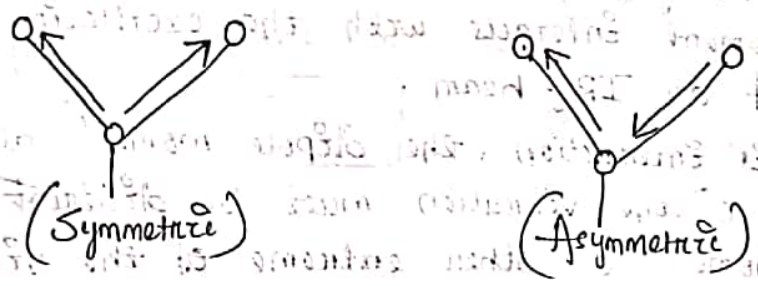
There are two types of stretching vibration.

(a) Symmetric Stretching :-

In this type, the movement of the atoms w.r.t a particular atom in a molecule is in the same direction.

(b) Asymmetric Stretching :-

In this type of vibration, one atom approaches the central atom while the other atom departs from it.



② Bending :-

In this type of vibration the position of the atom change w.r.t the original bond axis.

→ The bending vibrations are four types.

(a) Scissoring :-

In this type of bending vibration, two atoms approach each other

(b) Rocking :-

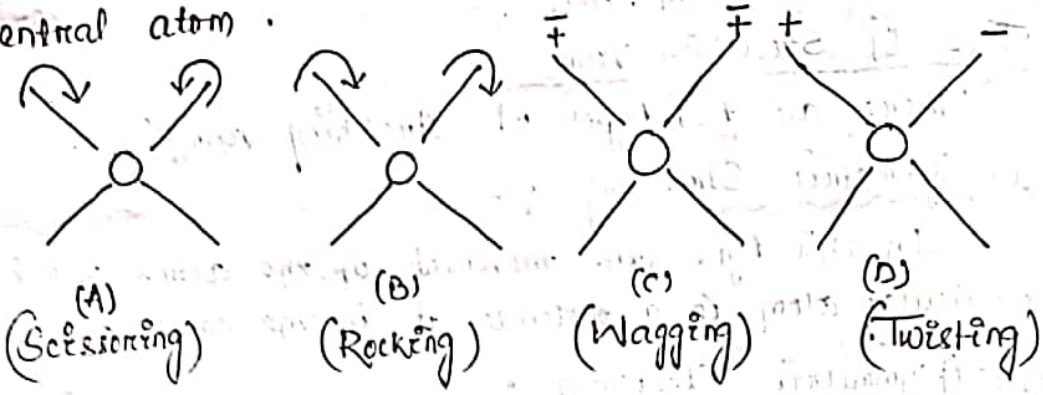
In this type, the movement of the atom takes place in the same direction.

(c) Wagging :-

Two atoms move 'up' and 'down' the plane w.r.t the same direction.

(d) Twisting :-

In this type, one of the atoms moves up the plane while the other moves down the plane w.r.t the central atom.



Fundamental Vibration

The IR light is absorbed when the oscillating dipole moment interacts with the oscillating electric vector of an IR-beam.

→ For this interaction, the dipole moment at one extreme of the vibration must be different from dipole moment at other extreme of the vibration in a molecule.

→ Only those vibrations are IR-active which are not centro-symmetric.

→ The IR-spectrum of a molecule results due to the transition between two different vibrational energy levels.

→ The vibrational motion resembles the motion observed for a ball attached to a spring i.e. harmonic oscillation

→ A chemical bond can be visualised as two balls attached to a spring. But it differs from this system, since in Infra-red contain vibrational energy levels only are allowed in molecules.

→ The vibrational energy of a chemical bond is quantised and can have the value,

$$E_{vib} = \left(v + \frac{1}{2}\right) h\nu$$

Where, 'v' is vibrational no. i.e. 0, 1, 2, 3, ...

h = Planck's constant

= 6.627×10^{-34} J.s

ν = Vibrational frequency of the bond.

→ We know that,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

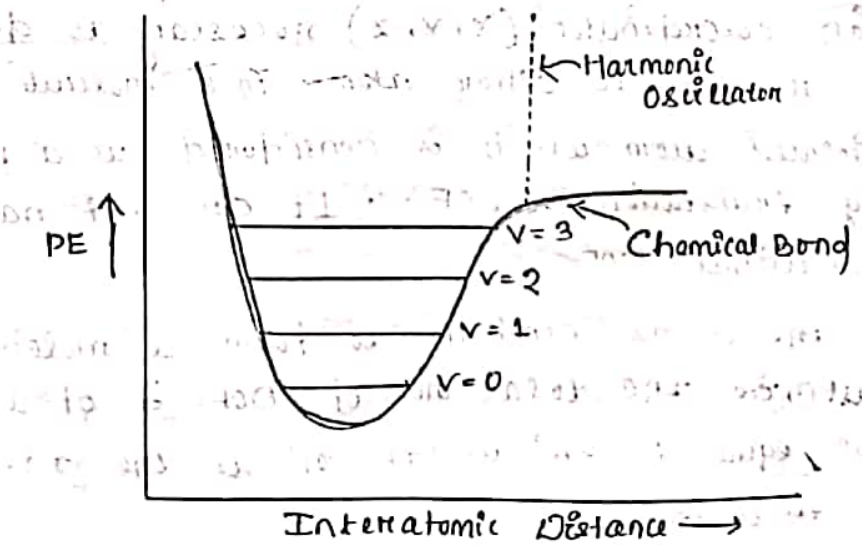
Here $\mu = \frac{m_1 m_2}{m_1 + m_2}$

The energy difference between the two vibrational energy levels can be written as:

$$\Delta E_{vib} = h.\nu$$

→ At ordinary temperature, where molecules are in their lowest vibrational energy levels, the potential energy diagram approximates that the harmonic oscillator. But at higher temperatures, the deviations occur.

→ Absorption of radiation with energy equal to the difference between two vibrational energy levels will cause a vibrational transition to occur.



→ Transitions from the ground state (v=0) to the 1st excited state (v=1) absorb light strongly and give rise to intense bands called the fundamental bands.

→ The energy difference (ΔE_{vib}) is given by,

$$\Delta E_{vib} = \Delta E_{vib\,(v=1)} - \Delta E_{vib\,(v=0)}$$

$$= \frac{3}{2} h\nu - \frac{1}{2} h\nu$$

$$= h\nu$$

→ This give the frequency of a fundamental band transitions from the ground state (v=0) to the second excited state (v=2) with the absorption of IR radiation give rise to weak bands called overtones.

→ The energy of the 1st overtone is given by,

$$\Delta E_{vib} = E_{vib\,(v=2)} - E_{vib\,(v=0)}$$

$$= \left(2 + \frac{1}{2}\right) h\nu - \frac{1}{2} h\nu$$

$$= 2h\nu$$

→ Polyatomic molecule may exhibit more than one fundamental vibrational absorption bands. The no. of these fundamental bands is related to the DOF in a molecule.

→ The no. of DOF is equal to the sum of coordinates necessary to locate all the atoms of a molecule in space.

→ Each atom has three DOF corresponding to the three cartesian co-ordinates (x, y, z) necessary to decide its position relative to other atoms in a molecule.

→ An isolated atom which is considered as a point mass has only translational DOF. It can not have vibrational and rotational DOF.

→ When the atoms combine to form a molecule, no DOF are lost, i.e the total no. of DOF of a molecule will be equal to '3n' where 'n' is the no. of atoms present in a molecule.

$3n$ DOF = Translational + Rotational + Vibrational

→ Rotational DOF result from the rotation of a molecule about an axis through the centre of gravity.

Since, we are concerned with the no. of fundamental vibration modes of a molecule. So, we calculate only the no. of vibrational DOF of a molecule.

Linear Molecule :–

For a linear molecule of n-atoms

Total DOF = $3n$

Translational DOF = 3

Rotational DOF = 2

Vibrational DOF = $3n-3-2 = 3n-5$

→ Each vibrational DOF corresponds to the fundamental mode of vibration and each fundamental mode corresponds to a band. Hence, theoretically there will be $3n-5$ possible fundamental bands for the linear molecule.

Non-linear Molecule :–

For non-linear molecule of n-atoms

Total DOF = $3n$

Translational DOF = 3

Rotational DOF = 3

Vibrational DOF = $3n-3-3 = 3n-6$

→ There ~~are~~ may appear some additional bands called Combination bands, difference bands and overtones.

→ Thus, due to these a large no. of bands will be observed as compared to the theoritical number.

→ If there are two fundamental bands at x and y, then the addition bands can be expected at,

(i) $2x$, $2y$ (overtones)

(ii) $x+y$, $x+2y$, $2x+y$ etc. (Combination bands)

(iii) $x-y$, $x-2y$, $2y-x$ etc. (Difference bands)

Combination :- More than 1 vibration can be excited at the same time.

Difference :- difference in fundamental bands (hot band) to excited state.

→ It may be noted that these additional bands are usually 10-100 times less intense as compared to the fundamental bands.

Factors Affecting Vibrational Frequencies :

① Effect of H-bonding :-

Hydrogen bonding brings about remarkable downward frequency shifts. Stronger the hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value.

→ Intermolecular hydrogen bonds give rise to broad bands whereas bands arising from intramolecular hydrogen bands are sharp and well defined. Intermolecular hydrogen bonds are concentration dependent.

→ The bands due to intramolecular hydrogen bonding are independent of concentration.

→ The absorption frequency difference between free and associated molecule is smaller in case of intramolecular hydrogen bonding than that in intermolecular association.

→ Hydrogen bonding in O–H and N–H compounds deserve special attention. Mostly non-associating solvents like carbon disulphide, chloroform are used because some solvents like benzene, acetone etc. influence O–H and N–H compounds to a considerable extent.

→ As nitrogen atom is less electronegative than the oxygen atom, hydrogen bonding in amines is weaker than that in alcohols and thus, the frequency which shifts in amines are less dramatic.

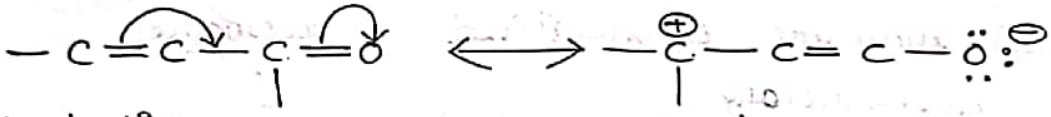
For Example :- Amine shows N–H stretching at 3500 cm^{-1} in dilute solution while in condensed phase spectra absorption occurs at 3300 cm^{-1}.

② Conjugation :—

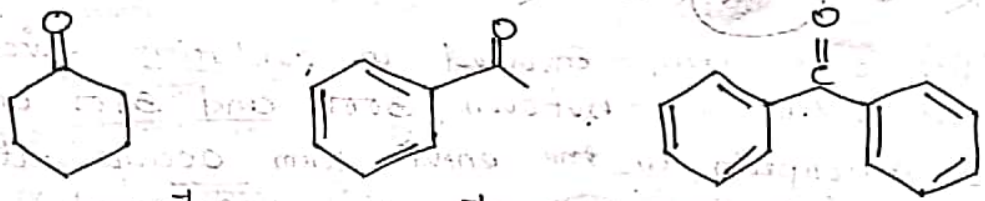
Conjugation of a carbonyl group with olefinic bond or aromatic ring results in the delocalisation of the π-e^- of both unsaturated groups.

→ It reduces the double bond character of both the bonds causing the lowering of carbonyl frequency from 1718 cm^{-1} to about 1690 cm^{-1} and C=C stretching frequency from 1645 cm^{-1} to 1620 cm^{-1}.

→ The lowering of absorption frequencies of both C=C and C=O group is due to resonance.

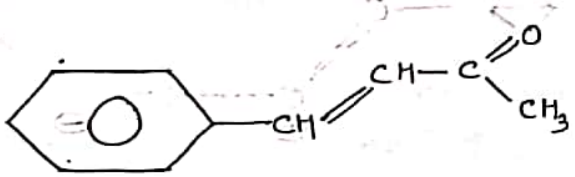


→ Introduction of second double bond in conjugation with carbonyl group results in an additional shift of ~15 cm^{-1} in the same direction.



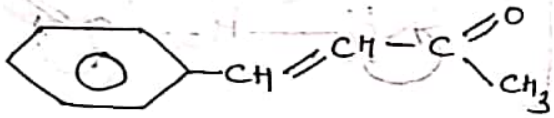
$\nu_{C=O}$ → 1717 cm^{-1} 1700 cm^{-1} 1670 cm^{-1}

→ The effect of conjugation is maximum when chromophores are coplanar. The steric effects disturb the coplanarity and reduce the effect of conjugation.



S = trans

$\nu_{C=O}$ 1675 cm^{-1}



S - cis

$\nu_{C=O}$ ⇒ 1700 cm^{-1}

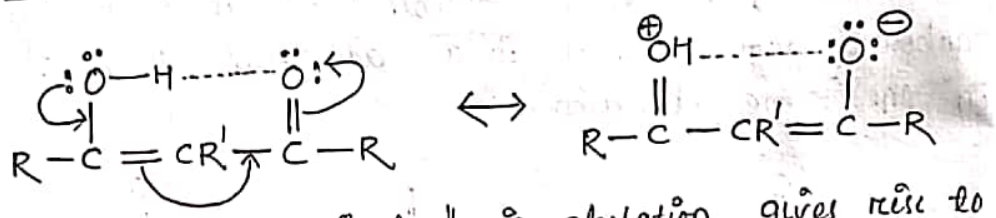
③ Resonance :—

The hydrogen bonded structure are further stabilised by resonance. Due to this, the stretching absorption occurs at much lower values.

→ In enols and chelates, hydrogen bonding is exceptional strong and absorption due to other O—H structure occurs at very low values.

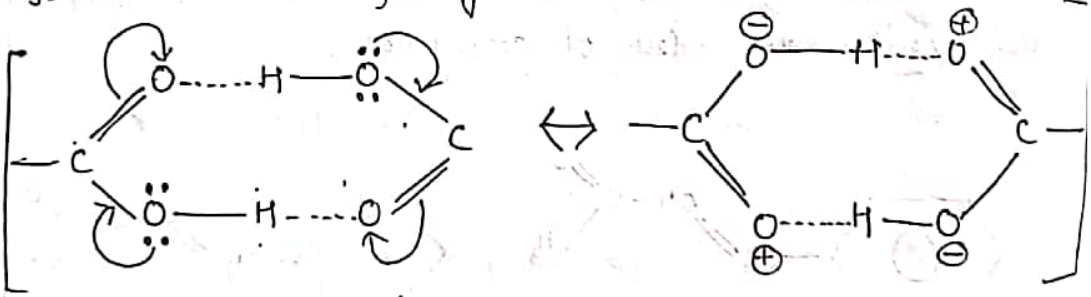
→ As these bonds are not broken easily on dilution by an inert solvent, free O—H structure may not be seen at low concentrations. It is due to the fact that the bonded structure is stabilised by resonance.

Ex:- Acetylacetone



→ The O—H group involved in chelation gives rise to broad absorptions between 3000 and 3500 cm^{-1}. The $\nu_{C=O}$ absorption in the enolic form occurs at 1630 cm^{-1} and that in the keto form at 1725 cm^{-1}.

→ Mostly, the acids exist as dimers and the bridges formed are stabilised by resonance.



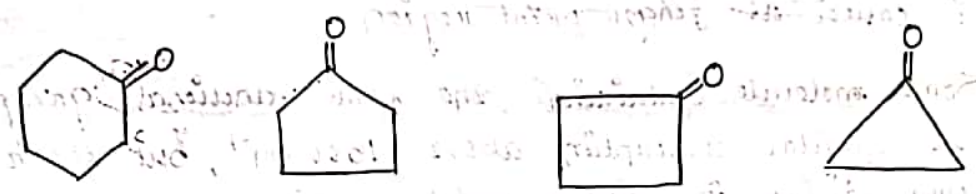
→ The formation of bridges lowers the force constant and thus $\nu_{C=O}$ and ν_{O-H} decrease. The larger decrease in the frequency of three isomers indicates the exceptional strengths of hydrogen bonds.

(4) Ring Size :-

It is found that various stretching and bending vibrations associated with C=O bonds in unsaturated molecules are regarded as normal.

→ But the deformation in the normal geometry of the molecule when a ring system usually change the vibrational frequency of functional group in the obtained molecule.

→ Consider the $\nu_{C=O}$ frequencies in cycloalkanones.



Cyclohexanone · Cyclopentanone Cyclobutanone Cyclopropanone

$\nu_C = 1717\ cm^{-1}$ $1745\ cm^{-1}$ $1780\ cm^{-1}$ $1825\ cm^{-1}$

$$\text{Bond} \propto s - \text{character} \propto \frac{1}{p}\text{-character} \propto \frac{1}{\text{Angle}}$$

→ In cyclohexanone, C=O structure occurs at $1717\ cm^{-1}$. It represents an unsaturated acyclic system.

→ In compounds with rings smaller than cyclohexanone, the angle 'θ' decreases than the normal tetrahedral angle. It causes strain which raises the wave number of absorption.

→ In smaller rings, the increased interaction offers resistance to the motion of the carbonyl carbon during stretching vibration.

Due to this, force constant increases and hence frequency of absorption is raised.

s character ↑, Electronegativity ↑, Bond strength ↑ K↑, P↑

Finger Print Region :-

For identification of two identical compounds, IR spectroscopy has an important role.

The region below 1500 cm^{-1} is rich in many absorptions which are caused by bonding vibrations and from the stretching vibration of C–C, C–O & C–N bonds.

→ In a spectrum, the number of bending vibrations is usually more than no. of stretching vibration. This region is usually rich in absorption bands and shoulders in it & is called as finger print region.

→ Some molecule containing the same functional group shows similar absorption above 1500 cm^{-1}, but their spectra differ in finger print region.

→ The identity of intra-red spectra of two compounds is much more characteristic than the comparison of their many physical properties.

→ It is not possible to distinguish the IR-spectra of straight chain alkanes containing 30 carbon atoms or more.

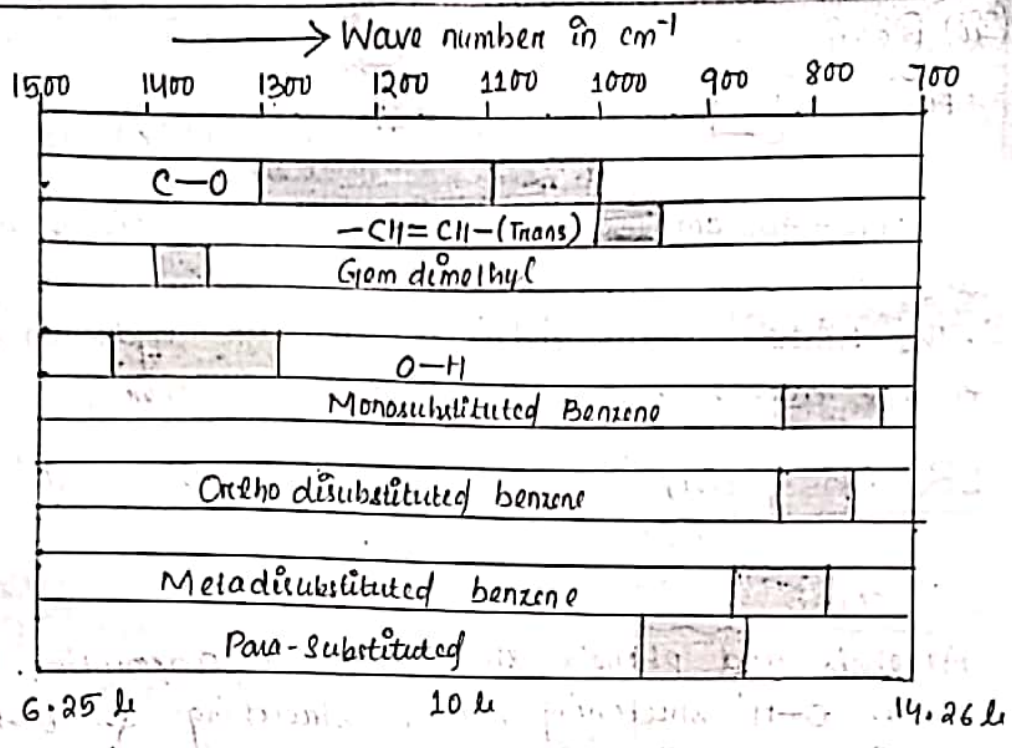
→ Also it is not possible to distinguish between two enantiomers even if their spectra are run with the same machine under exactly identical condition.

→ Finger Print region can be subdivided into three regions as below :

(i) 1500 – 1350 cm^{-1}

(ii) 1350 – 1000 cm^{-1}

(iii) Below 1000 cm^{-1}

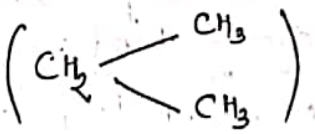


[fig. Characteristic absorption in finger print region]

Some characteristic absorptions in each of the above regions are as follows:

(i) Region: 1500-1350 cm^{-1} :- The appearance of a doublet near 1380 cm^{-1} and 1365 cm^{-1} shows the presence of 3°-butyl group in the compound.

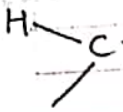
→ Gem-dimethyl shows ~~the presence of~~ a medium band near 1380 cm^{-1}.



(ii) Region: 1350 – 1000 cm^{-1} :— Alcohols, esters, lactones acid anhydrides show characteristic absorption band in this region due to C—O stretching.

→ Primary alcohols form two strong bands at 1350 – 1260 cm^{-1}. Phenol absorbs near 1200 cm^{-1} .etc.

(iii) Region : Below 1000 cm^{-1} :-



deformation at 700 cm^{-1} (s) and that at 970 - 960 cm^{-1} (s) distinguishes between cis & trans alkenes.

→ The higher value indicates that the hydrogen atoms in the alkene are trans w.r.t each other.

IR Absorption positions of O, N & S containing Functional Groups

① Alcohols & Phenols :

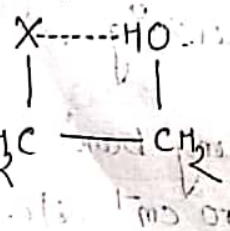
Alcohols and phenols show prominent absorption band due to 'O-H' stretching, 'C-O' stretching & 'O-H' bending vibration.

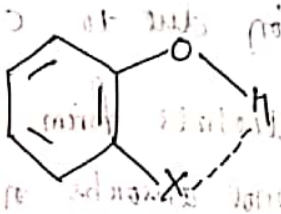
(a) O-H Stretching Vibration :- The longer the O-H bond, the lower is the vibration frequency, broader and more intense is the absorption band.

→ In alcohols & phenols, the sharp free monomeric band appears in 3650 - 3590 cm^{-1} range can be observed in the vapour phase.

→ Intermolecular hydrogen bonding increases as the conc. of the solution increases. Hence, additional band appear at lower frequencies of range 3550 - 3220 cm^{-1} at the expense of free hydroxyl bond.

→ Weak intermolecular hydrogen bonding occurs when O-H group is situated adjacent to a proton acceptor group :





(b) C–O Stretching vibration :– The C–O stretching vibrations in alcohols & phenols result in a strong band near 1260 – 1000 cm^{-1}.

→ The C–O stretching mode is coupled with the adjacent C–C stretching vibration. Hence, in primary alcohols this vibration is called C–C–O stretch vibration.

(c) O–H Bending vibration :– The O–H in plane bending vibration occurs in the 1420 – 1330 cm^{-1} region.

→ In primary and secondary alcohols, the O–H in plane bending with the C–H wagging vibrations to form two bands near 1420 cm^{-1} & 1330 cm^{-1}.

② Aldehydes :

(a) C–H Stretching vibration :–

Aldehyde C–H stretching vibrations occur in the 2830 – 2700 cm^{-1} region.

The appearance of two intense bands in this region is attributed to fermi resonance between C–H stretch and 1st overtone of the C–H bending vibration that appears near 1390 cm^{-1}.

→ Aromatic aldehydes with strongly electronegative group in the ortho position absorb at 2900 cm^{-1}.

P-Tolualdehyde shows its aldehydic C–H stretch at 2830 – 2735 cm^{-1}.

(b) C–O Stretching Vibration :–

A strong absorption band is observed near 1720 cm^{-1} due to C=O stretching.

→ The presence of this band shows that the compound may be an aldehyde, ketone, carbonylic acid, acid halide, acid anhydride, ester, amide, lactone.

→ Aliphatic aldehyde absorb near 1740 – 1720 cm^{-1}.

→ ~~Electrophilic substitution~~

→ Electronegative substitution on the α-carbon increases the frequency of carbonyl absorption. Acetaldehyde absorbs at 1745 cm^{-1} but trichloroacetaldehyde absorbs at 1768 cm^{-1}.

③ Ketones :-

(a) C=O stretching vibration :—

Ketones show a strong C=O stretching absorption in the region of 1870 – 1540 cm^{-1}.

→ The absorption frequency for a saturated aliphatic ketone increased when absorption is observed in nonpolar solvents.

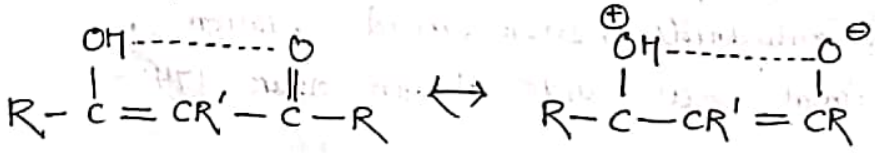
The overal range of solvent effect does not exceed by 25 cm^{-1}.

→ Replacement of an alkyl group of a saturated aliphatic ketone by a heteroatom, shift the carbonyl absorption.

→ The direction of shift depends on whether the (i) Inductive effect or (ii) resonance effect predominates.

→ β-diketones normally exist in keto and enol tautomerised forms. The enolic form does not show the normal absorption of conjugated ketones. It exhibits the intense broad band in the 1640 – 1580 cm^{-1} region.

→ The intense & displaced absorption results from intramolecular H-bonding, the bonded structure being stabilized by resonance.



(4) Carboxylic Acid :—

(a) C=O stretching Vibration :— The carboxylic acid group which consist of C=O and OH unit is the easiest to detect due to the presence of intense C=O stretching band in the region 1770 cm^{-1} along with broad O-H band near 3300 - 2500 cm^{-1}.

→ The monomers of saturated aliphatic acids absorb near 1760 cm^{-1}.

→ The carboxylic dimer has a centre of symmetry; Hydrogen bonding & resonance weaken the C=O band resulting in absorption at lower frequency than the monomer.

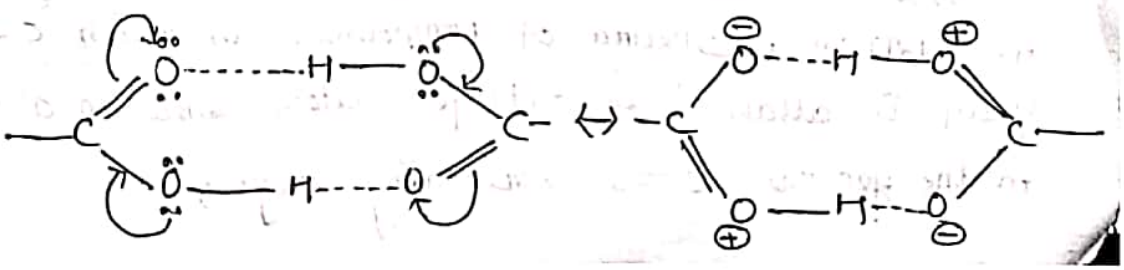
→ The C=O group, in dimerised aliphatic acid absorb in the region of 1720 - 1706 cm^{-1}.

→ Intramolecular H-bonding reduces the frequency of carbonyl stretching absorption to a greater degree than Intermolecular H-bonding. That's why salicylic acid absorbs at 1665 cm^{-1} while p-hydroxy benzoic acid absorbs at 1680 cm^{-1}.

→ Substitution in the α-position with electronegative atom or group such as halogens causes a minor increase in the C=O absorption frequency.

Due to -I-effect of -OH group $\nu_{C=O}$ absorption for acids should occur at higher wave number as compared to aldehydes.

→ But actually, it is not so ∴ $\nu_{C=O}$ absorption for acid is lowered due to internal conjugation acting in opposite direction.



(b) O–H Stretching Vibrations :-

The absorption caused by ν_{O-H} stretching is observed near 3570 cm^{-1} in very dilute solution of an acid.

→ The O–H stretching occurs as a broad band in the region of 3000 – 2500 cm^{-1}.

⑤ Amines :-

Amines are the alkyl derivatives of ammonia. These can be identified by absorption due to N–H str. near 3500 – 3300 cm^{-1}.

→ Primary amines show two sharp bands, secondary amines exhibit only one band while 3° amines do-not absorb in the N–H region.

→ Since, 'N' atom is less electronegative than oxygen atom, the 'N–H---N' hydrogen bonds are weaker as compared to 'O–H---O' bonds.

Hence, frequency shifts due to hydrogen bonding in amines are smaller.

→ The dilute solution of primary amine in an inert solvent give two sharp bands due to asymmetric and symmetric N–H stretching vibration between 3500 – 3300 cm^{-1}.

Seee In secondary amines N–H stretch occur near 3500-3300 cm^{-1} region.

→ In case of aromatic amines, ~~lower~~ ν_{N-H} have lower absorption values than that of aliphatic amines due to –I and +E-effect.

⑥ Sulphur Compounds :-

Thiobenzophenone & its derivatives absorbs moderately near 1217 cm^{-1}. Spectra of compounds in which 'C=S' group is attached to nitrogen atom show an absorption in the general 'C=S' stretching region.

→ In addition, several other bands in the broad region of 1560-700 cm^{-1} can be attributed to vibrations involving interaction between C=S and C-N stretching.

→ The thioenol tautomer of ethyl thiobenzoyl acetate absorbs broadly at 2415 cm^{-1} due to bonded S-H stretching absorption.

Application of IR spectroscopy in simple functional group analysis :—

→ This technique is useful in establishing the structure of an unknown organic compound.

→ It detects the functional groups present in that compound by studying the absorption bands at a particular wave number or wave length.

→ The shift in the position of a band gives additional information regarding the factors which causes this shift.

→ If no peak or band is present in a particular region, then it is a sure test for the absence of groups which absorb in that region.

① Identification of funal group.

② Determination of funal group.

③ Studying the progress of reaction

④ Detection of Impurities