1.2. INFRARED SPECTROSCOPY

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1.2. INFRARED SPECTROSCOPY

1.2.1. Introduction:

The absorption of infrared radiation by an organic compound causes the various bands in a molecule to stretch and bend. Some of the frequencies are absorbed and some other are transmitted without being absorbed. If we plot the percentage transmittance or percentage absorbance against wave number or frequency, infrared spectrum is obtained. The most important region for organic chemist is $4000-650~{\rm cm^{-1}or}~2.5-15\,\mu$. The absorption of 1R radiation can be expressed in terms of wave length or wave numbers. Generally IR spectra of organic compounds are plotted as percentage transmittance against wave number. The relation ship between wave length and wave number is as follows.

$$Wave number = \frac{1}{Wave length in centimeters}$$

If the wave length is $2.5\mu = 2.5 \times 10^{-4}$ cm

Wavenumber(
$$v$$
) = $\frac{1}{2.5 \times 10^{-4}}$ = 4000 cm⁻¹

The transitions of energy involved in infrared absorption are associated with vibrational changes with in the molecule. The molecules are constantly under going vibrations at room temperature. Each bond in the molecule has its characteristic stretching and bending vibrations which are quantized and are capable of absorbing light of that frequency lying in the IR region. The stretching vibration of two atoms connected to a bond can be compared to the vibrations of two balls attached to a spring. It requires more energy to stretch than to bend it. Thus stretching absorption of bond appears at higher frequency than the bending absorption of the same bond. For non linear polyatomic molecules, there will be 3n-6 nodes of vibration (3n-5 if linear) which include both stretching and bending vibrations.

1.2.2. Hooke's Law. Calculation of Vibrational frequency:

The stretching frequency ν of a bond with reasonable accuracy can be calculated applying

Hooke's law of simple harmonic motions. The Hooke's law is $v = \frac{1}{2\pi (K/\mu)^{1/2}}$

Where
$$\mu$$
 = reduced mass is equal to $\frac{m_1 m_2}{m_1 + m_2}$

v is the frequency of absorption

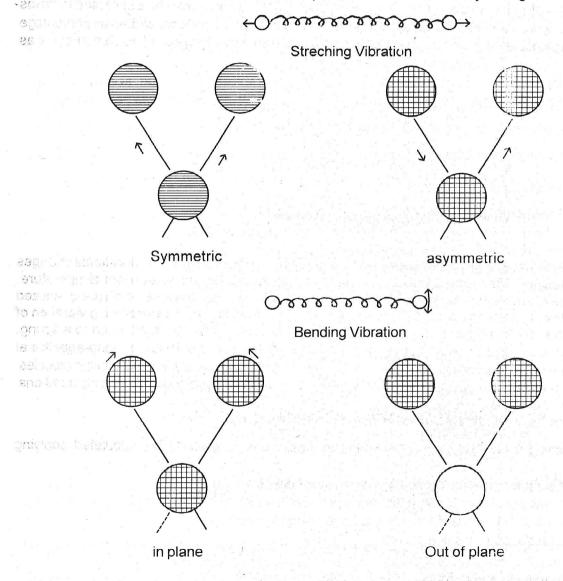
k = force constant of the bond m1 and m2 are the masses of the atoms attached to the covalent bond.

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From the equation it is clear that the vibrational frequency of a bond will increase when the bond strength increases and also when this reduced mass of the system decreases. Thus greater the mass lower the frequency of absorption and carbonyl bond will have higher vibrational frequency than C-O bond and C-H will have higher frequency of absorption than C-O.

1.2.3. Molecular Vibrations:

In stretching vibration the distance between two atoms increases or decreases, however the atoms remain in the same bond axis. The vibration occur at higher frequency. In bending the distance between these atoms remain constant and position of this atoms may change.



Some of the vibrations may have the same frequency - degenerate and their bands may overlap. Some vibrations may not be intense because a particular vibration should produce fluctuating dipole for it to be IR active. Otherwise it cannot interact with this fluctuating electric fields of the infrared light. So for vibration to be noticed in the spectrum it should lead to a change in the dipole moment of the

molecule. Otherwise these vibrations will be IR inactive and will show less or no absorption. The absorption band intensity depends on the difference between the dipole moments of the molecule in the ground state and the vibrational excited state. Molecules with center of symmetry are IR inactive. Eg. CO₂

$$O = C = O$$

Overtone bands appear as weak at the integral multiplets of fundamental vibrations. A fundamental vibration at 800 $\,\mathrm{cm}^{-1}$ will give a overtone band at 1600 and 2400 $\,\mathrm{cm}^{-1}$ with decrease of intensities

$$\left(\frac{1}{10} \text{to} \frac{1}{100}\right)$$
. vibrational coupling occurs between two bands vibrating with similar frequencies if the

band are close in the molecule. A fundamental vibration may couple with overtone of some other vibration and this coupling is called fermi resonance. Fermi resonance takes place when the overtone and fundamental vibration have the same symmetry property and they must be predominantly associated with a group of atoms in the same part of the molecule n-butyl vinyl ether shows Fermi

resonance. The over tone of fundamental vibration at 810 $\,\mathrm{cm}^{-1}$ coincides with a band at 1640 $\,\mathrm{cm}^{-1}$.

The mixing of two bands in accordance with fermi resonance gives two bands at 1640 and 1630 cm⁻¹

1.2.4. Instrumentation:

A rod of silicon carbide or Nernst filament is heated electrically in this range of $1100-1800^{\circ}$ C to produce IR radiations. The pulse beam is divided into two beams as reference beam and sample beam. When the beam passes through the sample, it becomes less intense due to absorption of certain frequencies. Now there is difference in this intensities of the two beams. Let I₀ be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample

Absorbance :
$$A = log \left(\frac{I_O}{I} \right)$$

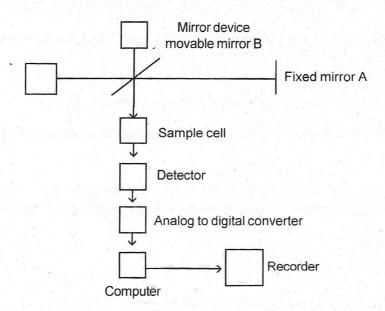
$$T = \frac{1}{I_O}$$

$$A = Log \left(\frac{1}{T} \right)$$

The detector (bolometer) changes its resistance upon heating with the radiation. The change in the temperature will cause an unbalanced signal across this circuit and the signal will be amplified and recorded. Poly styrene is used to calibrate this spectral chart.

The solid sample can be loaded by mixing with KBr in disc form. A blank disc is prepared with pure KBr and placed in the path of reference beam. KBr is transparent to the infrared region and a complete spectrum can be scanned by mixing 2% of solid sample with it. The solid samples can also be determined as a mull or a paste in nusol. Liquid samples placed as a thin film between two sodium. chloride plates which are transparent to IR radiation. It is also most convenient to determine the IR spectrum in solution. Good solvents are those which have poor absorptions in IR region. Like

 $\mathrm{CHCl_3}, \mathrm{CCl_4}, \mathrm{CS_2}$ etc. are good solvents in IR. FT IR instrument contains a number of added advantages. A monochromator is not necessary in FT IR. Data undergo analog to digital conversion. Results of several scans are combined and hence a neat spectrum for small amount of sample can be obtained.



Schematic representation of FT IR spectrometer

1.2.5. Finger print region:

The region below 1500 $\,\mathrm{cm}^{-1}$ is rich in many absorptions which are caused by bending vibrations and the C-C, C-O and C-N stretching vibrations. The bending vibrations are more than stretching vibrations and this region is called finger print region. Some compounds contain the same functional

group show similar absorption in functional group region (above 1500 cm⁻¹) but their spectra differ in finger print region. The compounds identity by IR spectra is much more characteristic than any other physical properties.

1.2.6. Applications of IR spectroscopy:

Infrared region $(4000-650~{\rm cm}^{-1})$ is of prime importance for the study of an organic compound. All groups absorb characteristically with in a definite range.

1.2.6.1. Identification of an alkane residue: The compounds are made up of carbon and hydrogen only. Hydrocarbons are saturated, and unsaturated aliphatics cyclics or aromatics. Alkane residues are detected from C-H stretching and C-H bending absorptions. Most of the organic compounds possess alkane residve, C-H absorption bands in a spectrum are of little diagnostic value.

The absorption due to C-H stretching occurs at 2840 − 3000 cm⁻¹

- $_{-{
 m CH}_3}$ group shows two distinct bands at 2962 and 2872 cm $^{-1}$. The former is due to asymmetric stretching and the latter is due to symmetrical stretching.
- → CH₂ the asymmetrical stretching and symmetrical stretching occur at 2926 and 2853 cm⁻¹
 respectively
- $\scriptstyle{\oplus}$ Symmetrical bending of $-CH_3$ appears at 1375 cm $^{-1}$ and asymmetrical bending near 1450 cm $^{-1}$
- ⊕ CH₂ group scissoring absorption appears between 1485 1340 cm⁻¹
- ⊕ Gem diethyl exhibits in plane out of plane symmetrical bending with equal intensity at 1385 and 1370 cm⁻¹
- Example 2 Cyclic alkanes absorptions are same as in the open chain compounds. However the ring strain moves the CH stretching band to higher frequency. Cyclopropane, C-H stretching band appears at 3100 cm⁻¹

1.2.6.2. Alkenes:

- + The = C H stretching band absorbs at 3100-3040 cm⁻¹
- + Non substituted = C H (str)at 3040 3010 cm⁻¹ and C-H bending at 700 cm⁻¹ and 915 905 cm⁻¹.
- + The C=C stretching band appears weakly at 1670 1640 cm⁻¹
- + Conjugated C = C stretching band at 1600 1650 cm⁻¹
- When Fluorine is attached to olefinic carbon v C=C increases, but when chlorine, bromine and iodine are attached it decreases.
- Due to ring strain in cyclic compounds then ν C=C is greater than unstrained cyclic and as well as open chain olefin.
- → Cumulative alkene absorb around near 2000 3000 cm⁻¹

Alkynes:

- $v-C \equiv C-$ of alkynes occurs around 2260 2100 cm⁻¹ symmetrically substituted alkynes no $vC \equiv C$ is observed
- Terminal alkynes give intense $vC \equiv C$ than non terminal ones.
- ••• \equiv C-H stretching band appears around 3350 3260 cm⁻¹
- \equiv C-H bending appears around 650 610 cm⁻¹.

Aromatic Hydrocarbons

- vAr-H stretching band occurs is the region 3050 3000 cm⁻¹; vC=C around 1650 1450 cm⁻¹ and C-H bending vibrations at 900-700 cm⁻¹
- Monosubstituted benzene will be identified with a band at 710 690 cm⁻¹ & 770 730 cm⁻¹
- ★ Metasubstituted benzene shows two peaks at 710 690 and at 800 750 cm⁻¹
- Ortho, Para disubstituted benzene show one band each at 770-735 cm⁻¹ and 840 800 cm⁻¹ respectively.

1.2.6.3. Alcohols and phenols

vO-H stretching band absorb at 3700-3500 cm $^{-1}$; vO-H stretching intermolecular hydrogen bond region at 3400 – 3200 cm $^{-1}$; vO-H stretching intramolecular hydrogen bond region at 3570 – 3450 cm $^{-1}$; chelate O-H stretching bond occurs in the region 3000-3520 cm $^{-1}$; primary alcohols vC-O stretching bond region at 1350 – 1260 cm $^{-1}$ another strong bond near 1050 cm $^{-1}$ and secondary alcohols vC-O stretching absorption at 1100 cm $^{-1}$ in addition to another strong band at 1350 – 1260 cm $^{-1}$; vC-O stretching region of tertiary alcohols can be distinguished due to appearance of strong bond at 1150 cm $^{-1}$ and another region at 1410 – 1310 cm $^{-1}$; 1,2 cyclohexane diols in cis - form vO-H stretching region at 3626 cm $^{-1}$ in addition to another region 3600 cm $^{-1}$. The phenols free O-H stretching region at 3600 cm $^{-1}$; phehols show characteristic strong C-O stretching bond at 1200 cm $^{-1}$ and another region at 1410 – 1300 cm $^{-1}$

1.2.6.4. Ethers, epoxides and peroxides

Aliphatic ethers exhibit strong bond around region at 1150 - 1085 cm⁻¹ due to asymmetrical C-O-C stretching the symmetrical stretching of C-O-C is weak appearing around region at 1075 - 1020 cm⁻¹.

The aromatic ethers, the asymmetrical C-O-C stretching region at $1275 - 1200 \text{ cm}^{-1}$ vC = C of vinyl ethers appear around at $1660 - 1610 \text{ cm}^{-1}$

1.2.6.5. Aldehydes & Ketones

The vC=0 of aliphatic ketone and cyclohexanes absorbs at 1715 cm $^{-1}$, while the aryl ketones exhibit at 1670 cm $^{-1}$. Aliphatic aldehyde vC=0 around region at 1740 – 1720 cm $^{-1}$. The hyper conjugative overlap of C-H in a ketone reduce its carbonyl double bond character and lower its vC=0 relative to aldehydes.

Aryl aldehydes occurs in the region at 1710 – 1685 $\,\mathrm{cm}^{-1}$ of $\,\nu\mathrm{C}$ = O of $\,\alpha,\beta$ – unsaturated aliphatic aldehydes appears at 1705 – 1685 $\,\mathrm{cm}^{-1}$

Aryl aldehydes with strong electronegative group is the ortho position may have its $\nu C-H$ as high at 2900 cm⁻¹

 ν C – H bending region at 1390 cm $^{-1}$ for aldehydes. Internal hydrogen bonding at ν C = O 1666 cm $^{-1}$ (Salicylaldehyde) decreases ν C = O

 $\alpha_1 \beta$ unsaturated ketones (saturated) vC=O stretching region at 1685 – 1665 cm⁻¹

 $\alpha_1 \beta$ unsaturated (Five membered) $\nu C = O$ stretching regions at 1725 – 1710 cm⁻¹

 $\alpha_1\beta$ unsaturated (Six membered) ν C = O stretching region at 1680 – 1665 cm⁻¹

Cyclohexanone vC = O stretching region at 1725 – 1705 cm⁻¹

Cyclopentanone vC = O stretching region at 1746 cm⁻¹

Cyclopropanone vC = O stretching region at 1885 cm⁻¹

 β Diketones usually exist is mixture of keto and enol form. The enolic form doesnot show the normal absorption of conjugated ketone. Instead, a broad bond appears in the region at $1640-1580~{\rm cm}^{-1}$, much intense than normal carbonyl absorption. This is due to intramolecular hydrogen bonding, the bonded structure being stabilized by resonance.

Quinones absorb at 1690 - 1655 cm⁻¹ with conjugation it may shift to 1655 - 1635 cm⁻¹

1.2.6.6. Carboxylic acid

Carboxylic acids usually exist as dimers. Hence vOH appears in the region corresponding to hydrogen bonded OH at $3300-2500~{\rm cm}^{-1}$

vC = 0 is very intense than ketones appearing around at 1760 cm⁻¹ for monomeric aliphatic acid. For dimers it appears region at 1720 cm⁻¹

Internal hydrogen bonding decreases the ν C = O to a greater extent than intermolecular hydrogen bonding. Example salicylic acid absorbs at 1665 cm $^{-1}$ while p-hydroxy benzoic acid absorbs at 1680 cm $^{-1}$

Aryl carboxylic acid vC = O stretching absorbs at 1700 – 1680 cm $^{-1}$ The carboxylate anion vC = O stretching region at 1610 – 1550 cm $^{-1}$. Two bonds arising from C-O stretching and O-H bending appears near 1320 – 1210 and 1440 - 1395 cm $^{-1}$.

1.2.6.7. Esters, Lactones, acid halides and anhydrides.

The carbonyl stretching bond of saturated aliphatic ester appears in the region at $1750-1735~\text{cm}^{-1}$ where $\alpha_1-\beta$ unsaturated esters and benzoates have their $\nu\text{C}=\text{O}$ 1730-1715 cm⁻¹ α -Halo substituents increases the $\nu\text{C}=\text{O}$ values saturated lactones have its $\nu\text{C}=\text{O}$ in the same region as in the case of esters.

 $\alpha_1 \beta$ unsaturated esters $\nu C = 0$ stretching region at 1730 – 1715 cm⁻¹, β lactones $\nu C = 0$ stretching absorbs at 1820 cm⁻¹ γ -lactone $\nu C = 0$ stretching region at 1780 – 1760 cm⁻¹, δ lactone $\nu C = 0$ stretching absorbs at 1750 – 1735 cm⁻¹.

The $\alpha_1 \beta$ unsaturated γ - lactones $\nu C = O$ stretching region at 1760 – 1740 cm⁻¹

The unconjugated acid halides absorb in the region at $1815-1785~{\rm cm}^{-1}$. While fluorides absorb at $1869~{\rm cm}^{-1}$; conjugated halides absorb at slightly lower frequency. The anhydrides display two stretching bonds in the carbonyl region due to asymmetric and symmetric stretching modes. Saturated anhydrides absorb near $1818-1750~{\rm cm}^{-1}$; while conjugated anhydrides absorb at $1775-1720~{\rm cm}^{-1}$. The higher frequency bond is more intense than the lower frequency bond.

The five membered $\alpha_1\beta$ unsaturated ν C = O stretching region at 1850 – 1800 cm $^{-1}$ and another region at 1800 – 1750 cm $^{-1}$

1.2.6.8. Amides and Lactams: The NH stretching vibration for primary amides absorbs at 3520
 3400 cm⁻¹ as a doublet and moves to lower frequency if hydrogen bonded.

The secondary amides absorbs at $3500-3400~cm^{-1}$ for NH stretching; Tertiary amides ν C=0 stretching region at $1670-1630~cm^{-1}$ while NH bending region at $1550-1610~cm^{-1}$ the β -lactams ν C=0 stretching region at $1760-1730~cm^{-1}$ the γ -lactams ν C=0 stretching region at $1700~cm^{-1}$ the δ -lactams ν C=0 stretching region at $1680~cm^{-1}$. The lactams exhibit similar features along with expected ring strain effects.

1.2.7. Effect of Hydrogen Bonding:

Hydrogen bonding brings about remarkable downward frequency shift stronger the hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value. Two types of hydrogen bonds can be readily distinguished in infrared technique. Generally, intermolecular hydrogen bond gives rise to broad bands where as band arising from intramolecular hydrogen bonds are sharp and well defined. Intermolecular hydrogen bond are concentration dependent on dilution, the intensities of such bonds are independent of concentraction. The absorption frequency difference between free and associated molecule is smaller in case of intermolecular 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, chlorofrom, carbontetrachloride are used because some solvents like benzene, acetene etc., influence O-H and N-H compounds to a considerable extent. The nitrogen atom is less electronegative than an oxygen atom. Hydrogen bonding in amines is weaker than that in alcohols and thus, the frequency shift in amines are less dramatic. For example, amine show N-H stretching at $3500~{\rm cm}^{-1}$ in dilute solutions while in condensed phase spectra, absorption occurs at $3300~{\rm cm}^{-1}$.

In aliphatic alcohols, a sharp bond appears at $3650~{\rm cm}^{-1}$ in dilute solutions due to free O-H group while a broad band is noticed at $3350~{\rm cm}^{-1}$ due to hydrogen bonded O-H group. Alcohols are strongly hydrogen bonded in condensed phases these are usually associated as dimers and polymers which result in the broadening of bands at absorption frequencies. In vapour state or in inert solvents molecules exist in free state and absorbs strongly at $3650~{\rm cm}^{-1}$. Alcohols can be written in the following resonating structures.

Resonating structure of alcohols.

Structure III is the hydrid of structures I and II. This results in the lengthening of the original O-H group. The electrostatic force of attraction with which hydrogen atom of one molecule is attracted by the oxygen atom of another molecule makes it easier to pull hydrogen away from the oxygen atom. Thus, small energy will be required to stretch such a bond (O-H) and hence absorption occurs at lower wave number.

Hydrogen bonding in enols and chelates are particularly strong and absorption due to O-H stretching occurs at very low values. As these bonds are not broken easily on dilution by an inert solvent free O-H stretching may not be seen at low concentrations. It is due to the fact that the bonded structure is stabilized by resonance consider acetyl acetone.

$$\overrightarrow{C}$$
: \overrightarrow{OH} $\overrightarrow{OH$

The O-H group involved in chelation gives rise to broad absorptions between 3000-2500 cm⁻¹.

The v_{co} absorption is the enolic form occurs at 1630 cm⁻¹ and that in the keto form at 1725 cm⁻¹. From the intensities of the two peaks it is possible to determine the quantities of the enolic and the ketonic forms.

Mostly the acids exist as dimers and bridges formed as stabilized by resonance.

The formation of bridges lowers the force constant and thus $\nu C = O$ and $\nu O - H$ decrease. The larger decrease in the frequency in these dimers indicates the exceptional strengths of hydrogen bonds.

The carboxylic acid dimers very broad at $3000-2500~{\rm cm}^{-1}$ due to O-H stretching. In vapour phase $v{\rm C}={\rm O}$ absorption occurs at $1770~{\rm cm}^{-1}$ in acetic acid and is the liquid state, absorption band appears at $1739~{\rm cm}^{-1}$. The benzoic acid shows a broad band at $3000-2500~{\rm cm}^{-1}$ due to O-H stretching. π cloud interactions are also noted when acidic hydrogen interacts with Lewis bases such as alkenes and benzene. For examples, the frequency of O-H stretching in phenols is lowered by $40-100~{\rm cm}^{-1}$. When spectrum is taken in benzene solution as compared to that in carbon tetrachloride solution. Due to this interaction, lengthening and hence weakening of O-H bond occurs.

It is possible to distinguish between intermolecular and intramolecular hydrogen bonding by IR spectroscopy. As the dilution increases, there will be no change in the appearance and position of the hydroxyl stretching band in the case of intramolecular hydrogen bonded system but that will go on changing as the dilution progresses in the case of intermolecular hydrogen bonded system.

1.2.8. Suggested Readings

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- 17. Fundamentals of Photochemistry, K.K. Rohtagi Mukherji, Wiley Eastern
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