Infrared Spectroscopy

Infrared spectroscopy deals with Infrared region of the electromagnetic spectrum

Role:- It is applied for identification of molecular compounds, which is based on the fact that diffrent chemical functional groups absorb Infrared light at diffrent wavelength depending upon the nature of the functional groups.

* Only two enantiomers have same IR spectrum
* Atom has a spherical symmetry & can only have electronic transitions. While the molecule loses its symmetry & can rotate & vibrate also. Molecules are associated with quantised energy levels called Electronic, vibrational & rotational. Each Electronic level within a molecule is associated with a no. of Vibrational levels with less energy spacing & each Vibrational level in turn is associated with set of rotational levels with even less energy separations

$$E_{rot} < E_{vib} < E_{elect}.$$

* IR radiation possesses relatively small amount of energy & therefore it induces transition b/w vibrational & rotational level of a molecule & hence it is called Vibrational-rotational spectrum of the molecule.

Hooke's law:

A molecule may be considered as a collection of balls + springs; where the balls are atoms + springs are considered as covalent bonds. As a consequence, a vibrating diatomic molecule can be considered as harmonic oscillator

The wave no. of its vibration ($\bar{\nu}$)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

c = velocity of light
k = force const.
μ = reduced mass of diatomic system

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

Selection rule:

Each atom has three degree of freedom, corresponding to motion along any of the three Cartesian coordinates (x, y, z).

→ for polyatomic molecule of 'n' atoms, total 3n degree of freedom

However, 3 degree of freedom for translational motion, Additionally 3 degree of freedom for rotations of the entire molecule

for non linear molecule:

→ 3N-6 degree of freedom are fundamental vibrations

→ 3N-5 vibrational modes as for linear molecule, only 2 degree of freedom are sufficient to describe rotation

Selection rule:-

Among 3N-6 or 3N-5 fundamental Vibrations, those that produces a net change in dipole moment may result in IR activity & those give polarisability change may give rise to Raman activity.

Infrared Region of the Electromagnetic Spectrum:-

NEAR IR	IR	FAR IR
10^{-4}	10^{-3}	10^{-2}
λ (cm)	($\bar{\nu}$ = 4000 cm^{-1}	400 cm^{-1})

IR spectrum

Plotting transmittance as a function of Wavelength.

fingerprint Region & functional gp. Region

Absorption bands in the 4000-1500 cm^{-1} region exhibits absorption bands corresponding to gp. of functional groups & is called as "functional Group Region".

finger print Region:-

The area from 1300 cm^{-1} to 667 cm^{-1} region makes it difficult to assign all the absorption bands because it contains apart from fundamental stretching vibrations, many bands resulting from sum or difference of their vibrational frequencies. This part of the spectrum is called characteristic of compound & bcoz of unique pattern found therein, it is

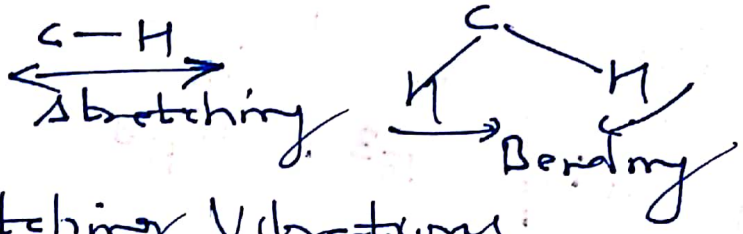
often called fingerprint Region.

Absorption of IR Radiations

Radiation in IR region corresponds to the stretching + bending Vibrational frequencies of the bonds in most covalent molecules.

Molecular Vibrations

The covalent bonds of molecules are not rigid, but are like stiff springs that can be stretched & bent.



1 → Stretching Vibrations

During stretching the distance b/w the two atoms increases or decreases but the atoms remains in the same bond axis.

a) Symmetrical Stretching
(Both the atoms move in or out simultaneously)

b) Asymmetrical Stretching
(One atom move in while the other move out)

2 → Bending Vibrations

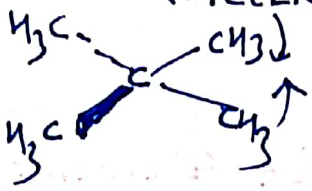
Consider a example of a three atom system. Including two terminal atoms bonded with a nodal one, wherein the bonding distance b/w the atoms remains constant but the position of the atoms effectively change relative to the original bond axis resulting in either decrease or increase in bond angle.

it requires less energy to bend a bond as wether than stretch. There are two types of bending Vibrations

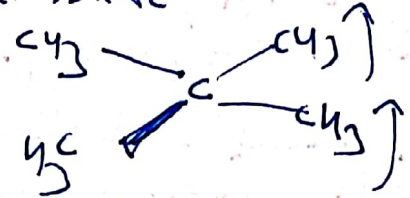
1) In plane bending.
2) Out of plane bending.

In plane bending :- Two terminal atoms tend to move towards or away from each other remaining in the same plane

a Scissoring - Both the atoms swing in/inert towards opposite directions.

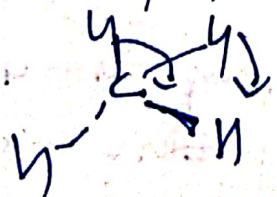


b Rocking - Both the atoms swing to the same side



Out of plane bending :-
In this bending Vibration mode, both the atoms bend out of the molecule plane of the system.

a Wagging - In the Wagging Vibration both the atoms swing up & down out of the plane of paper



b Twisting - One atom swing up & other swing down relative to the plane of paper.

factors affecting the absorption frequency

1 Hybridisation :-

force const. 'k' is dependent on the hybridization, higher is the s character higher will be the strength of the bond, & therefore higher will be the observed frequencies of C–H bond. The Order of bond strength is $sp > sp^2 > sp^3$

2 Electronic effects

a Inductive effect :-

When an electronegative element is attached to an atom involved in the formation of a bond, it results in the ↑ in absorption frequency of atom

Eg1 Halogen attached to –C(=O)– gp will increase the frequency of absorption of –C(=O)– group.

Ester –C(=O)– → 1714 cm^{-1}

Eg2 –OH gp attached to the –C(=O)– group.

1665 – 1710 cm^{-1}

Eg3 Anhydrides

1761 – 1832 cm^{-1}

b Resonance effect

When a group containing the unpaired electron is in conjugation with the –C(=O)– group, it results in increased single bond character, & lowering of –C(=O)– frequency

Eg1 $R-\overset{O}{\overset{\|}{C}}-NH_2 \leftrightarrow R-\overset{O^-}{\overset{|}{C}}=NH_2^+$ (1681 cm^{-1})

Eg2 If a carbonyl gp is in conjugation with another double bond, its double bond character decreases ($1690\ cm^{-1}$)

3 Hydrogen Bonding :-

→ Alcohols, Phenols & Carboxylic acids in condensed phase are strongly H-bonded. They undergo Intermolecular association leading to formation of dimers, trimers, which results in wide range of absorptions, & hence broadening of the absorption band.

Inter molecular H-bond

→ In dilute solution / inert solvent or vapour phase, the proportion of free molecule ↑ & leads to absorption at a higher wave no.

Thus H-bonding involves a lengthening of the original O-H bond leading to the weakening of the bond. (its force const. is decreased) & stretching frequency decreases.

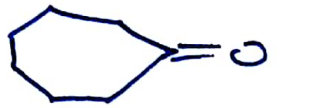
$\nu = \frac{1}{\lambda} = \bar{\nu} \propto \nu$

Eg1 $-\overset{O}{\overset{\|}{C}}-O-H$ (monomeric form, vapour state) ↓ 1760

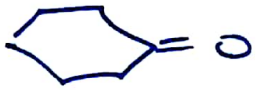
Eg2 Acids in conc. solution / neat solution or in solid state tend to dimerise via H-bonding. This dimerisation weakens the $-C^{\delta+}-$ gp & lowers the frequency to about $1710\ cm^{-1}$

4 Ring strain & Size

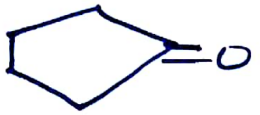
Incorporation of the $-\overset{\overset{O}{\|}}{C}-$ group in a small ring ↑ the stretching frequency



1705 cm⁻¹



1715 cm⁻¹



1745 cm⁻¹

5 Isotope effect

Stretching frequency of a free

O–H band = 3600 cm⁻¹

O–D band = 2600 cm⁻¹

Imp!

C=O 1725–1700 Carboxylic acids

C=O 1740–1720 (Aldehyde)

C=O
NH2 C=O 1715 (1690–1640)

C=O 1830–1800, 1775–1740 (Anhydride)

C=O 1750–1735 (Ester)

C=O 1725–1705 (Ketone)