

Infrared Spectroscopy (IR or Vibrational Spectroscopy) ①

deals with infrared region of electromagnetic spectrum. It is mostly based on absorption spectroscopy.

This technique can be used to identify and study chemicals. Sample may be solid, liquid or gaseous.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared, named for their relation to the visible spectrum.

⇒ The Higher-Energy near-IR ($14000 - 4000 \text{ cm}^{-1}$) ($0.8 - 2.5 \mu\text{m}$)

⇒ The mid-Infrared ($4000 - 400 \text{ cm}^{-1}$) ($2.5 - 25 \mu\text{m}$)

⇒ The Far-infrared ($400 - 10 \text{ cm}^{-1}$) ($25 - 1000 \mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

⇒ Vibrational spectroscopy is based on periodic changes in dipole moment caused by molecular vibrations of molecules.

Degrees of Freedom

is the number of variables required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinates (x, y, z) are adequate so its degree of freedom is three.

If molecule is made of N atoms, the degree of freedom becomes $3N$, because each atom has 3 degrees of freedom.

Since these atoms are bonded together, all motions are not translational; some become rotational, some others vibration.

⇒ For a non-linear molecule, 3 translational motions along three axes; 3 rotational along three axes so vibrational degree of freedom = $3N - 6$

⇒ For a linear molecule, rotation around intermolecular axis is not considered, so 2 rotational axes, so vibrational degree of freedom = $3N - 5$

e.g. For a diatomic molecule $N = 2$, calculate vibrational degrees of freedom

$$\begin{aligned} V &= 3N - 5 \text{ (linear)} \\ &= 3 \times 2 - 5 \\ &= 6 - 5 = 1 \end{aligned}$$

For a linear CO_2 , $N = 3$

$$\begin{aligned} V &= 3N - 5 \\ &= 3 \times 3 - 5 \\ &= 4 \end{aligned}$$

For a non-linear H_2O , $N = 3$

$$\begin{aligned} V &= 3N - 6 \\ &= 3 \times 3 - 6 \\ &= 3 \end{aligned}$$

Find the No. of vibrational modes for the following

- molecules:
- NH_3 (Non-linear) $3N-6 = 3 \times 4 - 6 = 6$
 - C_6H_6 (Non-linear) $3N-6 = 3 \times 12 - 6 = 30$
 - C_{10}H_8 (Non-linear) $3N-6 = 3 \times 18 - 6 = 48$
 - CH_4 (Non-linear) $3N-6 = 3 \times 5 - 6 = 9$
 - C_2H_2 (linear) $3N-5 = 3 \times 4 - 5 = 7$

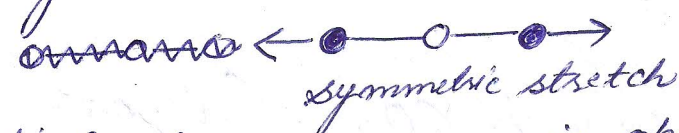
Normal modes of vibration

Dipole moment changes during the vibration.

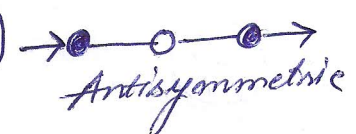
Two types of vibrations:

1) Stretching vibrations (changes of bond lengths)

(a) Symmetric stretching (all bonds move in same direction)



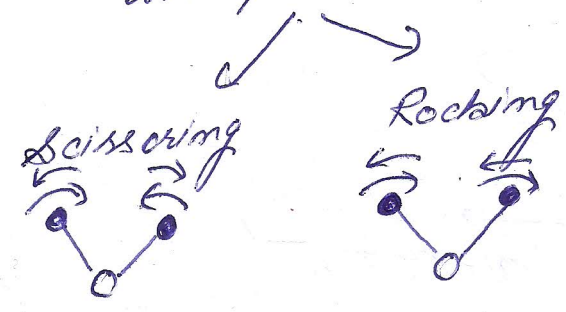
(b) Antisymmetric stretching (bonds move in opposite direction)



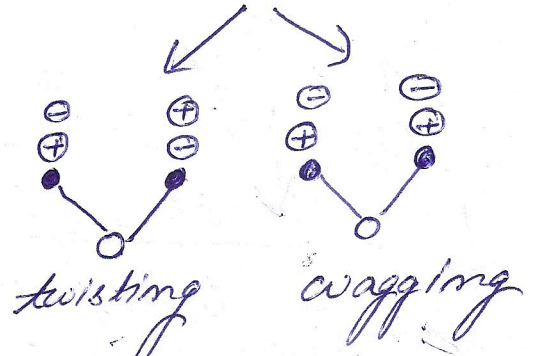
one atom approaches the central atom while the others depart from it.

2) Bending vibrations (changes of bond angles)

in-plane



out-of-plane



Bending vibrations require lesser energy and hence occur at higher wavelength than stretching vibrations. (4)

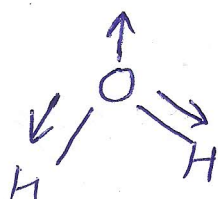
Theory of

vibrations in H_2O (nonlinear)

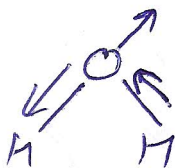
$$V = 3N - 6$$

$$= 3 \times 3 - 6 = \underline{\underline{3}}$$

Three vibrations in H_2O are



$$\nu_{\text{sym}} : 3652 \text{ cm}^{-1}$$



$$\nu_{\text{asym}} : 3756 \text{ cm}^{-1}$$

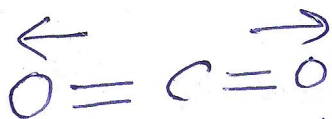


$$\text{Bending } \nu_{\text{bend}} = 1596 \text{ cm}^{-1}$$

vibrations in CO_2 (linear)

$$V = 3N - 5$$

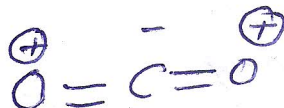
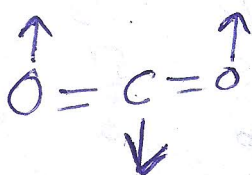
$$= 3 \times 3 - 5 = \underline{\underline{4}}$$



Symmetric stretching
Dipole moment = zero
IR Inactive



Asym. stretching
 $\nu = 2350 \text{ cm}^{-1}$
IR-Active



Bending vibrations $\nu = 667 \text{ cm}^{-1}$

Vibrational frequency = (5)

The value of the stretching vibrational frequency of a bond can be calculated by the application of Hooke's law (considering a vibrating molecule (diatomic) as a simple harmonic oscillator).

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

$\bar{\nu}$ = vibrational frequency (cm^{-1})

μ = reduced mass

k = Force constant of the bond and relates to the strength of the bond.

c = Velocity of the radiation = $2.998 \times 10^{10} \text{ cm sec}^{-1}$

The value of vibrational frequency or wave number depends upon: Bond strength and reduced mass. Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

Example 1: Force constant for C-H bond = $5 \times 10^5 \text{ gm sec}^{-2}$
mass of carbon atom (m_1) = $20 \times 10^{-24} \text{ gm}$
mass of hydrogen atom (m_2) = $1.6 \times 10^{-24} \text{ gm}$

⑥

$$\begin{aligned}
 \nu &= \frac{1}{2\pi} \sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}} \\
 &= \frac{1}{2 \times 22} \left[\frac{5 \times 10^5 \text{ gm sec}^{-2}}{\frac{20 \times 10^{-24} \text{ gm} \times 1.6 \times 10^{-24} \text{ gm}}{(20 + 1.6) \times 10^{-24} \text{ gm}}} \right]^{1/2} \\
 &= 9.3 \times 10^{13} \text{ sec}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \bar{\nu} &= \frac{\nu}{c} = \frac{9.3 \times 10^{13} \text{ sec}^{-1}}{3.0 \times 10^8 \text{ m sec}^{-1}} = 3.1 \times 10^5 \text{ m}^{-1} \\
 &= 3100 \text{ cm}^{-1}
 \end{aligned}$$

⇒ C=C stretching is expected to absorb at higher frequency than C-C stretching. It is due to the higher bond strength (value of k) of the double bond compared to the single bond.

⇒ Similarly, O-H stretching absorbs at higher frequency compared to C-C bond. because the reduced mass of O-H is less as compared to C-C bond.

(7)

⇒ But if we compare $^{16}\text{O}-^1\text{H}$ bond with $^{19}\text{F}-^1\text{H}$ bond. F-H bond has more reduced mass than O-H bond so expected to absorb at lower frequency than O-H bond. But F-H bond is stronger due to more electronegativity of Fluorine as compared to ~~the~~ Oxygen and absorbs at the higher frequency than O-H bond.

⇒ Example 2. Calculate the wave number of stretching vibration of a C-C double bond. Given Force Constant ($k = 10 \times 10^5 \text{ dynes cm}^{-1}$)

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 12}{12 + 12} = 6 \text{ amu}$$

$$= \frac{6}{6.02 \times 10^{23}} \text{ gm} = 9.97 \times 10^{-24} \text{ g}$$

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

$$= \frac{1}{2 \times 3.142 \times 3 \times 10^{10} \text{ cm}^{-1} \text{ s}} \sqrt{\frac{10 \times 10^5 \text{ gm sec}^{-2}}{9.97 \times 10^{-24} \text{ gm}}}$$

$$= 0.1680 \times 10^4 \text{ cm}^{-1}$$

$$= 1680 \text{ cm}^{-1}$$

Example 3 The reduced mass of a diatomic molecule ^⑧ is $2.5 \times 10^{-26} \text{ kg}$ and its vibrational frequency is 2900 cm^{-1} . Calculate the force constant.

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

$$k = 4\pi^2 c^2 \mu \bar{\nu}^2$$

$$= 4 \times (3.142)^2 (3 \times 10^8 \text{ m s}^{-1})^2 (2.5 \times 10^{-26} \text{ kg}) (2900 \times 10^2 \text{ m}^{-1})^2$$

$$= 7476.4 \text{ N m}^{-1} \quad (1 \text{ N} = 1 \text{ kg m s}^{-2})$$

Example 4 The force constant for CO is 1840 N m^{-1} . Calculate the vibrational frequency (cm^{-1}).

$$^{12}\text{C} = 19.9 \times 10^{-27} \text{ kg}$$

$$\mu = 1.138 \times 10^{-26} \text{ kg}$$

$$^{16}\text{O} = 26.6 \times 10^{-27} \text{ kg}$$

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

$$= \frac{1}{2 \times 3.142 \times 3 \times 10^8 \text{ m s}^{-1}} \sqrt{\frac{1840 \text{ kg s}^{-2}}{1.138 \times 10^{-26} \text{ kg}}}$$

$$= 2.132 \times 10^5 \text{ m}^{-1}$$

$$= 2.132 \times 10^5 \times 10^{-2} \text{ cm}^{-1}$$

$$= 2132 \text{ cm}^{-1}$$

Example 5: The force constant of HI is 880 N m^{-1} . (9)
At what wave number is the fundamental vibration expected?

$$\begin{aligned}\bar{\nu} &= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2 \times 3.142 \times 3 \times 10^8 \text{ m/s}} \sqrt{\frac{800 \text{ kg s}^{-2} (1+19) \times 6.02 \times 10^{23}}{1 \times 19 \times 10^{-3} \text{ kg}}} \\ &= 396071.8 \text{ m}^{-1} \\ &= 3960.7 \text{ cm}^{-1}\end{aligned}$$

No. of fundamental vibrations: $\Rightarrow$

a molecule must possess dipole moment or change in dipole moment during a vibration. For a vibrational transition, Infra-red radiation is absorbed.

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

The vibrational motion resembles the motion of a ball attached to a spring i.e. harmonic oscillator.

$\Rightarrow$ A chemical bond can be imagined as two balls attached to a spring.

The vibrational energy of a chemical bond is quantised and

(10)

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

v = vibration quantum No = 0, 1, 2, 3, ...

h = Planck's constant

ν = vibrational frequency of a bond.

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

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

for an allowed

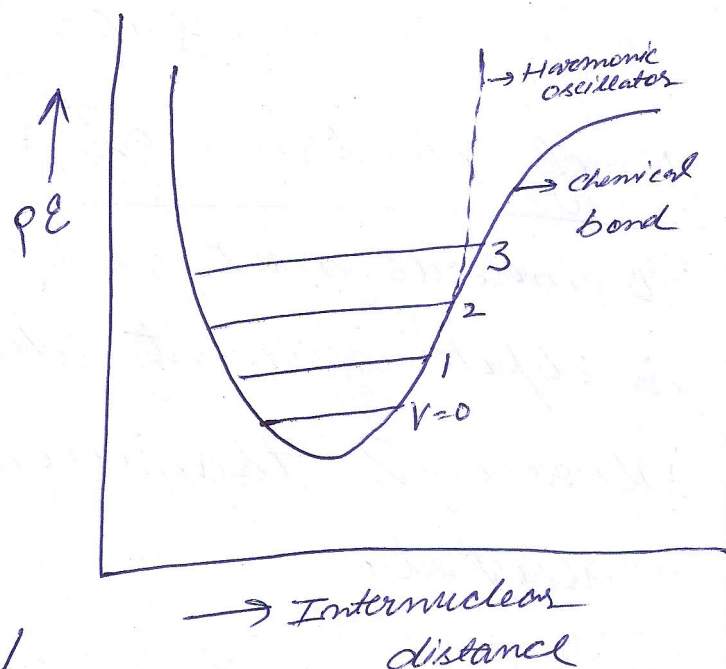
transition, $\Delta v = \pm 1$

⇒ Transition from $v=0$ to $v=1$

gives intense peaks called fundamental band.

⇒ Transition from $v=0$ to $v=2$ gives rise to weak peaks called overtone.

⇒ If a molecule has centre of symmetry, then symmetric vibrations are IR inactive (e.g. CO_2)



The Anharmonic Oscillator

Real molecules don't exactly obey the laws of simple harmonic motion; real bonds, although elastic, are not so homogeneous as to obey Hooke's law. If the bond between atoms is stretched with higher energy, there comes a point at which it will break - the molecule dissociates into atoms. For small compressions and extensions the bond may be taken as perfectly elastic, but for large compressions and extensions, molecule behaves as Anharmonic oscillator.

And the Schrodinger equation for Energy of vibrational levels changes

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) h\nu - \left(v + \frac{1}{2}\right)^2 h\nu x_e \text{ cm}^{-1}$$

x_e = anharmonicity constant.

So $E_{\text{vibrational}}$ decreases as ΔE becomes smaller.

The selection rule for the anharmonic oscillator is $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

Zero point Energy:-

(12)

$$E_{\text{vib}} = \left[v + \frac{1}{2} \right] h\nu_0$$

when molecule is present in lowest vibrational level ($v=0$)

$\boxed{E_0 = \frac{1}{2} h\nu_0}$ (This residual energy is called Zero point Energy)

The Diatomic Vibrating Rotator: $\Rightarrow$

A diatomic molecule has rotational energy separations of $1-10 \text{ cm}^{-1}$, while average vibrational separations of HCl were 3000 cm^{-1} .

Combined rotational-vibrational energy is simply the sum of the separate energies.

$$E = E_{\text{rot.}} + E_{\text{vib}}$$

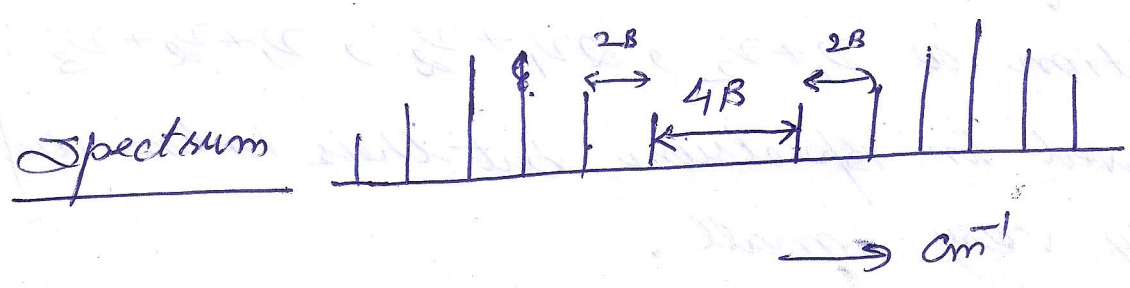
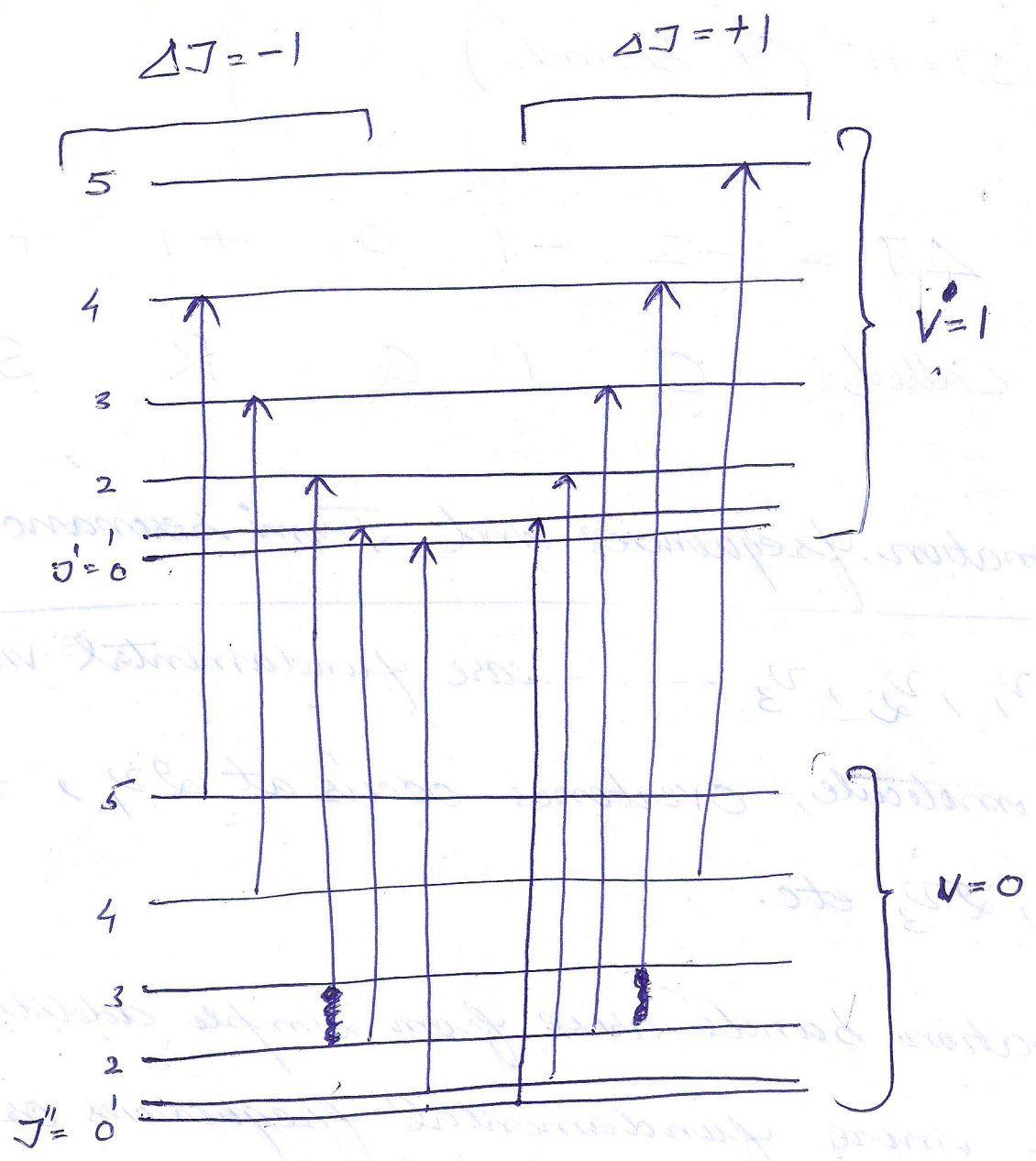
$$E(\text{cm}^{-1}) = BJ(J+1) + \left(v + \frac{1}{2} \right) h\nu_0$$

Selection rule for the combined motion

$$\Delta v = \pm 1, \pm 2 \text{ etc.} \quad \Delta J = \pm 1$$

we may have $\Delta V = 0$, but corresponds to the purely rotational transitions.

But $\Delta J = 0$ is not possible, means a vibrational change must be accompanied by a simultaneous rotational change.



According to the Born-Oppenheimer approximation (4)

rotation is unaffected by vibrational changes.
So B is identical in the upper and lower vibrational states.

$$\Delta J = -1 \text{ (P branch)}$$

$$\Delta J = +1 \text{ (R branch)}$$

$$\Delta J = -2 \quad -1 \quad 0 \quad +1 \quad +2$$

Called O P Q R S branch

Combination frequencies and Fermi resonance

If ν_1, ν_2, ν_3 ----- are fundamental vibrations in a molecule, overtones occur at $2\nu_1, 3\nu_1, \dots$
 $2\nu_2, 2\nu_3$ etc.

Combination bands arise from simple addition of two or more fundamental frequencies or overtones.

Such combination as $\nu_1 + \nu_2, 2\nu_1 + \nu_2, \nu_1 + 2\nu_2 + \nu_3$ etc. are observed in spectrum but their intensities are normally very small.

Similarly the difference bands, for example, $\nu_1 - \nu_2$, $2\nu_1 - \nu_2$, $\nu_1 + \nu_2 - \nu_3$ have small intensities but are often to be found in a complex spectrum.

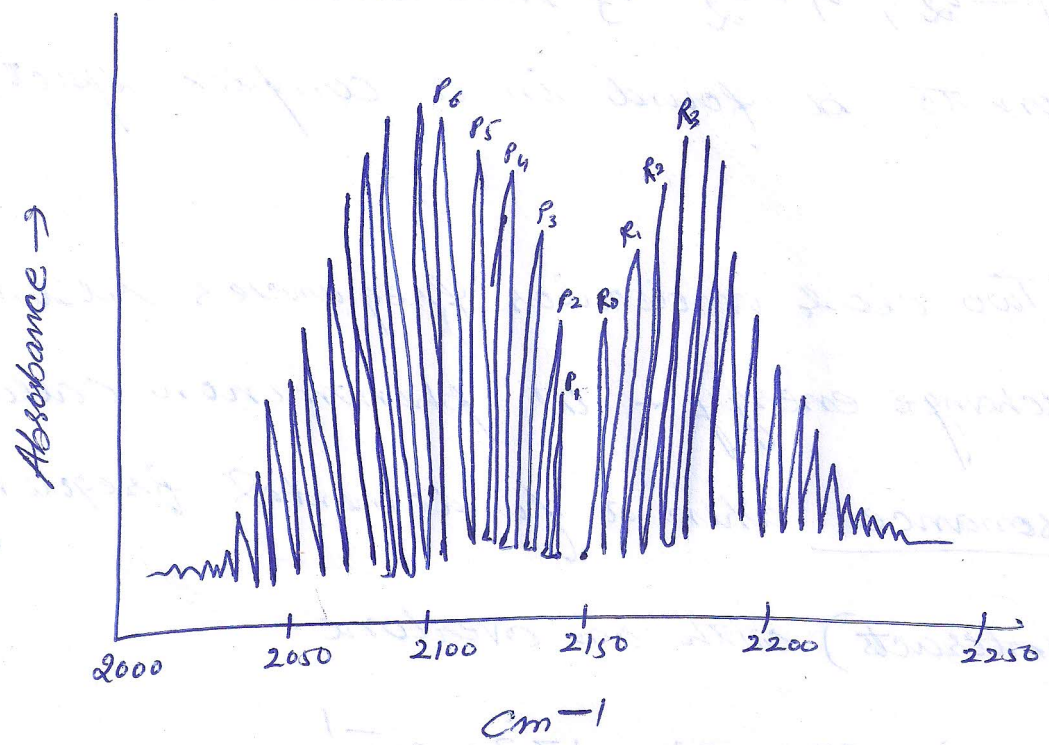
⇒ Two close molecular frequencies resonate and exchange energy - the phenomenon called Fermi resonance when a fundamental frequency resonates (interacts) with an overtone.

e.g. in CO_2 $\nu_1 = 1330 \text{ cm}^{-1}$
 $\nu_3/\nu_4 = 667 \text{ cm}^{-1}$

↓
 overtone for this vibration occurs at $2\nu_3 = 1334 \text{ cm}^{-1}$

Now ν_1 and $2\nu_3$ are very close to one another so these two interact and ^{higher} one is raised to higher frequency and lower one is depressed so the above two bands are observed at 1285 cm^{-1} and 1385 cm^{-1} . Their mean (average) is at about 1330 cm^{-1} .

The Vibrational - Rotational spectrum of carbon monoxide



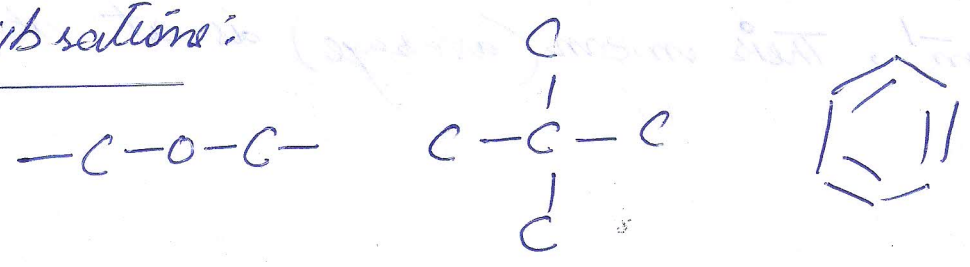
Band centre (separation between P and R branches) is about 2143 cm^{-1} .

$$2B = 3.83 \text{ cm}^{-1}$$

$$B = 1.915 \text{ cm}^{-1}$$

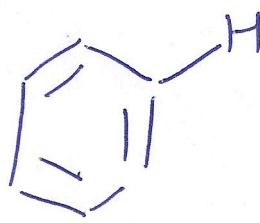
Normal modes of vibrations are divided into two classes: the skeletal vibrations
the functional group vibrations

Skeletal vibrations:



For organic molecules, the skeletal vibrations fall in the range $1400-700\text{ cm}^{-1}$. This region ($1400-700\text{ cm}^{-1}$) is called finger print region as peaks in this region are specific for a specific compound or no two compounds (which are different in structure) cannot have same peaks in finger print region.

Functional group region $\Rightarrow$ varies between $1400-4000\text{ cm}^{-1}$.
Here in this region, peaks due to functional groups are recorded in the spectrum.

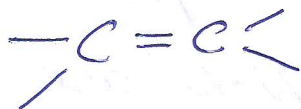
<u>Functional group</u>	<u>Approximate IR Frequency (cm^{-1})</u>
$-\text{OH}$	3600
$-\text{NH}_2$	3400
$\equiv\text{C}-\text{H}$	3300
	3060
$=\text{C}-\text{H}_2$	3030

Functional groupStretching frequency (cm⁻¹)

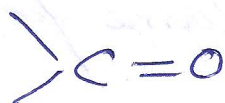
2250



2220



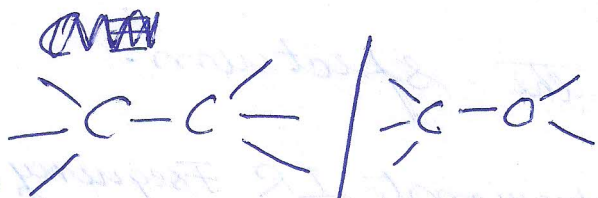
1650



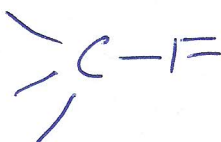
1750–1600



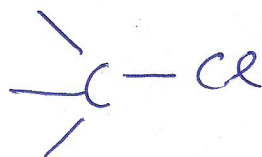
1600



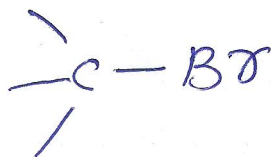
1200–1000



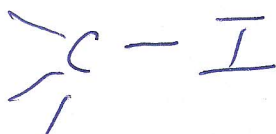
1050



725



650



550

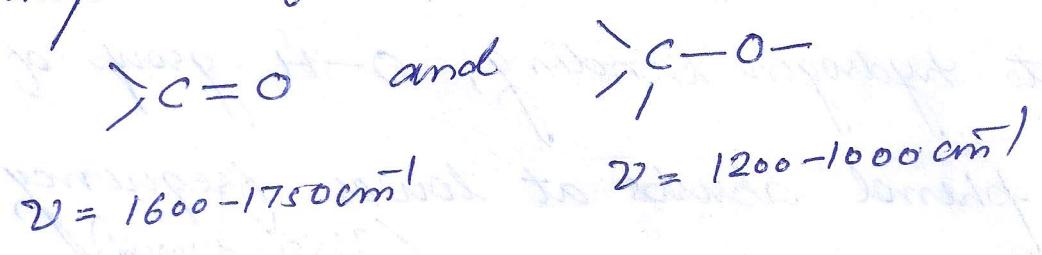
Factors affecting vibrational frequencies

1) Bond order :- more is the bond order (no. of bonds)

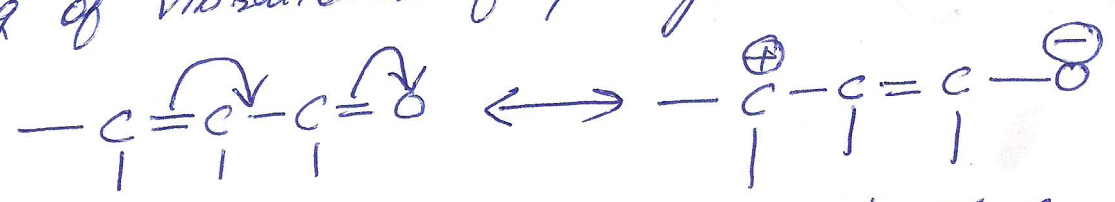
more will be the vibrational frequency.

	<u>Force constant</u> dynes cm^{-1}	<u>Bond order</u>	<u>Stretching frequency</u>
e.g. >C-C<	5×10^5	1	1300-800
>C=C<	10×10^5	2	1640-1600
$\text{-C}\equiv\text{C-}$	15×10^5	3	2300-2100

another example is of

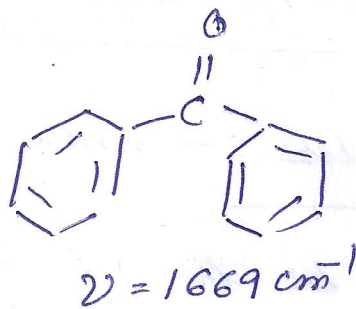
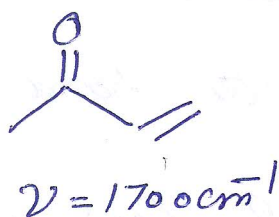
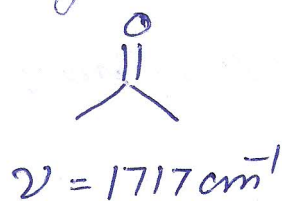


2) Conjugation : $\Rightarrow$ conjugation of a carbonyl group with an olefinic bond or aromatic ring results in the delocalization of the π electrons, reduces the double bond character causing a lowering of vibrational frequency.

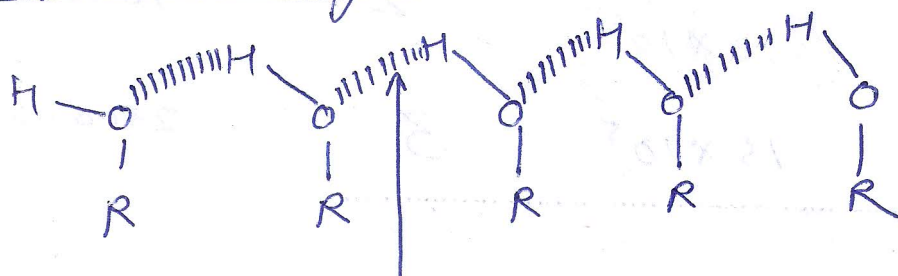


due to resonance stretching frequencies of C=C and

C=O groups decreases.



Hydrogen bonding



Hydrogen bonding

due to hydrogen bonding, O-H group of alcohol and phenol absorbs at lower frequency (broad bands) ($3550 - 3200 \text{ cm}^{-1}$).

But in vapour phase or in non polar solvents

hydrogen bonding disappears or breaks, so O-H group absorbs at higher frequency (near 3600 cm^{-1}) (sharp peaks).

Applications of Infrared spectroscopy: $\Rightarrow$

① Identification of an organic compound

The infrared spectrum of an organic compound (in fingerprint region) can help in identification of a compound.

e.g. $\text{CH}_3\text{CH}_2\text{OH}$ (Ethanol)

CH_3OH (Methanol)

Both Ethanol and Methanol have same functional group so spectrum in functional group region may be same but fingerprint regions of both ~~the~~ compounds are different due to different skeletons.

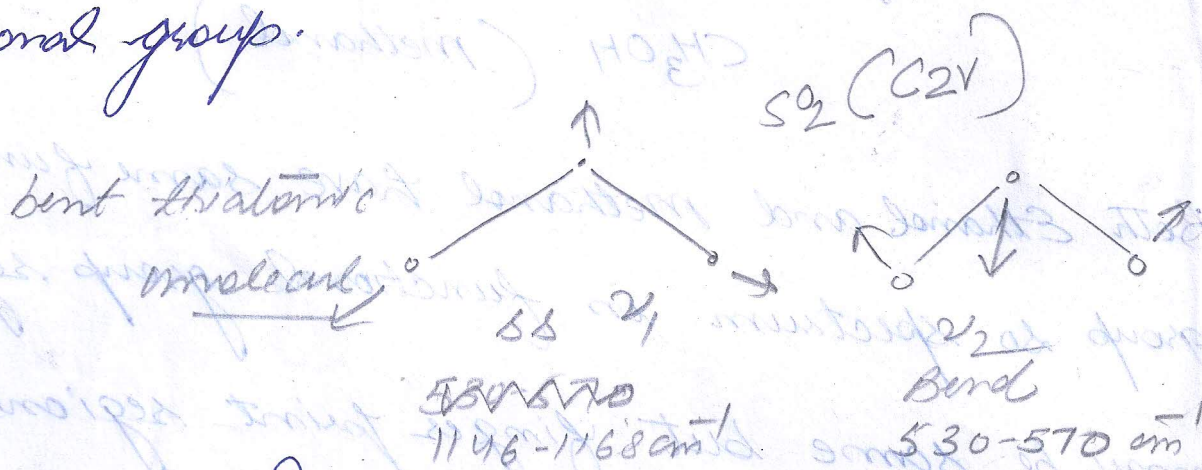
② Detection of functional groups (Qualitative analysis)

If a compound contains carbon, hydrogen and oxygen, only $\rightarrow$ compound can be $\text{O}-\text{H}$, $\text{C}=\text{O}$ or $\text{C}-\text{O}-\text{C}$ or ester, carboxylic acid etc.

If peak appears in $(1650-1870\text{ cm}^{-1})$ region, carbonyl may be present.

If peak appears in $(3700-3200\text{ cm}^{-1})$ region, $-OH$ group can be present.

So presence or absence of a peak for a functional group can ascertain the presence or absence of a functional group.

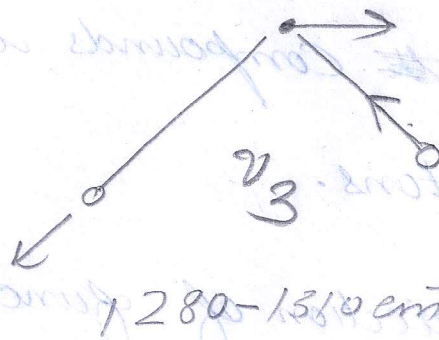


propenyl cation

NO hyperconjugation

propene

hyperconjugation



29

C
O