

BSc chemistry - 5th semester

Title of the course - DSC-6 (discipline specific core course)
Subject code - 21BSCS6CHE6L

Paper - 2

Syllabus

(15 hrs) Part - IV

(5 hrs) * Infrared Spectroscopy.

- Introduction to infrared spectroscopy.
- Intensity of absorption band.
- Position of absorptions
- C-H, >C=O, O-H & N-H absorption bands with explanation for variation in stretching frequencies.
- Identification of H-bonding in alcohols, phenols & carboxylic acids using IR-spectroscopy.

(5 hrs) * UV and visible Spectroscopy.

- Types of electronic transitions.
- Chromophores and auxochromes.
- Bathochromic shift & hypsochromic shift.
- Intensity of absorption.
- Woodward-Fieser rules for calculating λ_{max} of conjugated dienes such as alicyclic, homoannular and hetero annular dienes.
- Applications of UV spectroscopy.

(5 hrs) * Mass Spectrometry.

- Principle
- Determination of m/e ratio
- Instrumentation.
- Determination of molecular mass & isotopic abundance
- Molecular ion peaks & base peak.
- McLafferty rearrangement with respect to 2-hexanone, hexanoic acid & methyl hexanoate.

Course objective

Students learn about

- (5) Applications of infrared spectroscopy, UV-visible spectroscopy and mass spectroscopy in organic chemistry.

Course outcome

After the completion of this course, the student would be able to

- (6) Identify the molecules using the data from infra-red spectroscopy, UV-VIS spectroscopy & mass spectrometry.

Total Marks : 100 → 60 sem exam (2 hrs). } 75%.

→ 40 IA marks } attending

10+10 → C₁ i.e 1st IA (30)+Assignment

10+10 → C₂ i.e 2nd IA (30)+class room activity.

Exam pattern:

- (Q) 7 & 8(h) Q. No 1: Any six ($2 \times 6 = 12$) out of 8 (2 from each unit)
- Q. No 2: Any three ($4 \times 3 = 12$) out of 4 (from unit-I).
- Q. No. 3: Any three ($4 \times 3 = 12$) out of 4 (from unit-II)
- Q. No. 4: Any three ($4 \times 3 = 12$) out of 4 (from unit-III)
- 1, 2, 3, 4. Q. No. 5: Any three ($4 \times 3 = 12$) out of 4 (from unit-IV)

References:

→ Spectroscopy is that branch of science which deals with the study of interaction of electromagnetic radiation with matter.

The term electromagnetic radiation represents the radiant energy emitted from any source in the form light, heat etc.

→ They have dual character.

→ These waves are associated with electric and magnetic fields. All electromagnetic radiations travel with the velocity of light

$$[C = r\lambda] \quad \underline{\underline{v = c/\lambda}}$$

→ Each photon is a packet of energy whose energy is given by Plank's equation

$$[E = hv]$$

where h is plank's constant i.e. $h = 6.632 \times 10^{-34}$ Js.

→ When the different types of electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequency the complete arrangement is called as "Electromagnetic Spectrum".

wavelength λ (cm)	EMR	Energy scale / mol	Interaction
higher frequency 10^{-9}	gamma rays	10^6	IONIZATION
bigger wavelength 10^{-7}	X rays	10^4	
10^{-5}	UV	10^2	Electronic transitions
10^{-4}	VISIBLE	10	
10^{-3}	Infrared	1	Molecular vibration
10^{-1}	microwave	10^{-2}	
10^2	Radio waves	10^{-4}	Rotational motion Nuclear spin transitions
lower frequency 10^4		10^{-6}	
longer wavelength			

→ Matter upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called as Infrared spectrum or Vibrational spectrum and process is known as Infrared spectroscopy or Vibrational Spectroscopy.

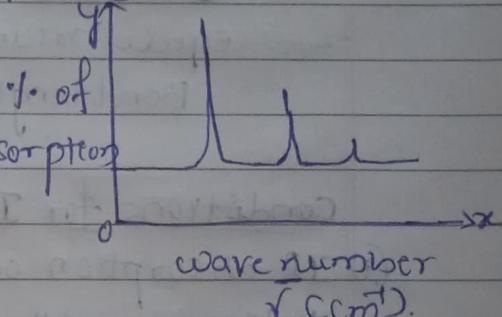
→ Infrared spectrum is a plot of absorption (%) versus wavenumber (cm^{-1})

wave number is

reciprocal of wavelength absorption

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

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



→ Wave numbers are directly proportional to frequency.

Range of IR.

- (i) Near IR : 0.8 to 2.5 μm (12000cm^{-1} - 4000cm^{-1}).
- (ii) Middle IR : 2.5 to 15 μm (4000cm^{-1} - 667cm^{-1}).
group frequency regions: 4000cm^{-1} - 1500cm^{-1} .
Fingerprint region: 1500cm^{-1} - 667cm^{-1}
- (iii) Far IR: 15 to 1000 μm (667cm^{-1} - 10cm^{-1}).

→ Molecules (Atoms)

→ continuous motion (natural vibrations)

→ Applied IR frequency

→ Absorption of IR frequency

→ Vibrations at many rates

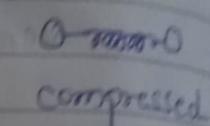
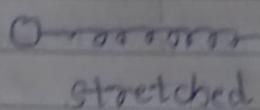
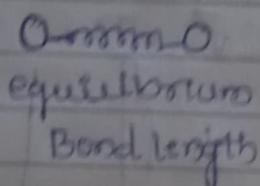
→ IR spectra

→ Characteristic functional groups & Bonds.
Fingerprint of a molecule

Principle of IR Spectroscopy

→ Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses or atoms.

Note: Specific bonds respond (absorb) to specific frequencies.

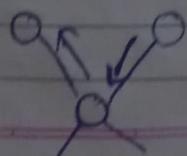
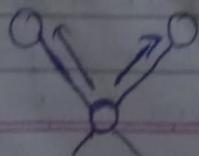


Conditions for IR Absorption

- IR absorption only occurs when IR radiation interacts with a molecule undergoing a change in dipole moment (μ) as it vibrates.
i.e. $\Delta\mu > 0$
- IR absorption only occurs when the incoming IR photon has sufficient energy for transition to the next allowed vibrational state to take place
i.e. $\Delta E = h\nu$

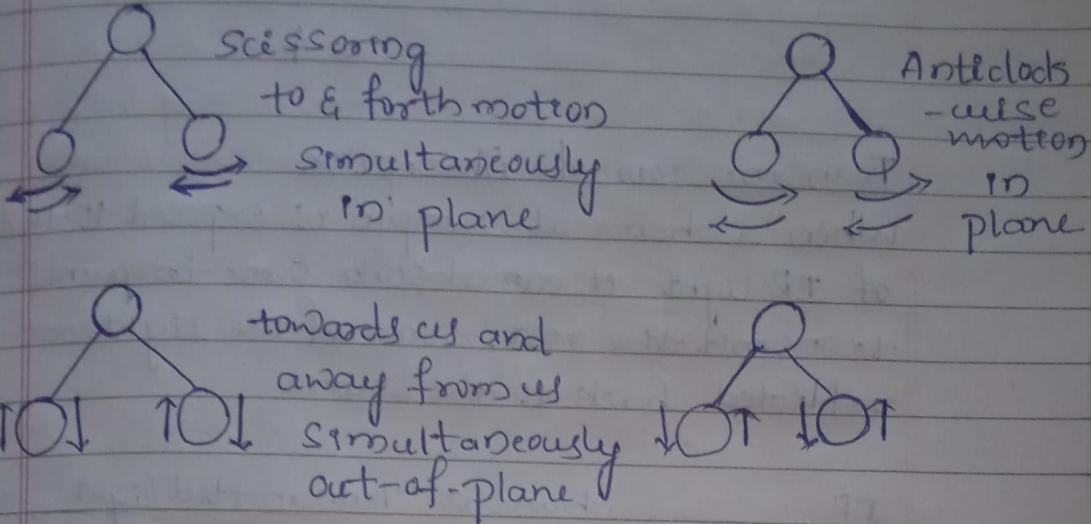
Modes of vibrations

- Vibrations can involve either changes in bond length (stretching) or bond angle (bending).
- Some bonds can stretch in-plane (symmetric stretching) or out-of-plane (asymmetric stretching)



Symmetric Stretching Asymmetric Stretching

→ Bending vibrations can be either in-plane (scissoring, rocking) or out-of-plane (wagging, twisting).



Degrees of Freedom

Number of cartesian coordinates which defines the position of an atom in space are called as degrees of freedom.

→ For one atom there are three degrees of freedom then compound/molecule containing n number of atoms then it has $3n$ degrees of freedom which is given by -

$$\text{Total } 3n \text{ DOF} = \text{Translational DOF} + \text{Rotational DOF} + \text{Vibrational DOF}$$

Total DOF	Type of molecule	Translational DOF	Rotational DOF	Vibrational DOF
3n	Linear	3	2	$3n - 5$
3n	Non-linear	3	3	$3n - 6$

Ex: HCl, For HCl, $n=2$

Since it is linear molecule

$$\begin{aligned}\text{Vibrational DOF} &= 3n - 5 \\ &= 3(2) - 5 \\ &= 1\ #\end{aligned}$$

Ex: CO_2 , for CO_2 $n=3$

Since it is linear molecule

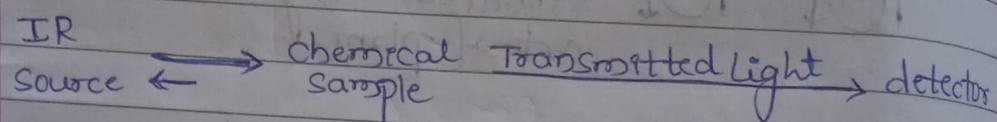
$$\text{Vibrational DOF} = 3n - 5$$

$$= 3(3) - 5$$

$$= 4$$

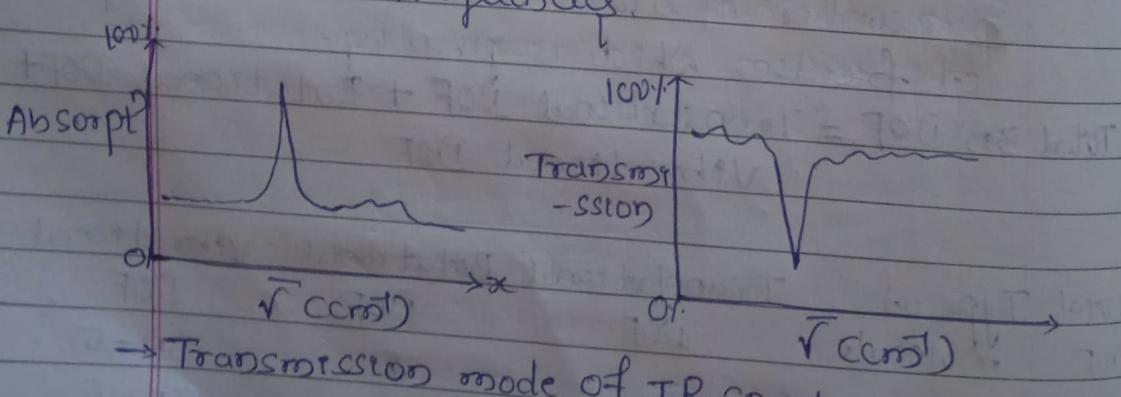
Transmission vs Absorption.

When a chemical sample is exposed to the action of IR light, it can absorb some frequencies and transmit the rest. Some of the light can also be reflected back to the source.



→ From all the frequencies it receives, the chemical sample can absorb certain specific frequency and allow the rest to pass through it (transmitted light).

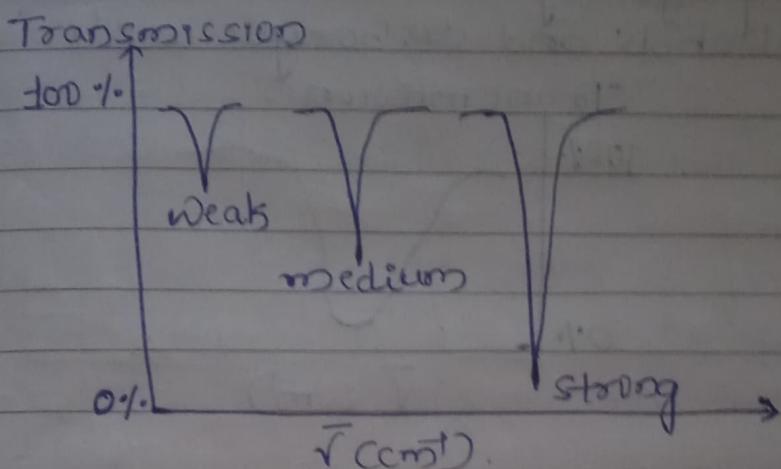
The detector detects the transmitted frequency and by doing so also reveals the values of the absorbed frequencies.



→ Transmission mode of IR spectrum is the most commonly used representation.

- * Intensity of Absorption bands.
IR bands can be classified as strong, medium or weak, depending on their relative intensities in the infrared spectrum.

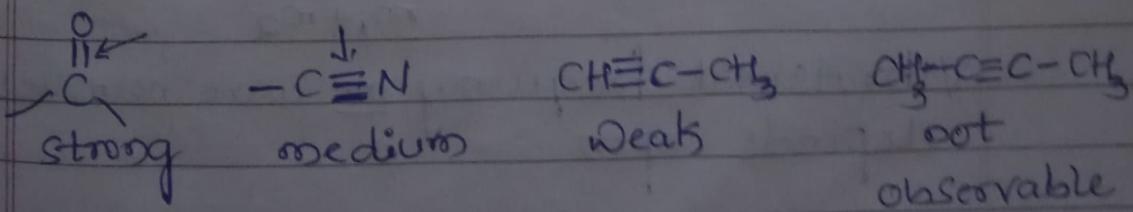
→ A strong band covers most of the y-axis. A medium band falls to about half of the y-axis and a weak band falls to about one-third or less of the y-axis.



→ Not all covalent bonds display bands in the IR spectrum; only polar bonds do so. These are referred to as IR active.

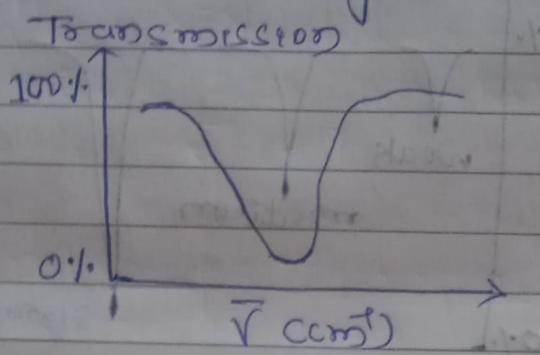
→ The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question.

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



→ Infrared band shapes come in various forms. Two of the most common are narrow and broad. Narrow bands are thin and pointed like a dagger. Broad bands are wide and smoother.

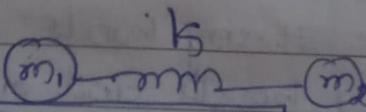
A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids.



* Vibrational Frequency.

The value of stretching vibrational frequency of bond can be calculated by using Hooke's law.

→ Hooke's law states that the vibrational frequency of a bond is directly proportional to the bond strength and inversely proportional to the masses at the ends of the bond.



$$\boxed{\bar{f} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}}$$

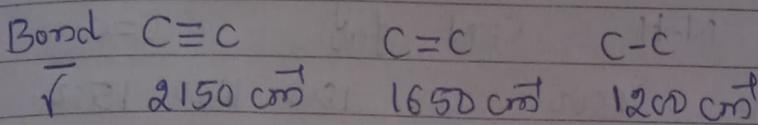
where $m = \frac{m_1 \cdot m_2}{m_1 + m_2}$ Reduced mass.

Vibrational frequency or wave number depends upon

(i) Bond strength.

The frequency of vibration will be directly proportional to strength of bond (K).

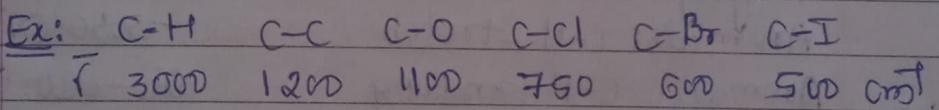
Ex: stretching vibration of triple bond will appear at high frequency than that of either a double or single bond.



since triple bond strength is greater than double and single bond hence it has highest stretching vibration frequency.

(ii) Mass.

Vibrational frequency is inversely proportional to the masses at the ends of bond.



* Position of IR absorptions.

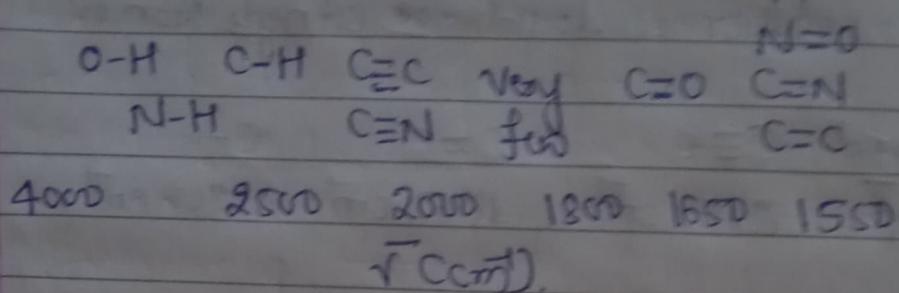
In general, the IR spectrum can be split into four regions for interpretation.

$4000 - 2500 \text{ cm}^{-1}$: Absorption of single bonds formed by hydrogen and other elements eg. $O-H$, $N-H$, $C-H$.

$2500 - 2000 \text{ cm}^{-1}$: Absorption of triple bonds eg. $C \equiv C$, $C \equiv N$.

$2000 - 1500 \text{ cm}^{-1}$: Absorption of double bonds eg. $C=C$, $C=O$

1500 - 400 cm⁻¹: This region often consists of many different complicated bands called the fingerprint region. It is rarely used for identification of particular functional groups.



* <u>Functional Group</u>	<u>Characteristic Absorption</u> (cm ⁻¹)
Alkyl C-H stretch	2950 - 2850 (m, w)
Alkenyl C-H stretch	3100 - 3010 (m)
Alkene C=C stretch	1680 - 1620 (v)
Alkyne C-H stretch	~3300 (s)
Alkyne C≡C stretch	2260 - 2100 (v)
Aromatic C-H stretch	~3030 (v)
Aromatic C-H bending	860 - 680 (s)
Aromatic C=C bending	1700 - 1500 (m, w)
Alcohol / phenol O-H stretch	3950 - 2900 (broad)
Carboxylic acid O-H stretch	3000 - 2500 (broad)
Aniline N-H stretch	3500 - 3300 (m)
Nitrile C≡N stretch	2260 - 2220 (cm)
Aldehyde C=O stretch	1740 - 1690 (s)
Ketone C=O stretch	1750 - 1680 (s)
Ester C=O stretch	1750 - 1735 (s)
Carboxylic acid C=O stretch	1780 - 1710 (s)
Anilide C=O stretch	1690 - 1650 (s)
Anilide N-H stretch	3700 - 3500 (cm)

* Factors affecting Vibrational frequency

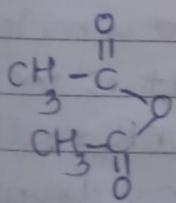
→ Mainly there are four factors responsible for shifting the vibrational frequencies from their normal values.

(i) Coupled Interactions.

- An isolated C-H bond has only one stretching vibrational frequency whereas methylene group shows two stretching vibrations. Symmetrical and asymmetrical because of mechanical coupling or interaction between C-H stretching vibrations in the -CH_2 group.
- Asymmetric vibrations occur at higher frequencies or wave numbers than symmetric stretching vibrations.

These are known as coupled vibrations because these vibrations occur at different frequencies than that required for an isolated C-H stretching.

Ex: A strong vibrational coupling is present in carbonylic acid anhydrides in which symmetrical and asymmetrical stretching vibrations appear in the region $1720 - 1825 \text{ cm}^{-1}$



The interaction is very effective probably because of the partial double bond character in the carbonyl oxygen bonds due to resonance which also keeps the system planar for effective coupling.

Requirements.

- For interaction to occur, the vibrations must be of same symmetry species
- There must be a common atom between the groups for strong coupling between stretching vibrations.
- For coupling of bending vibrations, a common bond is necessary.
- Interaction is greatest when coupled groups absorb individually near the same frequency.
- Coupling is negligible when groups are separated by one or more carbon atoms and the vibrations are mutually perpendicular.

(ii) Fermi Resonance.

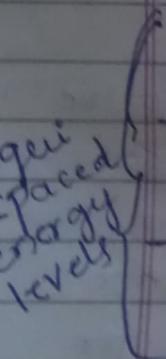
When a matter incident with

v_1 IR radiation of frequency (v_1)

there by matter undergo vibrational transitions

v_0 . from $v_0 \rightarrow v_1$, then the

frequency required for this transition is called as Fundamental Vibrational frequency.



v_3
 E_3 2nd overtone

v_2
1st overtone

v_1

FVF

No

If in a molecule when it is incident with IR radiation

vibrational transitions from $v_0 \rightarrow v_1$

$v_0 \rightarrow v_2$

$v_0 \rightarrow v_3$.

are occurred since these energy levels are quantized or equally spaced

Then $E_2 = 2E_1 \rightarrow$ 1st overtone

$E_3 = 3E_1 \rightarrow$ 2nd overtone

$E_4 = 4E_1$

In general, Overtones are multiples of Fundamental vibrational frequencies.

$\nu_0 \rightarrow \nu_1$

Ex: If a molecule has 1400 cm^{-1} as a fundamental vibrational frequency then -

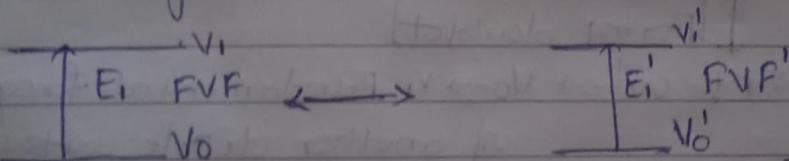
$\nu_0 \rightarrow \nu_2$ 2800 cm^{-1} is its 1st overtone

$\nu_0 \rightarrow \nu_3$ 4200 cm^{-1} is its 2nd overtone

$\nu_0 \rightarrow \nu_4$ 5600 cm^{-1} is its 3rd overtone

(Higher overtones are not considered/observed).

→ Let us consider a molecule with two functional groups, when it is incident with IR radiation it undergoes two sets of vibrational transitions



that is from $\nu_0 \rightarrow \nu_1$ with E_1 as a fundamental vibrational frequency and $\nu_0' \rightarrow \nu_1'$ with E_2 as a fundamental vibrational frequency. These two different fundamental vibrational frequencies are coupled to form new frequency of absorptions.

$$E_2 = E_1 + E_1'$$

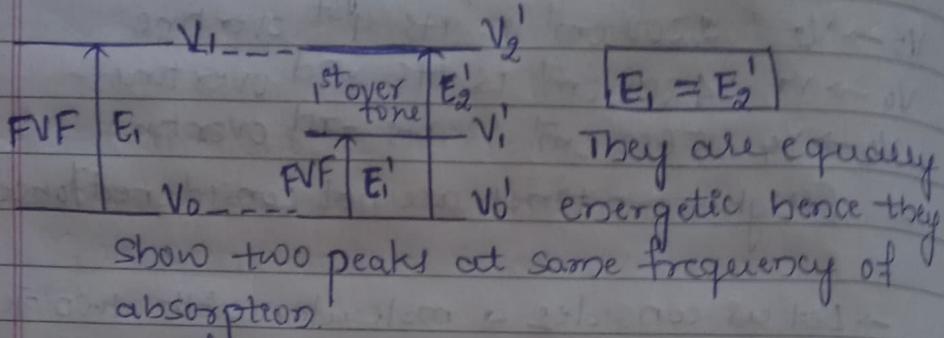
These are known as combination bands.

"Combination bands are formed by coupling of two fundamental vibrational frequency of absorption".

Ex: $1400\text{ cm}^{-1} \rightarrow \nu_0 \rightarrow \nu_1 \rightarrow$ Fundamental frequency
 $750\text{ cm}^{-1} \rightarrow \nu_0' \rightarrow \nu_1' \rightarrow$ Fundamental frequency

$2150\text{ cm}^{-1} \rightarrow$ combination bond

→ Let us consider a molecule with two dipoles when it is incident with IR radiation it undergoes two sets of vibrational transitions that is from $\nu_0 \rightarrow \nu_1$ with E_1 as a fundamental frequency and $\nu_0' \rightarrow \nu_1'$ with E_1' as a fundamental frequency along with from $\nu_0' \rightarrow \nu_2'$ with E_2' as its 1st overtone.



Ex: $1400 \text{ cm}^{-1} \rightarrow \nu_0 \rightarrow \nu_1$ Fundamental frequency
 $2800 \text{ cm}^{-1} \rightarrow \nu_0 \rightarrow \nu_2$ First overtone

↑ [Fermi doublet]
 $2790 \text{ cm}^{-1} \rightarrow \nu_0 \rightarrow \nu_1$ Fundamental frequency of another dipole within molecule

When this fundamental frequency 2790 cm^{-1} is resonance with 2800 cm^{-1} of overtones they form doublet at this frequency is known as Fermi resonance and doublet is known as Fermi doublet.

→ Fermi Resonance occurs when there is coupling of either overtones or combination bands with the fundamental frequency of another dipole within the molecule.

In this way overtones, combination bands and Fermi resonance shows some extra peaks in IR spectrum.

(iii) Hydrogen Bonding.

→ It occurs in any system containing a proton donor ($X-H$) and a proton acceptor.

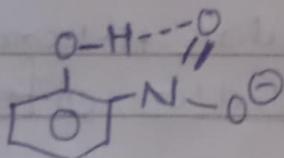
Hydrogen along with more electronegative atoms like fluorine, oxygen and nitrogen hence most of the times Hydrogen bond formed in case of alcohols, phenols, amines & carboxylic acids.

There are two types of Hydrogen bonding.

(i) Intra-molecular H-bonding.

The hydrogen bond is formed within the same molecule.

Ex:

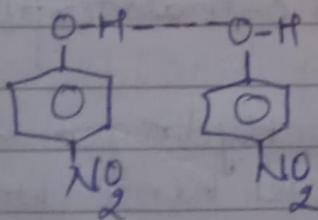


O-nitrophenol

(ii) Inter-molecular H-bonding.

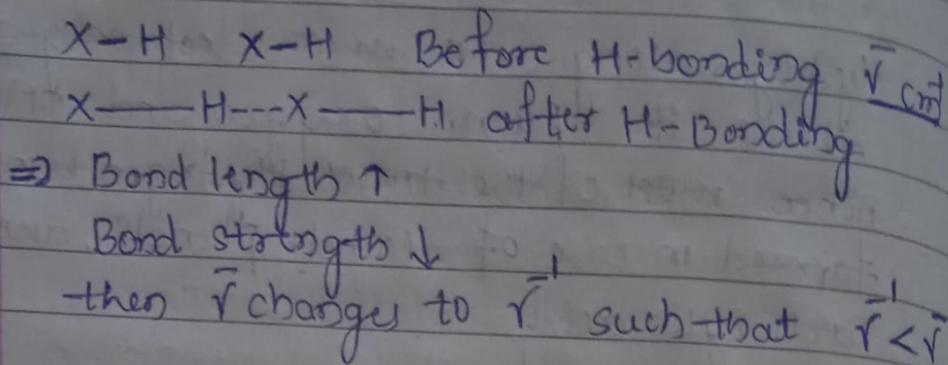
The hydrogen bond is formed between two different molecules.

Ex:



→ When hydrogen bond is formed (whether it is intra or intermolecular) - there is change in bond length of $X-H$ (where $X=N, O, F$) depends on the extent of hydrogen bonding.

Bond strength decreases that will resulting low absorptioal vibrational frequency from normal value



- Intramolecular H-bonding gives rise to broad bands, while intra molecular H-bonds give sharp and well defined bands.
- Intra and inter-molecular H-bonds can be distinguished by dilution effect.

Intra molecular H-bonding remains unaffected by dilution and as a result the absorption band also remains unaffected whereas in intermolecular H-bonds all broken on dilution and as a result there is a decrease in the bonded O-H absorption

as a dilution increases, hydrogen bond (intermolecular) decreases hence broad band slowly change into sharp band

- The strength of H-bonding is also affected by
 - Ring Strain
 - Molecular geometry.
 - Relative acidity and basicity of the atoms.

Ex: In aliphatic alcohols, a sharp band appears at 3650 cm^{-1} in dilute solutions due to free O-H group while a broad band appears at 3350 cm^{-1} due to H-bonded -OH group.

Ex: In case of anines, N-H stretching occurs at 3550 cm^{-1} in dilute solutions while in condensed phase spectra absorption occurs at 3350 cm^{-1} due to H-bonded -NH group.

(iv) Electronic effects.

The frequency shift from the normal position of absorption occurs because of electronic effects such as

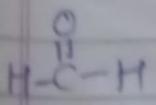
- (a) Inductive effect
- (b) Mesomeric effect
- (c) Field effect

Under influence of these effects the bond strength changes and its absorption frequency shift from normal value.

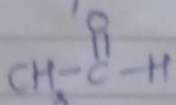
Inductive effect.

→ Introduction of alkyl groups (electron releasing groups) cause positive inductive effect (+I effect) which will show lengthening or weakening of the bond. Due to this absorption takes place at lower wave number or frequency.

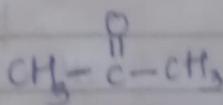
Ex: Compare wave numbers of C=O absorption for following compounds.



Formaldehyde
 1750 cm^{-1}



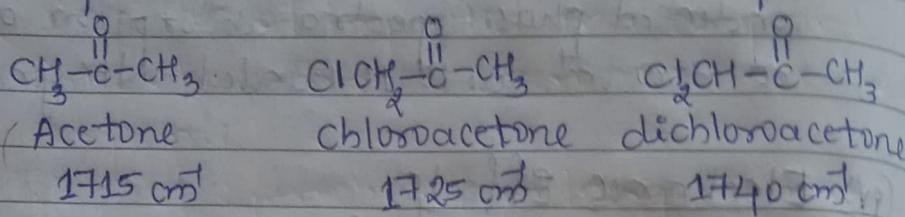
Acetaldehyde
 1745 cm^{-1}



Acetone
 1715 cm^{-1}

→ Introduction of electronegative groups (electron withdrawing groups) cause negative inductive effect (-I effect) which will show more dipole moment of the bond. Due to this absorption takes place at higher wave number or frequency.

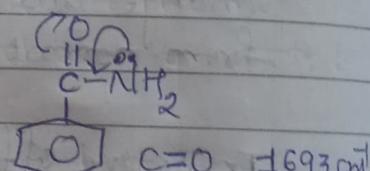
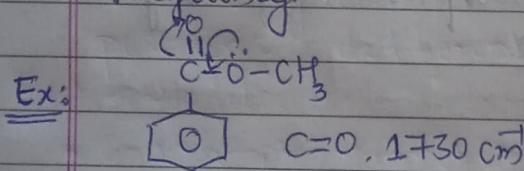
Ex: Compare wave numbers of C=O absorption



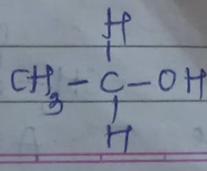
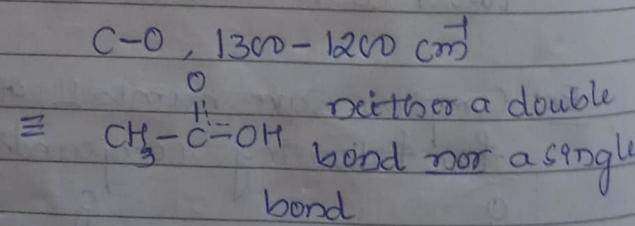
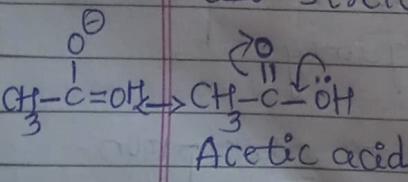
Mesomeric Effect

In many cases mesomeric effect works along with the inductive effect and shift the vibrational frequency.

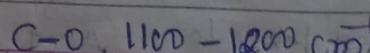
→ Conjugation causes lengthening or weakening of bond leading to lowering of vibrational frequency.



But in case of carboxylic acids and alcohols C=O stretching shows opposite effect



Ethanol

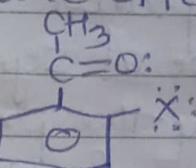
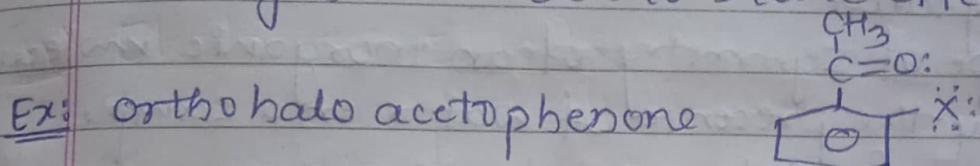


Field Effect

In ortho substitution, inductive effect, mesomeric effect works along with steric effect.

In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called field effect.

It is generated due to steric effect.



IR Spectrometers: Advantages.

- 1) All kinds of material can be analyzed.
- 2) provides lot of information.
- 3) fast and easy.
- 4) Very small amount of sample is required.
- 5) Less expensive.

Disadvantages.

- 1) IR spectra cannot be obtained for mono atomic substances e.g. helium, argon.
- 2) IR spectra cannot be obtained for H-mono-nuclear diatomic molecules like N_2, O_2 .
- 3) Works best for pure substance but not for complex mixtures.

Applications of IR spectroscopy

- Identification of functional groups and structure elucidation of organic compounds
- Quantitative analysis of number of organic compounds
- Study of covalent bonds in molecules
- studying the progress of reactions
- Detection of impurities in a compound
- Ratio of cis-trans isomers in a mixture of compounds
- shape of symmetry of an inorganic molecule
- Study the presence of water in a sample
- study of Beta-enol tautomerism

Limitations of IR spectroscopy

- Cannot determine the molecular weight of the compound.
- Does not give information about the relative positions of different functional groups in a molecule.
- Gas samples cannot be analysed as they lack sensitivity.
- From the single IR spectrum of an unknown substance it is not possible to know whether it is pure compound or a mixture of compound.