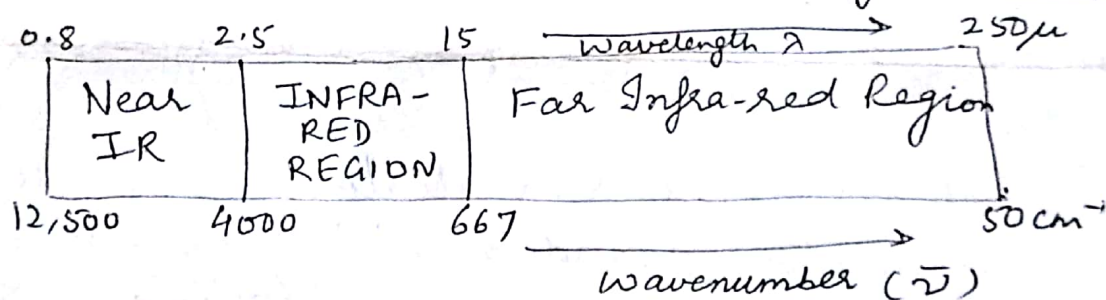


INFRA-RED (IR) SPECTROSCOPY

Infrared Spectroscopy gives information about the molecular vibrations. The vibrational energy separation is very large as compared to rotational energy separation. When a molecule absorbs radiation in IR region, there is Vibrational-rotational spectrum. The IR spectrum consists of vibrational band with a number of rotational lines.

- The ordinary infra-red region extends from 2.5μ to 15μ . The region from 0.8μ to 2.5μ is called Near infra-red and that from 15μ to 200μ is called Far infra-red region.



$$\bar{\nu} = \frac{1}{\lambda (\text{cm})}$$

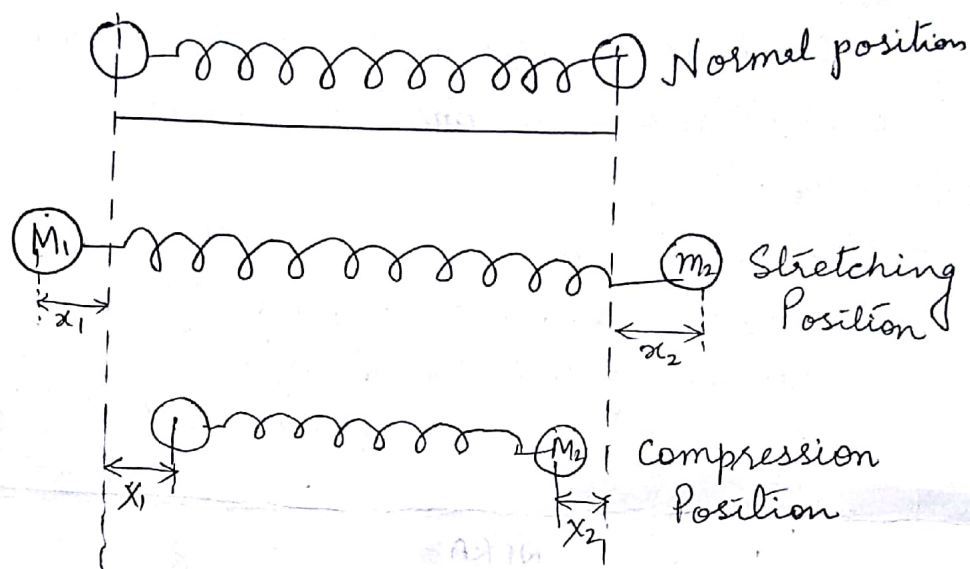
$$1\mu = 10^{-4}\text{ cm}$$

- IR-spectroscopy is one of the most powerful analytical technique for structure elucidation.
- The absorption bands gives valuable information about
 - (i) Functional groups
 - (ii) Bonds present in a chemical substance.
- The plot of % transmission of IR radiation versus wavelength is known as infrared spectrum.

MOLECULAR VIBRATION

The vibrational energy depends upon :

- (i) Masses of the atoms present in a molecule.
- (ii) Strength of the bonds
- (iii) The arrangement of atoms within the molecule.



Let us consider a diatomic molecule in which atoms A and B oscillate against each other just like a harmonic oscillator.

- The vibration frequency of a diatomic molecule

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \text{ cm}^{-1}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ = reduced mass

m_1 & m_2 are the masses of atoms A and B respectively in gram.

K = force constant

c = Velocity of light = 3×10^{10} cm/sec

Bond bending is more imp than bond stretching in interpretation of alkene & aromatic comp.

(2)

Therefore, in case of a diatomic molecule the vibrational frequency depends upon -

(i) Force constant

(ii) Reduced mass

When a bond is elastic, it will stretch and compress periodically with a certain fundamental frequency depending upon the

(i) Masses of the atoms

(ii) Elasticity of the bond

According to Hook's law -

$$\text{Restoring force } F = -K(x_2 - x_1) \\ = -Kx$$

\therefore force constant of a bond depends upon the strength of the bond.

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

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

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

$$K \propto \bar{\nu}$$

The energy difference between the two successive vibrational levels is given by

$$\Delta E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \text{ ergs}$$

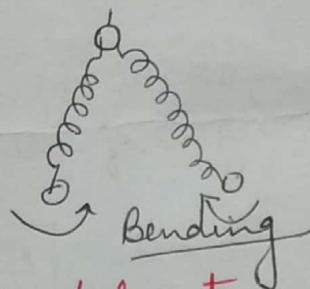
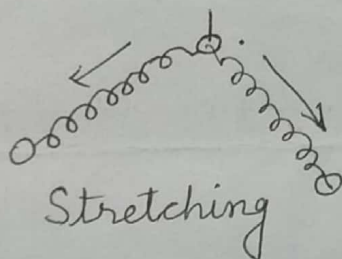
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \text{ cm}^{-1}$$

TYPES OF VIBRATION

There are 2 types of fundamental vibrations -

- (i) Stretching Vibration
- (ii) Bending Vibrations

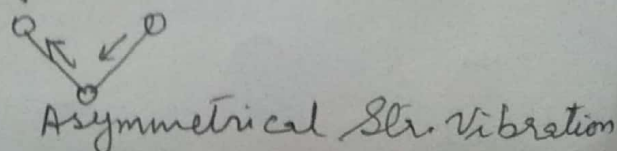
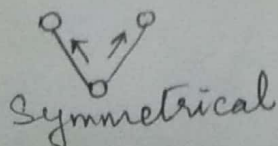
(i) Stretching Vibrations - Vibrations in which distance between two atoms increases or decreases but the atoms remain in the same bond axis are known as stretching vibrations. In stretching vibrations two bonded atoms continuously oscillate without altering the bond angle. It is denoted by $\nu(\text{nm})$.



Types of Stretching Vibrations :-

There are 2 types of stretching vibrations:-

- (a) Symmetrical Stretching Vibration:- The mode of stretching vibration in which both the atoms move in and out simultaneously is known as symmetric stretching vibration.
- (b) Asymmetrical stretching Vibration - The mode of stretching vibration in which one atom 'moves in' while the other moves out is known as asymmetrical stretching vibration.



(3)

Stretching vibrations require more energy and hence occur at shorter wavelength.

$$\nu_{C-C} < \nu_{C=C} < \nu_{C\equiv C}$$

(ii) Bending Vibrations :- "Vibrations in which positions of atoms

change relative to the original bond axis are known as bending vibrations". Bending vibrations require lower energy and occur at longer wavelength as compared to the stretching vibration. They are also known as deformation vibrations. It is denoted by δ (delta).

eg $\delta(N-H) = 1590 \text{ cm}^{-1}$

Types of bending Vibrations:- These are of 4 types-

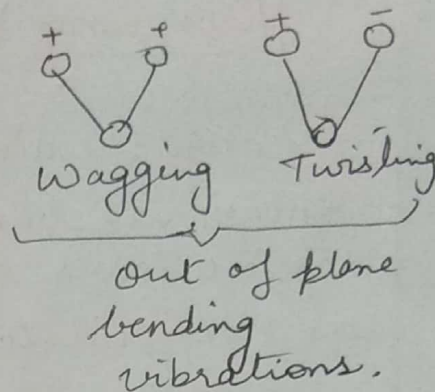
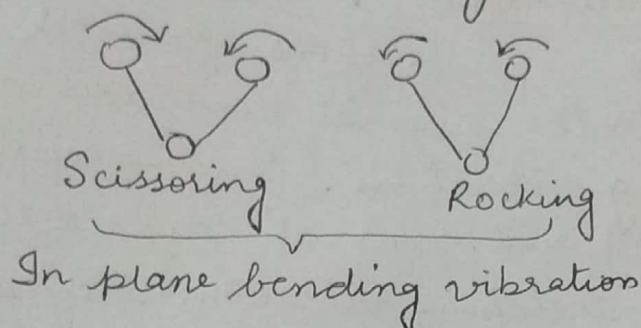
- | | |
|----------------|--------------|
| (a) Scissoring | (b) Rocking |
| (c) Wagging | (d) Twisting |

(a) Scissoring - The mode of bending vibrations in which two atoms approach each other is known as scissoring.

(b) Rocking - The mode of bending vibration in which both the atoms move to the same side and then both to the other side i.e. the movement of atoms takes place in one direction is known as rocking.

(c) Wagging - The mode of vibration in which two atoms move up and below the plane wrt the central atom is known as wagging.

(d) Twisting - The mode of bending vibration in which one of the atoms moves up the plane while the other moves down the plane with respect to the central atom is known as twisting.



FUNDAMENTAL VIBRATIONS AND OVERTONES

Fundamental vibrations :- The vibration corresponding to the transition from the ground state (ν_0) to the first excited state (ν_1) is known as fundamental vibration. The fundamental vibration absorbs light strongly and it gives rise to intense bands known as fundamental bands & the corresponding frequency is known as fundamental frequency. According to quantum mechanics :-

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

$$\text{If } \nu=1 \therefore \left(1 + \frac{1}{2}\right) h\nu = \frac{3}{2} h\nu \text{ --- (1)}$$

$$E_{\text{vib}} (\nu=0) = \left(0 + \frac{1}{2}\right) h\nu = \frac{1}{2} h\nu \text{ --- (2)}$$

$$\Delta E_{\text{vib}} (\nu=0) = E_{\text{vib}} (\nu=1) - E_{\text{vib}} (\nu=0)$$

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

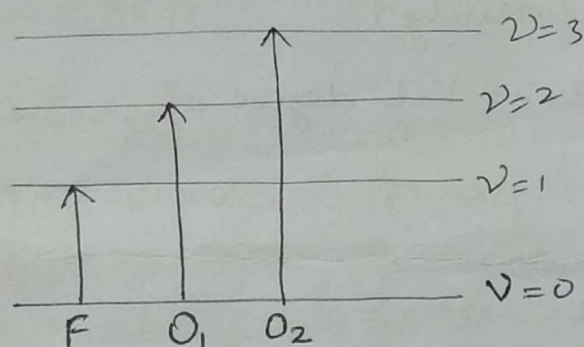
$$\boxed{\Delta E_{\text{vib}} = h\nu}$$

Does covering as more and more
interpretation of alkene & aromatic comp.

Overtone :- Vibrational bands other than fundamental bands are known as overtones e.g. Transition from the ground ($\nu=0$) state to the second excited state ($\nu=2$). Therefore, energy for the first overtone is given by -

$$\begin{aligned}\Delta E_{\text{vib}} &= E_{\text{vib}}(\nu=2) - E_{\text{vib}}(\nu=0) \\ &= \left(2 + \frac{1}{2}\right) h\nu - \left(0 + \frac{1}{2}\right) h\nu \\ \Delta E_{\text{vib}} &= \frac{5}{2} h\nu - \frac{1}{2} h\nu = 2h\nu\end{aligned}$$

Similarly, second, third overtones can be calculated -



Number of Fundamental Vibrations

Non-Linear polyatomic molecules :- Let 'n' be the number of atoms in the polyatomic molecule. Therefore total degree of freedom of the molecule = $3n$

⇒ Total degree of freedom = Translational degree of freedom

+ Rotational degree of freedom + Vibrational degree of freedom

Translational degree of freedom = 3

Rotational

"

"

"

= 3

$3n = 3 + 3 + \text{Vibrational degree of freedom}$

$$\boxed{\text{Vibrational degree of freedom} = 3n - 6}$$

eg- (i) CH_4 $n=5$

$$\text{Vibrational degree of freedom} = (3 \times 5 - 6) = 9$$

(ii) C_6H_6 $n=12$

$$\text{Vib. degree of freedom} = 3 \times 12 - 6 = 30$$

For linear molecules — Total degree of freedom = $3n$

$$\text{Translational degree of freedom} = 3$$

$$\text{Rotational degree of freedom} = 2 \text{ (only 2)}$$

because there is no degree of freedom about its axis of linearity)

$$3n = 3 + 2 + \text{Vib. degree of freedom}$$

$$\boxed{\text{Vib. degree of freedom} = 3n - 5}$$

eg- (1) CO_2 $\text{O}=\text{C}=\text{O}$

$$\text{Vibrational degree of freedom} = (3n - 5)$$
$$3 \times 3 - 5 = 4$$

(2) $\text{HC} \equiv \text{CH}$

$$\text{vib. degree of freedom} = 3 \times 4 - 5 = 7$$

Dipole Moment & Infrared Spectrum

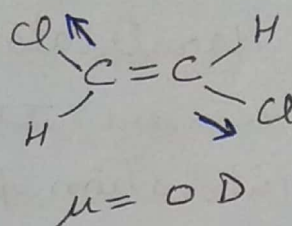
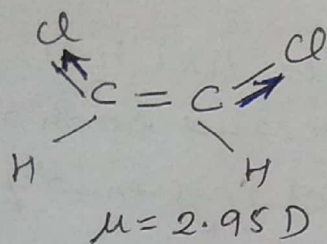
Generally the absorption of infrared radiation of particular frequency by a molecule can occur only if the dipole moment of the molecule is different in the two vibrational levels. The IR light is absorbed when the oscillating dipole moment interacts with oscillating electric vector of an infrared beam. If no change in dipole

... as more imp than ...
aromatic comp.

(5)

moment accompanies the vibrations, then the mode is infrared inactive or the molecule is said to be infrared inactive or the molecule is said to be infrared inactive.

Eg- Why trans dichloroethylene show no $C=C$ stretching absorption while cis isomer shows this bond.



The $>C=C<$ in trans isomer is non-polar having zero dipole moment. On stretching, the dipole moment does not change and hence no absorption of infrared radiation take place whereas cis-isomer has a dipole moment, hence cis isomer shows $C=C$ stretching absorption band. However, both the isomers shows bands for $C-H$ & $C-Cl$ stretching.

SELECTION RULE

The selection rules are -

- (i) The dipole moment of the molecule should change during the course of vibration.

ie. $\frac{d\mu}{dq} \neq 0$

@ Therefore, homodiatomic molecules (like H_2 , O_2 , N_2) do not give rise to IR spectra. These molecules are known as IR-inactive.

(b) Heterodiatomic molecules/ other molecules (like HCl , HBr ----) give rise to IR-spectra.

(c) Triatomic molecules/ other molecules having centre of symmetry are IR-inactive because the symmetric stretching of the bond produces no change in dipole moment.

eg CO_2 , CS_2

(d) Angular triatomic molecules like H_2O , SO_2 , H_2S etc are IR-active because each mode of vibration produces a change in dipole moment.

~~Diatomic~~

(ii)

$$\Delta v = \pm 1$$

Since the vibrational spectra are usually determined by absorption spectroscopy, hence the rule $\Delta v = \pm 1$ is the only part of this selection rule.

$\Delta v = +1$ Fundamental band

$\Delta v = +2$ First overtone

$\Delta v = +3$ Second overtone & so on

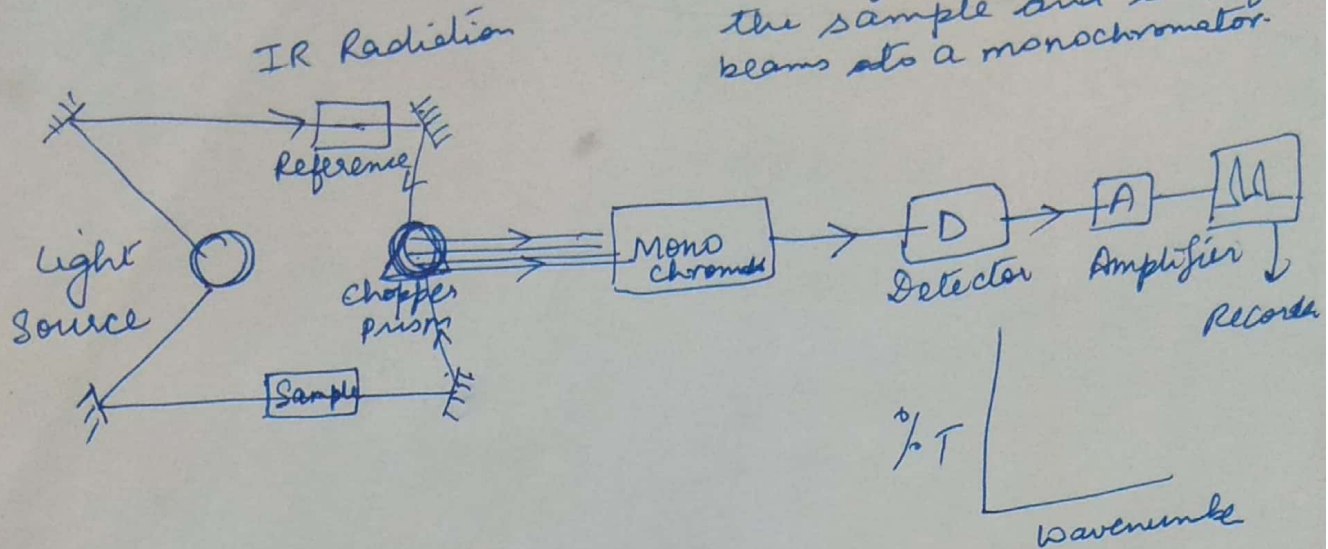
IR Spectra an Important tool for Identification of Organic Compounds

The entire IR-region is divided into two broad regions -

- (i) Functional group Region :- The functional group region extends from $4000-1500\text{ cm}^{-1}$. It is particularly useful for detecting the presence of functional groups. Different functional groups absorb at characteristic frequencies in this region of the spectrum.
- (ii) Finger Print Region - The region below 1500 cm^{-1} is very useful for establishing the identity of a compound. Two identical compounds under similar conditions and in same medium, differ in their IR spectra in the region below 1500 cm^{-1} and hence can be identified easily. The region below 1500 cm^{-1} is
- (a) Rich in many absorptions caused by bending vibrations.
 - (b) Rich in many absorptions resulting from the stretching vibrations of C-C, C=O and C-N bonds.
 - (c) Rich in absorption bands and shoulders because the no. of bending vibrations is usually more than the no. of stretching vibrations. Therefore, it

Instrument

Chopper - rotates at a definite speed reflects the sample and the reference beams into a monochromator.



Light Source

Nernst glower → which consists of rod of the sintered mixture of ^{oxides} Zirconium, Ytterbium and Erbium (90:7:3)

- This rod is heated to 1500°C to produce IR rad.
- Non conducting at room temp. so heating is reqd.

Globar (SiC) → rod of SiC can also be heated to produce IR radiation.
Produce less intense IR rad.

- Light from the source is split into 2 beams.

Monochromator → Various types of Monochromator

- Prism (alkali metal halides)
 - NaCl
 - KBr
 - LiF
 - CsBr

- Grating ~~mm~~
Small thin prism are present

Detectors

Bolometer

- ~~Thin metal conductor is used.~~
- Detector converts infra-red energy into electrical energy.

| Bond Type | Functional Gr. | Stretching | Bending |
|-----------|-----------------------|-------------------------|--------------|
| C-H | Alkane | 2970-2850(s) | 1470-1350(s) |
| C-H | Alkene | 3080-3020(m) | 1000-675(s) |
| C-H | Alkyne | 3300(s) | |
| C-H | Aldehyde | 2900 (m) 2700 (m) | |
| C-H | Aromatic | 3100-3000(v) | 800-675s |
| O-H | Alcohols (H-bonds) | 3500-3300(s) (broad) | |
| O-H | Alcohols (NO H-bonds) | 3650-3590(s) | |
| OH | Acid | 3000-2500(s) broad. | |
| N-H | Amine | 3500-3300(m) | |
| N-H | Amide | 3500-3350(v) | |
| C-C | Alkane | 1200-800 (w) | |
| C=C | Alkene | 1680-1620 (w) | |
| C=C | Aromatic | 1600-1450 (v) | |
| C≡C | Alkyne | 2260-2100 (v) | |
| C-O | Alcohol, ether, ester | 1300-1000(s) | |
| C=O | Ketone | 1725-1705(s) | |
| C=O | Aldehyde | 1740-1720. | |
| C=O | Ester | 1750-1735 (s) | |
| C=O | Acid | 1725-1700(s) | |
| C=O | Amide | 1690-1650 | |

| | | |
|-----------------|-------------|------------------------------------|
| C-N | Alkyl amine | 1220 - 1050 (W) |
| C-N | Aryl amine | 1360 - 1250 (S) |
| C≡N | Nitrile | 2260 - 2100 (V) |
| NO ₂ | Nitro | 1580 - 1560 (S) 1400 - 1380 (S) |

Hydrogen Attached to sp^3 Hybrid Atoms

| H-O | H-C | H-N |
|-----------------------------|---|---|
| Alcohol (3500-3300) (broad) | Methyl (CH ₃) Methylene (CH ₂) Methine (CH) | Amines |
| Phenol " | 3500-2850 cm ⁻¹ | Primary ↓ 2 peaks (3500-3300) |
| Carboxylic Acid (3000-2500) | - C-H bending (1470-1350 cm ⁻¹) | Secondary ↓ only one peak |
| | | Tertiary amines do not absorb in N-H region |

Hydrogen Attached to sp^2 and sp Hybrid Atoms

| C-H bending (1600-650 cm ⁻¹) | | |
|--|-----------------------------------|--|
| H-C | | |
| Alkenes (3000 cm ⁻¹) | Aromatic (3100 cm ⁻¹) | Aldehyde (2700 cm ⁻¹ 2900 cm ⁻¹) |

Bond bending is more imp than bond stretching in the interpretation of alkene & aromatic comp.