

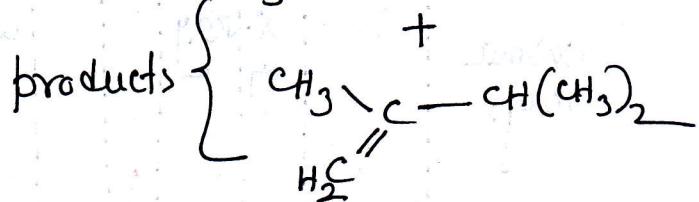
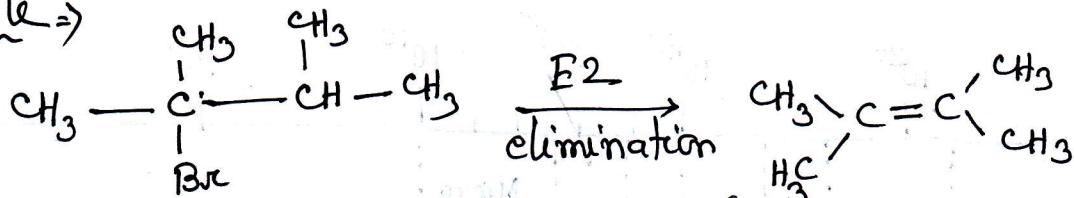
# Spectroscopy of Organic Compounds

Spectroscopy Definition  $\Rightarrow$  Study of the quantized interaction of electromagnetic radiations with matter

Why to study Spectroscopic techniques

↓  
to determine the structure of organic compounds

Example  $\Rightarrow$



{ How to know the structures of the products?

↓  
classical methods (chemical test)

- Establishment of molecular formula (from elemental analysis)
- Chemical reactions (test for functional groups)
- Prediction of one or more structures from the results obtained
- Confirmation of the predicted structure by synthesis

Disadvantages  $\Rightarrow$  Cumbersome, laborious, time-consuming

Advantages of Spectroscopic techniques =

- Very small sample requirement (ug to mg)
- Within a few minutes structural information are obtained.

Bohr's principle  $\Rightarrow$  interaction of light with matter (molecule)

electromagnetic radiation

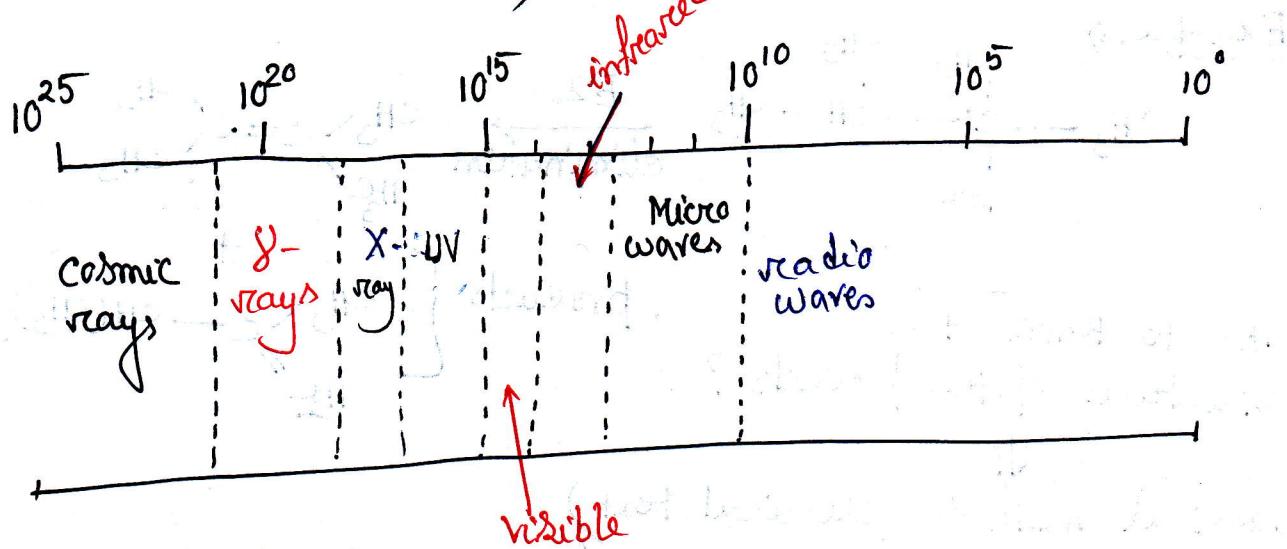
Characterized by frequencies, Wavelengths, Wave numbers

( $\nu$ )

( $\lambda$ )

( $\bar{\nu}$ )

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



$10 \text{ nm} - 200 \text{ nm} \Rightarrow$  Far ultraviolet

$200 \text{ nm} - 380 \text{ nm} \Rightarrow$  Near ultraviolet

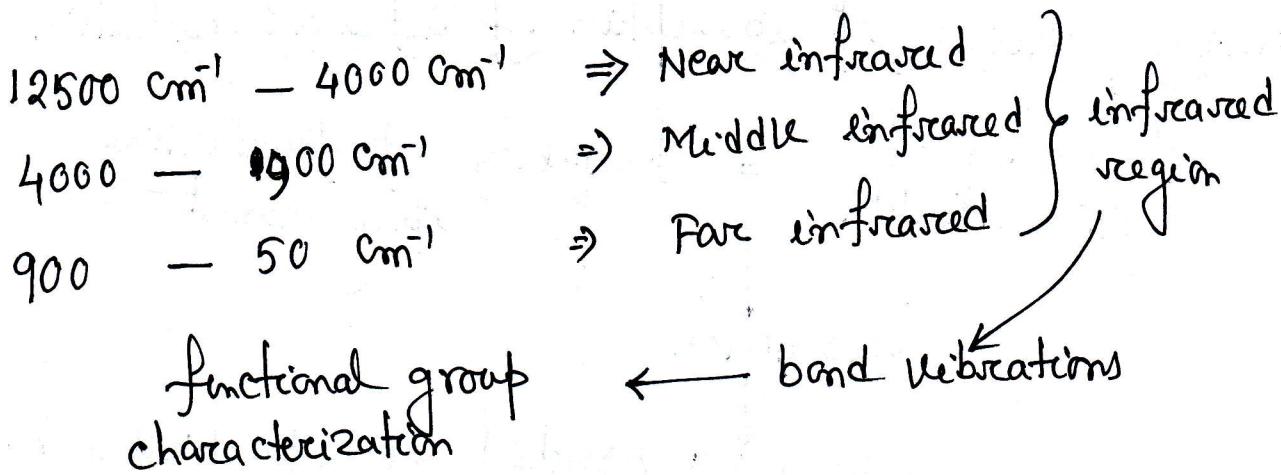
$400 \text{ nm} - 780 \text{ nm} \Rightarrow$  Visible region

Ultraviolet — Visible region

electronic transitions  
between molecular orbitals

deals with the conjugation of the molecules

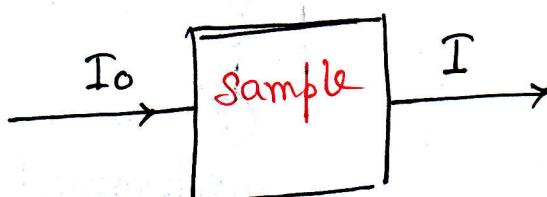
→ electronic spectrum



Terms  $\Rightarrow$  radiant power, intensity, absorbance, transmittance

Intensity  $\Rightarrow$  characterized by radiant power

proportional to no. of photons propagating  
in the beam per second



$$\text{Transmittance} \quad T = \frac{P}{P_0} = \frac{I}{I_0}$$

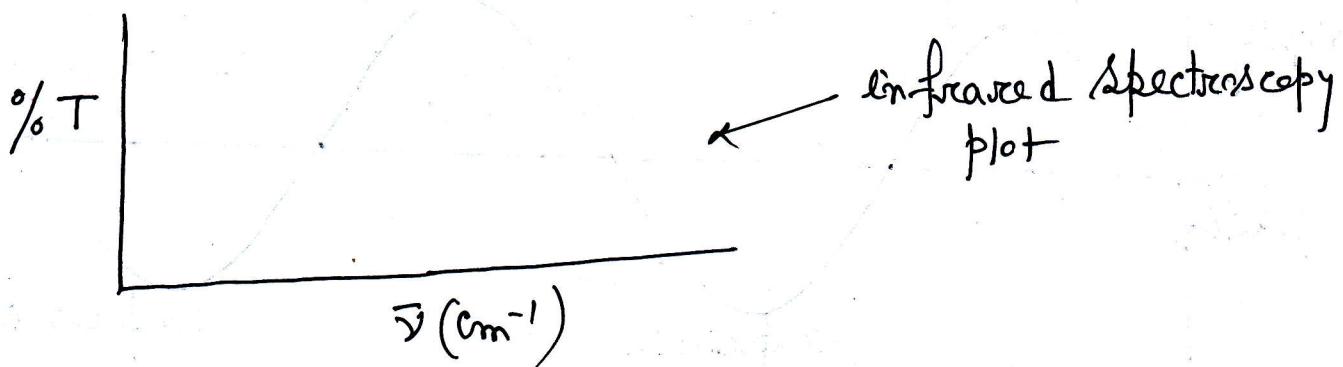
$$\% T = \frac{I}{I_0} \times 100$$

Absorbance

$$A = \log_{10} \left( \frac{P_0}{P} \right)$$

$$= \log_{10} \left( \frac{I_0}{I} \right)$$

Therefore,  $A = \log_{10} \left( \frac{1}{T} \right)$



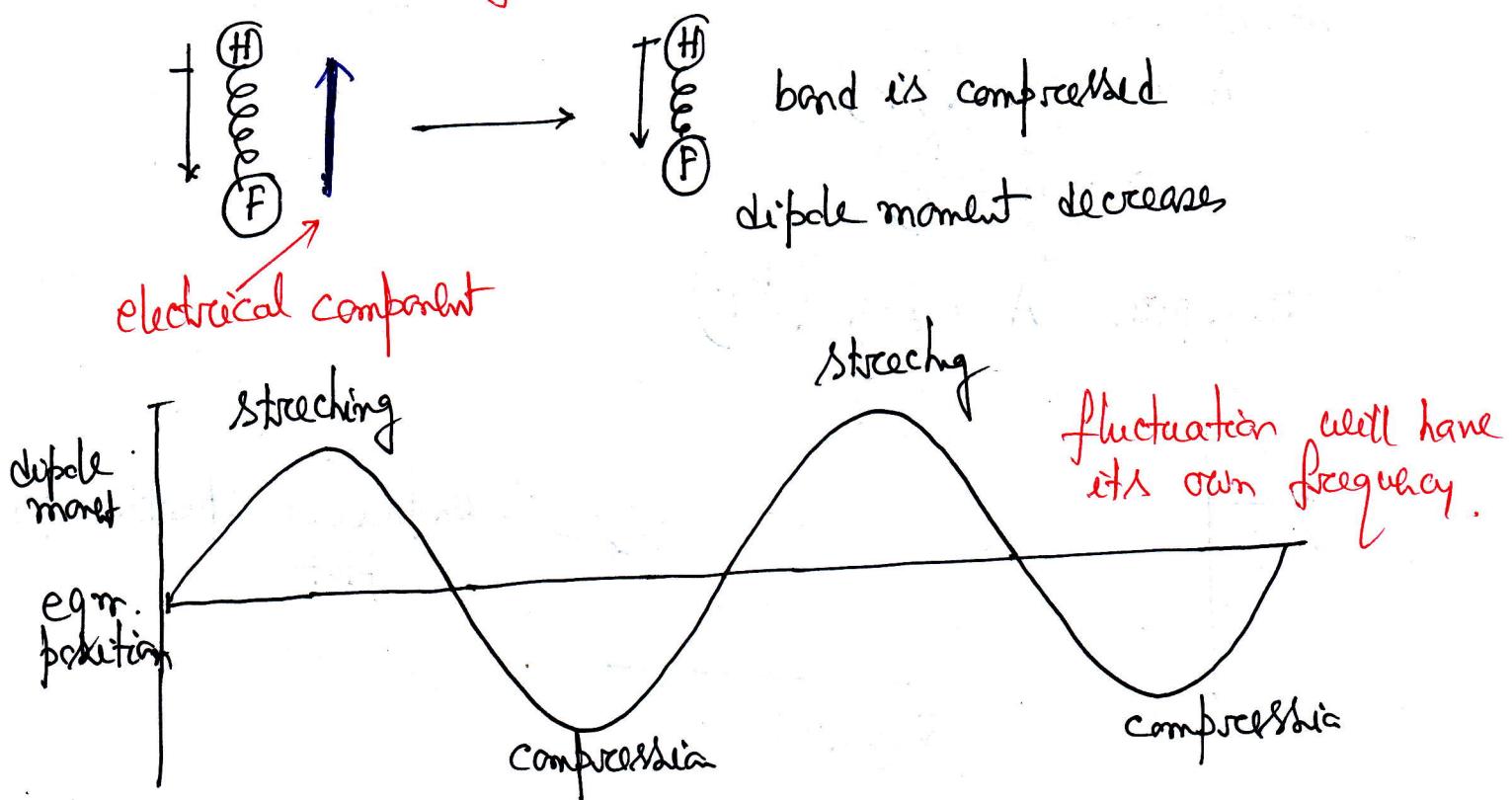
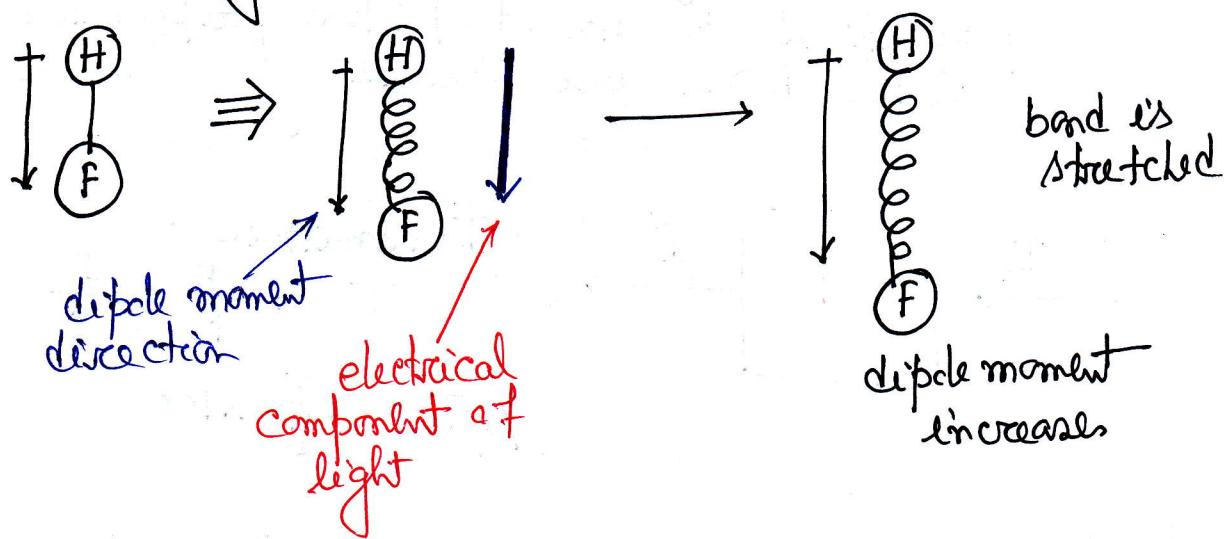
## 4 Basic principle of absorption of infrared radiation

$$\text{frequency of IR radiation} = \text{frequency of fluctuating dipole moment}$$

↓  
resonance

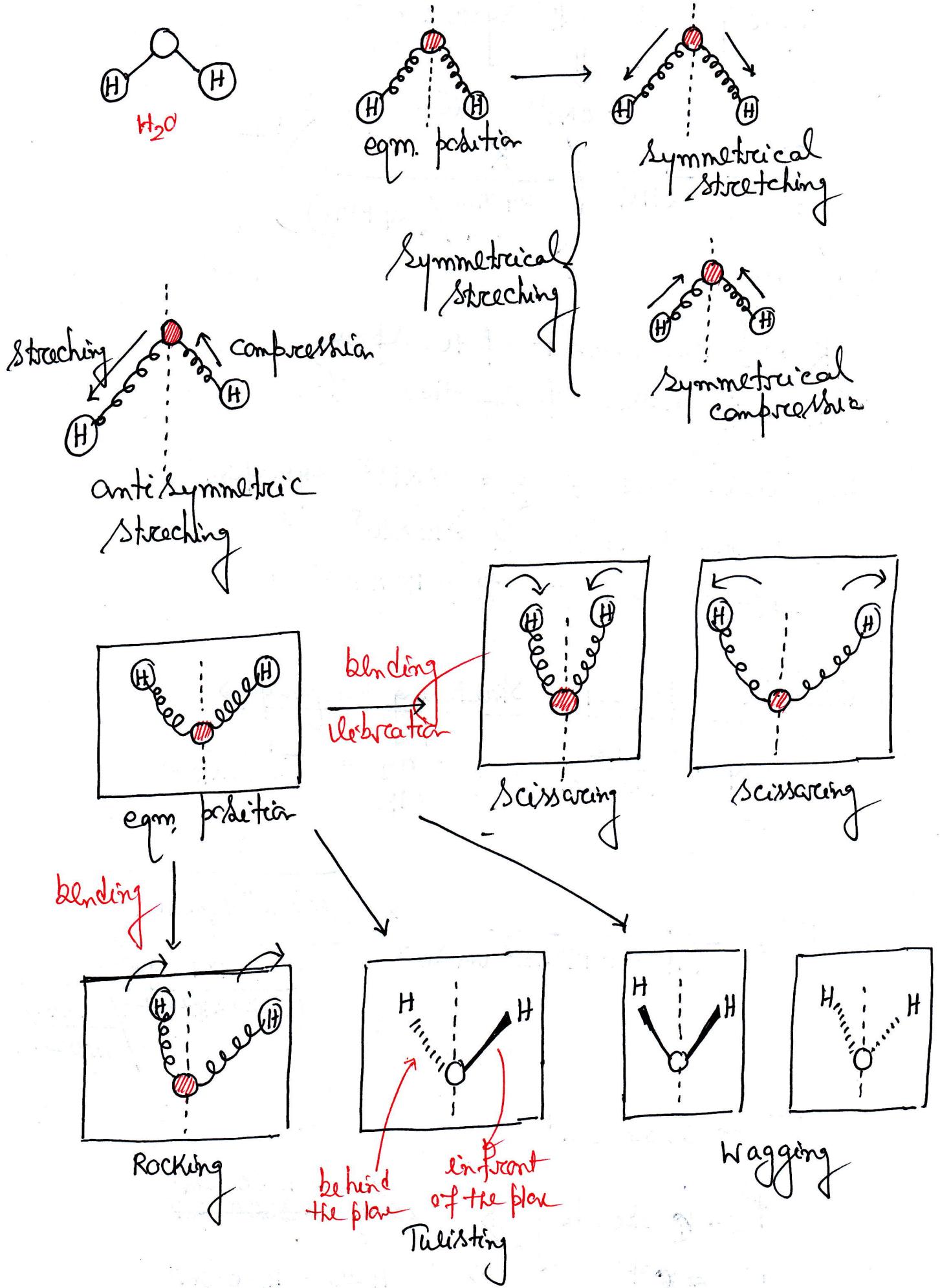
↓  
energy is absorbed by a particular bond  
↓  
signal produced

Fluctuating dipole moment  $\Rightarrow$



Bond's natural vibrations =>

5



6 How to calculate the frequency of vibration of Spring and ball system?



Hooke's law

$$\bar{v} = \frac{1}{2\pi C} \left( \frac{R}{m_1 m_2 / (m_1 + m_2)} \right)^{1/2}$$

↑  
wave no.

$R$  = force constant of the Spring

$m_1, m_2$  = masses of the two balls.

for single bond  $\Rightarrow R = 5 \times 10^5$  dynes/cm

double bond  $\Rightarrow R = 10 \times 10^5$  "

triple bond  $\Rightarrow R = 15 \times 10^5$  "

Calculate  $\Delta p^3 C - H$  Stretching frequency  $\Rightarrow$

$$m_1 = \frac{12}{6.023 \times 10^{23}}, \quad m_2 = \frac{1}{6.023 \times 10^{23}}$$

(C) (H)

$$\bar{v} = \frac{1}{2\pi \times 2.998 \times 10^8 \text{ cm sec}^{-1}} \times \sqrt{\frac{5 \times 10^5 \text{ dynes/cm}}{(6.023 \times 10^{23})^2 \frac{12+1}{6.023 \times 10^{23}} \text{ gm}^2}}$$

$$\bar{v} \approx 3032 \text{ cm}^{-1}$$

$$\Delta p^3 C - H \text{ Stretching} \Rightarrow \frac{800 - 1200 \text{ cm}^{-1}}{2800 - 3000 \text{ cm}^{-1}}$$

$$\Delta p^2 C = \Delta p^2 \Rightarrow 1620 - 1680 \text{ cm}^{-1}$$

$$\Delta p C = - \Delta p \Rightarrow 2100 - 2260 \text{ cm}^{-1}$$

$$\Delta p^3 C - H \Rightarrow 2840 - 3000 \text{ cm}^{-1}$$

$$\Delta p^2 C - H \Rightarrow 3060 - 3100 \text{ cm}^{-1}$$

$$\Delta p^1 C - H \Rightarrow 3000 \text{ cm}^{-1}$$

Relative contributions of bond strengths and reduced mass must be considered while applying Hooke's law

Problem 1  $\bar{\nu}_{O-H} > \bar{\nu}_{O-D}$  Why?

$$R_{O-H} \approx R_{O-D}$$

$$m_D \approx 2m_H$$

Therefore  $\mu_{O-D} \gg \mu_{O-H}$

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

$$\bar{\nu}_{O-H} > \bar{\nu}_{O-D}$$

Problem 2  $\bar{\nu}_{F-H} = 4138 \text{ cm}^{-1}$  } Why?  
 $\bar{\nu}_{C-H} = 3040 \text{ cm}^{-1}$

$$R_{F-H} > R_{C-H}$$

$k$  factor outweighs  $\mu$  factor.

Problem 3  $\bar{\nu}_{C-O} = 1060 - 1150 \text{ cm}^{-1}$  } Why.  
 $\bar{\nu}_{C=O} = 1710 - 1740 \text{ cm}^{-1}$

$\mu \Rightarrow$  same

$$R_{C=O} > R_{C-O}$$

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

## Characteristic Infrared absorption frequencies (bands)

Alcohols, phenols (-OH)  $\Rightarrow$   $3200 \text{ cm}^{-1} - 3650 \text{ cm}^{-1}$  (strong, broad)

Amines ( $-\text{NH}_2$ ,  $\text{NHR}$ )  $\Rightarrow$   $3000 - 3200 \text{ cm}^{-1}$  (strong, broad)

Carboxylic acid (-OH)  $\Rightarrow$   $\sim 2500 \text{ cm}^{-1}$  (strong, broad)

Carbonyl ( $\text{C=O}$ )  $\Rightarrow$   $\sim 1720 \text{ cm}^{-1}$  (sharp, strong)

Carbonyl ( $>\text{C=O}$ )  $\Rightarrow$   $\sim 1710 \text{ cm}^{-1}$  (sharp, strong)

Amide ( $-\text{C}(=\text{O})\text{NH}-$ )  $\Rightarrow$   $\sim 1680 \text{ cm}^{-1}$  (sharp, strong)

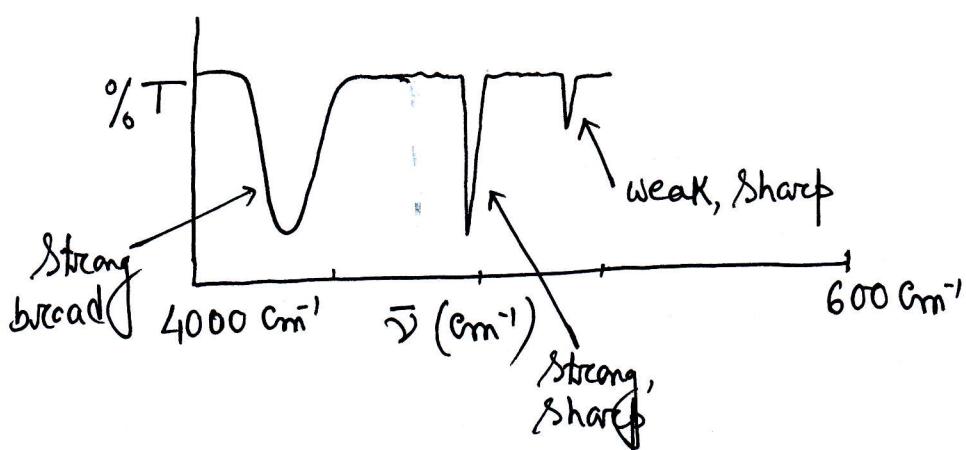
$\text{C}\equiv\text{C}$  - - - - -  $\Rightarrow$   $2250 - 2100 \text{ cm}^{-1}$  (sharp, weak)

$\text{C}\equiv\text{N}$  - - - - -  $\Rightarrow$   $2260 - 2240 \text{ cm}^{-1}$  (sharp, strong)

$\text{C}=\text{C}$  - - - - -  $\Rightarrow$   $1680 - 1600 \text{ cm}^{-1}$  (sharp, weak)

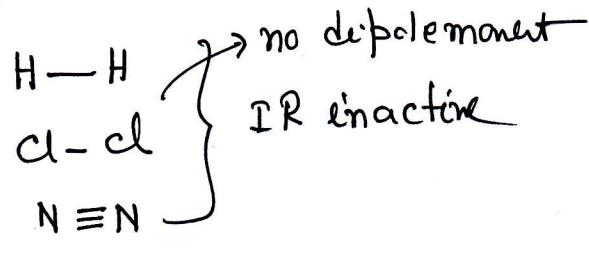
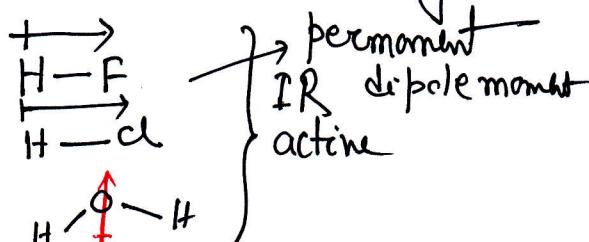
$\delta p^2\text{CH}$  - - - - -  $\Rightarrow$   $3100 - 3000 \text{ cm}^{-1}$

$\delta p \text{ C-H}$  - - - - -  $\Rightarrow$   $\sim 3300 \text{ cm}^{-1}$  (weak, sharp)



\*\* Criteria for a molecule/bond to be IR active  $\Rightarrow$

1. The bond must have fluctuating dipole moment during its vibration (stretching or bending)

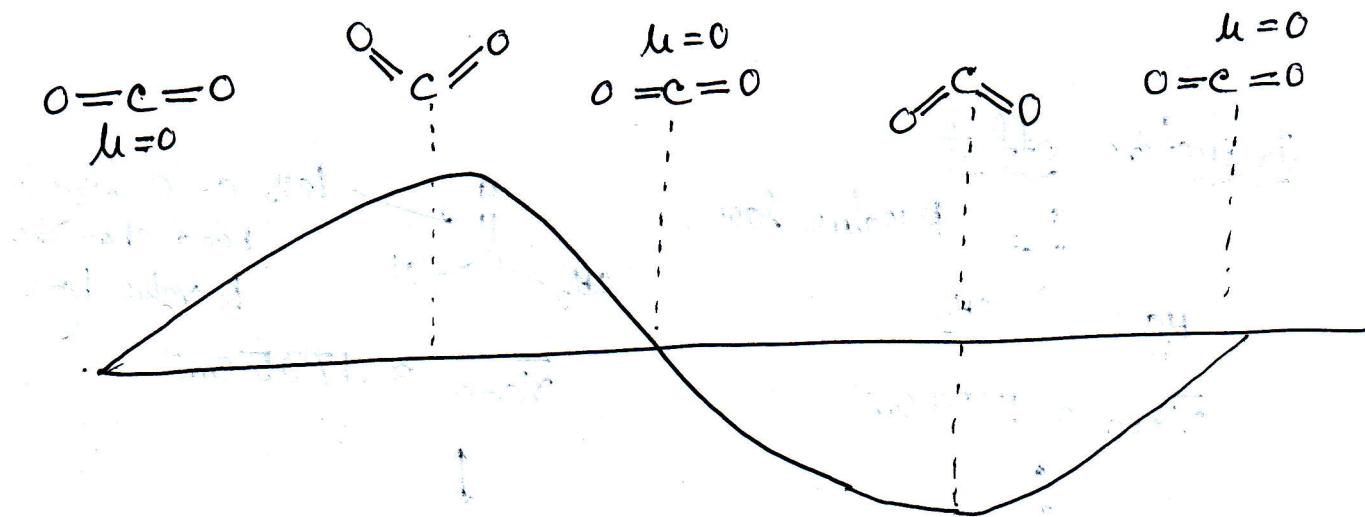
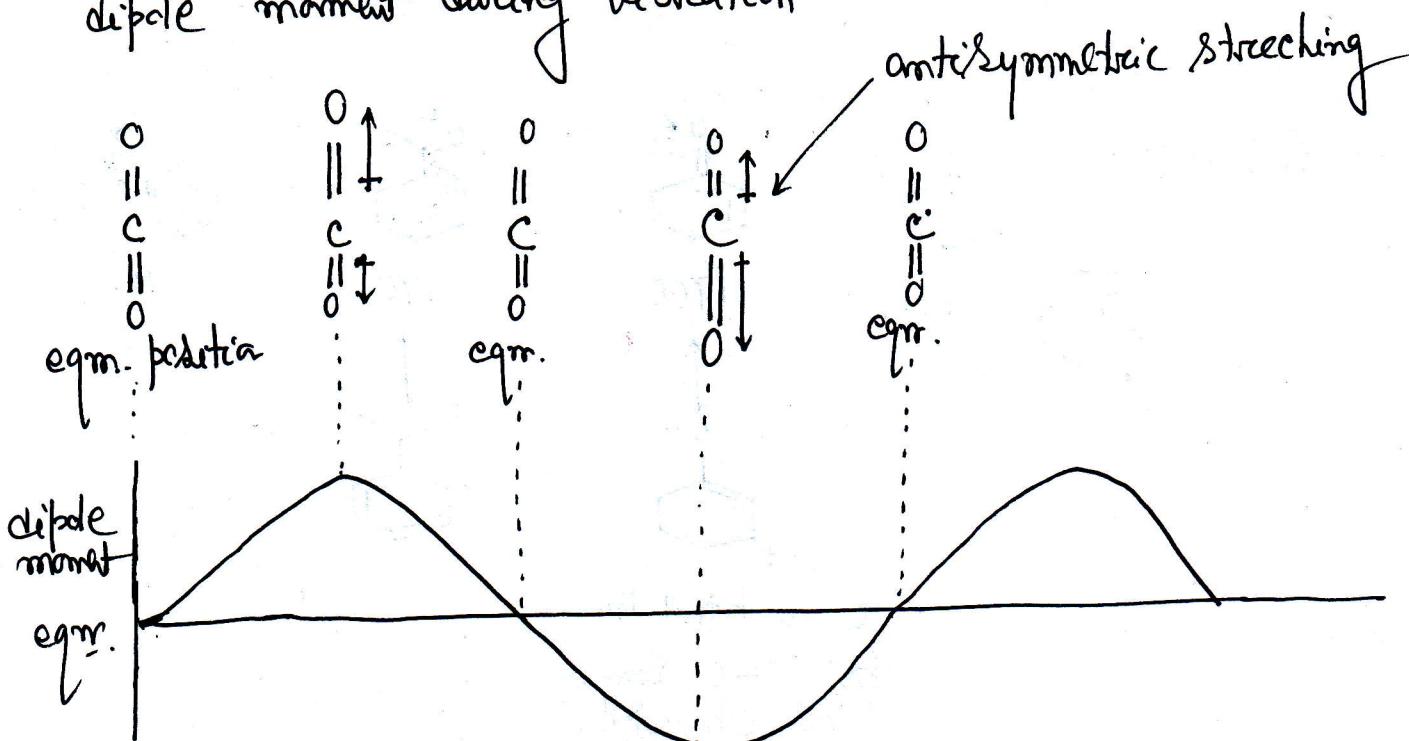


8 Will  $\text{CO}_2$  molecule exhibit IR spectrum?

8

$\text{O}=\text{C}=\text{O}$  } linear, symmetric  
no permanent dipole moment

But there exists fluctuating dipole moment during vibration



Therefore,  $\text{CO}_2$  exhibits IR spectrum.

# 9 Structure - Spectrum relationship

9

factors affecting the value of absorption frequency.

1. Resonance

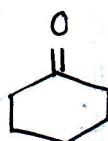
2. Inductive

3. H-bonding

4. Steric

5. Electronegativity

1. Resonance



$\bar{\nu}_{C=O}$  (cm<sup>-1</sup>)

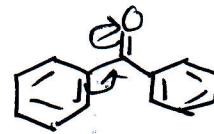
1717



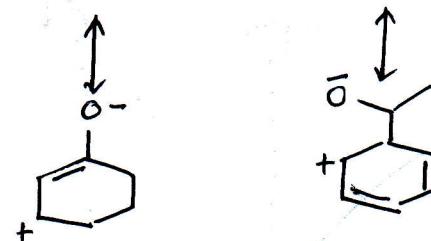
1700



1700

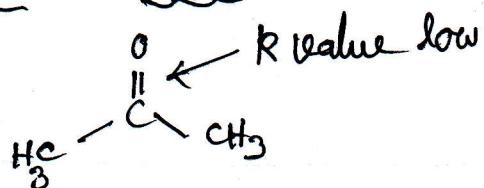


1669

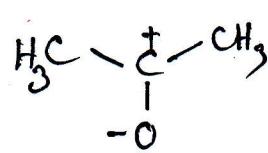


c = o bond has  
now c - o single  
bond character

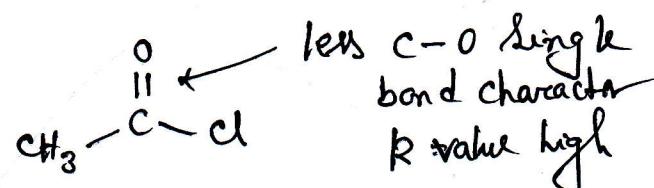
2. Inductive effect



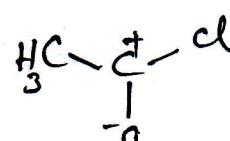
$\bar{\nu}_{C=O} \approx 1720 \text{ cm}^{-1}$



stabilized by  
+ I effect

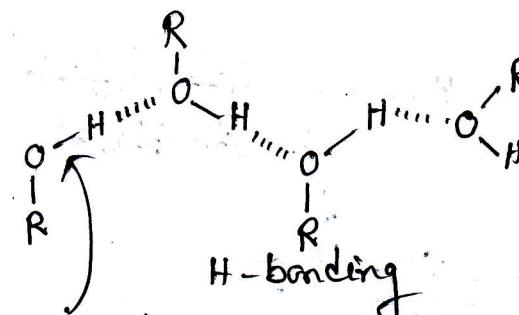
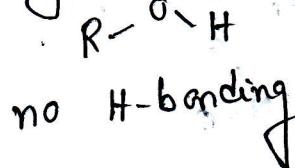


$\bar{\nu}_{C=O} \approx 1795 \text{ cm}^{-1}$



destabilized by  
- I effect

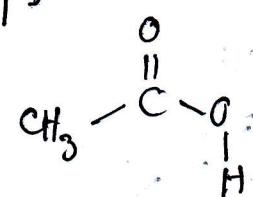
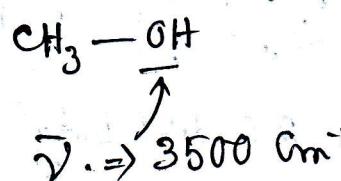
3. H-bonding effect  $\Rightarrow$



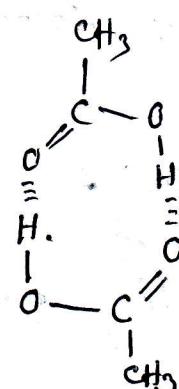
bond becomes weak  $\rightarrow k$  value low

$\downarrow$   
low  $\bar{\nu}_{O-H}$  value

\* Higher the extent of H-bonding lower will be value of absorption frequency



more polar  
 $O-H$  bond  
 $\downarrow$   
higher extent of H-bonding



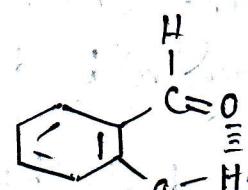
$\bar{\nu}_{O-H} \approx 2500 \text{ cm}^{-1}$

\* H-bonding depends on dilution

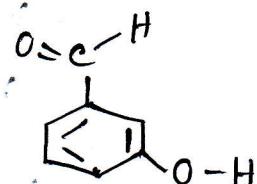
i) High dilution  $\rightarrow$  less H-bonding  $\rightarrow$  higher absorption frequency.

ii) Concentrated soln.  $\rightarrow$  more H-bonding  
 $\downarrow$   
lower stretching frequency

\* Intramolecular H-bonding  $\Rightarrow$  no effect on dilution



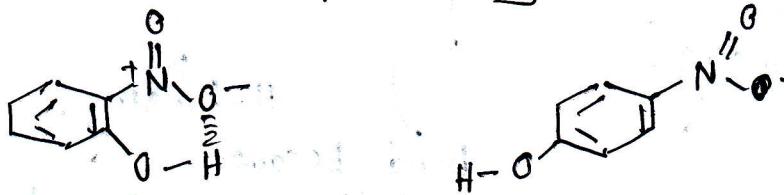
intramolecular H-bonding



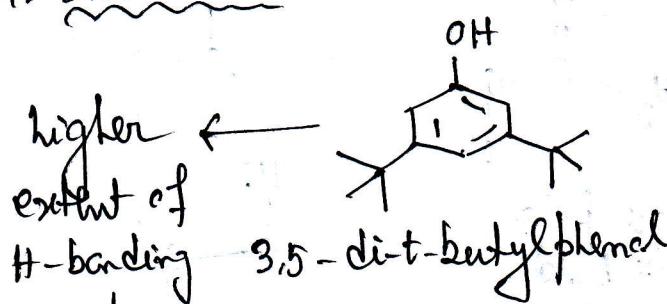
intermolecular H-bonding

$\bar{\nu}_{O-H}$  value depends on dilution factor.

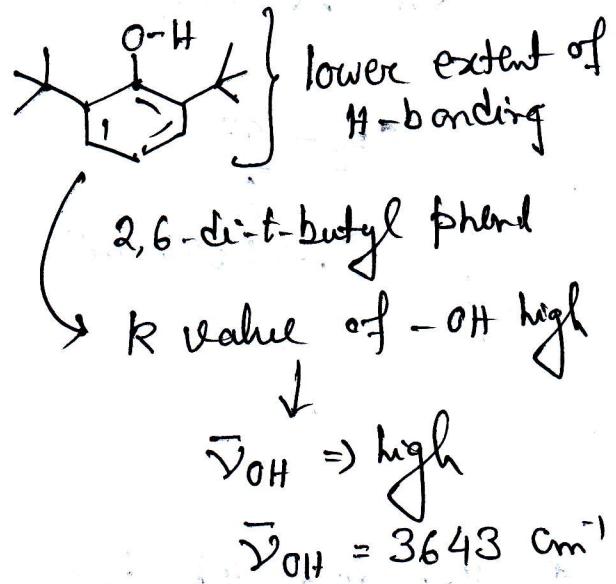
Problem] How to differentiate between 2-nitrophenol and 4-nitrophenol by IR spectroscopy.



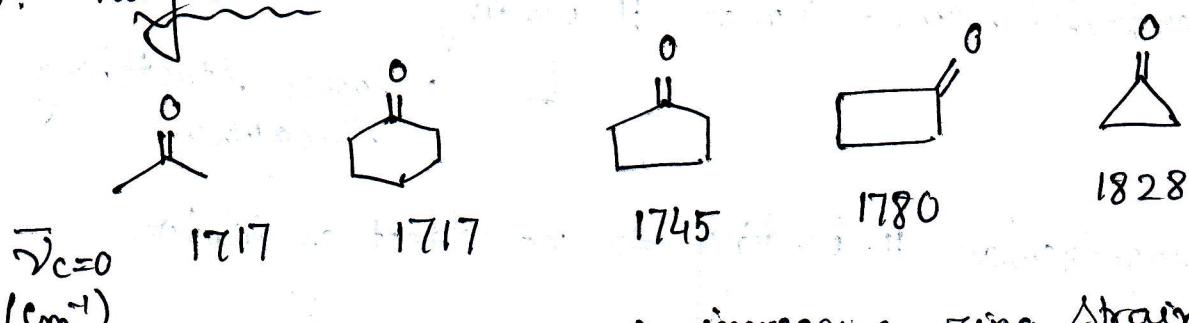
#### 4. Steric Factor



$\downarrow$   
K value of O-H is less  
 $\downarrow$   
 $\bar{\nu}_{O-H} \Rightarrow$  low     $\bar{\nu}_{O-H} \approx 3600 \text{ cm}^{-1}$



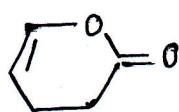
#### 5. Ring Strain



$\bar{\nu}_{C=O}$  value increases  
 increasing ring strain (angle strain)  
 internal (endocyclic) bond angle decreases  
 endocyclic bond s-character decreases  
 exocyclic bond (C=C) s-character increases

## Problem

## How to distinguish between

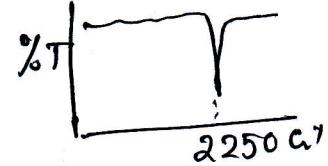


## Problem 1

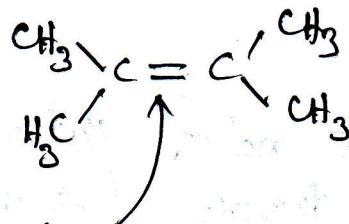
Distinguish between  $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}$        $\text{CH}_3\text{COCH}_3$

## Problem 1

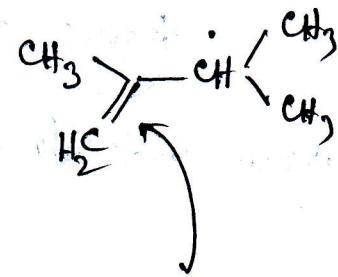
Distinguish between  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$   $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$ .



## Problem 1

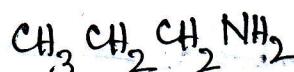


Symmetric  $c=c$   
 no fluctuating dipole moment  
 no  $\bar{\nu}_{c=c}$  band/peak



$V_{C=C}$  appears  
in IR spectrum  
at  $\text{---}$  value

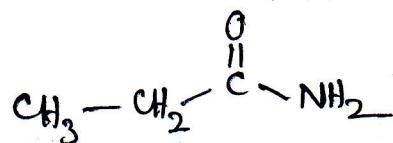
## Problem 1



$$\bar{\nu}_{N-H} \approx 3300 \text{ cm}^{-1}$$

(Strong, broad)

no carbonyl stretching

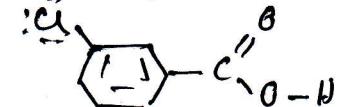


$$\bar{\gamma}_{N-H} \approx 3300 \text{ cm}^{-1}$$

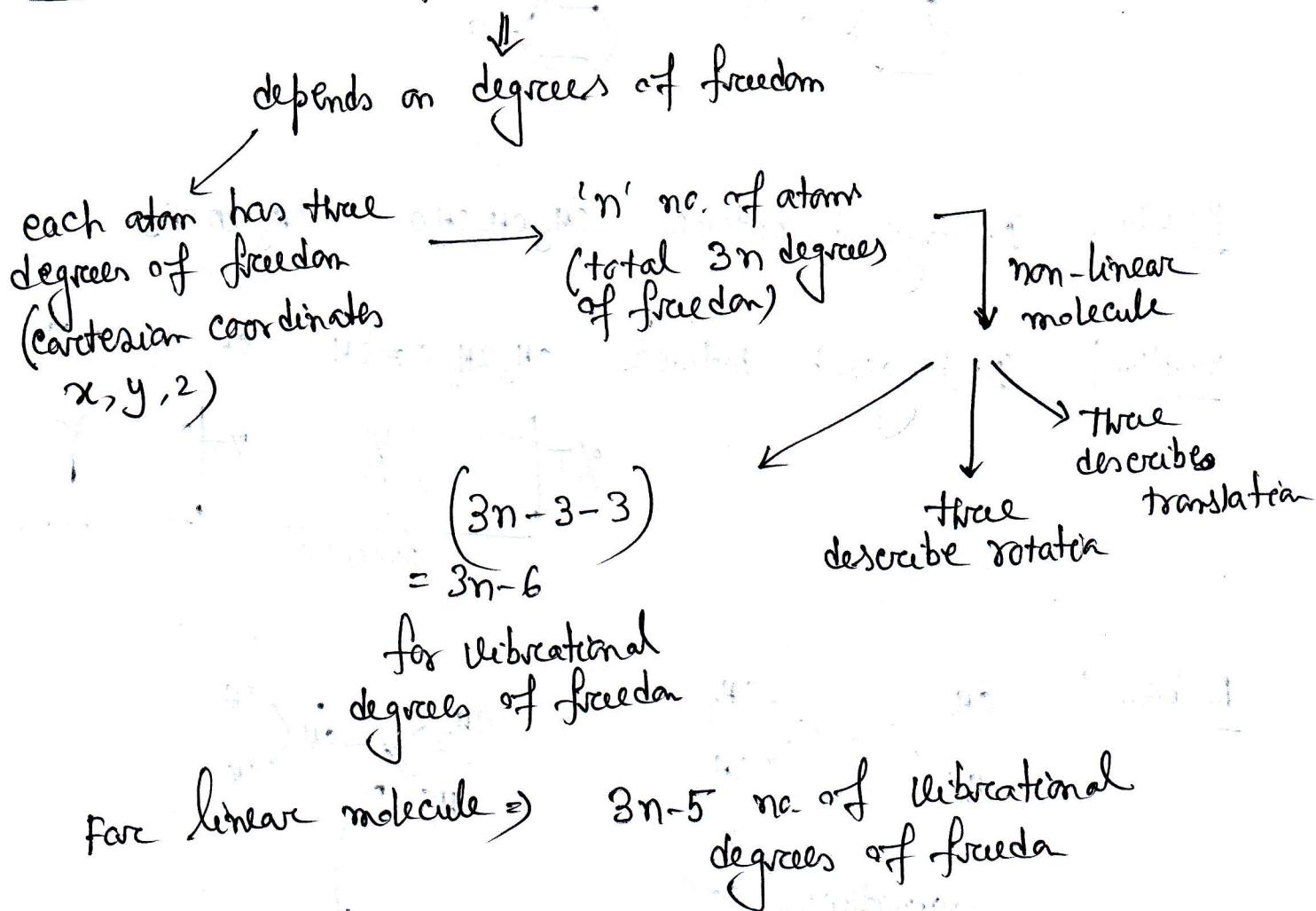
$$\bar{V}_{c=0} \approx 1680 \text{ cm}^{-1}$$

## Preproblem

Distinguish between m-chlorobenzoic acid and p-chlorobenzoic acid by IR spectroscopy.



Problem Number of fundamental vibrations



Problem calculate the no. of fundamental vibrations in the following molecules:

methane, ethanol, acetylene, ethylene, oxygen

Fingerprint region | Different compounds  $\rightarrow$  different IR spectra

IR spectrum is called fingerprint of a compound

The region below  $1500 \text{ cm}^{-1}$  is called fingerprint region because every compound has unique ~~and~~ absorption pattern in this region, just as every person has unique fingerprints.