3. Infrared spectroscopy.

D D M M Y Y Y Y

Infrared spectroscopy deals with study of molecular phenomenon of radiation. The infrared spectrum lies between visible and microwave. for convient it is divided into 3 region.

112500 4000 667 50

Near IR	Middle IR	Far IR

0.8 2.5 15 200

IR studies of organic compound are carried out in middle infra red region for so far all practical purpose 4000 – 667 cm^{-1} radiation range is simply called as infrared region.

The infrared radiation are obtained heating a rod of oxides, glass and pots absorb IR radiation.

IR radiation are less energytics to cause electronic transition but they are energytics in a to induce both vibrational and rotational transition.

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* Fandamental modes of vibration

At all temperature absolute zero, the constituent atoms of the molecule vibrate and rotate in a variety of ~~wave~~ ways.

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The motion leading to change in bond distance (stretching) or bond angle (bending) is called vibrational motion. The stretching and bending vibrations together are known as fundamental modes of vibrations.

The number of fundamental modes of a polyatomic molecule can be ~~can~~ calculated from the number of atoms (N) present in the molecule and their degree of freedom. The number of degrees of freedom is equal to the sum of the coordinates necessary to locate all the atoms of the molecule in space. Thus for a non-linear molecule having N number of atoms,

No. of fundamental modes of vibration = 3N-6

3N is degree of freedom because three cartesian coordinates are needed to locate each atom in space. Out of these atomic degree of freedom, three decribe translation of the molecule as a whole and three describe rotation of the molecule as a whole. These six degree cannot lead to internal vibration so they are subtracted.

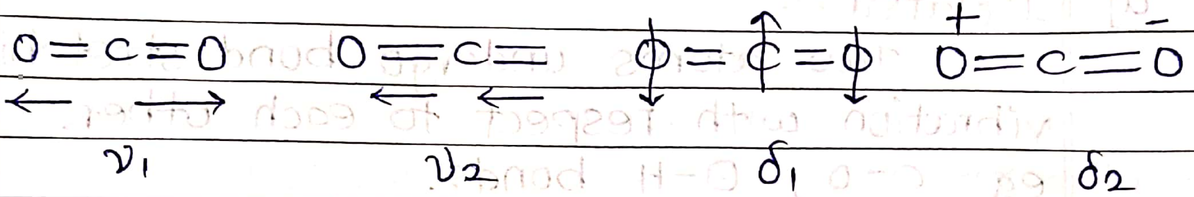
For linear molecule there are only two axis about which the molecule as a whole can rotate. So,

The number of fundamental modes = 3N-5.

CO_2 is linear triatomic molecule. so, as per the formula,

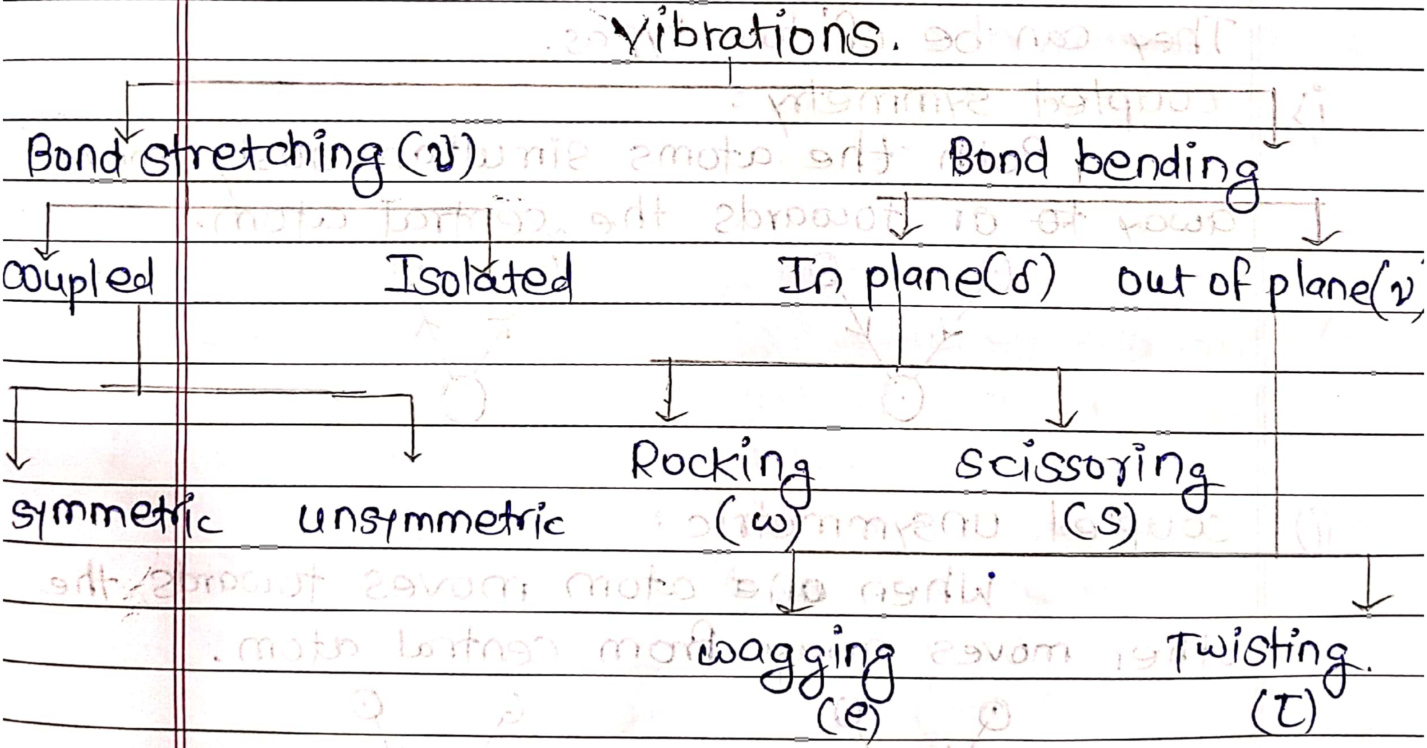
No. of fundamental modes of vibration $= 3\times3-5$
$= 4.$

These four modes can be represented as below.



The arrows indicate movement of atoms along bond axis. whereas +ve and -ve sign signify vibrations perpendicular to the plane of paper.

The fundamental vibrations are grouped and sub grouped as under.



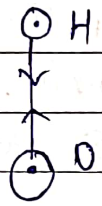
1. Bond stretching

There vibrations where in a pair of atoms constantly vibrate along their bond axis changing the bond length but maintaining constant bond angle, show they can two types

a] Isolated :

Two atoms undergo bond stretching vibration with respect to each other.

eg. C=O , O-H bonds.

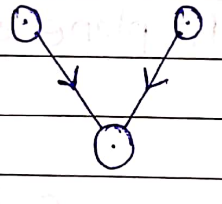


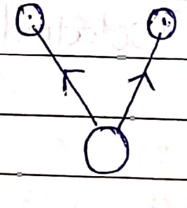
b] coupled :

They are streching vibrations of two atoms with respect to a common central atom. They can be of two types.

i) coupled symmetry :

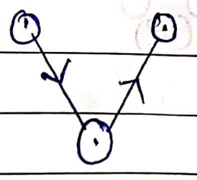
Both the atoms simultaneously move away ~~to~~ or towards the central atom.

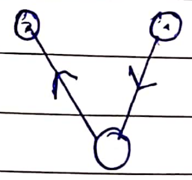




ii) coupled unsymmetric :

When one atom moves towards, the other moves away from central atom.





Stretching vibrations are respected by nu (ν) followed by chemical group in bracket. eg. $\nu(C=O)$ 1600 cm^{-1}. The stretching vibrations generally require higher ~~frequ·~~ energy than the bending vibrations. so give the absorption bands at higher frequency (4000-1400 cm^{-1})

2) Bond bending

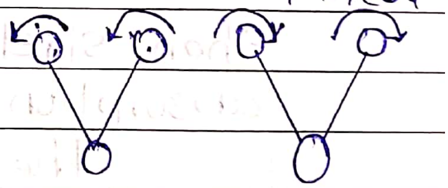
The central atoms remain fixed to a point on a fixed plane but the two atoms bound to it vibrate to change the bond angle keeping the bond length constant. so, the shape of the molecule changes hence it is also ~~known~~ called deforming vibration. They are of two types.

a) In-plane bending vibration :

The vibrating atoms remain in same plane along with the common atom. They are of two types.

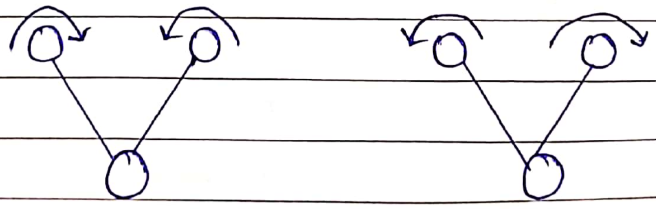
i) Rocking vibrations :

The vibrating atoms move simultaneously back or forth (↶ ↷)



ii) Scissoring vibrations :

The vibrating atoms move back and forth towards each other.

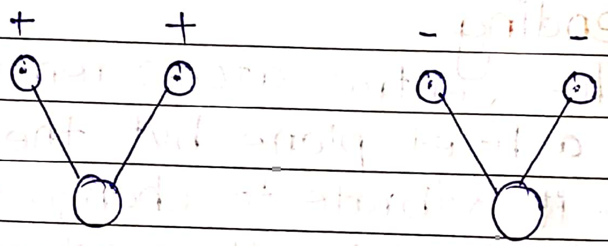


b) Out of plane

The vibrating atoms move out of the plane of central atom. They can be of two types.

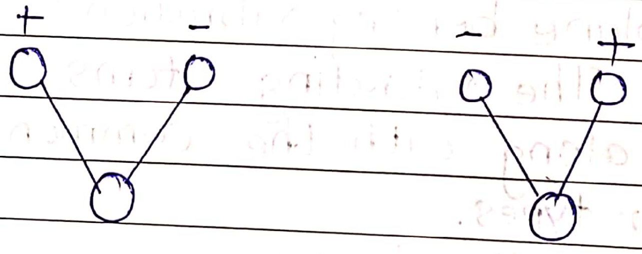
i) Wagging vibration :

The vibrating atoms simultaneously move back (-) or forth (+) of the common plane



ii) Twisting vibration :

The vibrating atoms move in opposite direction to the common plane.



Bending vibrations require lesser energy than stretching vibrations so, they give the absorption band at lower frequency.

The intensity of absorption due to stretching vibration is more than that due to deforming vibrations.

* Conditions for the absorption of IR-radiation.

1) The natural frequency of vibrations of the molecule must be equal to the frequency of incident radiations.

2) Changes in vibrations must stimulate changes in dipole moment of the molecule

The non-polar like N_2, C_2, O_2 Cl_2, cannot absorb IR-radiation as they do not have permanent dipole moment

A polyatomic molecule like CO_2 with no permanent dipole moment also absorb IR-radiation because, when it vibrates it's dipole moment changes.

3) The intensity of absorption must be proportional to the rate of change of dipole. If the rate of change of dipole is slow, absorption of radiation is weak and if it is fast absorption of radiation is strong.

Selection Rule -

1) IR-active transition -

The vibrations that generate oscillating dipole moment absorb in IR and are known as IR-active transitions.

eg. H-Cl, I-Cl, C≡O, $CHCl_3$, C≡N,

2) IR-inactive ~~radia~~ transitions -

The vibrations does not generate and

oscillating dipole moment do not absorb in IR, are known as IR- inactive transitions eg. O_2, C_2, N_2, H_2 etc

3) Allowed and forbidden transitions -

Only the transitions from v_0 to the next higher level ($v_0 \rightarrow v_1$) or ($v_1 \rightarrow v_2$) etc. are allowed and called fundamental transitio They form an idealized system by acting as perfectly hormonic oscillator.

So, overtone bands are also seen and their frequency will be $2v$, $3v$ etc. These ar known as forbidden transitions detected as weak overtones in the spectrum.

Imp

* Regions of IR spectrum.

IR absorption in 4000-650 cm^{-1} i.e. (2.5-1.5 μm) frequency range is called fundamental group region as it stimulate fundamental vibrations of ~~also~~ almost all the common diatomic groups of organic compound. ~~form~~ from analytical point of view organic chemist divide this fundamental region into group frequency region and finger print region.

I] Functional group region -

The high energy or high frequency region that lies between 4000 - 1400 cm^{-1} is called functional group region. A functional group is a diatomic unit joined by a covalent bond.

The absorption bands seen in this region of IR- spectra are due to stretching modes of fundamental vibrations of diatomic groups like C-O, C-N, N-H, C=O, C≡N etc.

The vibrational frequency of each one of these group is characteristic of it's own type only and is called group frequency. The group frequency region is sub-divided into four smaller frequency ranges corresponding to bonds of hydrogen, single bonds, double bonds and triple bonds.

Correlation chart.

C-H → 3000 cm^{-1}

≡C-H → 3300

=C-H → 3100

-C-H → 3000

C-C → 1100

C=C → 1650

C≡C → 2150

C≡N → 2250

$\overset{O}{\overset{\|}{C}}-H$ → 2700 - 2900 cm^{-1}

Fermi (2700-2800)

Resonance (2800-2900)

OH-3600 cm^{-1}

Intermolecular (3300-3400)

Intramolecular (3200-3300) cm^{-1}

$\overset{O}{\overset{\|}{C}}$ / $\overset{O}{\overset{\|}{C}}-H$ / $\overset{O}{\overset{\|}{C}}-OH$ → 1700 - 1725 cm⁻¹

$\overset{O}{\overset{\|}{C}}-OR$ → 1735 - 1750 cm⁻¹

$\overset{O}{\overset{\|}{C}}-O\overset{O}{\overset{\|}{C}}$ → 1760 - 1810 cm⁻¹

$\overset{O}{\overset{\|}{C}}-NH_2$ → 1650 - 1680 cm⁻¹

$\overset{O}{\overset{\|}{C}}-X$ → 1810 cm⁻¹

NO_2 → 1350 1550
symmetric Asymmetric.

2) Finger print region :-

It is low energy or low frequency region between 1400 - 667 cm⁻¹ (7.5 - 15 µm) The absorption band in this region are due to both stretching and bending modes of vibration.

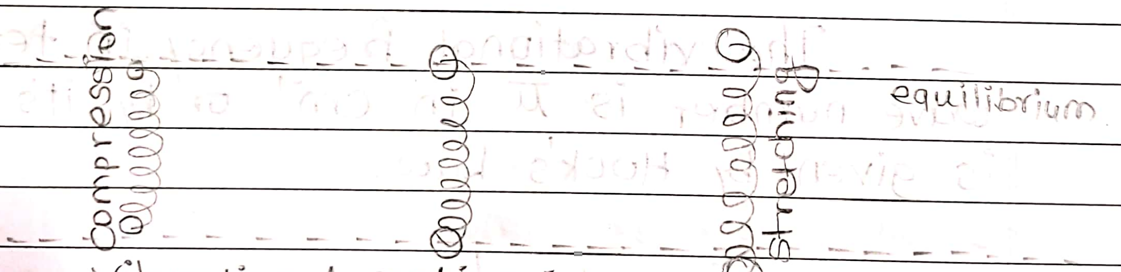
most single bond gives absorption bands in this range. but because of their near about same energy and strong interaction with neighbouring bonds, the bands cannot be assigned to a particular group. Hence they are called Combination bands. small difference in the constitution of a molecule result in significant changes in peak distribution in this region of spectrum. Hence, it is called finger print ~~of the molecule as~~ it is

A few important functional group frequencies like (c-o-c) (ester, ether) c-c (alkane, alkyl group) and c-cl (alkyl halide) are also found in this region.

The region 909 - 650 cm^{-1} (11-15 μm) is known as aromatic region. It is valueable to identify aromatics and ortho, para, meta substitution patterns in aromatic ring.

* Hook's Law :

The vibrations of a diatomic group i.e masses m_1 and m_2 joined by a covalent bond act as simple hormonic oscillator. It is just like a vibrating a spring joined to two balls. as shown in fig.



Vibrational motion in a diatomic molecule.

The force which tends to bring the vibrating atoms to the equilibrium position is called restoring force (F) and it is directly proportional to the displacement (x).

$$F = -K \cdot x$$
$$= -K \quad \ldots\ldots \text{(when } x=1\text{)}$$

The restoring force is negative sign as it acts in direction opposite to that of displacement. The proportionality constant (k) is called force constat defined as the force required to stretch a bond through unit distance.

Hook's law states that vibrational frequency (v) of a covalent bond diatomic pair is directly proportional to the square root of the ratio of force constant (k) and reduced mass (μ).

$$v \propto \sqrt{\frac{k}{\mu}} \begin{matrix} \leftarrow \text{Force constant} \\ \leftarrow \text{Reduced mass} \end{matrix}$$

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

The vibrational frequency in terms of wave number is $\bar{\nu}$ in cm^{-1} or by it's wavelength is given by Hook's Law.

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

where, $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$

i.e. $\bar{\nu} \propto \sqrt{\frac{k}{\mu}}$ .... $\left(\frac{1}{2\pi c} - \text{constant}\right)$

It is change in diatomic pair changes K and μ values so changes the wave no. $\bar{\nu}$. These forms the basic of IR-spectroscopy. The following illustrations will support this statement.

i) The reduced mass (μ) remaining constant vibrational frequency increases with increasing the bond strength (K-value).

eg.

ν cm^{-1}	2150	1650	1100
Bond Types	C≡C	C=C	C−C
Bond strength	strongest	stronger	strong.

ii) The bond strength remaining constant vibrational frequency increases with decreasing reduced mass (μ). eg. assume the single bonds shown below. have nearly same k value.

$\bar{\nu}$ cm^{-1}	3000	1200	1100
Bond Type	C−H	C−C	C−O
$\bar{\nu}$ value	least	moderate	highest.

The vibrations are quantized between specific energy levels. Hook's eqn is given below. The vibrational quantum number (v) can have ~~the~~ values of 0, 1, 2, 3,. . . . . etc.

$$E_v = \left[v + \frac{1}{2} \right] h\nu$$

By absorbing IR-radiation the molecule undergos transtion from lowest vibrational

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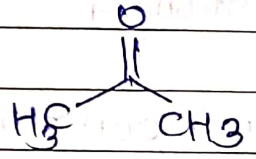
level (E_0; $v=0$) to succeeding level (E_1, $v=1$) The frequency of exciting radiation is given by eq.

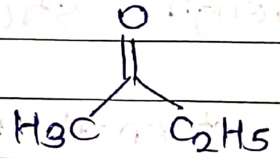
$$\nu = \frac{E_1 - E_0}{h}$$

* Factors affecting IR absorption frequency.

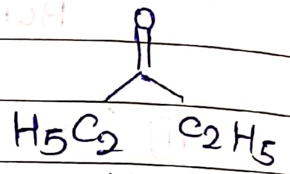
By Hooks law stretching frequency of a chemical bond depends on, bond strength, reduced mass. It ~~means~~ eg. carbonyl bond C=O in a series of saturated aliphatic ketones.



acetone



butanone



pentanone.

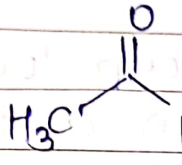
The carbonyl group C=O frequency in all these ketones is expected to be same (1710 - 1715 cm^{-1}). But actually the value is not fixed but varies in a reasonable range.

Many factors either internal or external which influence the bond strength affect bond frequency and cause minor shift in IR-band position. The major influencing factors are disscussed below.

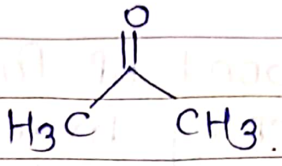
i) Inductive effect:

The electron releasing (+I) group weakens the bond by lengthening it. This lowers stretching frequency and IR band shift to lower side (red shift).

eg.



acetaldehyde

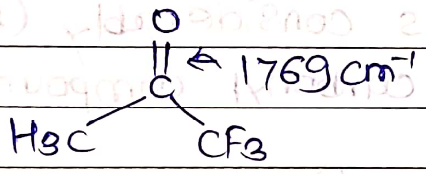


acetone.

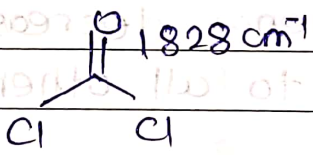
An extra methyl (+I) group, 8 in acetone, decrease double bond character of C=O bond. This raises the vibrational frequency and push IR-absorption to lower 1710 cm⁻¹ side.

An electron withdrawing (-I) group, stabilizes the bond (raise k) by shortening it This lowers the stretching frequency and shift IR band to higher side (blue shift).

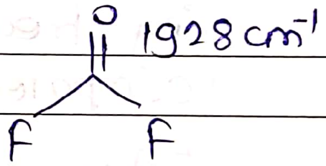
eg. Notice the C=O bond frequency in following ketones.



Trifluro-acetone



Carbonyl Chloride



Carbonyl Fluroide.

Fluorine and chlorine are highly electronegative atoms exert highest (-I) industive effect. so when they are directly linked to C=O group exteremé shift is observed.

2ii) Resonance (R) effect:

Resonance we lengthens so weakens

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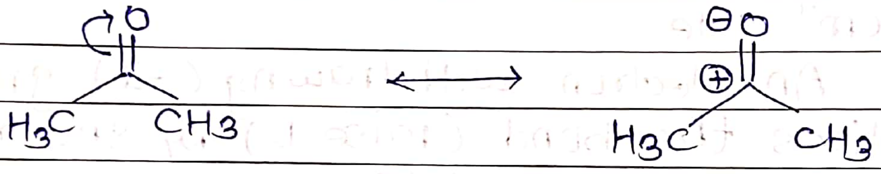
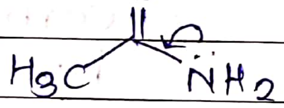
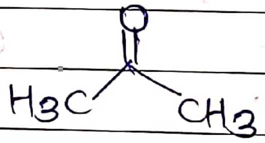
the bond of functional group lowering it's stretching frequency. eg. in acetone the electron donating (+R) effect of methyl groups assist resonance and staibilize the single bond structure (b). As a single bond is weaker than a double bond, the C=O bond frequency decrease to 1710 cm^{-1} as compared with acetalehyde (1720 cm^{-1}).



Resonance effect is prominently seen in all acid derivatives (amide, esters, acid halides etc). In amides the (+R) effect of nitrogen is far more than it's (+I) effect. so the stretching frequency decreases considerably (~~19~~ 1690 cm^{-1}) compared to all other carbonyl compounds.

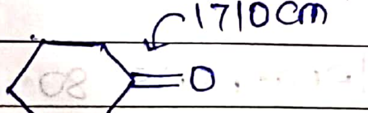
eg.





The C=O stretching frequency is lowered by conjugation with double bond as double bond exerts +R effect to increase resonance. So double bond character decreases and absorption shifted to lower side.

eg. α-β enones.

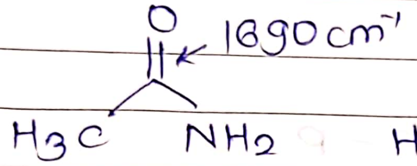


cyclohexanone.

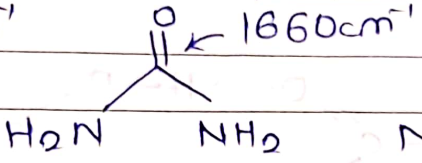
$-\overset{|}{C}=\overset{|}{C}-C=O$ 1685 cm^{-1}

α-β-unsaturated ketone.

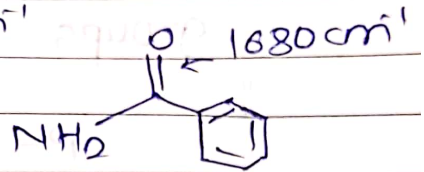
In amines the +R effect of nitrogen far exceeds than it's +I effect. This decreases the stretching frequency considerably to as low as 1690 cm⁻¹ compared to all other carbonyl compounds.



acetamide

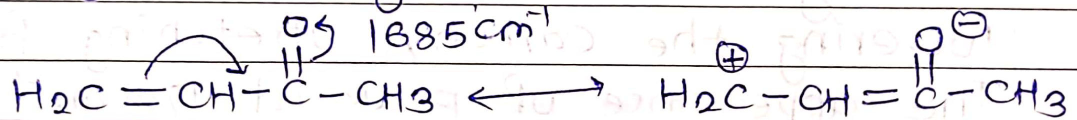


urea

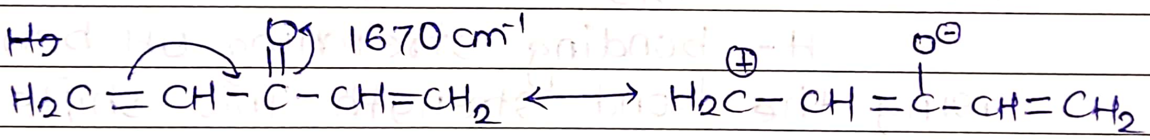


benzamide.

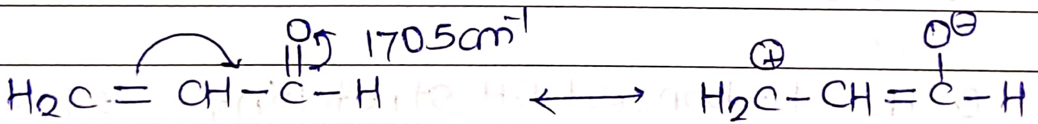
If their conjugation is extended the carbonyl stretching frequency decreases to longer side. eg.



$$H_2C=CH-\overset{O}{\overset{||}{C}}-CH_3 \longleftrightarrow H_2\overset{\oplus}{C}-CH=\overset{O^{\ominus}}{\overset{|}{C}}-CH_3$$



$$H_2C=CH-\overset{O}{\overset{||}{C}}-CH=CH_2 \longleftrightarrow H_2\overset{\oplus}{C}-CH=\overset{O^{\ominus}}{\overset{|}{C}}-CH=CH_2$$



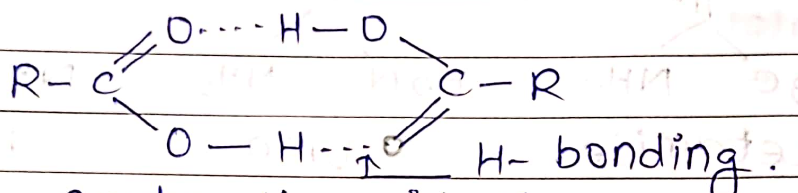
$$H_2C=CH-\overset{O}{\overset{||}{C}}-H \longleftrightarrow H_2\overset{\oplus}{C}-CH=\overset{O^{\ominus}}{\overset{|}{C}}-H$$

iii) Hydrogen bonding :

Hydrogen bonding lowers the absorption frequency of functional group. The H-bonding increases the bond length to weaken the bond and pushes the absorption to lower side. Thus it affects the stretching frequencies of groups like >C=O, -COOH, -OH, -NH_2 etc. and assists their identification.

a) carboxylic acids :

In solid or pure liquid form strong hydrogen bonding occurs and exists as dimmers. This affects the stretching frequencies of both carboxyl and hydroxyl groups.



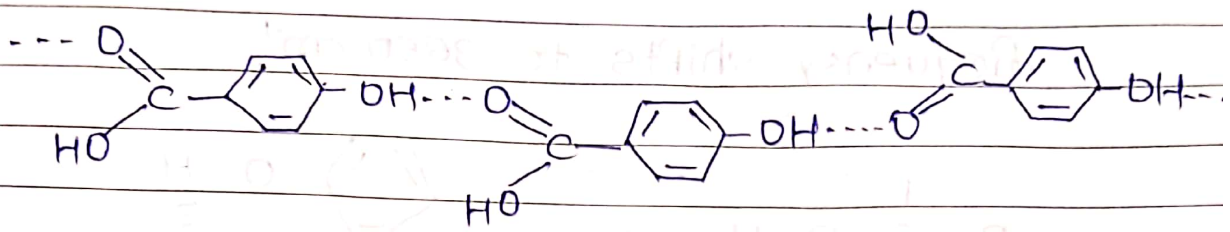
carboxylic acid dimer.

The involvement of >C=O both in H-bonding weakens the C=O bond thereby lowering the carbonyl stretching frequency. The appearance of peak at 1721 cm^{-1} indicates the acid exists as dimer.

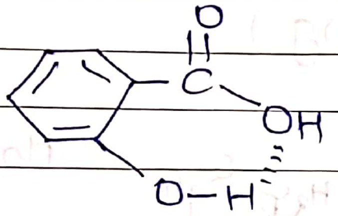
H- bonding stretching OH bond decreasing the bond strength. This shifts absorption to ~~we~~ lower side.

O-H	H-bonded OH stretching frequency	2700-3500 cm^{-1}
O-H	free OH stretching frequency,	3500 cm^{-1}.

Intramolecular hydrogen bonding shows greater ~~than~~ effect on C=O, O-H stretching than intermolecular H- bonding e.g. p-Hydroxy benzoic acid, O- Hydroxy benzoic acid.



P- Hydroxy benzoic acid (intramolecular H- bonding) 3300- 3400 cm^{-1}



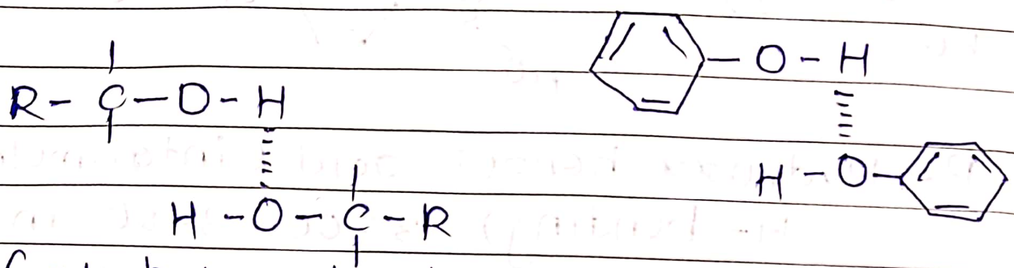
O- Hydroxy benzoic acid (intramolecular H- bonding) 3200-3300 cm^{-1}

Effect of dilution on H- bonding:

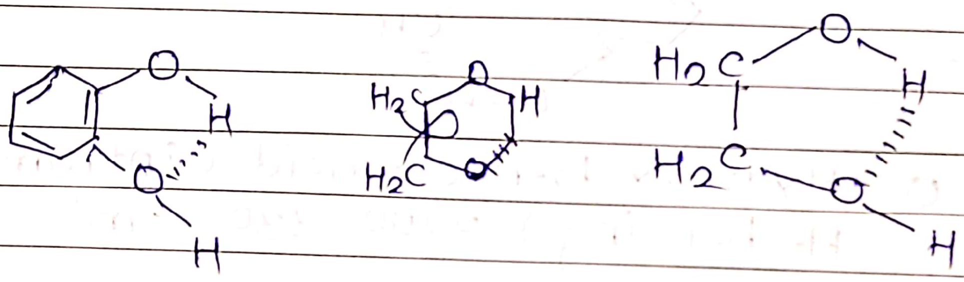
Dilution with aprotic solvent prevents intermolecular H-bonding. This stabilizes O-H bond and shifts the IR-absorption to higher side, so it is called dilution effect. eg. Lack of H- bonding shifts $>C=O$ and $-O-H$ group frequencies to higher side 1760 cm^{-1} and 3550 cm^{-1} respectively.

b) Alcohols and Phenols:

Strong inter or intramolecular H-bonding effects operate in alcohols and phenols. H- bonded alcoholic O-H group show peak in 3200 - 3500 cm^{-1} range. But in gas phase or in extreme dilution in aprotic solvent H- bonding is missing so, stretching frequency shifts to 3650 cm^{-1}.



(alcohol and phenols (intermolecular H- bonding)



(alcohols and phenols intramolecular H- bonding)

Intramolecular H- bonds remain intact even after dilution so dilution effect is not observed. A a comparison of IR- spectra before and after dilution can be used to check the type of H-bonding.

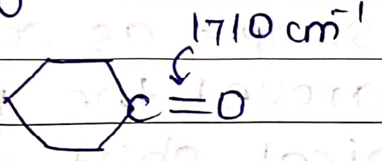
c) Amines and amides :

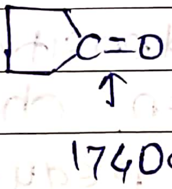
Strong H- bonding effects are observed in 1°, 2°- amines and 1°, 2° amides. The H- bonding effects ~~are observed~~ is not shown by 3° amines and amides as they lack N-H bonds.

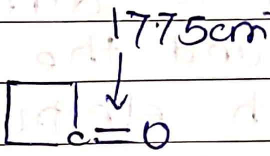
iv) Effect of strain :

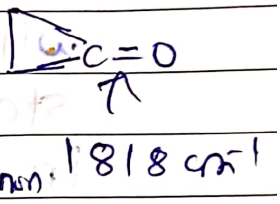
In cyclic compounds angle and ring strains cause large frequency shifts. eg. the C=O stretching frequency increases as the ring size decreases.

eg









cyclohexanone

cyclobutanon

cyclopentanon

cyclopropanone