UNITS – 1

UV AND IR SPECTROSCOPY AND THEIR APPLICATIONS

By,

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UNIT-I
UV and IR spectroscopy and its applications:-

Basic concepts of UV spectroscopy:-

① A molecule contains electronic, vibrational and rotational energy levels.

② Each electronic level is associated with a number of vibrational levels with less energy separations.

③ Each vibrational level in turn is associated with a set of rotational levels with even less energy separations.

Diagram showing energy levels E_0 and E_1 with vibrational levels V_0, V_1, V_2 and rotational levels.

→ vibrational levels.
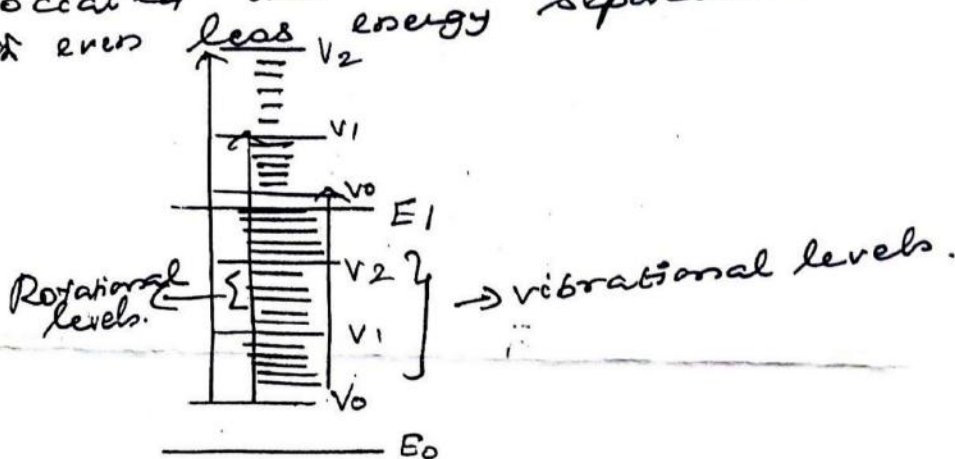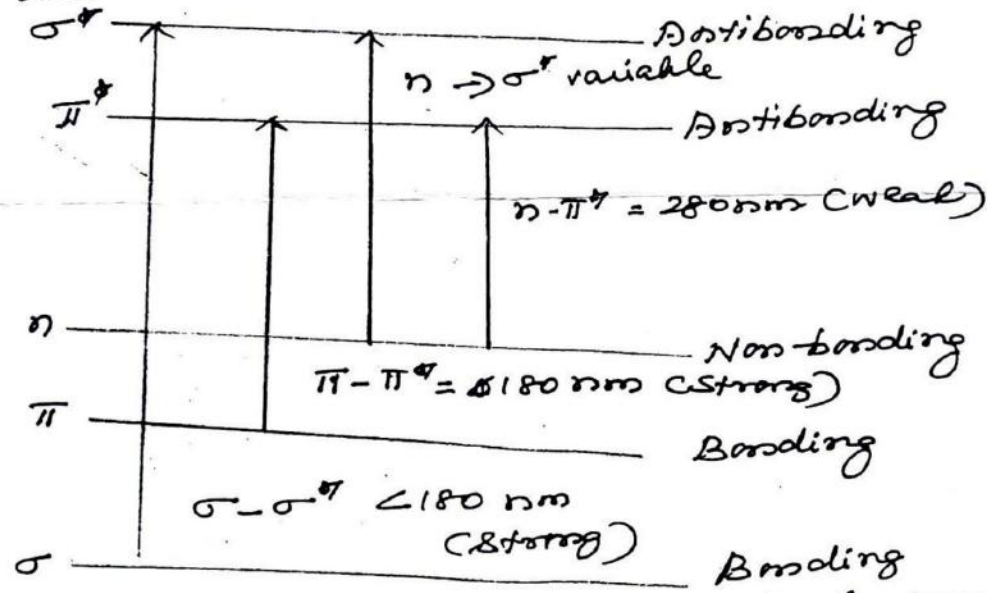
Electronic energy levels:-

④ Due to relatively larger amounts of energy associated with the UV radiation, they are capable of electronic excitations and induce transitions in the electronic, vibrational and rotational energy levels of a molecule.

⑤ Thus ultraviolet spectrum of a molecule results from transitions between electronic energy levels accompanied by changes both in vibrational and rotational states.

ELECTRONIC ENERGY LEVELS & ELECTRONIC TRANSITIONS.

① Absorption of ultraviolet radiation by an organic molecule leads to electronic excitation among various energy levels within the molecule.

② The transitions generally occur in between a bonding or lone-pair orbital and an unoccupied non-bonding or antibonding orbital.

③ The energy difference between various energy levels in most organic molecules varies from 30 to 150 kcal/mole.

④ The σ orbitals involved in forming σ-bonds are the lowest energy occupied molecular orbitals.

⑤ The π-orbitals lie at somewhat higher energy and the orbitals holding the unshared electron pairs (non-bonding orbitals) lie at even higher energy levels than the π-orbitals.

⑥ The unoccupied or antibonding orbitals (π* and σ*) are the orbitals of highest energy.

σ* ————————————————— Antibonding
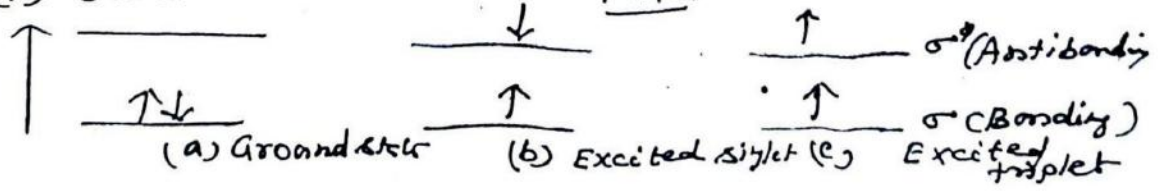   n → σ* variable
π* ————————————————— Antibonding

        n - π* = 280 nm (weak)

n ——————————————————— Non-bonding

        π - π* = 180 nm (Strong)

π ———————————————————— Bonding

    σ - σ* < 180 nm
         (Strong)

σ ———————————————————— Bonding

The change in energy ΔE for different transitions are in the order
$n \to \pi^* < n - \pi^* < n \to \sigma^* << \sigma - \sigma^*$

Electronic energy levels and electronic transitions. FIG 1

The important modes of electronic transitions, when a molecule absorbs radiation in ultraviolet or visible region.

ⓐ Transitions between bonding and Antibonding orbitals:-

(i) σ - σ* transition:-   FIG 2

↑ ———————   ↓ ————   ↑ ——— σ*(Antibonding)

  ↑↓ ————   ↑ ————   ↑ ——— σ (Bonding)
 (a) Ground state   (b) Excited singlet (c) Excited triplet

Electronic excitation takes place ②
when one of the σ bonding electrons(b) is promoted.
to the σ* level as shown in fig 2 (b) (c) and in
2 (b) without any inversion of spin and in 2 (c)
with inversion of spin. C is known as
excited triplet state. Triplet state possesses
lower energy than the corresponding excited
singlet state. Normally the absorption of visible
or UV radiation causes electronic transition
from singlet ground state to the excited
singlet state.

From fig (1), it is seen, that σ-σ*
transition requires very high energy. This
energy is available only in the far UV region.
This transition occurs is only saturated
hydrocarbons with no non-bonding electrons.

② σ-σ* transition:-
This type of transition takes place in
saturated compounds containing one hetero atom
with unshared pare of electrons (n electrons).
Some compounds undergoing this type of transitions are
saturated halides, alcohols, ethers, aldehydes, ketones,
Amines etc. Such transitions require comparitively
less energy that that required for σ-σ* transition.
water absorbs at 167 mμ, methyl alcohol at 174 mμ
and methyl chloride at 169 mμ.
In saturated alkyl halides, the energy
required for such a transition decreases with
the increase in the size of the halogen atom.

π-π* transition:-
This type of transition occurs in
the unsaturated centres of the molecule (i.e) in
compounds containing double or triple bonds and
also in aromatics. The excitation of π electron
requires smaller energy and hence transition
of this type occurs at longer wavelength. A π electron
of a double bond is excited to π* orbital. For
example alkenes, alkynes, carbonyl compounds,
cyanides, azo compounds show π-σ* transition.
This transition requires still lesser energy

as compared to $n \rightarrow \sigma^*$ transition and therefor absorption occurs at longer wavelengths.

$n-\pi^*$ transition:-

In this type of transition, an electron of unshared electron pair on hetero atom gets excited to π^* antibonding orbital. This type of transition requires least amount of energy out of all transitions and hence occurs at longer wavelength. Saturated aldehydes show both the type of transitions. (low energy $n-\pi^*$ and high energy $\pi-\pi^*$).

CHROMOPHORE :-

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region. The absorption occurs irrespective of the fact whether colour is produced or not. Some of the important chromophores are ethylenic, acetylinic, carbonyl, acids, esters, nitrile group etc.
There are two types of chromophores.
(a) chromophores in which the group contains π electrons and they undergo $n-\pi^*$ transitions. Such chromophores are ethylenes, acetylenes etc.
(b) Chromophores which contain both π electrons and non-bonding electrons. Such chromophores undergo two types of transitions (i.e) $\pi-\pi^*$ and $n-\pi^*$. Examples of this type are carbonyls, nitriles, azo compounds, nitro compounds etc.,
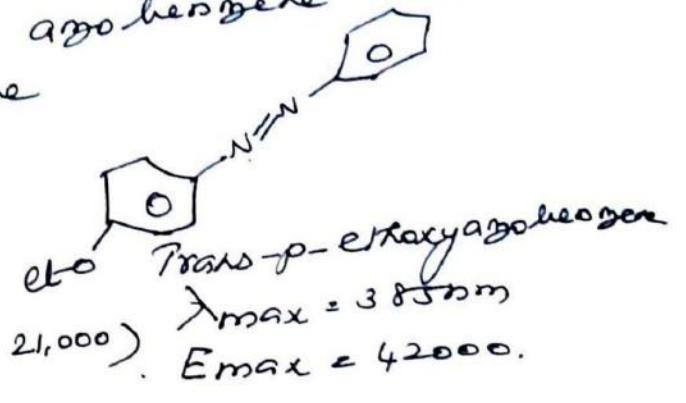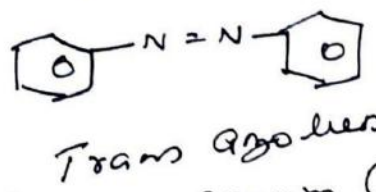
AUXOCHROME :-

An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum. An auxochromic group is called colour enhancing group. Some common auxochromic groups are OH, OR, NH2, NHR, NR2, SH etc. The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons.

In aniline, $\ddot{N}H_2$ acts as a chromophore. But in anilinium ion, there is no lone pair on nitrogen atom and so ε_{max} is reduced as given.

Aniline
$\lambda_{max} = 280 nm$
$\varepsilon_{max} = 1430$

$\lambda_{max} = 254 nm$
$\varepsilon_{max} = 160$
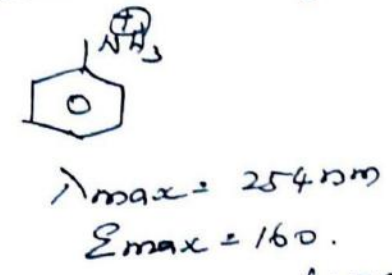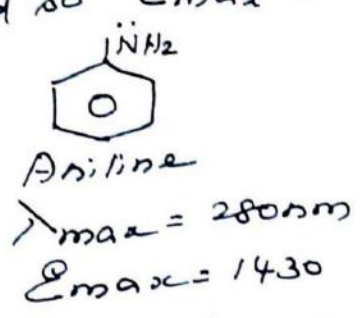
If we consider azobenzene and trans-p-ethoxyazobenzene

Trans Azobenzene
$\lambda_{max} = 320 nm$ $(\varepsilon_{max} = 21,000)$

Trans-p-ethoxyazobenzene
$\lambda_{max} = 385 nm$
$\varepsilon_{max} = 42000$.

Mechanism:-

All auxochromic groups contain non-bonding electrons. Due to this, there is extension of conjugation of the chromophore by sharing the non-bonding electrons.

$$H_2C = CH - \ddot{N} - (CH_3)_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = \overset{\oplus}{N} - (CH_3)_2$$
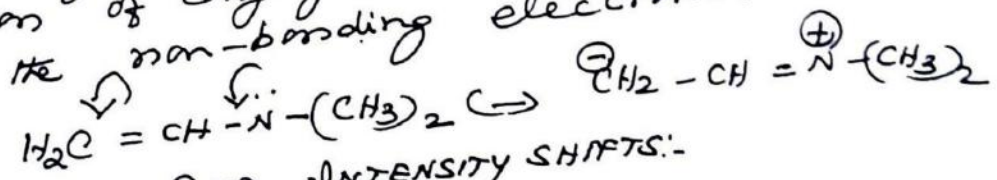
ABSORPTION AND INTENSITY SHIFTS:-

ⓐ BATHOCHROMIC EFFECT:-

Absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome or by the change of solvent. Such an absorption shift towards longer wavelength is called red shift or bathochromic shift. The $n-\pi^*$ transition for carbonyl compounds experiences bathochromic shift when the polarity of the solvent is decreased.

ⓑ HYPSOCHROMIC SHIFT:-

It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength. The absorption

to shifted towards shorter wavelength is called blue shift or hypsochromic shift.

(c) HYPERCHROMIC EFFECT!-

It is the effect leading to increased absorption intensity. The intensities of primary and secondary bands of phenol are increased in phenolate.

(d) HYPOCHROMIC EFFECT!-

It is the effect leading to decreased absorption intensity. The intensities of primary and secondary bands of benzoic acid are decreased in benzoate.

FACTORS AFFECTING THE POSITION OF UV BANDS!-

① CONJUGATION.-

(i) A conjugated system requires lower energy for $\pi - \pi^*$ transition than an unconjugated system.

(ii) For example, in the conjugated butadiene (λ_{max} = 217 nm) and the $\pi + \pi^*$ orbitals have energies much closer together than those in ethylene.

(iii) Energy absorption for butadiene can occur by π_2 (bonding) $\rightarrow \pi_3^*$ (antibonding) transition (HOMO $\rightarrow$ LUMO). The energy difference is 136 kcal/mole. But for $\pi - \pi^*$ transition of ethylene energy difference is (176 Kcal/mole) giving a λ_{max} at a longer wavelength.

Greater the number of alternate multiple bonds, for example $-C=C-C=C-C=C-$ or $-C=C-C=O$ etc. λ_{max} for divinylethylene $H_2C=CH-CH=CH-CH=CH_2$ is 265 mM whereas for diallyl $H_2C=CH-CH=CH_2$ is only 180 mM.

When the conjugated system is extensive, (i.e) when the molecule contains

a number of conjugated double bonds, the wavelengths of absorption maxima becomes sufficiently high and hence the absorption occurs in the visible region and the compound appears coloured. For example α-carotene with 10 conjugated double bonds absorbs at the violet end of the visible spectrum and hence is red in colour.

As the conjugation increases, the energy gap between HOMO and LUMO decreases.

II. STERIC HINDRANCE & COPLANARITY:-

(i) Longer the conjugated system, higher will be the absorption maximum and larger will be the value of the extinction coefficient.

(ii) If in a structure, the π-electron system is prevented from achieving coplanarity, there is a marked shift in the absorption maximum and extinction coefficient.

(iii) Since steric crowding which distorts the geometry of the chromophore which is turn prevents effective π-orbital overlap. conjugation is reduced.

(iv) Due to this, there will be a departure in the value of absorption maximum calculated from the empirical rules.

(v) $\pi-\pi^*$ transition for biphenyl(I) which readily achieves coplanarity absorbs at 250 mμ and εmax 19,000. But in 2-methyl biphenyl (II) $\pi-\pi^*$ transition undergoes blue shift and intensity is diminished as the two rings remain no longer coplanar. For this molecule absorption maximum is 237 mμ and εmax 10250.
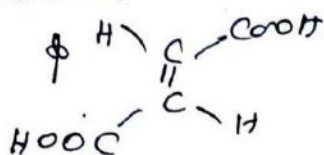
$H_3C-C-O^H_{\overset{\|}{O}}$

$O=C-OH$

I

II
Me
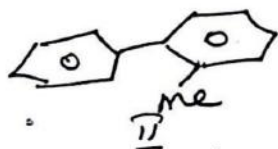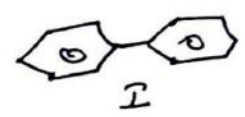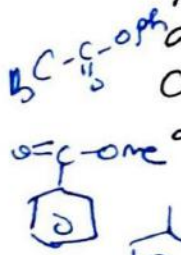
(vi) If the compound containing alkene chromophore is capable of existing as geometrical isomers.

(vii) The trans isomer is found to absorb at longer wavelength with higher value of extinction coefficient as compared to cis-isomer.

(viii) It is due to more effective π-orbital overlap and it achieves effective coplanarity.

(ix) Due to greater crowding in __cis form__

(since both bulky groups are on the same s..
the geometry of the albene chromophore is
distorted and departure from coplanarity
results.
(x) Thus $\pi-\pi^*$ transition is cis-cinnamic acid
takes place at lower wavelength with lower
extinction coefficient

ϕ — H \ C — COOH
|| C — H
HOOC / C — H

Absorption maxima = 272 mμ
ε_{max} = 15,900.

Tram cinnamic acid

H \ C — COOH
|| C — COOH
H /
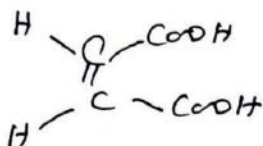
Absorption maxima = 268 mμ
ε_{max} = 10700.

Cis - cinnamic acid

III CONFORMATION AND GEOMETRY IN POLYENE SYSTEMS:-

(i) In long-chain conjugated polyenes, steric
hindrance to coplanarity can arise when
cis-bonds compared to are present.
(ii) All trans methyl carotenoid, its isomer
with a central cis-double bond, absorbs at
shorter wavelength due to partial chromophore.

IV SOLVENT EFFECTS IN POLYENES AND KETONES:-

(i) The position and intensity of an absorption
band is greatly affected by the polarity of the
solvent used.
(ii) Such solvent shifts are due to the differences
in the relative capabilities of the solvents to
interact electrostatistically with polar
chromophores (e.g carbonyl).
(iii) $n-\pi^*$ transition :- In this, the ground state is more
polar than the excited state. This stabilization is
more pronounced with hydrogen bonding solvents
(such as water/etoH). The non-bonded electrons
on the oxygen will coordinate with hydroxylic
solvents, thus lowering the net energy of $\underline{n}$ electron

So energy difference is increased in the presence ⑤ of polar solvent, λ_{max} is decreased and Absorption occurs is shifted towards shorter wavelength and consequently the intensity becomes less.

(iv) $\pi - \pi^*$ transition :- By increasing the polarity of the solvent, the dipole-dipole interactions with the solvent molecules lower the energy of the excited state and the energy difference is decreased. λ_{max} is increased and absorption is shifted towards longer wavelength with increased intensity.

(v) $n - \pi^*$ transition :-

Hydrogen bonding also takes place in $n - \pi^*$ transition. Two cases arise.

① If the polar chromophores (e.g. carbonyl) are more polar in the excited state than in the ground state the increase in polarity of the solvent stabilises the non-bonding electrons in the excited state due to hydrogen bonding. So the absorption band is shifted towards longer wavelength with increased intensity.

② If the polar chromophores are more polar in the ground state, the increase in polarity of the solvent causes the absorption band to shift towards a shorter wavelength. In this case, stabilization of the non-bonding electrons takes place to a greater extent in the ground state due to hydrogen bonding than in the excited state.

n–π* Transition
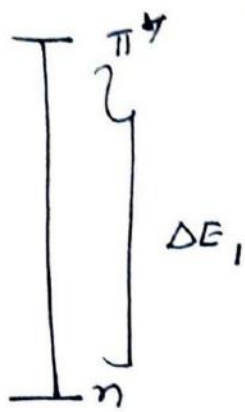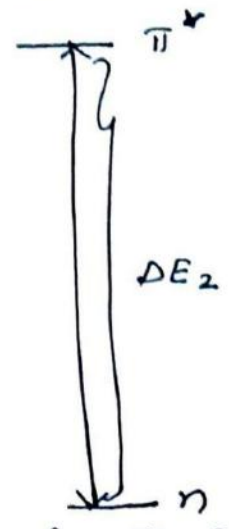
ΔE_1

In the absence of polar solvent

ΔE_2

n

In the presence of polar solvent.

$$\Delta E_2 > \Delta E_1$$

π–π* – Transition

ΔE_1

In the absence of polar solvents
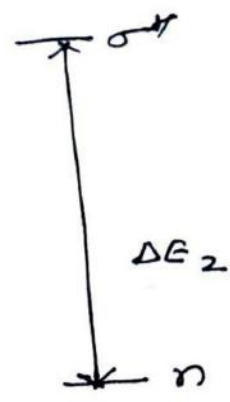
$\Delta E_2 < \Delta E_1$

ΔE_2
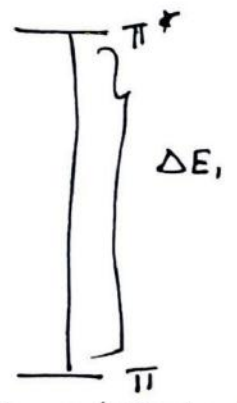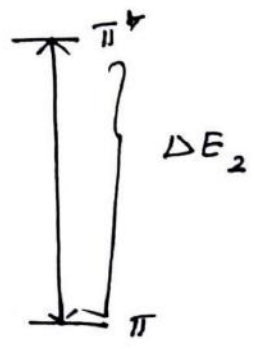
In the presence of polar solvents

S viii

$n-\sigma^*$ Transition (Excited state is more polar)

σ^*

ΔE_1

n

In the absence of polar solvents

σ^*

ΔE_2

n
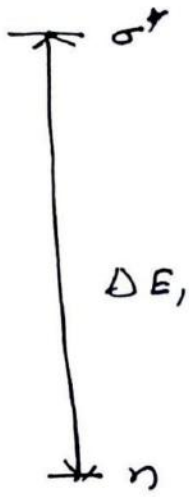
In the presence of polar solvents

$\Delta E_1 > \Delta E_2$ $\Delta E_2 < \Delta E_1$

S ix

$n-\sigma^*$ Transition (Ground state is more polar)

σ^*

ΔE_1

n

In the absence of polar solvents

$\Delta E_2 > \Delta E_1$

σ^*

ΔE_2

n
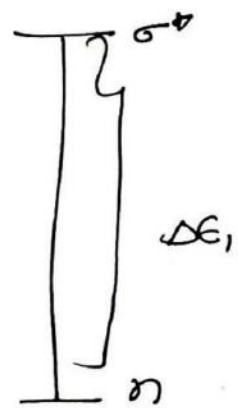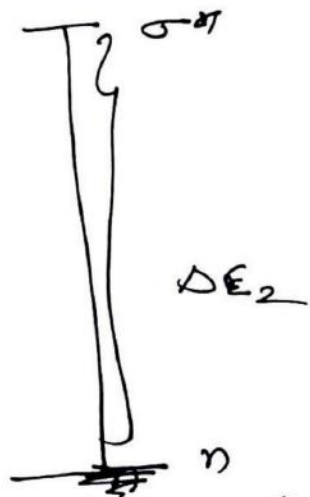
In the presence of polar solvents.

WOODWARD-FISHER RULES FOR CALCULATING ABSORPTION MAXIMUM IN DIENES

Table T$_2$-8 Conjugated dienes and Trienes.

Solvent–Ethanol

Transition involved—$\pi \rightarrow \pi^*$

Parent value for Butadiene system or a cyclic conjugated diene	217 mμ
Acyclic Triene	245 mμ
Homoannular conjugated diene	253 mμ
Heteroannular conjugated diene	215 mμ
Increment for each substituent	
Alkyl substituent or ring residue	5 mμ
Exocyclic double bond	5 mμ
Double bond extending conjugation	30 mμ
Auxochrome	
—OR	+ 6 mμ
—SR	+ 30 mμ
—Cl*, —Br*	+ 5 mμ
—NR$_2$	+ 60 mμ
OCOCH$_3$	0 mμ

(*d*) **Exocyclic and Endocyclic conjugated double bonds** : Exocyclic double bond is a double bond, part of the conjugated system, formed by any carbon atom of any ring but present outside the ring. Endocyclic double bond is present inside the ring. Such double bonds are shown in the following examples :

(Exo) (Endo)

(Exocylic double bond to ring A)

(Contain two exocyclic, double bonds)
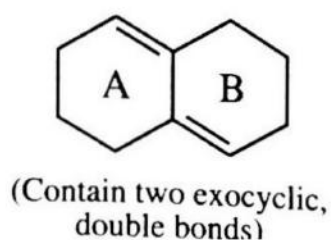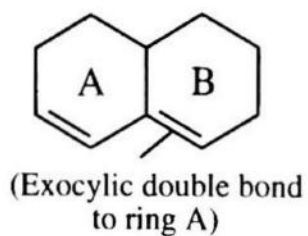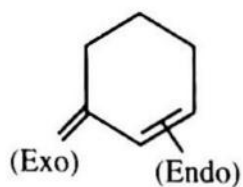
Some examples illustrating the above rules are as follows :

EXAMPLE 1. *Calculate the absorption maximum in the ultra-violet spectrum of 2, 4- Hexadiene.*

SOLUTION. The basic unit in 2, 4. hexadiene is butadiene. There are two alkyl substituents (one on each double bond) on it. Thus,

$$(CH_3—CH=CH—CH=CH—CH_3)$$
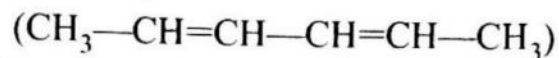
$$\begin{array}{lll} \text{Basic value} & = & 217 \text{ m}\mu \\ \text{2-alkyl substituents } (2 \times 5) & = & \underline{10 \text{ m}\mu} \\ \text{Calculated value} & = & 227 \text{ m}\mu \end{array}$$

The observed value* is also found to be 227 mμ.

EXAMPLE 2. *Calculate the absorption maximum in the UV spectrum of*

$$\langle\rangle = C - CH = CH + CH_3$$
$$\underset{CH_3}{\overset{\displaystyle |}{+}}$$
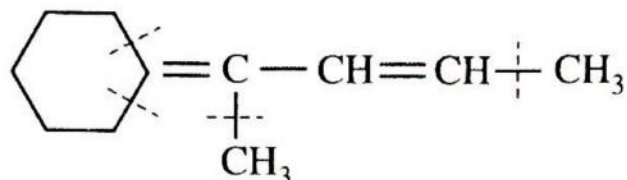
It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exo-cyclic double bond.

The value of absorption maximum is calculated as follows :

Basic value	=	217 mμ
2-alkyl substituents (2 × 5)	=	10 mμ
2-Ring residues (2 × 5)	=	10 mμ
1-Exocyclic double bond	=	5 mμ
Calculated value	=	**242 mμ**

The observed value is also found to be 242 mμ.

EXAMPLE 3. *Calculate* λ_{max} *for*
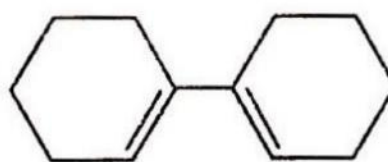
It is an example of heteroannular diene and there are four ring residues on the double bonds. Thus,

Basic value $= 215$ mμ

Four Ring residues (4×5) $= \underline{20 \text{ m}\mu}$

Calculated value $= \mathbf{235 \text{ m}\mu}$

The observed value is also found to be 234 mμ,.

EXAMPLE 4. *Calculate the absorption maximum for the compound*

in ethanol.
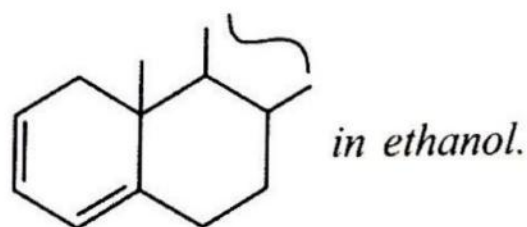
SOLUTION. It is an example of homoannular conjugated diene and there are three ring residues on it. Moreover, it contains an exocyclic double bond in it. Thus,

Basic value	=	253 mμ
3-Ring residues (3 × 5)	=	15 mμ
1-exocyclic double bond	=	5 mμ
Calculated value	=	273 mμ
Observed value	=	274 mμ

EXAMPLE 5. *Calculate the absorption maximum for the compound*

in ethanol.
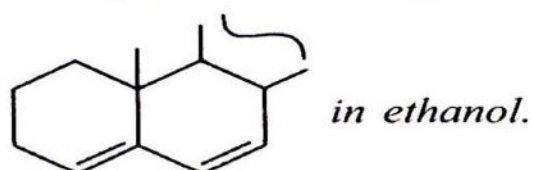
SOLUTION. It is an example of heteroannular diene and there are three ring residues in it. Moreover, it contains one exocyclic double bond in it. Thus,

Basic value	=	215 mµ
3-Ring residues	=	15 mµ
1-exocyclic double bond	=	5 mµ
Calculated value	=	**235 mµ**

The observed value of absorption maximum in the ultra-violet spectrum of this compound is also found to be 235 mµ.

EXAMPLE 6. *Calculate the value of absorption maximum for the compound*
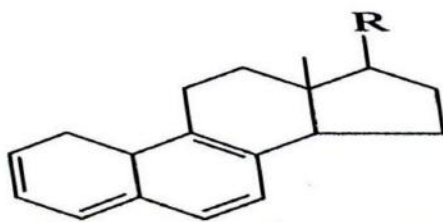
SOLUTION. It is a homodiene system. There are five ring residues on the double bonds, one exocyclic bond and also two double bonds which extend conjugation.

Basic value	=	253 mμ
2-double bonds extending conjugation	2 × 30 =	60 mμ
5-Ring residues	5 × 5 =	25 mμ
1-Exocyclic double bond	1 × 5 =	5 mμ
Calculated value	=	**343 mμ**
Observed value	=	345 mμ

EXAMPLE 7. *Calculate* λ_{max} *for the compound.*
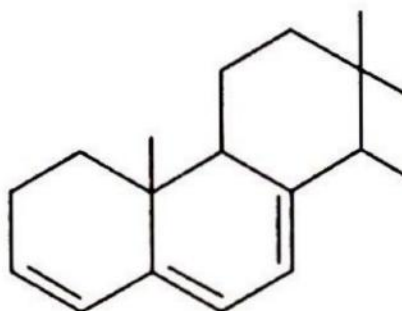
SOLUTION. It is a homoannular conjugated diene system. It contains four ring residues; two exocyclic double bonds and one double bond which extend conjugation. Thus, λ_{max} for this compound is calculated as:

Basic value	=	253 mµ
4-Ring residues	(4 × 5) =	20 mµ
2-exocyclic double bonds	(2 × 5) =	10 mµ
1-double bond extending conjugation	=	30 mµ
Calculated value	=	**313 mµ**
Observed value	=	312 mµ

POLY-enes and POLY-ynes

Note. If a conjugated polyene contains more than four double bonds, then Fieser-Kuhn rules are used. According to this approach, both λ_{max} and ε_{max} are related to the number of conjugated double bonds as well as other structural units by the following equations.

$$\lambda_{max} = 114 \times 5\,M + n\,(48.0 - 1.7n) - 16.5\,R_{endo} - 10\,R_{exo}$$

$$\varepsilon_{max} = (1.74 \times 10^4)n$$

where

n = no. of conjugated double bonds.

M = no. of alkyl or alkyl like substituents on the conjugated system.

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.

R_{exo} = no. of rings with exocyclic double bonds.

Consider the case of Lycopene :

(Lycopene)
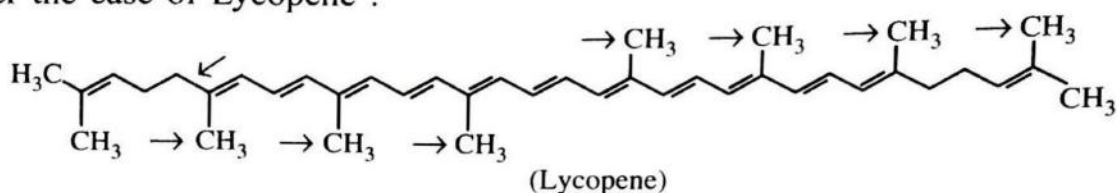
In this compound, only eleven double bonds are in conjugation. Thus, $n = 11$. In addition to this, there are eight substituents (methyl groups and chain residues). Thus, $M = 8$. As there is no ring system, there are neither exo nor endocyclic double bonds in this conjugated system. λ_{max} can be calculated as under :

$$\lambda_{max} = 114 + 5(8) + 11 [48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm}$$

The observed value of λ_{max} is found to be 476 nm (hexane)

$$\varepsilon_{max} \text{ (calculated)} = 19.1 \times 10^4.$$

Similarly, λ_{max} can be calculated for β-carotene.
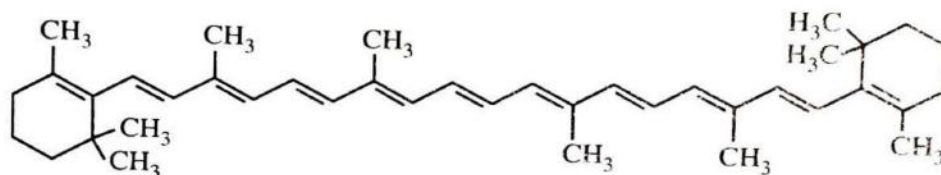
The calculated value of λ_{max} is found to be 453.3 nm and ε_{max} 19.1 × 10⁴.

6

7 C₄H₉

8

9 C₈H₁₇
AcO   H
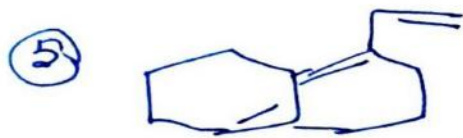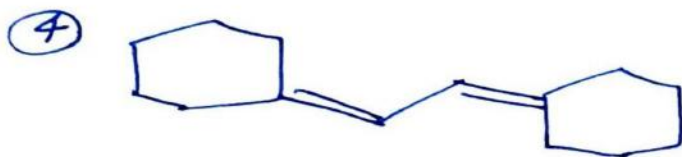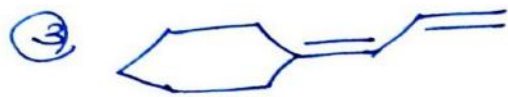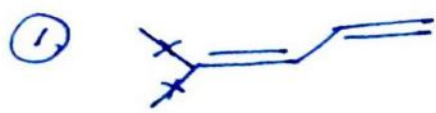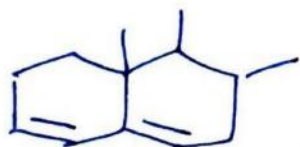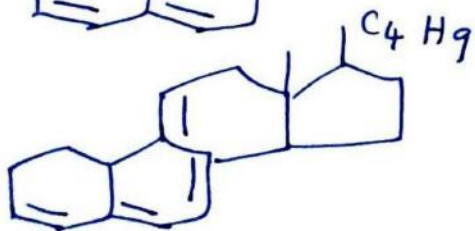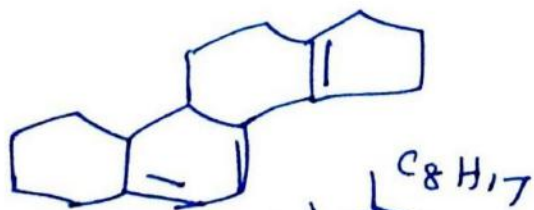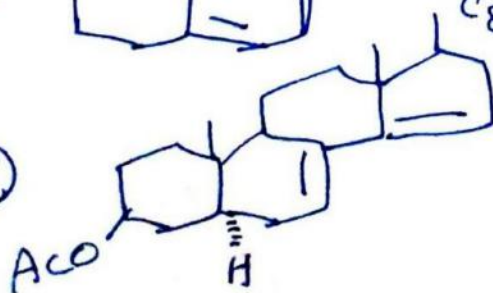
10

PERIYAR ARTS COLLEGE, CUDDALORE-1.

P.G. DEPARTMENT OF CHEMISTRY.

Assignment - I

IN ORGANIC CHEMISTRY - III Date:- 14.08.2020.

FOR II M.SC., CHEMISTRY.

Calculate λ_{max} for the following dienes:-

①

②

③

④

⑤

⑥

⑩

⑦

⑧

⑨

⑪ $H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$

⑫
$\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$

⑬ $= CH - CH = CH_2$

⑭ $= CH - CH =$

⑮

⑯

⑰

⑱

⑲

All the best!

⑳
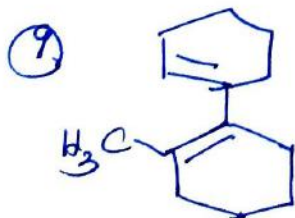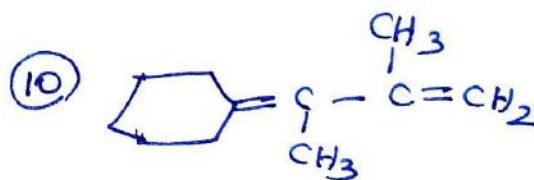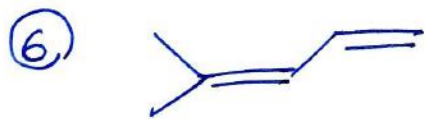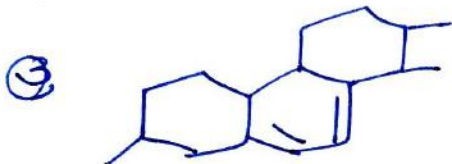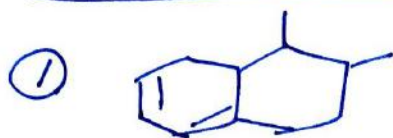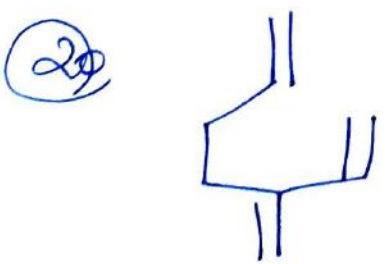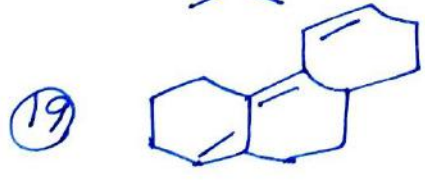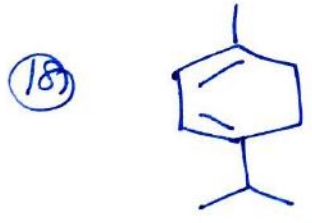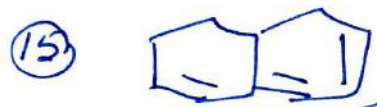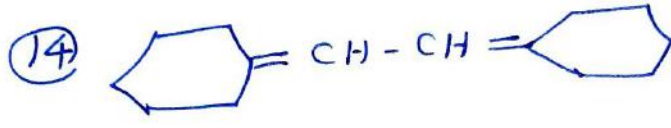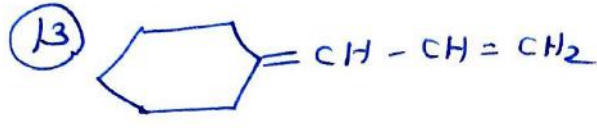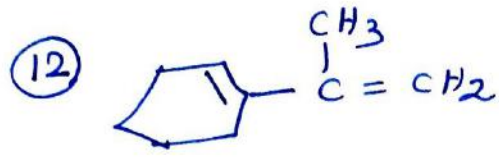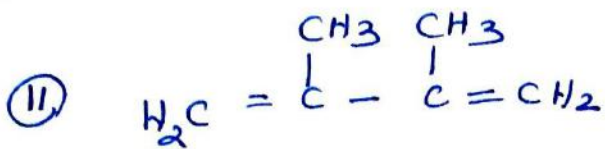
INFRA-RED SPECTROSCOPY

PRINCIPLE:-

① The absorption of infra red radiations $(0.8\mu$ to 2.5μ - near IR region
2.5μ to 15μ - (ordinary ")
15μ to $200mm$ - Far IR region) causes excitation of a molecule from a lower to higher vibrational level.

② Each vibrational level is associated with a number of closely spaced rotational levels. So IR spectrum is considered as vibrational-rotational spectra.

③ Only those molecules which undergo change in dipole moment will absorb in infra red region. So vibrational transitions which are accompanied by change in dipole moment are called as infra red active transitions. Thus they are responsible for absorption of energy in IR region.

④ The vibrational transitions which are not accompanied by change in dipole moment of the molecule are not directly observed and these are infra red inactive

⑤ Vibrational transitions of $C=O$, NH, OH etc, bands are accompanied by a change in dipole moment and thus absorb strongly in the IR region.

⑥ But transitions in the carbon-carbon bonds in symmetrical alkenes and alkynes are not accompanied by change in dipole moment and hence do not absorb in IR region.

Molecular Vibrations:-

Atoms in a molecule are not held rigidly. The molecule may be visualised as consisting of balls of

different sizes tied with springs of varying strengths. Balls and springs correspond to atoms and chemical bonds respectively. When infra-red light is passed through the sample, the vibrational and rotational energies of the molecules are increased.

Two kinds of fundamental vibrations are.

   (a) Stretching   (b) Bending.

STRETCHING VIBRATIONS:-

In this type of vibrations, the distance between the two atoms increases or decreases but atoms remain in the same bond axis.

Stretching vibration.
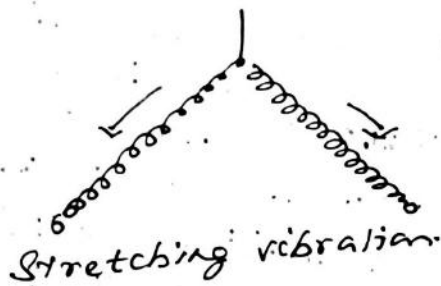
Types:- (i) Symmetric stretching
      (ii) Asymmetric stretching.

(i) Symmetric Stretching:-

The movement of the atoms with respect to a particular atom in a molecule is in the same direction.
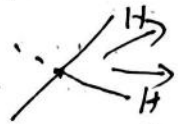
(ii) Asymmetric Stretching:-

In these vibrations, one atom approaches the central atoms while the other departs from it.
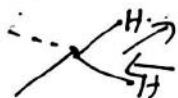
BENDING VIBRATIONS:-

In this type of vibrations, the positions of the atoms change with respect to the original bond axis. More energy is required to stretch a spring than to bend it. So stretching absorptions appear at high frequencies as compared to the bending absorption of the same band.

TYPES:-

① SCISSORING:- In this type, two atoms approach each other.

bending.

② ROCKING:- The movement of the atoms take place in same direction.
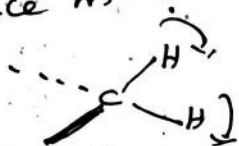
③ WAGGING:- The two atoms move up and down the place with respect to the central atom.

④ TWISTING:- One of the atoms moves up the plane while the other moves down the plane with respect to the central atom.

SHORT NOTES ON FINGER PRINT REGION:-

No two components that are closely related can have identical/superimposable bands. The fingerprint region of an IR spectrum is useful for establishing the identity of two compounds.

Fingerprint region is divided into 3 regions:-

(i) 1500-1350 cm^{-1} region:-

The appearance of a doublet near 1380 cm^{-1} and 1365 cm^{-1} (s) shows the presence of (m) t-butyl group in the compound. Gem dimethyl shows a medium band near 1380 cm^{-1}. Out of the two bands for the nitro compound, one appears in the fingerprint region near 1350 cm^{-1}.

(ii) 1350-1000 cm^{-1} region:-

C-O stretching of alcohols, esters, lactones, acid anhydrides show characteristic absorption in this region. Primary alcohols form two strong bands at 1350-1260 cm^{-1} and near 1050 cm^{-1}. Phenols absorb near 1200 cm^{-1}. Esters show two strong bands between 1380-1050 cm^{-1}. Absorption in the region 1150-1070 cm^{-1} is most characteristic of ethers (i.e.) C-O stretching in C-O-C group.

(iii) Region below 1000 cm^{-1}:-

$\diagdown$C = C-H deformation at $\approx$ 700 cm^{-1} (s) and that at 970-960 cm^{-1} (s) distinguishes between cis and trans alkenes. The higher value indicates that the hydrogen atoms in the alkene are trans to each other. A bond in the region 750-700 cm^{-1} shows monosubstituted benzene.

Various regions of IR radiation:-

The IR region is divided into 3 parts

(i) **Near IR region:-**

This is also known as overtone region and ranges from 0.8 to 2.5μ.

(ii) **Mid IR region:-** Gives useful information about the structure of the molecule. This is also known as vibration-rotation region and ranges from 2.5 to 50μ. Absorption spectra are produced from the electronic transitions between the vibrational & rotational levels of a molecule in its ground state.

(iii) **Far IR region:-** This is known as rotation region and lies in the spectral range of 50 to 1000μ. The far IR region contains a few absorptions of interest to organic chemists, notably Carbon-halogen bond absorptions and the absorptions associated with rotational changes within the molecule.

Explain how IR spectrum can be used to study intra and intermolecular hydrogen bonding in organic compounds.

① By using IR spectrum, we can be able to describe and distinguish inter and intramolecular hydrogen bonding in organic compounds.

② The free OH stretching frequency is greater than the OH stretching frequency which involves in hydrogen bonding in organic compounds.

③ Since the bond length increases and strength of OH bond decreases due to hydrogen bonding and so stretched frequency decreases.

④ In very dilute solution, there is no intermolecular hydrogen bonding. In ethanol only intermolecular hydrogen bonding is present. In dilute solution, only one band at 3650 cm^{-1} is shown.

⑤ But in concentrated solution of ethanol, a sharp band appears at 3650 cm^{-1} and a broad band at 3350 cm^{-1}

The sharp band is OH stretching in free alcohol molecules and the broad band is OH stretching in hydrogen bonded alcohol molecules. (intermolecular hydrogen bonding).

$$R-O\cdots H-\overset{\overset{R}{|}}{O}\cdots H-\overset{\overset{R}{|}}{O}\cdots H-\overset{\overset{R}{|}}{O}\cdots$$

$$\overset{|}{H}$$

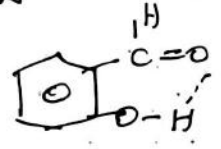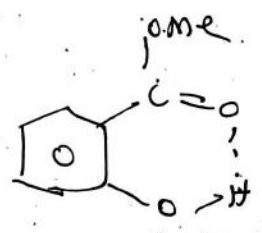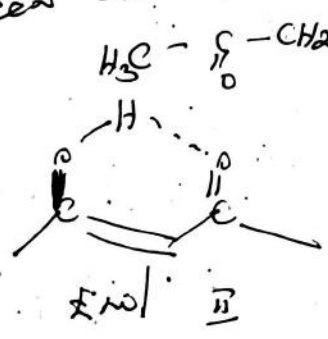Intermolecular hydrogen bonding)
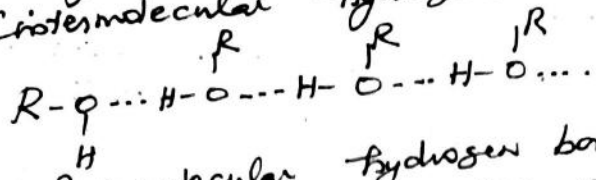
⑥ If we take IR spectrum of salicylaldehyde we can find a band at $2800 cm^{-1}$ for OH stretching frequency. This frequency is very much lower than that of OH stretching frequency in intermolecular hydrogen bonding. This discrepancy is due to the formation of intermolecular hydrogen bonding as follows.

⑦ Hydrogen bonding in enols and chelates is particularly strong and the observed OH stretching frequencies are low. Since these bands are not easily broken on dilution by an inert solvent and a band due to OH st. frequency may not be seen at low concentration.

$$H_3C-\overset{O}{\underset{||}{C}}-CH_2-\overset{O}{\underset{||}{C}}-CH_3$$

Enol II

Chelate III
methyl salicylate.

⑧ Since intramolecular hydrogen bonding is much stronger than intermolecular hydrogen bonding and so O-H bond becomes much weaker in I, II & III, where intramolecular hydrogen bonding is present and so OH stretching frequency is shifted to lower region.

(9) On dilution, intramolecular hydrogen bonding is not at all affected, because it is present within the molecule itself. So the band is never affected on dilution.

In this way, we can distinguish between intra and intermolecular hydrogen bonding by using IR spectrum.

FERMI RESONANCE

FUNDAMENTAL BANDS:-

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands. No of fundamental bands is calculated using the formula $(3N-5)$ for a linear molecule and $(3N-6)$ for a non-linear molecule.

Transitions from the ground state $(V=0)$ to the second excited state $(V=2)$ with the absorption of infrared radiations give rise to weak bands called overtones.

In addition to overtones, combination bands, difference bands appear. If there are two fundamental bands at x and y, then the additional bands can be expected at

(i) $2x, 2y$ (overtones)
(ii) $(x+y), (x+2y), (2x+y) ... $ etc.}
      (combination bands)
(iii) $(x-y), (x-2y), (2y-x)$ etc., ...
      (difference bands)

All these additional bands are 10-100 times less intense as compared to fundamental bands.

Definition :-

A molecule transfers its energy from fundamental band to overtone and back again if they have same frequency. Quantum mechanically resonance, pushes the two levels apart and mixes their character so that each level becomes partly fundamental and partly overtone in character. This type of resonance gives rise to a pair of transitions & equal intensity is known as Fermi resonance as it was discovered by **FERMI**.

1) When an overtone / combination band falls near a strong fundamental vibration, it causes a decrease in the intensity & the fundamental vibration and a large increase in the intensity & the overtone / combination vibration.

2) The requirements of such effective coupling are

(a) The vibrations must be of the same symmetry.

(b) Strong coupling requires a common atom between the groups.

(c) When the coupled groups absorb individually near the same frequency.

(d) A common bond is required for coupling of bending vibrations.

One example of Fermi resonance is afforded by absorption of CO_2. Symmetric stretching band of CO_2 is IR inactive since it produces no change in dipole moment and it shows strong absorption at $1340 cm^{-1}$ in Raman Spectra.

⑤ The fundamental bending vibration occurs at $666 cm^{-1}$ and its first overtone occurs at $1334 cm^{-1}$. This overtone frequency is very close to $1340 cm^{-1}$. Fermi resonance occurs and mutual perturbation of $1340 cm^{-1}$ (fundamental) and $1334 cm^{-1}$ (overtone) gives rise to two bands at $1285.5 cm^{-1}$ and $1388.3 cm^{-1}$ having intensity ratio of $1:0.9$.

⑥ Another example of Fermi resonance is given by aldehydes in which CH stretching absorption usually appears as a doublet ($2820 \neq 2720 cm^{-1}$) due to interaction between CH stretching (fundamental) and overtone of CH deformation (bending)

⑦ Fermi resonance is also shown by the spectrum of n-butyl vinyl ether. In this case the overtone of the fundamental vibration at $810 cm^{-1}$ (ie) $1620 cm^{-1} \neq 810 \times 2$) chances to coincide with the band at $1640 cm^{-1}$ due to CH bending. The mixing of these two bands (overtone and fundamental CH bending) in accordance with the Fermi resonance gives two bands of almost equal intensity at $1640 cm^{-1}$ and $1630 cm^{-1}$.

IR SPECTROSCOPY.

VIBRATIONAL FREQUENCIES :-

The energy needed to vibrate a molecule will be absorbed in IR region. The position of the absorbed light in the spectrum can be specified in units of frequencies which are known as vibrational frequencies.

Each bond in an organic molecule absorbs light of specific frequency and perfect stretching and bending frequency. The stretching energy of a bond is greater than the bending energy. Thus stretching absorptions of a bond appear at higher frequencies in the IR Spectrum than the bending absorptions of the same bond

The vibrational frequency of a bond can be calculated using Hook's law.

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

where

ν = frequency.
k = force constant of the bond.
R = Reduced mass of the system.

CALCULATION OF FORCE CONSTANT :-

The force constant of a bond k is a diatomic molecule is related to the frequency of absorption ν according to the formula.

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

where 'R' is the reduced mass and can be calculated from the relation

$$\frac{1}{R} = \frac{1}{m_1} + \frac{1}{m_2}$$

FACTORS INFLUENCING VIBRATIONAL FREQUENCIES :-

① BOND STRENGTH :-

The vibrational frequency increases when the bond strength increases. This is in accordance with Hooke's law $C=C$ & $C=O$ stretching frequency. are greater than $C-C$ & $C-O$ stretching frequency.

② REDUCED MASS :-

The vibrational frequency increases when the reduced mass of the system decreases.

Example :

$C-H$ and $O-H$ stretching will have higher frequencies than $C-C$ and $C-O$ stretching respectively.

Exceptions :-

According to reduced mass, stretching. frequencies fall along the series

$$C-H > N-H > O-H > F-H$$

But actually the follow the series. $F-H > O-H > N-H > C-H$ due to increasing electronegativity.

③ VIBRATIONAL COUPLING :-

When the two bonds vibrate with similar frequency, vibrational coupling takes place. For this to happen the two bonds should be close to one another in the molecule.

(E.g) we expect one stretching absorption frequency for an isolated $C-H$ bond, but in the case of methylene group (CH_2), two absorptions occurs which correspond to symmetric and antisymmetric. vibrations as follows.

Symmetric   Anti-symmetric
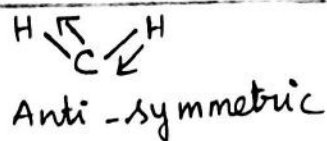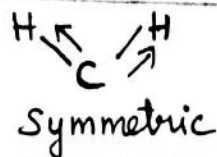
In such cases anti-symmetric vibration always occur at higher frequencies while symmetric vibrations occur at lower frequencies. These are called coupled vibrations since these vibrations occur at different frequencies that that required for an isolated C–H stretching.

④ HYDROGEN BONDING :-

Stronger the hydrogen bonding, greater is the absorption shift towards lower frequencies than the normal value. Intra and intermolecular hydrogen bonds can be distinguished in infrared spectroscopy.

INTER MOLECULAR HYDROGEN BONDS	INTRA MOLECULAR HYDROGEN BONDS
i) Give rise to broad bands	Give rise to sharp well defined bands
ii) concentration dependendent: on dilution, the intensities of bands decrease and finally di appear.	Independent of concentration
iii) The absorption frequency difference between free and associated molecules is larger.	Smaller. $0462 \ 2575282$

① FACT :-

The frequency shifts due to hydrogen bonds in amines is less than those for alcohols.

EXPLANATION :-

Nitrogen atom is less electronegative than oxygen. So hydrogen bonding in amines is weaker

than in alcohols. Amines show N-H stretching at
3500 cm^{-1} in dilute solutions while In condensed
phase spectra. absorption occurs at 3300 cm^{-1}. Absolute
alcohols show O-H group stretching at 3650 cm^{-1}
in dilute solutions. while they show hydrogen bonded.
O-H group stretching at 3350 cm^{-1}

② .FACT :-

A number of cyclic and acyclic 1:2 diols
show two bands, while isolated diols in ccl4 show
one band in the OH stretching mode region.

EXPLATION:

In ccl4 there is no intermolecular hydrogen.
bonding Thus 1:2-diols show 2 bands in dilute
solution. One is due to intramolecular hydrogen
bonding and another is due to free O-H stretching.
vibration.

⑤ ELECTRONIC EFFECT:-

i) Vibrational frequency of a bond depends on the
bond strength or the force constant .

ii) Force constant measures the force required to.
stretch a bond.

iii) Due to electronic effects, such as inductive.
effect, mesomeric effect (through resonance) and.
field effect (through space) force constant changes.

iv) So the vibrational frequency changes from the.
normal value.

v) INDUCTIVE EFFECT:

Due to the presence of a polar covalent
bond in a molecule, the process on electron shift
along a chain of atoms is called inductive effect.

vi) When an alkyl group is introduced into a molecule electron releasing inductive effect arises (+I effect). The length of the bond increases and the bond becomes weaker. Because of this absorption occurs at lower frequency.

vii) The frequency change for $C=O$ absorption, by the introduction of CH_3 group is shown below.

Formaldehyde	HCHO	$1750 \ cm^{-1}$
Acetaldehyde	H_3C-CHO	$1745 \ cm^{-1}$
Acetone	$H_3C-\underset{O}{\overset{}{C}}-CH_3$	$1715 \ cm^{-1}$

viii) When electronegative atoms are introduced into a molecule, $-I$ effect (electron withdrawing inductive effect) arises and the vibrational frequency of $C=O$ increases as shown below

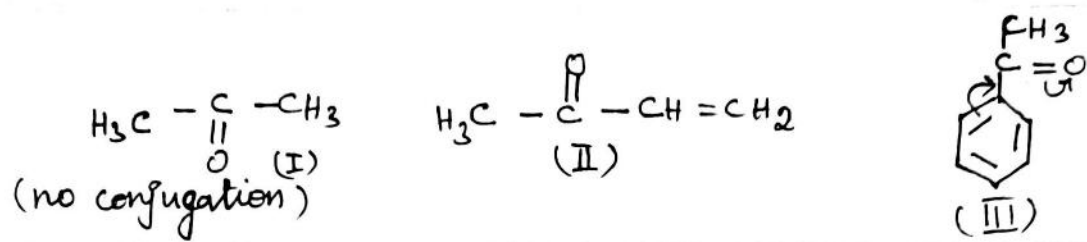|		
Acetone	$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$	$1715 \ cm^{-1}$
chloro acetone	$Cl:CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	$1725 \ cm^{-1}$
Dichloro acetone	$Cl_2CH-\underset{O}{\overset{}{C}}-CH_3$	$1740 \ cm^{-1}$

ix) MESOMERIC EFFECT :-

This involves displacement of electrons leading to centres of high or low electron density in a molecule. This effect operates along with inductive effect.

x) Mesomeric effect is particularly important in systems with an extended conjugation of multiple bonds, such as α, β-unsaturated carbonyl compounds, benzenoid compounds. etc,,

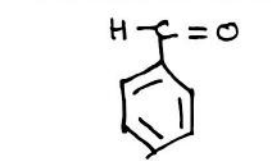xi) Conjugation lowers the absorption frequency of $C=O$ stretching.

xii) when two electron withdrawing groups ((eg.) $C=O$ NO_2 etc ..) are adjacent to multiple bond mesomeric effect causes the weakening of the bond and consequently the absorption frequency decreases.

(E.g) absorption frequency of $\diagdown C=O$ of acetone(I) methyl vinyl ketone (II) and acetophenone (III) are 1715 cm^{-1}, 1706 cm^{-1} and 1693 cm^{-1} respectively.

$$H_3C - \overset{\overset{}{\underset{\overset{\|}{O}}{C}}}{} - CH_3 \quad (I)$$
(no conjugation)

$$H_3C - \overset{\overset{O}{\|}}{C} - CH=CH_2 \quad (II)$$

(III)

In II, conjugation is due to α, β-unsaturation. and is III, it is due to aromatic ring

⊗ In some cases, lone pair of electrons on an atom may enter into conjugation with a neighbouring double bond (E.g)

$$H-\overset{}{C}=O$$
Benzaldehyde
$\gamma_{C=O} \Rightarrow 1715$ cm^{-1}
IV
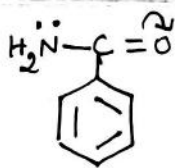
$$H_2\overset{..}{N}-\overset{}{C}=\overset{\frown}{O}$$
Benzamide
$\gamma = 1663$ cm^{-1}
V
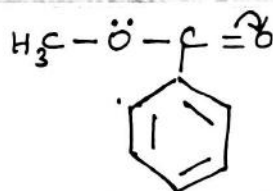
$$H_3\overset{}{C}-\overset{..}{O}-\overset{}{C}=\overset{\frown}{O}$$
phenyl acetate
$\gamma = 1730$ cm^{-1}
VI

Since conjugation lowers the absorption frequency. Because of greater conjugation in amide, $\bar{\gamma}_{C=O}$ in amide is less than in ester.

(Nitrogen is less electronegative than oxygen so the lone pair on N is more labile and participates more in conjugation).

⑥ FIELD EFFECT:

   This effect operates in orthosubstituted compounds. Inductive effect is considered when the compound is meta substituted. In para substituted compounds both inductive and mesomeric effects are considered and the domination of one effect over the other gives rise to higher or lower the frequency of absorption.

   But in ortho substituted compounds, steric effect is also considered along with other effects. In this case, the lone pair of e^-s (non-bonding electrons) on two atoms cause electrostatic repulsions leading to diminishing conjugation and consequently the vibrational frequencies of both the groups change. This effect is called field effect.

  (For eg)

   In ortho halo acetophenone, the nonbonding electrons present in oxygen and halogen repell each other. This causes a change is the state of hybridisation of $c=o$ group and also make it to go out of plane with respect to double bond on the ring.
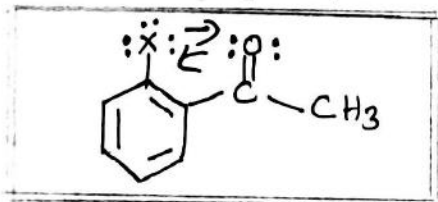
  Thus conjucation decreases and so absorption occurs at higher frequency. In ortho substituted compounds, $\gamma_{c=o}$ is more in cis isomer than in trans isomer. So α-haloketo derivatives of steroids, $>C=O$ str. frequency is higher, when cl is in equatorial than when it is is ascual. Since is equatorial Conformer, non-bonding electrons on oxygen and cl undergo repulsion more and so $>C=O$ str. freq is more

⑦ · BOND ANGLES :-

i) In ketones, the highest $C=O$ frequencies arise in the strained cyclobutanones and this is explained in terms of bond angular strain the $>C-\underset{\underset{O}{\overset{||}{C}}}{}-C<$ bond angle is reduced below the normal $120°$ leading to increased 's' character in the $C=O$ bond. The bond is <u>shortened</u> & <u>strengthened</u> and so $\gamma_{C=O}$ increases. If the bond angle is pushed outwards above $120°$ the opposite effect operates and for this reason. di-tert-butyl ketone has a very low $\gamma_{C=O}$ ($1697 cm^{-1}$)

* In cycloalkenes 'II $\gamma_{C=C}$ falls with increasing strain, but reaches a minimum is cyclobutene. In cylobutene, stretching of $C=C$ involves only bending of the attached $C-C$ bonds. In all others, (where the internal angles are not $90°$), $C=C$ stretching must involve some stretching of the adjacent $C-C$ bonds, which involves increasing $C=C$ stretching frequency.

$$\left(\overline{\underline{(CH_2)_6}} \right)$$

II
$\gamma_{C=C}$ $1610-1650 cm^{-1}$

cyclobutene
$1566 cm^{-1}$
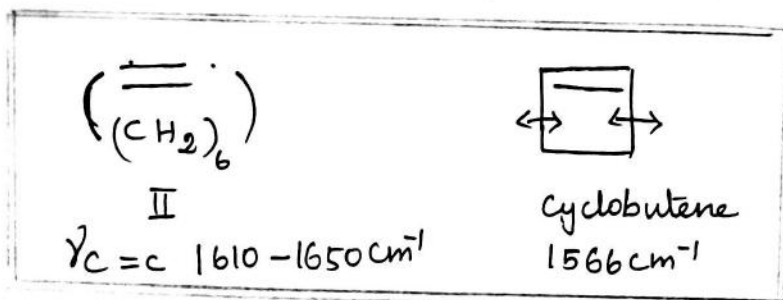
C-H stretching vibrations move to higher frequency in the sequence alkane – alkene – alkyne.

As hybridisation goes from $SP^3 - SP^2 - SP$, the 'S' character of the C-H bond increases, bond lengths become <u>shorter</u> and frequencies <u>rise</u>.

(the same symmetry)

SHORT NOTES ON METAL-LIGAND STRETCHING VIBRATION:- OR CHANGES IN IR SPECTRA OF DONOR MOLECULES UPON COORDINATION:-

(i) In acetone, carbonyl frequency is $1715.5 \, cm^{-1}$. Upon complexation with several Lewis acids, a decrease in the frequency of this band is observed. This decrease has been attributed to the effect of oxygen coordinated to the acid. Oxygen coordination has several effects upon the vibration.

(ii) The carbonyl force constant is decreased by drawing π-electron density out of the carbonyl group. This causes the observed decrease in the carbonyl frequency and indicates oxygen coordination. The absence of any absorption in the carbonyl region on the high frequency side of the complexed carbonyl band further supports for oxygen coordination (iii) If there were nitrogen coordination in the complexes, the nitrogen lone-pair would be involved resulting in a decreased C-N vibration frequency and a higher energy carbonyl absorption.

(iv) The decrease in the carbonyl stretching frequency of urea upon complexation to Fe^{3+}, Cr^{3+}, Zn^{2+} or Cu^{2+} is interpreted as indicating oxygen coordination in these complexes.

(v) Nitrogen coordination is observed in the compounds $Pd(NH_2CONH_2)_2Cl_2$ and

$Pt(NH_2CONH_2)_2Cl_2$ and the spectra show the expected increase in the C-O stretching frequency as well as a decrease in the C-N frequency.

(vi) Decrease in the P-O-stretching frequencies indicative of oxygen coordination are observed when triphenylphosphine oxide and hexamethylphosphoramide $OP[N(CH_3)_2]_3$ are coordinated to metal ions, phenol or iodine.

(vii) The S-O stretching frequency decreases in the palladium complex of dimethyl sulfoxide compared to free sulfoxide. This is an indication of sulphur coordination in this complex. The N-O stretching frequency of pyridine-N-oxide is decreased upon complexation.

(viii) IR spectra has been very valuable in determining whether the thiocyanate ion NCS⁻ is bonded in a metal complex via the nitrogen atom or the sulfur atoms. Since both modes of bonding have been detected, the anion is said to be <u>ambidentate</u>. The CN stretching frequency occurs at a lower frequency in the <u>N-bonded</u> isomer than in the <u>S-bonded</u> isomer. For nitrogen coordinated complexes the C-S stretching frequency occurs at 780 - 760 cm⁻¹ region and at 690-720 cm⁻¹ region for sulfur bonded ones. The NCS bend is also diagnostic occuring in the 450 - 440 cm⁻¹ region for N-bonded isomer and 400 - 440 cm⁻¹ for S-bonded isomer.

<u>Short notes on FingerPrint region.</u>

Ar-NO$_2$	N=O str	1570 - 1310
		1370 - 1300
C-NO$_2$	N=O str	1620 - 1535
		1375 - 1275

CHARACTERISTIC ABSORPTION FREQUENCIES OF FUNCTIONAL GROUPS

S.No	Types of vibration	Class of compound		Frequency cm^{-1}
01.	C-H str	(i) Alkanes	(i)	2960 - 2850
		(ii) Alkenes	(ii)	3100 - 3010
		(iii) Alkynes	(iii)	~ 3300
		(iv) Aromatics	(iv)	3150 - 3020
		(v) Aldehydes	(v)	2820
				2775 - 2720
02.	C=C str	Alkenes	②	1675 - 1600
03.	C≏C str	Aromatics	③	1600 - 1450
04.	C≡C str	Alkynes	④	2260 - 2100
05.	C=O str	Aldehydes	⑤	1740 - 1720
06.	C=O "	Ketones	⑥	1725 - 1705
07.	C=O "	Carboxylic acids	⑦	1725 - 1700
08.	C=O "	Esters	⑧	1750 - 1730
09.	C=O "	Amide	⑨	1680 - 1630
10.	C=O "	Anhydride	⑩	1850 - 1800
				1790 - 1740
11.	C=O "	Acid chlorides	⑪	~ 1790
12.	O-H "	Alcohols & phenols (dilute solution)	⑫	3650 - 3580
13.	O-H "	(Alcohols & phenols (Hydrogen bonded)	⑬	3550 - 3200
14.	O-H "	Carboxylic acids	⑭	2700 - 2500
15.	N-H "	1° amines, amides	⑮	~ 3500
16.	N-H "	1° amines, amides (H bonded)	⑯	~ 3400
17.	N-H "	2° amines, amides free	⑰	3500 - 3300
18.	N-H "	2° amines, amides (H - bonded)	⑱	3310 - 3140
19.	C≡N "	Nitriles, Nitro groups	⑲	2260 - 2220
				Asy - 1620 - 1585
				Sym - 1375 - 1275

1.Which of the following diatomic molecule do not absorb in IR region?

Hcl   HBr N_2 o_2 H_2

- N_2, O_2 and H_2 these diatomic molecules do not have dipolemoment
- There is no change in dipolemoment
- Therefore N_2, O_2 and H_2 do not absorb in IR region.

2.Arrrange, the following lactones in order of thier decreasing carbonyl frequency and give reasons.
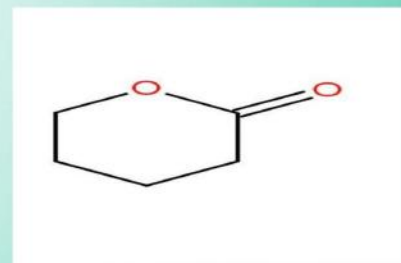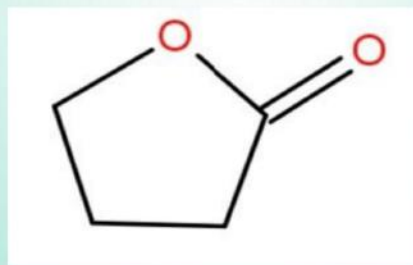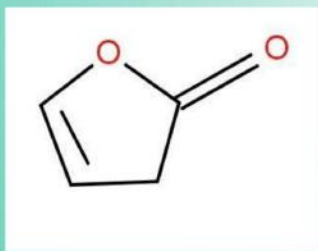
Decreasing order of CO stretching frequency I>II>III

- In structure I due to mesomeric effect , double bond adjacent to single bonded oxygen atom of lactone I raises the C=O stretching frequency. So 5 membered ring absorbs at higher frequency than 6 membered ring .

Structure II &III bond angle related.
- In structure(II) bond angle will be lower than structure(III).so bond angle is less and bond strain will be more bond strength is high Therfore stretching frequency is high for structure(II).
- InStructure(III)bond angle more compared to structure(II)bond strain is less bond strength is low and so stretching frequency is low.

3.CO stretching frequency of 2,4,6 cyclo hepta trienone is low why?
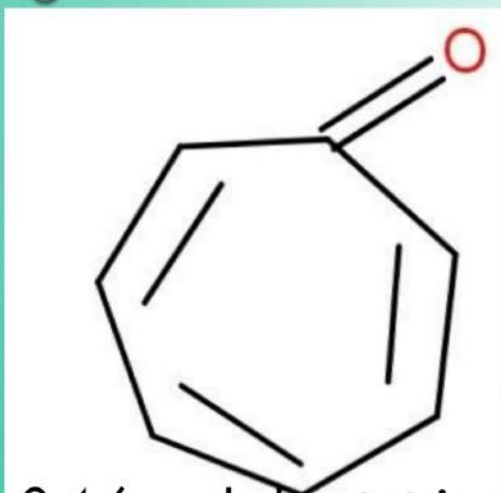
2,4,6-cyclo heptatrienone
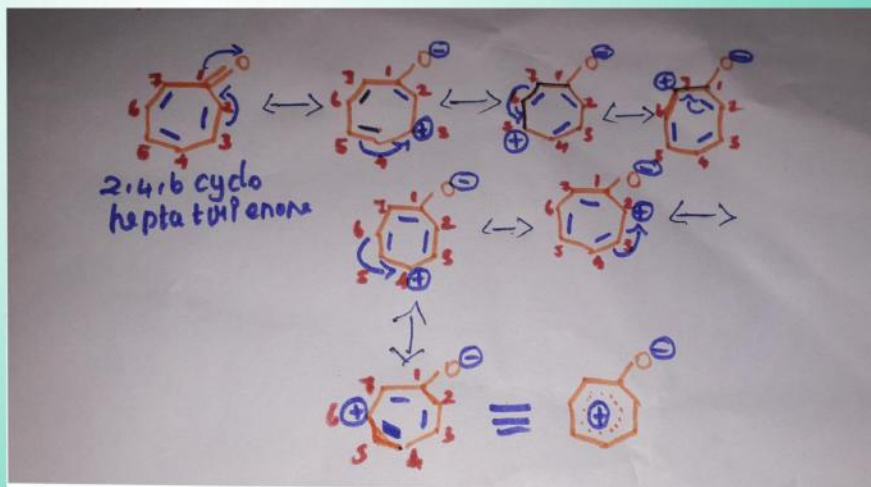
Due to 6 resonance structres C=O bond is weakened much and so low co stretching frequency.

4.Cis -1,2 dichloro ethylene is infrared active why?Trans 1,2 dichloro ethylene Ir inactive Explain.
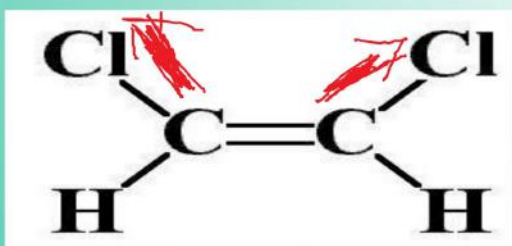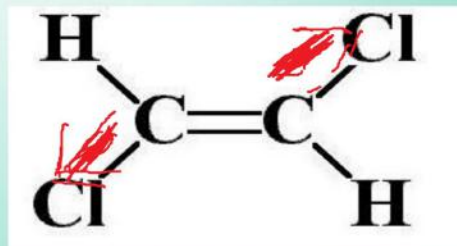
Cis -1,2-dichloro ethylene   trans-1,2-dichloro ethylene

Condition: There will be change in dipolemoment

- Dipolemoment is a vector quantity
- It is a directional properity
- In trans isomer two chlorine atoms are on opposite sides, dipolemoment values are cancelled.Therefore trans-1,2-Dichloroethylene **IR inactive .**
- In cis isomer two chlorine atoms are on the same side,so that vector quantity is cancelled and it will be added .There will be change in dipolemoment. Therefore cis 1,2-Dichloroethylene **IR active.**

Qn.no-1
Explain C=O stretching of the following compounds ?
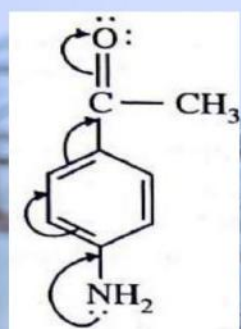
I
p-Amino
Acetophenone
ν C=O 1677 cm^{-1}
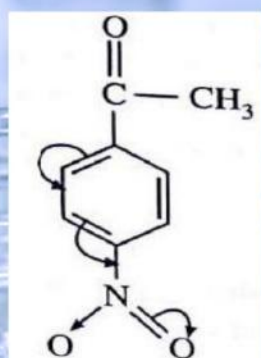
II
p-Nitro
Acetophenone
ν C=O 1700 cm^{-1}
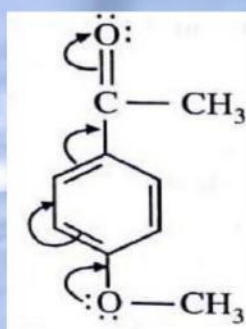
III
p-Methoxy
Acetophenone
ν C=O 1684 cm^{-1}
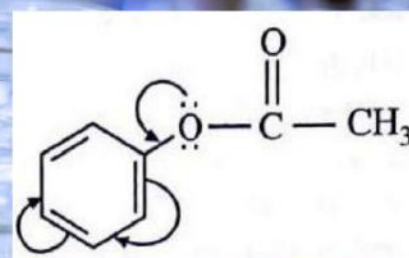
IV
Phenyl Acetate
ν C=O 1770 cm^{-1}

Explanation,

Electronic effect – Absorption frequency will change, according to substitution of neighborhood.so the frequency shifts due to electronic effect they are inductive effect, mesomeric effect and field effect.

The force constant and bond strength changes and its absorption frequency shifts from the normal value.

Let us compare the following compounds.,

☐The lone pair of electrons present in the conjugated double bond system.

☐The mobility of the lone pair of electrons matters.

☐In I & III compounds,As nitrogen atom is less electronegative than oxygen atom.

☐The nitrogen atom is more labile and its goes more conjugation, so frequency is less due to C=O is loosed and bond strength decrease.
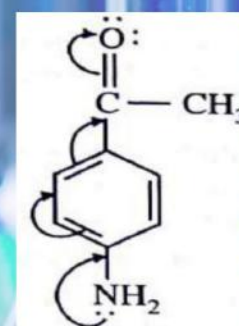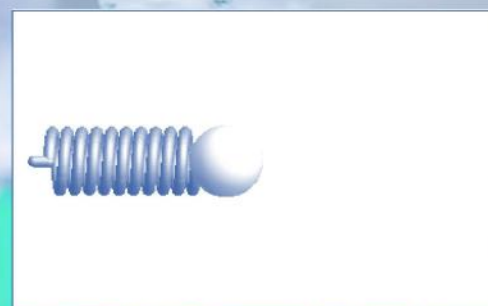
I
p-Amino
Acetophenone
v C=O 1677 cm^{-1}
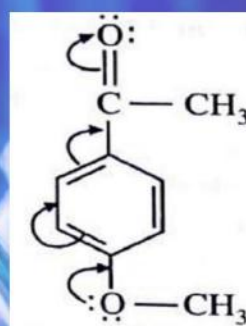
III
p-Methoxy
Acetophenone
v C=O 1684 cm^{-1}

❑Let us compare the compound II & IV, we should observed the inductive effect.

❑It is nothing but, there are two possibilities,

❑ +I effect – introduction of alkyl group (EDG) – bond lengthened so it is bond weakened.

❑Therefore force constant decreases and wavenumber also decreases.

❑ -I effect – introduction of electronegative group(EWG) – bond shortened so it becomes bond strengthened.

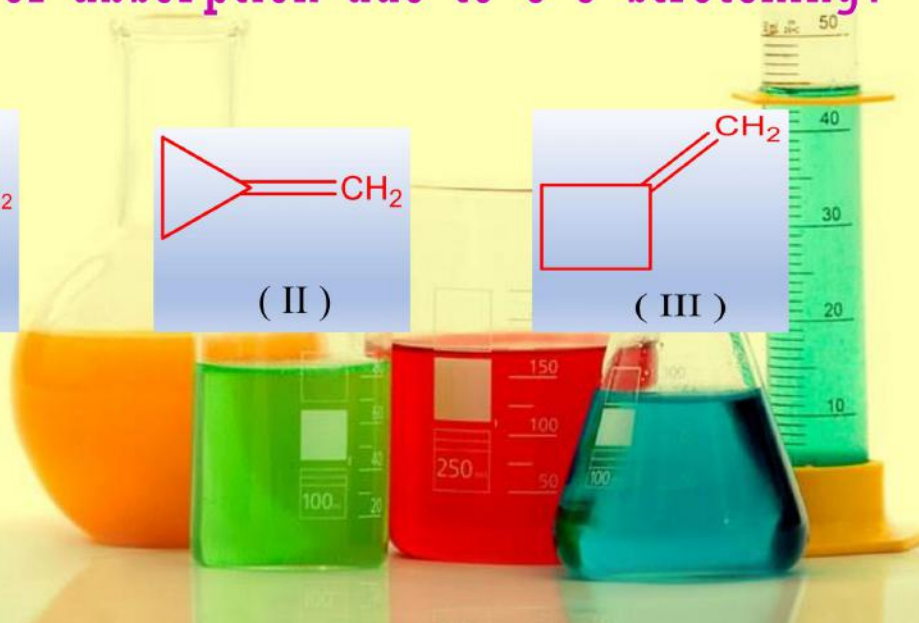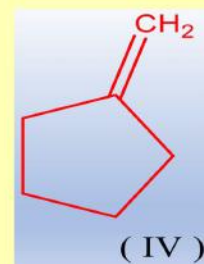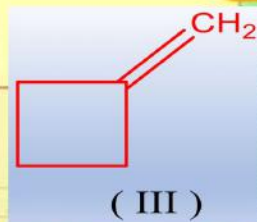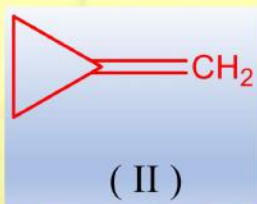❑Therefore force constant increases and wavenumber also increases.
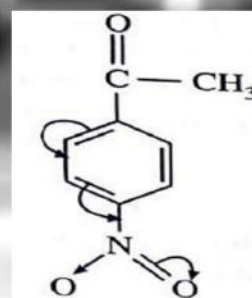
II
p-Nitro
Acetophenone
ν C=O 1700 cm⁻¹
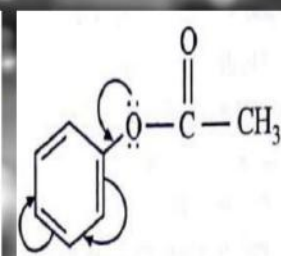
IV
Phenyl Acetate
ν C=O 1770 cm⁻¹

Qn.no-2

Arrange the following compounds in order of their increasing wavenumber of absorption due to C-C stretching?

(I)

(II)

(III)

(IV)
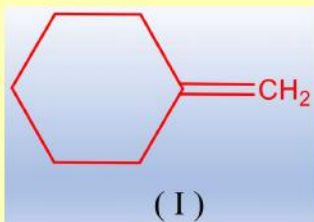
- The increasing order of wave number absorption is


(I) < (IV) < (III) < (II)

- The exocyclic **olefinic** double bond shows an increasing **C=C** stretching frequency as **the size** of the ring decreases.
- Thus with the **increases in ring strain, C=C** stretching requires more energy and wave number of absorption.
- If bond angle **less**, bond strain will be more.
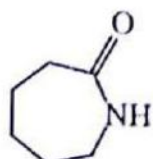
BOND ANGLE $\alpha \dfrac{1}{\text{FREQUENCY}}$

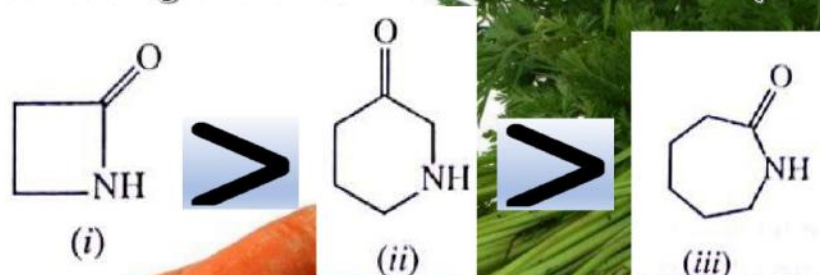**Arrange the following compounds in order of their decreasing wavenumber of absorption?**
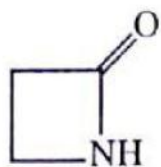
(i)
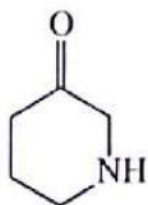
(ii)

(iii)

- The decreasing order of wave number absorption is

- In cyclic amides, if ring strain increased, the C=O stretching frequency also increased.
- We know that smaller rings have more strain than that of bigger ring, with the decrease in ring size, the fore constant of C=O bond increase and hence the absorption position is raised.

FORCE CONSTANT α BOND STRENGTH

Calculate the vibrational degree of freedom following molecules ?

O_2

N_2O

CH_2O

C_6H_6

$CHCl_3$

CH_4

Solution,

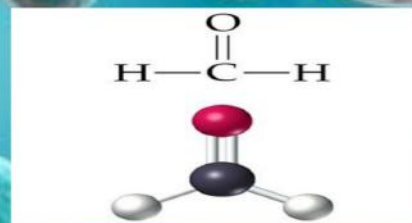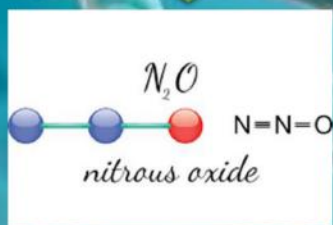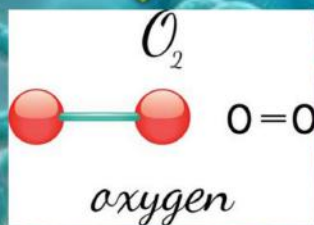**Vibrational degree of freedom for linear molecule = 3N - 5**
Vibrational degree of freedom for non-linear molecule = 3N - 6
Here, N = total no.of atoms in a molecule

Non-Linear
3N – 6
3(3) – 6 = 3

Linear
3N – 5
3(2) – 5 = 1

Non-Linear
3N – 6
3(3) – 6 = 3

O_2
O = O
oxygen

N_2O
N = N = O
nitrous oxide

CH_4
methane

Non-Linear
$3N - 6$
$3(5) - 6 = 9$

C_6H_6
benzene

Non-Linear
$3N - 6$
$3(12) - 6 = 30$

Chloroform

Cl
H
Cl   Cl

$CHCl_3$
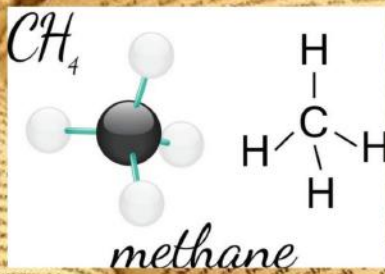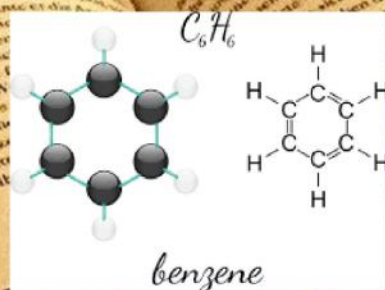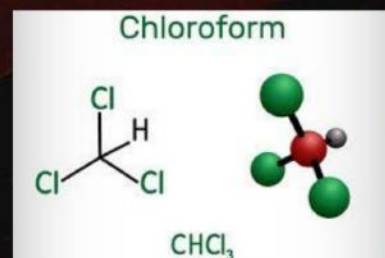
Non-Linear
$3N - 6$
$3(5) - 6 = 9$

PERIYAR ARTS COLLEGE, CUDDALORE-1

P.G. DEPARTMENT OF CHEMISTRY

II M.Sc., CHEMISTRY

ORGANIC CHEMISTRY-III

INTERNAL TEST-I   Date:- 17.08.2020.

Part-A

Answer all questions:- 6x5 = 30 marks.

1. Explain auxochromes and chromophores with examples.

2. Explain various types of electronic transitions of UV-visible spectra.

3. (a) what is Far IR region? Explain it. ③
   (b) List any 3 functional group and give its IR absorption range ③.

4. Explain the importance of finger print region in IR spectra.

5. Differentiate inter and intramolecular hydrogen bonding by IR spectra.

Part-B   2x10 = 20 marks.

6. Explain the factors influencing the position and intensity of absorption bands.

7. Explain the various factors that influence carbonyl stretching frequency.

All the best.