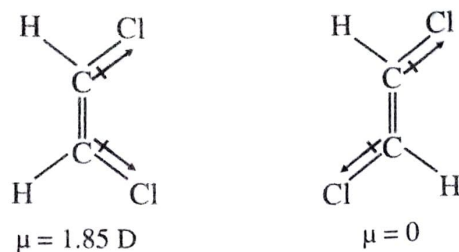change in the dipole moment. This technique clearly makes a distinction between cis and trans isomers. Consider 1, 2-dichloro ethene. Its geometrical isomers are :

$$\mu = 1.85 \text{ D} \qquad\qquad\qquad \mu = 0$$

For most of the vibrations, the change in the dipole-moment occurs in the cis isomer. On the other hand, trans isomer is non-polar with dipole moment equal to zero.

Accordingly the $C = C$ str absorption peak at 1580 cm^{-1} is not observed in case of trans-isomer since the vibration in it does not produce any change in the dipole moment. On the other hand, this peak (1580 cm^{-1}) appears due to $C = C$ str in cis isomer.

In the same way, it is observed that in methyl acetylene ($CH_3C \equiv CH$), the vibration due to $C \equiv C$ str is infra-red active whereas in dimethyl acetylene ($CH_3C \equiv C—CH_3$), the vibration is infra-red inactive.

11. Rotational Isomerism : Infra-red spectroscopy helps in the detection of Gauche (skew) and staggered conformations. The two conformations of 1, 2-dichloro ethane can be shown below :
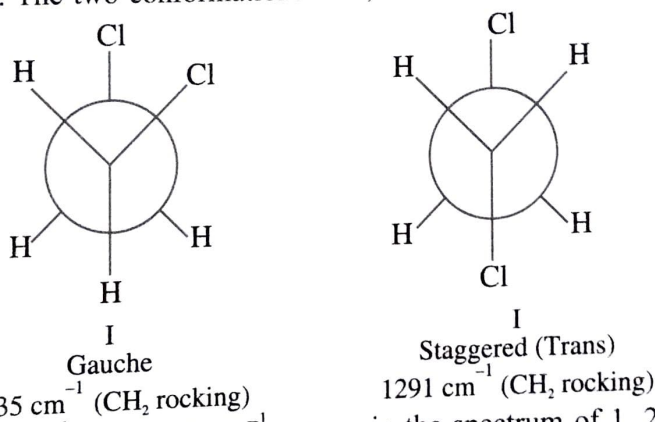
Two bands at 1291 cm^{-1} and 1235 cm^{-1} appear in the spectrum of 1, 2-dichloroethane. The staggered (trans) form predominates at lower temperature whereas gauche form dominates at higher temperature. The relative intensities of the bands depend upon temperature. The rocking vibration band at 1291 cm^{-1} becomes less intense as the temperature is raised. From the relative intensities of the bands, their relative abundance at a particular temperature can be estimated.

12. Detection of Impurity in a compound. Infra-red spectroscopy is also useful in the detection of impurity in a compound by comparing its spectrum with the spectrum of the authentic sample of the compound. Moreover, a pure sample always consists of sharp peaks and bands while impure sample will consist of poor bands and also some additional bands.

3.14 Simple Problems on infra-red Spectroscopy

1. *An organic compound with molecular mass C_8H_{18} shows the following characteristic absorption bonds :*
   (i) 2925 cm^{-1} (st),   (ii) 1465 cm^{-1},   (iii) 1380 cm^{-1} and   (iv) 720 cm^{-1}.
   Determine the structure of the compound.

   Ans. From the positions of the absorption bands, it is clear that the compound is a saturated hydrocarbon. A band at 2925 cm^{-1} shows C—H stretching whereas that at 1465 cm^{-1} is due to C—H bending for methyl and methylene. Absorption position of 1380 cm^{-1} is due to

C—H bending for methyl. Absorption at 720 cm^{-1} due to rocking motion for methylene. Hence the organic compound is n-octane (CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3).

2. *An organic liquid with molecular formula C_7H_8 burns with a sooty flame. It shows the following absorption bands in its Infra-red spectrum : (i) 3060 cm^{-1} (ii) 3040 cm^{-1} (iii) 2918, 2870 cm^{-1} (iv) 1500, 1450 cm^{-1} (v) 750 cm^{-1}. Deduce the structure of the compound.*

Ans. Since the compound burns with a sooty flame, it appears to be aromatic. The absorption at 3060 cm^{-1} is due to C—H str aromatic. Also a band at 3040 cm^{-1} is due to C—H stretching (aromatic). Two absorption positions due to C—H str for methyl group appear at 2918 cm^{-1} and at 2870 cm^{-1}. The aromatic ring is further confirmed as two absorption bands appear at 1500 cm^{-1} and 1450 cm^{-1} due to C==C stretching. The aromatic compound is mono substituted due to the appearance of a band at 750 cm^{-1}. Hence, the probable organic aromatic compound is toluene.

3. *The analytical data and the molecular mass determination gave C_8H_8O as the molecular formula of the compound. The compound burns with a sooty flame and gave an oxime with hydroxylamine hydrochloride. Following absorption bands appear in its Infra-red spectrum : (i) 2825 cm^{-1}, (ii) 2717 cm^{-1}, (iii) 3060 cm^{-1} and (iv) 1700 cm^{-1} (s) and 830 cm^{-1}. Deduce the structure of the compound.*

Ans. The organic compound is aromatic as it burns with a Sooty Flame. It also contains an aldehydic group as it forms an oxime with hydroxyl-amine hydrochloride.

Two bands at 2825 cm^{-1} and 2717 cm^{-1} are due to C—H str which are most characteristic of an aldehydic group. A band at 3060 cm^{-1} is due to C—H stretching in aromatic compounds. Benzene ring in it must be disubstituted as an absorption peak is formed at 830 cm^{-1}. Thus, C_6H_4— and CHO are the parts of the molecule. Clearly, CH_3 is left. Thus, the organic compound under investigation is p-Tolualdehyde (CH_3—⬡—CHO).

4. *An organic compound dissolves in sodium hydroxide to form a yellow coloured solution. It gives brisk effervescence with sodium bicarbonate solution. Its infra-red spectrum exhibits the following absorption bands : (i) 3060-3110 cm^{-1}, (ii) 3000-2520 cm^{-1} (b), (iii) 1602, 1510, 1450 cm^{-1} and (iv) 1620, 1375 cm^{-1} (s) and 830 cm^{-1}.*

Ans. Organic compound which dissolves in sodium hydroxide producing yellow coloured solution should contain —NO_2 group in it. The efferrescence with sodium bicarbonate shows that it contains a —COOH group in it. The presence of —COOH group is further confirmed from a broad band at 3000-2500 cm^{-1}. The absorption bands at 1602, 1510 and 1450 cm^{-1} are most characteristic of C==C stretching in aromatics. The presence of nitro group is revealed from the two bands at 1620 and 1375 cm^{-1}. The absorption position at 830 cm^{-1} shows that the compound is disubstituted. Hence, the most likely structure of the compound is p-Nitrobenzoic acid. (O_2N—⬡—COOH)
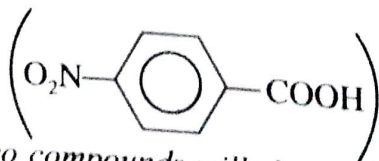
5. *Which of the following two compounds will show a higher wave number ? Give suitable reason for your answer.*
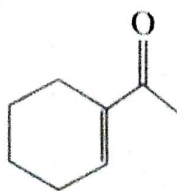
and
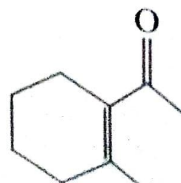
Ans. Compound (*ii*) will absorb (due to v C = O str) at a sightly higher wave number as compared to compound (*i*). It is due to steric hindrance. The effect occurs when the carbonyl group is forced slightly out of the plane of the double bond and due to this *p*-orbital overlap is reduced.

6. *Arrange the following compounds in order of their increasing wave number of absorption due to C=C stretching*

| (i) | (ii) | (iii) | (iv) |
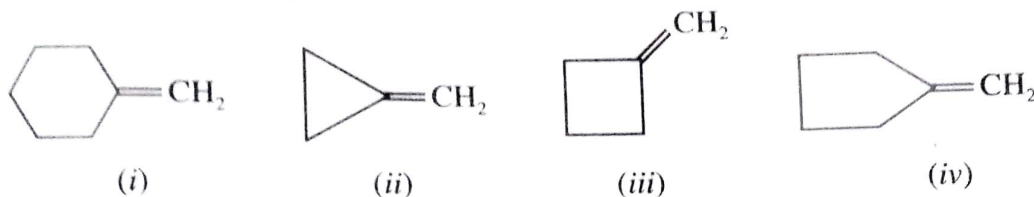
Assign reason for your answer.

Ans. The exocyclic olefinic double bonds show an increase in C=C stretching frequency as the size of the ring decreases. Thus, with the increase in ring strain, C=C str requires more energy and wave number of absorption is raised. The wave number of absorption has the order :

$$(i) \; < \; (iv) \; < \; (iii) \; < \; (ii)$$

7. *An organic compound with molecular formula C_8H_6 decolourises bromine in carbon tetrachloride and gives a white precipitate with ammonical silver nitrate solution. Give the probable structure of the compound. Its infra-red spectrum gives a band at 2150-2200 cm^{-1} and the region near 3300 cm^{-1} is transparent.*

Ans. The compound appears to be unsaturated as it decolourises bromine in carbon tetra chloride. It cannot be ethylenic as it gives, white precipitate with ammonical silver nitrate solution. The presence of $C \equiv C$ is further confirmed due to an absorption band at 2150-2200 cm^{-1}. Hence, the compound can be $C_6H_5—C \equiv CH$.

8. *How will you distinguish between :* (i) $p—CH_3CO—C_6H_4—OCH_3$ *and*
(ii) $CH_3CO—C_6H_4—NO_2$?

Ans. Methoxy group in the para position causes +M effect in *p*-methoxy acetophenone. Due to this, the force constant of C = O bond is decreased which results in the lowering of wave number of absorption. On the other hand, the $—NO_2$ group causes $—M$ effect and raises the bond order of C = O bond resulting in the absorption at higher wave number.

9. *Arrange the following compounds (Lactams) in order of their decreasing wave number of absorption :*


| (i) | (ii) | (iii) |
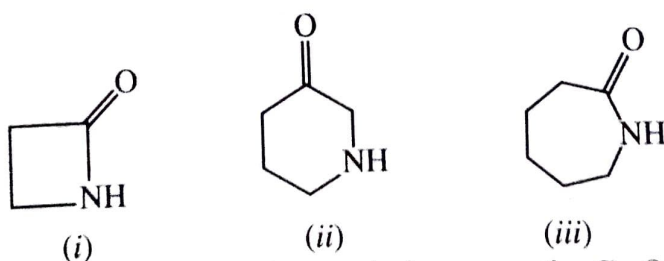
Ans. In cyclic amides or Lactams, the ring strain increases the C=O stretching frequency. We know that the smaller rings are more strained than the bigger rings. With the decrease in ring size, the force constant of C=O bond increases and hence the absorption position is raised. Hence, the decreasing order is :

(*i*) > (*ii*) > (*iii*)

10. *An aromatic organic compound decolourises bromine in carbon tetra-chloride and exhibits the following absorption position.*
(i) 3090 cm^{-1} (ii) 3040 and 3000 cm^{-1} (iii) 2820 and 2750 cm^{-1} (iv) 1685 cm^{-1}(s)
(v) 1630 cm^{-1} (vi) 1580 and 1450 cm^{-1} (vii) 750 cm^{-1}.

Ans. Absorption bands at 1580 and 1450 cm^{-1} confirms the presence of aromatic ring. A peak at 750 cm^{-1} shows that the ring is monosubstituted. A strong band at 1685 cm^{-1} shows the presence of carbonyl group. The carbonyl group is aldehydic as two characteristic peaks appear at 2820 cm^{-1}. Further the compound certains C=C due to the presence of a band at 1630 cm^{-1}. (also confirmed by the decolourisation of bromine) Thus, the structural units in the compound under investigation are : C_6H_5, C=C, CHO. Hence, the probable structure of the compound is :

$C_6H_5CH=CH-CHO$ or   ⬡—CH=CH—CHO. (Cinnamaldehyde)
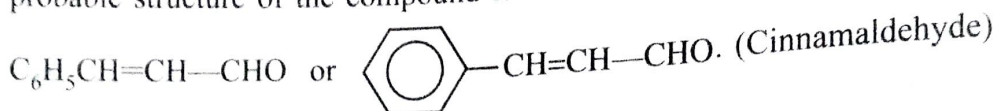
3.15 Short Questions with Answers

1. What is the range of infra-red radiations ?

Ans. The range of infra-red radiations is 2.5 μ–15 μ *i.e.,* 4000 cm^{-1} to 667 cm^{-1}.

2. What happens when a substance is irradiated with infrared radiations ?

Ans. When a substance is exposed to infra-red radiations, the various bonds in a molecule stretch and bend with respect to one another. The absorption of radiations between 1500 cm^{-1}-4000 cm^{-1} cause the bonds to stretch and the bands formed due to these absorptions are most characteristic of different functional groups. The absorption of radiations below 1500 cm^{-1} cause bending of bonds.

3. Can you distinguish a pair of enantiomers by infra-red spectroscopy ?

Ans. No. The enantiomers of an optically active substance cannot be distinguished by this technique.

4. Name the various types of bending vibrations.

Ans. These are Scissoring, Rocking, Wagging and twisting. For such vibrations, energy required is below 1500 cm^{-1}.

5. What is Hooke's law ?

Ans. Hooke's law helps to calculate approximately the value of stretching vibrational frequency of a bond. According to this law,

$$\bar{v} \text{ (wave no.)} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass.

$$\mu = \sqrt{\frac{m_1 m_2}{m_1 + m_2}}$$

6. Compared to the number of bonds in a molecule, there are generally more number of peaks in the infra-red spectrum. Explain.

Ans. In addition to the number of peaks / bands characteristic of different bonds in a molecule, the other peaks may be due to overtones, combination bands, difference bands etc. For example, if x cm^{-1} and y cm^{-1} are the frequencies of fundamental bands, then peaks of low intensity also appear at $2x, 2y, (x + y), (x − y)$ cm^{-1} etc.

7. How inductive effect brings about a change in the position of absorption for a particular bond ?

Ans. The presence of electron releasing groups. (+I effect) such as alkyl groups brings about a downward shift in wave number of absorption. For example, Acetaldehyde (CH_3CHO) gives C = O str band at 1745 cm^{-1} whereas acetone (CH_3COCH_3) due to additional methyl group absorbs at 1715 cm^{-1} due to C = O str. Similarly, the presence of —I groups

(F, Cl, NO, etc) raise the wave number of absorption from the normal value. For example, C—O str for acetone is at 1715 cm^{-1} whereas those for chloroacetone and dichloroacetone are at 1725 cm^{-1} and 1740 cm^{-1} respectively.

8. How hydrogen bonding change the position of absorption in the Infra-red spectroscopy ?

Ans. Hydrogen bonding brings about a remarkable downward shift in the wave number of absorption. For example, alcohol in the vapour state (Isolated molecule) shows O—H str at about 3600 cm^{-1} whereas that in the associated form gives a broad absorption band at 3200 cm^{-1}. Stronger the hydrogen bonding, more broadening of the band occurs at much lower wave number.

9. Can you distinguish the type of hydrogen bonding by Infra-red spectroscopy ?

Ans. Yes. It can be easily done by taking the infra-red spectra of the given compound at two different concentrations. If there is a shift in the absorption position of a particular peak or band, then the type of hydrogen bonding in the substance is intermolecular otherwise it is intra molecular. Intra-molecular hydrogen bonding in a substance does not depend upon the concentration of the solution.

10. Discuss the positions of absorption of a particular band in a substance in all the three states.

Ans. In the vapour state, the absorption band for stretching of a particular bond occurs at the highest wave number compared to that when the substance is in the liquid state which in turn occurs at higher wave number than when the same substance is in the solid state.

11. Linear molecules have (3n-5) vibrational degrees of freedom whereas non-linear molecules have (3n-6) vibrational degrees of freedom. Explain.

Ans. In non-linear molecules, three degrees of freedom describe rotation and another three describe translational. The remaining (3n-6) are the vibrational degrees of freedom. But in linear molecules, there are only two degrees of rotation.

12. Infra-red spectroscopy is the best technique to establish the identity of organic compounds. Explain.

Ans. In this technique, when a substance is exposed to infra-red radiations, almost all types of bonds in a molecule show absorption bands at characteristic wave numbers. Most characteristic stretching absorption bands appear above 1500 cm^{-1}.

13. Some of the fundamental vibrations are infra-red active while others are not. Explain.

Ans. Infra-red light is absorbed only when a molecule of the substance under examination undergoes a net change of dipole-moment. Total symmetry about a bond eliminates certain bonds and thus the number of bands which appear does not agree with the number of fundamental vibrations. Clearly, some of the fundamental vibrations in infra-red are active and some are inactive.

14. What happens to O-H str position when 10 ml of carbon tetrachloride is added to 2 ml of ethyl alcohol ?

Ans. Ethyl alcohol exhibits intermolecular hydrogen bonding and due to this, absorption band occurs at 3200 cm^{-1}. When carbon tetrachloride is added it, there is decrease in hydrogen bonding and thus, the absorption position is raised.

15. What do you mean by Finger print region ?

Ans. The region below 1500 cm^{-1} is rich in many absorptions which are caused by bending vibrations. In the spectrum, the number of bending vibrations is usually more than the number of stretching vibrations. This region is called Finger print region. Some substances containing the same functional group show similar absorption above 1500 cm^{-1} but their

absorption positions differ in the finger print region. Such compounds can be easily distinguished by comparing their finger print regions.

16. **In acetylene, —C ≡ C—H str appears at about 3300 cm⁻¹. How will you distinguish it from an O—H str in alcohol ?**

Ans. In alcohols, the O—H str absorption band appears between 3200-3600 cm⁻¹. ≡ C—H str at 3300 cm⁻¹ can be easily distinguished because O—H str band at this position will be broader and will change with change in concentration of solution. ≡ C—H str position will be a sharp peak and is concentration independent.

17. **How will you show that the compound under investigation is not aromatic ? Use Infra-red technique.**

Ans. The absence of bands due to C=C str at 1600 cm⁻¹, 1500 cm⁻¹ and 1450 cm⁻¹ shows that the given compound is not aromatic.

18. **How will you distinguish between CH_3CH_2CHO and CH_3COCH_3 ?**

Ans. For propanal, in addition to vC = O str at 1720 cm⁻¹, there will be a peak at C—H str at ~2720 cm⁻¹. The peak at ~2720 cm⁻¹ is most characteristic of an aldehyde and it will be missing in case of an aldehyde.

19. **The C—H str vibration in chloroform occurs at 3000 cm⁻¹. Calculate the C—D str frequency in deutero chloroform.**

Ans. The wave number for fundamental vibration can be calculated by using the expression:

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

For C—H str and C—D str; k is supposed to be the same. The ratio of their reduced masses (μ) can be calculated as under :

(i) For C—H ;
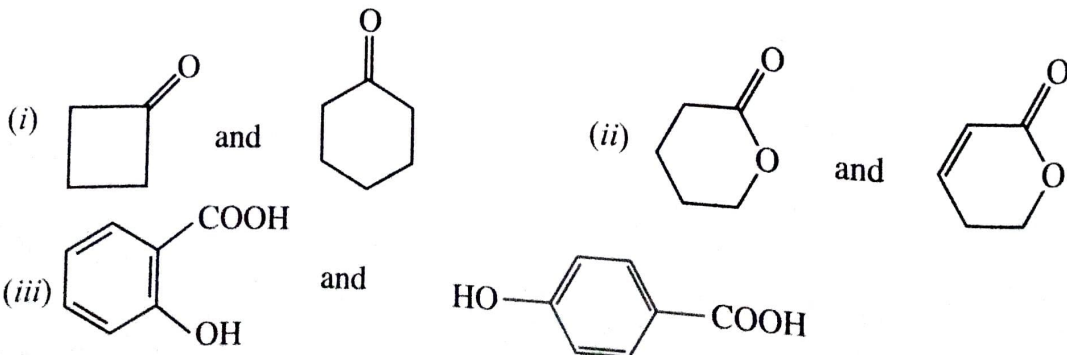$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 1}{12+1} = \frac{12}{13} = 0.92$$

(ii) For C—D ;
$$\mu = \frac{12 \times 2}{12+2} = \frac{24}{14} = 1.71$$

For calculating the wave number of absorption (C—D), we write

$$\frac{\bar{V}_D}{\bar{V}_H} = \sqrt{\frac{\mu_H}{\mu_D}} = \sqrt{\frac{0.92}{1.71}} = 0.73$$

Thus, the C—D str absorption band will appear at 3000 × 0.73 = **2190 cm⁻¹**.

20. **How will you distinguish between the following pairs on the basis of Infra-red spectroscopy ?**

Ans. (i) In cyclic ketones, vC = O str absorption increases as the size of the ring decreases (ring strain increases). Thus, cyclobutanone shows carbonyl absorption at higher

wave number (nearly 1788 cm^{-1}) whereas cyclohexanone absorbs at almost the same wavenumber at which saturated ketones absorb.

(*ii*) The $vC = O$ absorption in case of conjugated cyclic ketone absorbs at lower wave number as compared to the other. The absorption bands are sharp in both the cases.

(*iii*) In *o*-Hydroxy benzoic acid (salicyclic acid), we see intramolecular hydrogen bonding. The absorption band due to O—H str appears as a broad bond at nearly 3300 cm^{-1} and is concentration independent. But in *p*-hydroxybenzoic acid, the association is due to intermolecular hydrogen bonding. Absorption occurs at about 3000 cm^{-1} as a broad band. The position of absorption is raised as the solution is diluted by adding a non-aqueous solvent such as carbon tetrachloride.

21. **Which of the following diatomic molecules do not absorb in the Infra-red region.**

$$HCl, ClBr, N_2, H_2, O_2$$
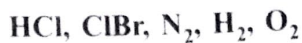
Ans. N_2, H_2 and O_2 are homodiatomic molecules. Their molecular vibrations are not accompanied by any change in dipole moment and hence they do not absorb in IR region.

22. **Why is methanol a good solvent for UV but not for IR spectroscopy ?**

Ans. The reason is that methanol (CH_3OH) does not absorb in UV, *i.e.* it is transparent above 200 *m*μ. But is absorbs strongly in the infra-red region (4000 cm^{-1} to 667 cm^{-1}).

23. **What is the effect of hybridisation of carbon on the stretching frequency of C—H bonds ?**

Ans. With the increase in s-character of hybridised carbon, the force constant (k) for C—H bond increases and hence the value of stretching frequency increases.

$$\overset{sp^3}{C}\text{—H str} \qquad \overset{sp^2}{=C}\text{—H str} \qquad \overset{sp}{\equiv C}\text{—H}$$
$$(2950–2850 \text{ cm}^{-1}) \qquad (3000–3100 \text{ cm}^{-1}) \qquad (3300 \text{ cm}^{-1})$$
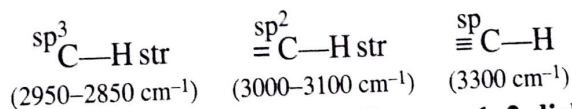
24. ***cis*-1, 2-dichloroethene is Infra-red active while trans-1, 2-dichloroethene is IR inactive. Explain.**

Ans. When the compound under examination is exposed to IR radiations, *cis*-1, 2-dichloroethene undergoes a net change in dipolemoment and hence absorbs in IR. Thus, it is IR active. On the other hand, trans-1, 2-dichloroethene is symmetrical and does not show any change in dipole-moment. Hence, it is IR inactive.

25. **How will you note the progress of the oxidation of 2-Propanol to Propanone in Infra-red spectroscopy ?**

Ans. 2-Propanol shows a strong band at 3400-3200 cm^{-1} due to O—H str. On the other hand, propanone shows a strong band at 1715 cm^{-1} due to C = O str. As oxidation of 2-propanol takes place, the intensity of O—H band decreases while that of C = O str increases. On complete oxidation, the band at 3400 cm^{-1}-3200 cm^{-1} will be missing and an intense band at 1715 cm^{-1} will appear.

26. **How will you distinguish between *cis* and *trans*-cinnamic acid ?**

Ans. *cis*-Cinnamic acid absorbs at a higher wave number as compared to its trans-isomer. It is partially explained due to the steric effect caused by the bulky groups on the same side of the double bond. Due to repulsive interactions, the C = O part of —COOH group goes out of the plane of the double bond. Thus, conjugation diminishes and hence $vC = O$ absorption occurs at a higher wave number.

27. **Can you detect an anhydride by Infra-red spectroscopy ?**

Ans. Yes. An anhydride can be detected by the formation of two bands which appear at :
(*i*) 1850-1800 cm^{-1} and (*ii*) 1790-1740 cm^{-1}. The presence of unsaturation causes lowering in absorption positions by 20-40 cm^{-1}.

28. **How will you distinguish between CH_3CONH_2 and $CH_3CH_2NH_2$?**

Ans. In case of a acetamide, a strong absorption band appears near 1600 cm^{-1} which is missing in ethylamine.

29. **Infra-red absorption due to carbonyl stretching occurs at higher frequencies than stretching of $C = C$ bond. Explain.**

Ans. This is explained in terms of π-bond of the $C = O$ bond, which is considerably stronger than the π-bond in $C = C$ bond.

30. **An acyl group is readily detected from the infra-red spectroscopy since the $C = O$ stretching frequency varies with the functional group, i.e. with G. From the following trends in the strong carbonyl stretching absorption peak in the 1700 cm^{-1} region identify a particular acid derivative in each case :**

$$\overset{\displaystyle O}{\underset{\displaystyle R\!-\!C\!-\!G}{\|}}$$
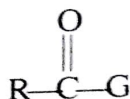
(i) $1700\text{-}1815 \text{ cm}^{-1}$,

(ii) $1740\text{-}1790 \text{ cm}^{-1}$ and $1800\text{-}1850 \text{ cm}^{-1}$ (two bands),

(iii) $1720\text{-}1750 \text{ cm}^{-1}$ and (iv) $1630\text{-}1690 \text{ cm}^{-1}$

Ans. (i) Must be acid chloride

(ii) The two absorption bands at the given positions show that the compound is an anhydride.

(iii) The absorption position at $1720\text{-}1750 \text{ cm}^{-1}$ shows that the compound is an ester

(iv) The absorption position at a much lower wave number is clearly due to $C = O$ str in an amide. The lowering is due to the fact that the lone pair on N-atom is in conjugation with the carbonyl group.
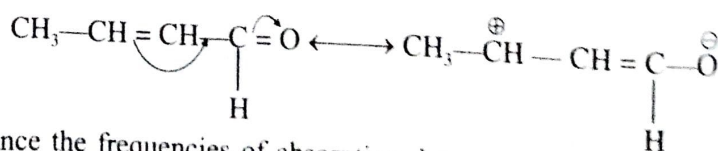
31. **The C—H frequency of is a compound observed at 2910 cm^{-1}. Predict the corresponding C—D stretching frequency whose hydrogen is replaced by deuterium.**

Ans. $\nu C\!-\!H = \sqrt{2} \cdot \nu C\!-\!D$

$$\therefore \quad \nu C\!-\!D = \frac{\nu C - H}{\sqrt{2}} = \frac{2910}{1.414} = 2058 \text{ cm}^{-1}.$$

32. **An aliphatic aldehyde containing unconjugated double bond shows $C = C$ and $C = O$ stretching at ~1645 cm^{-1} and $1720\text{-}1740 \text{ cm}^{-1}$ respectively. Explain why crotonaldehyde shows the corresponding absorptions at 1700 cm^{-1} and 1630 cm^{-1}**

Ans. In crotonaldehyde, C=C is in conjugation with C=O and can be written in the resonance structure as below :

$$CH_3\!-\!CH = CH\!-\!\underset{\underset{\displaystyle H}{|}}{C} = O \longleftrightarrow CH_3\!-\!\overset{\oplus}{CH} - CH = \underset{\underset{\displaystyle H}{|}}{C}\!-\!\overset{\ominus}{O}$$

Due to resonance the frequencies of absorption due to $C = O$ str as well as $C = C$ str get lowered.

33. **What do you mean by Fundamental vibrations and overtones ?**

Ans. The fundamental vibrations correspond (in quantum treatment) to the transition from the zeroth vibrational level i.e $v_0 \to v_1$. The term overtone is used for any multiple of the given fundamental frequency. Thus, the transition from $v_0 \to v_2$ and $v_0 \to v_3$ are the first and the second overtones of the fundamental.

34. How will you explain that the carbonyl stretching frequency of an aldehyde is slightly higher than that of the corresponding methyl ketone ?

Ans. In case of methyl ketone (CH_3—CO—), the electron donating group is methyl which leads to more single bond character in carbonyl and hence $\nu C = O$ stretching is lowered.

35. The carbonyl stretching frequency in 2, 4, 6-cycloheptatrienone is exceptionaly low. Explain.

Ans. The exceptional low value of $\nu C = O$ str in 2, 4, 6-cycloheptatrienone is due to the conjugation effect. The cyclohepta trienyl cation (II) which is tropylium cation
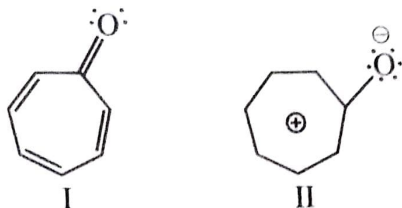
contains 6 π electron cloud and its structure is stable. As a result of strong resonance contribution, the $\nu C = O$ str frequency is quite low.

36. Saturated aliphatic monocarboxylic acid, show carbonyl stretching near 1755 cm^{-1} whereas the saturated aliphatic ketones absorb near 1720 cm^{-1}. Explain.

Ans. In monocarboxylic acid, the carbonyl group is bound to oxygen atom. Now two opposing effect strongly influence the carbonyl frequency. These effects are inductive effect and mesomeric effect. Out of these, inductive effect dominates and thus absorption frequency in case of carboxylic acid is more.

3.16 Important Tips for Interpreting an Infra-red Spectrum

Following are some useful tips for interpreting an infra-red spectrum.

(i) Always place more reliance upon the negative evidence. The absence of a band in a particular region is a sure indication of the absence of group/groups absorbing in that region. For example if there is no absorption in the region 1900–1600 cm^{-1}, the carbonyl group $\left(>C=O \right)$ must be absent in the compound.

(ii) Always start from the higher frequency end of the spectrum. Mostly stretching vibrations occur in the region above 1500 cm^{-1} and are most informative. The region 1500–1000 cm^{-1} may be used for confirming esters, alcohols, ethers etc.

(iii) To distinguish between intermolecular and intramolecular hydrogen bonding, the spectra of the sample are scanned at two different concentrations. Various solvents may be used to study association effects.

(iv) For easy detection of the various groups present in the compound, the infra-red region (4000 to 667 cm^{-1}) may be visualised as consisting of the following portions:

Table T$_3$—15. Characteristic absorption frequencies of functional groups

Type of Vibration	Class of Compound	Frequency (cm^{-1})	Intensity
C – H Str	(i) Alkanes	2960-2850	(s)
C – H Str	(ii) Alkenes	3100-3010	(s)
C – H Str	(iii) Alkynes	~ 3300	(s)
C – H Str	(iv) Aromatics	3150-3020	(s)
C – H Str	(v) Aldehydes	~ 2820,	(w)
		2775-2720	(w)

Sample Problems

Q. 1.   What happens when a molecule absorbs infrared radiation?

Sol.   Absorption of infrared radiation by a molecule induces transition between vibrational and rotational energy levels resulting in the formation of infrared spectrum. Thus, the infrared spectrum of a molecule results from transitions between vibrational and rotational energy levels and is called vibrational-rotational spectrum of the molecule.

Q. 2.   When does a molecule absorb infrared light?

Sol.   Infrared light is absorbed when oscillating dipole moment (due to molecular vibration) interacts with the oscillating electric vector of the infrared beam. These vibrations absorb infrared radiation at certain quantized frequencies and give rise to characteristic bands. When infrared light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased

Q. 3.   What is the basis of the classical theory of vibrational interactions?

Sol.   Interactions between the classical components of the electromagnetic radiation and electrical dipolar motions within the molecules are the basis of classical theory of vibrational interactions.

Q. 4.   What is an infrared spectrum? Explain briefly the normal infrared region.

Sol.   Infrared spectrum of a compound represents its energy absorption pattern in the infrared region and is obtained by plotting percent absorbance/transmittance of infrared radiation as a function of wave length/wave number over a particular range.

Normal infrared region

The normal infrared region (also called middle infrared region) extends from 4000 cm^{-1} to 667 cm^{-1} and results from vibrational plus rotational transitions. This region is particularly meant for organic chemists since the vibrations induced in organic molecules are absorbed in this region.

Q .5.   Give the wavelength, frequency and energy ranges pertaining to the normal infrared region of the spectrum.

Sol.   The range of the wavelength in the normal infrared region is from 2.5 to 16 μm (1 μm = 10^{-6} m) whereas the frequency range in wave number is from 4000 to 667 cm^{-1}. This corresponds to energy changes in the range from 2 to 10 kcal/mol.

Q. 6.   The stretching of a C–H bond in an alkane leads to absorption at ~ 2900 cm^{-1} in the infrared spectrum. What wavelength does this corresponds to? What is the energy change involved.

Sol. $\lambda = 1/v = 1/2900\ cm^{-1} = 3.45 \times 10^{-4}\ cm^{-1} = 3.45\ \mu m;\ E = hv = 8.3$ k cal/mol.

Q. 7.   Give the relationship for the conversion of wavelength to wave number.

Sol.   The wavelength in microns (μ) can be converted into wave number (cm^{-1}) by using the following relation. Wave number (cm^{-1}) = $1/\mu \times 10^4$.

Q. 8.   Explain why frequencies are generally expressed in terms of wave numbers by organic chemists?

Sol.   Frequencies are usually expressed in terms of wave numbers (cm^{-1}) by organic chemists, since the wave number is proportional to the frequency and, therefore, to the energy while the wavelength is inversely proportional to the energy.

$$E = hv$$

Q. 9.   Describe fundamental vibrations and overtones.

Sol.   The fundamental vibrations correspond in the quantum treatment to the first vibrational transition from the zeroth vibrational level to the first, v_0 to v_1.

The term overtone is used to apply to any multiple of a given fundamental frequency. The transition from $v_0 \rightarrow v_2$ and $v_0 \rightarrow v_3$ are the first and second overtones of the fundamental and require radiation of twice and three times of its frequency.

Q. 10.   Some of the fundamental vibrations are infrared active while the others are not. Explain.

Sol.   Infrared light is absorbed when a change in the dipole character of the molecule takes place. Total symmetry about a bond will eliminate certain absorption bands so that the number of absorption

bands does not coincide exactly with the number of fundamental vibrations and the molecules display somewhat simplified spectra. Thus, some of the fundamental vibrations are infrared active while the others are not.

Q. 11. Give the equation for calculating the frequency of vibration of a diatomic molecule.

Sol. A vibrating diatomic molecule behaves as a simple harmonic oscillator, oscillating with the frequency $\bar{v}$ as per the equation.

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

where k = force constant (dynes/cm) of the bond
μ = reduced mass, that is harmonic mean of the masses m_1 and m_2
(Harmonic mean = $m_1 \times m_2/m_1 + m_2$)
c = velocity of light

Q. 12. Explain the fact that ethylene and ethyne unlike propene and propyne, have no carbon to carbon multiple bond stretching bands.

Sol. Ethyne and ethylene are symmetrical molecules and do not give rise to a change in dipole moment when excited. A change in dipole moment occurs when propene and propyne are excited and a band is observed.

Q. 13. cis- 1, 2-Dichloroethylene is IR active with respect to $v_{c=c}$ whereas trans - 1, 2-dichloroethylene is not. Explain.

Sol. For most of the normal vibrations, dipole moment change occurs for cis-isomer, trans-isomers, however, are highly symmetrical and consequently remain forbidden.

Q. 14. How many fundamental vibrational frequencies would you expect to observe in the infrared spectrum of carbon-dioxide.

Sol. Carbon-dioxide, being linear, will have theoretically ($3n$-5 or $3 \times 3 - 5 = 4$) four fundamental vibrational modes as shown below:
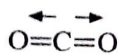
O=C=O	O=C=O	O=C=O	O=C=O
(a)	(b)	(c)	(d)
Sym. stretching (IR inactive)	Asym. stretching (IR active) $v_{max} = 2350$ cm^{-1}	Bending vibrations (identical motions) $v_{max} = 667$ cm^{-1}	
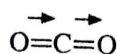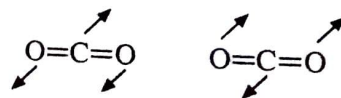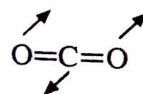
Thus, the two bands at 2350 cm^{-1} and 667 cm^{-1} pertaining to asymmetric stretching (b) and bending vibrations (c and d) constitute the fundamental spectrum of carbon-dioxide.

Q. 15. Calculate the vibrational degrees of freedom in the following molecules:
(i) O_2 (ii) N_2O (iii) CH_2O (iv) CH_4 (v) C_6H_6 (vi) $CHCl_3$

Sol. (a) For linear molecules, the vibrational degrees of freedom = $3n$-5
(b) For non-linear molecules, the vibrational degrees of freedom = $3n$-6
Thus, the vibrational degrees of freedom are (i) one (ii) three (iii) six (iv) nine (v) thirty (vi) six

Q.16. The C–H stretching frequencies of an alkane is observed at 2900 cm^{-1}. Predict the value of the corresponding C–D frequencies where hydrogen is replaced by deuterium.

Sol. $v_{C-H} = \sqrt{2}v_{C-D}$

$v_{C-D} = \sqrt{2}v_{C-H} = 2900/1.414 = 2060$ cm^{-1}

Q. 17. Arrange giving reasons, the following bonds in order of their decreasing vibrational frequencies.
C–Cl, C–Br, C–C, C–O, C–H, C–I

Sol. The C–H stretching occurs at about 2960 cm^{-1}. As the atom bonded to carbon increases in mass, the factor μ increases and consequently the frequency decreases. The decreasing order of vibrational frequencies will be

cm^{-1}	C–H	C–C	C–O	C–Cl	C–Br	C–I
v_{max}	2960	1200	1100	800	550	500

Q. 18. Compare the relative stretching frequencies for C–C, C=C and C≡C bonds.

Sol. Since the frequency of vibration is directly proportional in the force constant of the band, the increasing order of frequency is

C–C	C=C	C≡C
1200 cm^{-1}	1650 cm^{-1}	2150 cm^{-1}

Q. 19. Explain the effect of hybridization on the force constant of the bond.

Sol. Hybridization affects the force constant, k, of the bond. Bonds are stronger in the order sp > sp^2 > sp^3. Thus, the frequencies decrease as follows:

≡C–H	=C–H	–C–H
3300	3100	2960

Q. 20. How can you distinguish among hexane, I-hexene and I-hexyne on the basis of infrared spectroscopy.

$$CH_3CH_2CH_2CH_2CH=CH_2 \qquad CH_3CH_2CH_2CH_2C≡CH$$
$$\text{1-Hexene} \qquad\qquad\qquad \text{1-Hexyne}$$
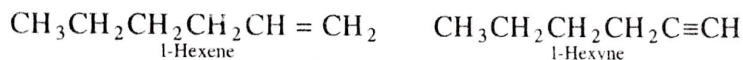
Sol. (i) The spectrum of I-hexyne, a terminal alkyne, exhibits a strong C_{sp}–H stretching absorption at 3300 cm^{-1} and weaker C≡C stretching absorption at 2120 cm^{-1}.

(ii) The spectrum of I-hexene displays C_{sp^2}–H stretching absorption at 3095 cm^{-1} together with C=C stretching absorption at 1640 cm^{-1}. In addition, two bands due to terminal C–H out-of-plane bending modes at 990 and 910 cm^{-1} will appear.

(iii) The stretching absorptions in hexane appear just below 3000 cm^{-1}.

Q. 21. The E$_2$ dehydrohalogenation of 2, 3-dimethyl-2-chlorobutane can lead to two possible products. Explain.

$$Me_2CH-\underset{\underset{Cl}{|}}{C}Me_2 \xrightarrow{-HCl} \underset{A}{Me_2C=CMe_2} + \underset{B\ \ Me}{Me_2CH-\underset{\underset{Me}{|}}{C}=CH_2}$$
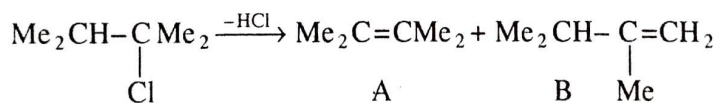
Sol. The product A, being symmetrical, does not exhibit C = C stretching absorption whereas the product B, being asymmetrical, displays the C=C stretching absorption at 1640 cm^{-1} and C–H out-of-plane bending of the terminal alkene at 890 cm^{-1}.

Q. 22. The dehydration of 1, 2-dimethyl cyclohexanol (cis or trans) can lead to the formation of three alkenes. Write their structures and explain how infrared spectroscopy can be used to differentiate among them.

Sol. The three products can easily be differentiated by C–H out-of-plane bending absorptions in the region from 800 to 1000 cm^{-1}. A, being a terminal methylene group, will absorb near 895–885 cm^{-1}, B, being a symmetrical tetra substituted alkene, will show no absorption in this region and C is a trisubstituted alkene, which absorbs near 840–790 cm^{-1}.
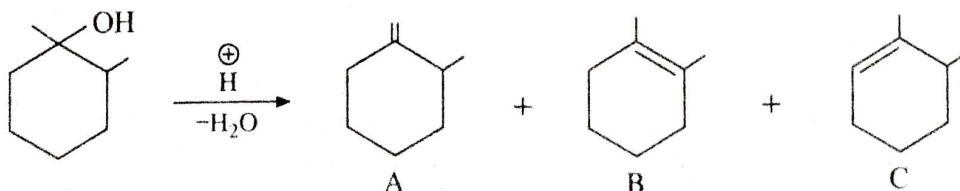
Q. 23.

Concentrated solutions of ethanol and 1,2-glycol in CCl_4 exhibit broad O–H stretch near 3350 cm⁻¹ in their IR spectra. On dilution with CCl_4, the spectrum of 1,2-glycol does not change but that of ethanol exhibits a sharp band at 3600 cm⁻¹ in addition to the broad band at 3350 cm⁻¹. Explain the observation.

Sol. Hint: Intermolecular hydrogen bonding is concentration dependent whereas intramolecular hydrogen bonding is not affected on dilution.

Q. 24.

2-tert-Butylphenol (I) exhibits infrared peaks at 3605 and 3643 cm⁻¹, whereas 2, 6-di-tert-butylphenol (II) exhibits the peak only at 3643 cm⁻¹. Explain.

Sol. The peak at 3643 cm⁻¹ exhibits the free hydroxyl stretching frequency which should be the same for both the compounds. The peak at 3605 cm⁻¹ in (I) corresponds to the stretching frequency of a hydrogen bonded hydroxyl which is inhibited in (II) by the presence of two bulky ortho-tert-butyl groups.

I

II
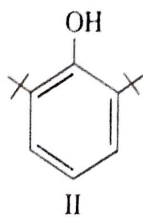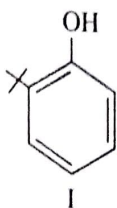
Q. 25.

Which of the following spectra pertaining to the hydroxyl group corresponds to
(i) the most concentrated solution (ii) the most dilute solution.

Sol. (i) The spectrum (c) corresponds to the most concentrated solution because hydrogen bonding between molecules becomes important as the concentration increases and accounts for the lower frequency band.

(a) (b) (c)
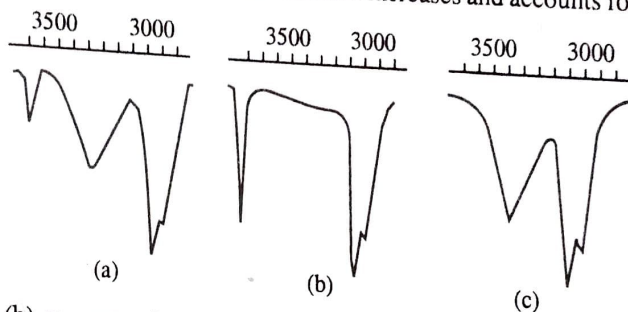
(ii) Spectrum (b) corresponds to the most dilute solution.

Q. 26. Which of the following spectra pertaining to hydroxyl group, provides the best evidence of intramolecular hydrogen bonding?

Very dilute solution (a) Dilute solution (b) Saturated solution (c)
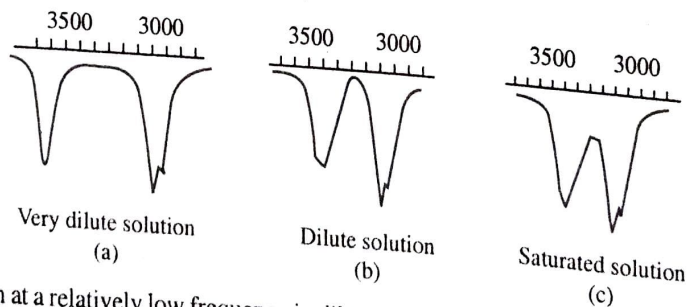
Sol. Absorption at a relatively low frequency in dilute solution indicates that hydrogen bonding is independent of concentration. This is characteristic of intramolecular hydrogen bonding (spectrum b).

Q. 27. Using infrared spectroscopy, how would you determine whether the oxygen in an organic compound is present as a carbonyl. hydroxyl or ether linkage.

Sol. Carbonyl would exhibit a strong absorption between 1800 and 1650 cm⁻¹. Hydroxyl would display a strong absorption between 3650 and 3100 cm⁻¹ together with strong absorption between 1250 and 1000 cm⁻¹. Ethers would show strong absorption between 1250 and 1000 cm⁻¹.

Q. 28. The carbonyl stretching frequency of an aldehyde is slightly higher than that of the corresponding methyl ketone..

Sol. Electron donation to carbonyl group leads to more single bond character and hence a lower frequency in ketones.

Q. 29. An aliphatic aldehyde containing unconjugated double bond exhibits C = O and C=C stretching at 1720–1740 cm^{-1} and near 1650 cm^{-1} respectively. Explain why crotonaldehyde exhibits the corresponding absorptions at 1700 cm^{-1} and 1630 cm^{-1}.

*Sol.* The resonance in crotonaldehyde may be depicted as follows:

$$CH_3-CH=CH-C\equiv O \longleftrightarrow CH_3-\overset{\oplus}{CH}-CH=C-\overset{\ominus}{O}$$
$$\qquad\qquad\qquad\overset{|}{H} \qquad\qquad\qquad\qquad\qquad\overset{|}{H}$$
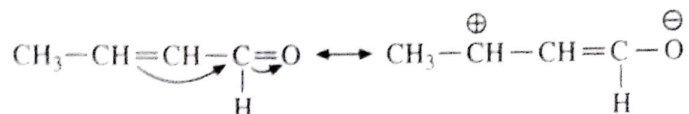
The effect of resonance is to lower both the frequencies of the carbonyl group (more single C–O bond charater) and of the carbon-carbon double bond absorption (more single carbon-carbon bond character).

Q. 30. 1-Acetyl-2-methylcyclohexene (II) exhibits carbonyl stretching frequency slightly higher (1693 cm^{-1}) than that of 1-acetylcyclohexene (I) (1686 cm^{-1}). Explain.
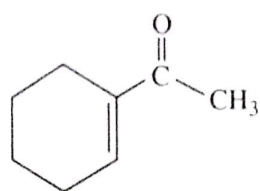
I
1-Acetylcyclohexene
$v_{C=O} = 1686$ cm^{-1}
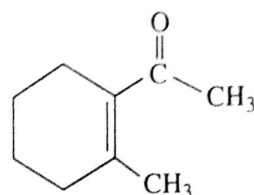
II
1-Acetyl-2-methylcyclohexene
$v_{C=O} = 1693$ cm^{-1}

Sol. The higher carbonyl stretching frequency in (II) is due to the steric effect, an effect occurring when carbonyl group is forced slightly out of the plane of the double bond so that p orbital overlap is reduced, which in turn lowers the resonance effect.

Q. 31. Explain the exceptionally low carbonyl stretching frequency in 2,4,6-cycloheptatrienone.

Sol. The exceptionally low carbonyl stretching frequency ($v_{C=O} = 1650$ cm^{-1}) in 2,4,6-cycloheptatrienone (I) is due to the conjugation effect.
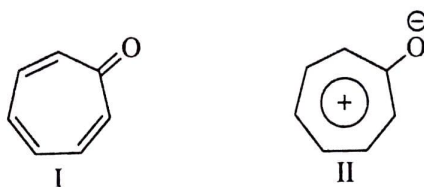
I
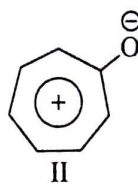
II

Because the cycloheptatrienyl cation, II (tropylium cation), contains six π electrons and consequently attains a stable aromatic structure, there are strong resonance contributions from the hybrid with a single-bond to oxygen resulting in an extremely low carbonyl stretching frequency.
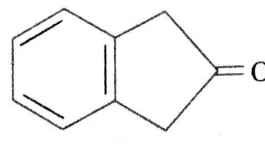
Q. 32. Arrange the following carbonyl compounds in order of their increasing carbonyl stretching frequency.
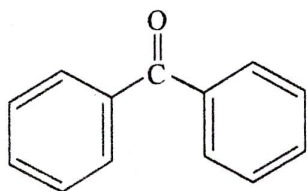

I
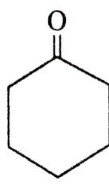
II

III

Sol.   The order of increasing carbonyl stretching frequency is I < II < III because I is conjugated (conjugation lowers the carbonyl frequency), II is a six membered ring ketone and hence frequency will be equal to acyclic ketone and III is a non conjugated five membered ring ketone.

Q. 33.   Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1} whereas the saturated aliphatic ketones near 1720 cm^{-1}. Explain.

Sol.   When a carbonyl group is bound to an oxygen atom, two opposing effects are present, both of which strongly influence the carbonly frequency.

Since the inductive effect is dominant in carboxylic acids over the mesomeric effect, the carboxyl stretching frequency in carboxylic acids is greater than that in ketones.

| Negative inductive effect | Mesomeric effect |
| (increases frequency) | (decreases frequency) |
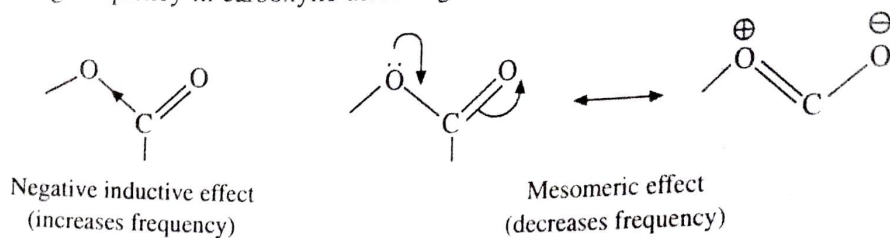
Q. 34.   Arrange, giving reasons, the following lactones in order of their decreasing carbonyl frequency.
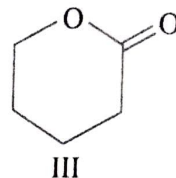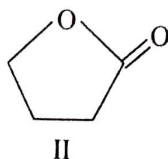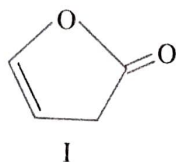
I   II   III

Sol.   The decreasing order of carbonyl frequency is I > II > III because a double bond adjacent to the singly bonded oxygen atom of an ester or lactone (I) raises the C=O stretching frequency. Five membered ring carbonyl compounds absorb at higher frequency than six membered ring compounds.

Q. 35.   The carbonyl stretching absorptions for the following lactones are 1720, 1745 and 1760 cm^{-1}. Match the absorptions with the appropriate structure and give a reason for each choice.


I   II   III
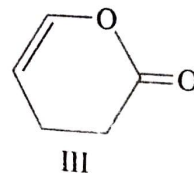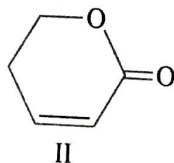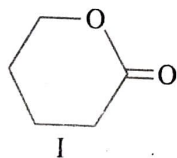
Sol.   The values of the carbonyl stretching for the three lactones are as follows:
I (1745); II (1720); III 1760 cm^{-1}. In the lactone III, the conjugation of the carbon–carbon double bond with the oxygen p orbital diminishes the normal resonance interaction of that oxygen with the carbonyl group resulting in an increase in the double bond character of the carbonyl group and consequently an increase in the carbonyl frequency occurs as compared to the saturated lactone (I).

Q. 36.   The carbonyl absorption of the carboxylate anion differs considerably from that of the parent acid. Explain.

Sol.   The carboxylate group is symmetrical due to resonance and the two CO bands are of equivalent strength, intermediate between C=O and C–O.
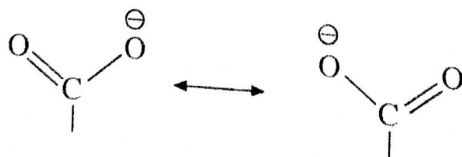
The two bands, one near 1600 and the other near 1400 cm^{-1}, observed in the case of carboxylate ion, are due to asymm. and symm. CO_2^- stretching absorptions as shown:

Asymmetric stretching   Symmetric stretching
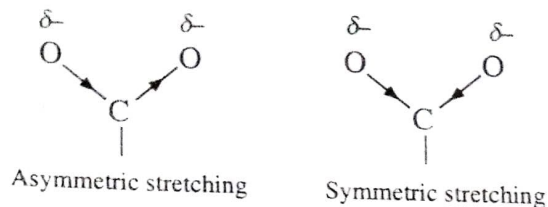
Q. 37. Arrange the following non conjugated carbonyl compounds in order of increasing carbonyl stretching frequency: aldehydes, esters, amides, acyclic ketones, acid fluorides and acid chlorides.

Sol. Amides, acyclic ketones, aldehydes, esters, acid chlorides and acid fluorides. The value of carbonyl stretching frequency will depend on the predominance of inductive or resonance effect.

Q. 38. Which of the following molecules has the highest carbonyl stretching frequency.

(a)   (b)   (c)   (d)   (e)   (f)
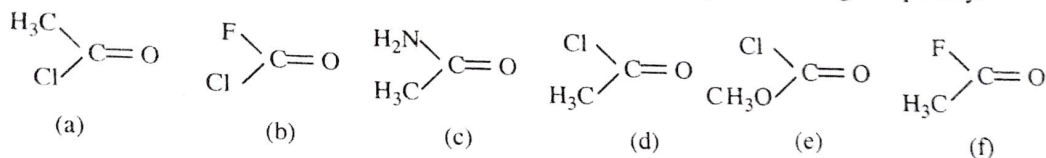
Sol. Except acetamide, the inductive effect is dominant and the highest carbonyl stretching frequency will be shown by (b) because it involves the largest net inductive withdrawal from the carbonyl group.

Q. 39. Deduce which of the following compounds would give a spectrum showing strong absorption at $1720 \ cm^{-1}$.

I   II   III
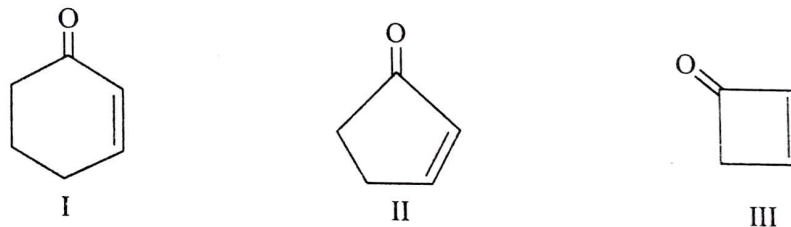
Sol. Since the C=O stretching frequency increases as the size of the ring decreases and decreases by introduction of olefinic bond in α, β, position, the ketone II will show strong absorption at $1720 \ cm^{-1}$.
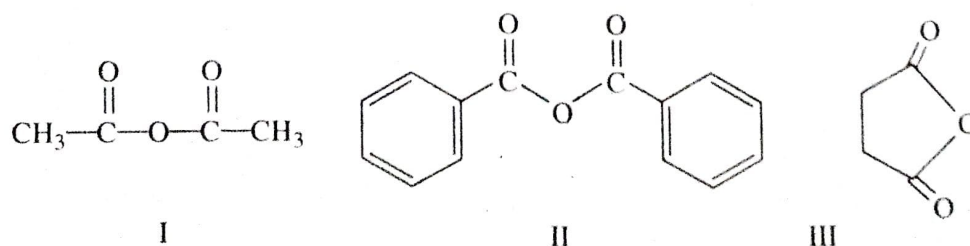
Q. 40. Which band in the spectrum enables us to distinguish between these two structures.

I   II
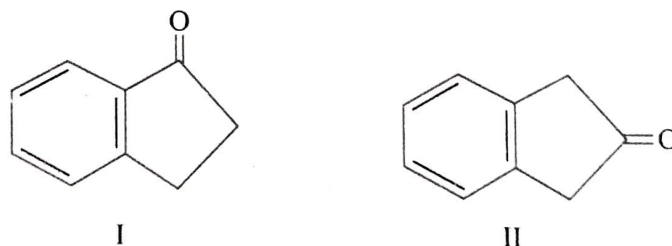
Sol. The carbonyl band. Its frequency indicates that the C=O group in the 5 membered ring is conjugated with the benzene ring in structure I.

Q. 41. Assign each of the following pairs of absorptions to one of the compounds below: 1865, 1780; 1815, 1750; 1775, 1720 cm^{-1}.
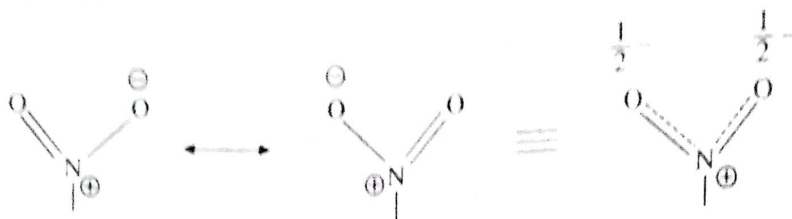

I   II   III

Sol (I) 1815, 1750, (II) 1775, 1720, (III) 1865, 1780 cm^{-1}. Conjugation lowers the absorption frequency. 5 membered ring C=O absorbs at higher frequency than 6 membered ring/open chain.

Q. 42. The nitro group is best regarded as a resonance hybrid between two equivalent forms. Explain its stretching mode.

Sol The situation is entirely analogous to the carboxylate anion. Two equivalent bonds to the same atom means that we can have asymmetric and symmetric stretching modes, both of which will be very strong because of the polar nature of the group.
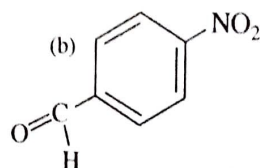
Q. 43. Assign each of the following pairs of frequencies to one of the compounds given below:
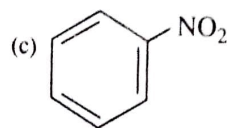(a) 1480 and 1319; (b) 1560 and 1360; (c) 1530 and 1355 cm^{-1}.
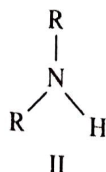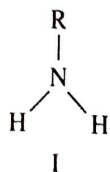
Sol.
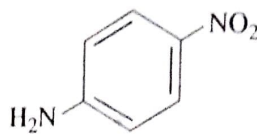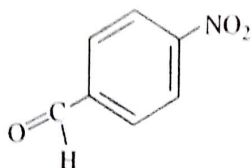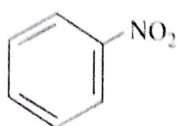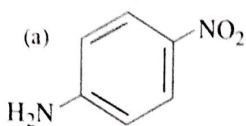
(a) 1480 and 1319

(b) 1560 and 1360

(c) 1530 and 1355 cm^{-1}

Q. 44. An amino group is electron donating and a carbonyl group is electron withdrawing. How would you distinguish between the N–H stretching absorption of a primary amine (I) and a secondary amine (II).

Sol. N–H stretching absorption of a primary amine would appear as a doublet, the two components corresponding to asymmetric and symmetric modes. The separation is usually 100 cm^{-1}. N–H stretching absorption of a secondary amine would generally have a single maximum.

Q. 45. Why β-diketones frequently exist as mixtures of enolic and ketonic forms? Mention the various stretching and bending vibrations encountered in the enol form.

$$R-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-R' \rightleftharpoons R-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-R'$$
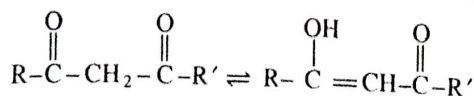
Sol. This is because that the enolic form is stabilised by hydrogen bonding. The enol form displays the following stretching and bending vibrations:
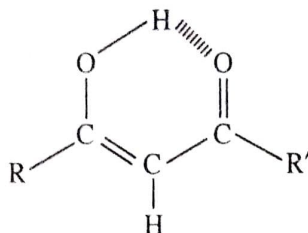
(i) C–H and OH stretching
(ii) C=O stretching
(iii) C=C–H out of plane bending

Q. 46. How would you distinguish between the compounds in each pair by infrared spectral studies:

(i) Phenol and cyclohexanol
(ii) cis and trans-2-butene
(iii) Ethylbenzene and o-xylene
(iv) Acetaldehyde and acetone

Sol. (i) Both the phenol and cyclohexanol would exhibit O–H stretching in the range 3450–3200 cm^{-1} with the phenol in the lower range. Phenol, however, would show the typical aromatic C–H stretching absorption above 3000 cm^{-1} whereas cyclohexanol shows C_{sp^3} –H stretching absorption below 3000 cm^{-1}. Phenol would also exhibit aromatic C–H out-of-plane bending vibrations in the range from 1000–650 cm^{-1}.

(ii) Both cis and trans–2– butenes display =C–H stretch at 3020 cm^{-1} and C=C stretching absorption near 1670 cm^{-1}. They differ in the out-of-plane bending; cis-2- butene absorbing at 670 cm^{-1} while trans-isomer absorbs strongly around 970 cm^{-1}.

(iii) Ethylbenzene, being monosubstituted benzene ring, displays two absorption bands due to C–H out-of-plane bending and C–C out-of-plane bending vibrations respectively at 750 and 700 cm^{-1} whereas o-xylene shows one band between 770 and 735 cm^{-1} due to C–H out-of-plane bending vibration.

(iv) Acetaldehyde can be easily distinguished from acetone by the appearance of a doublet in the region 2830–2695 cm^{-1}. This is due to the interaction between the fundamental C–H stretch and the first overtone of the C–H in-plane bending which occurs near 1390cm^{-1}.

Q. 47. The IR spectrum of benzoyl chloride shows a band at 1770 cm^{-1} with a shoulder at 1740 cm^{-1}. Explain.

Sol. A weak band near 1750–1735 cm^{-1} appearing in the spectra of aroyl chlorides probably results from Fermi resonance between the C=O band and the first overtone of a lower wave number band near 875 cm^{-1}.

Q. 48. A compound has molecular formula C_5H_{10}. It shows no absorption at 1380 cm^{-1} in the infrared spectrum. What is its structure.

Sol. The compound is cyclopentane.

Q. 49. An organic compound with the molecular formula C_8H_6 decolourises bromine in carbon tetrachloride and gives a white precipitate with ammonical silver nitrate solution. Its IR is given below. Identify the compound.
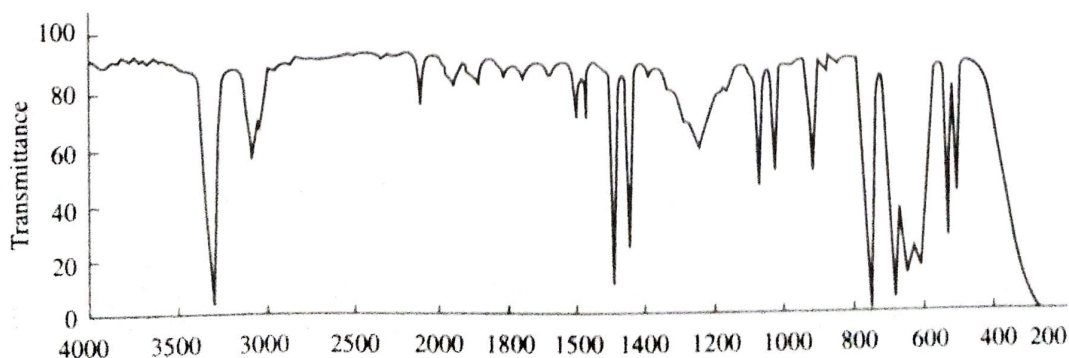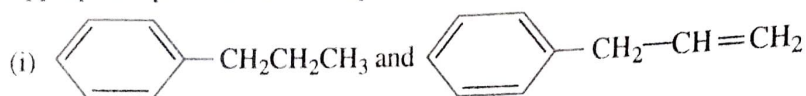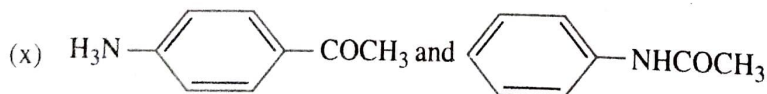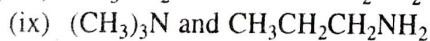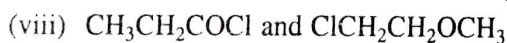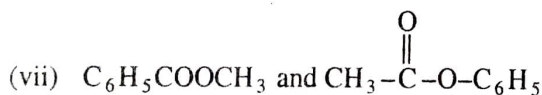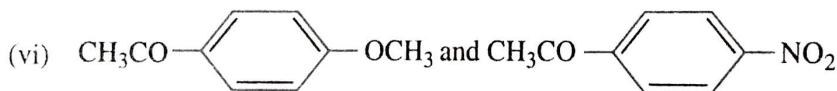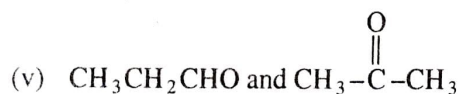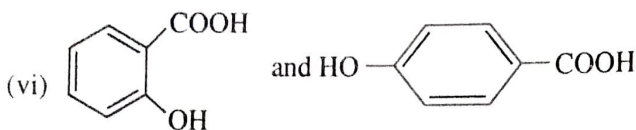
Sol.

(i) Reaction with bromine shows that it is unsaturated.
(ii) Reaction with ammonical $AgNO_3$ indicates 1-alkyne.
(iii) A sharp intense band at 3300 cm^{-1} indicates C_{sp}–H stretching vibration.
(iv) The weak bands in the region 3085–3040 cm^{-1} exhibit aromatic C–H stretching vibrations.
(v) The weak absorption at 2110 cm^{-1} is due to C≡C stretching vibrations.
(vi) The presence of monosubstituted benzene ring is confirmed by the absorption at 760 cm^{-1} (aromatic C–H out-of-plane bending) and 690 cm^{-1} (aromatic C–C out-of-plane bending.)
(vii) The broad and weak absorptions at 650 and 610 cm^{-1} correspond to the acetylenic C–H out-of-plane bending vibrations.

Hence the compound is phenylacetylene.

Q. 50. How would you distinguish between the following pairs of organic compounds. Name the vibrations and appropriate positions of absorptions in each case.

(i) [benzene ring]—$CH_2CH_2CH_3$ and [benzene ring]—CH_2—CH=CH_2

(ii) cis-stilbene and trans–stilbene

(iii) CH_3–C≡C–H and CH_3C≡N

(vi) [benzene ring with COOH and OH] and HO—[benzene ring]—COOH

(v) CH_3CH_2CHO and CH_3–$\overset{\overset{O}{\|}}{C}$–$CH_3$

(vi) CH_3CO—[benzene ring]—OCH_3 and CH_3CO—[benzene ring]—NO_2

(vii) $C_6H_5COOCH_3$ and CH_3–$\overset{\overset{O}{\|}}{C}$–O–$C_6H_5$

(viii) CH_3CH_2COCl and $ClCH_2CH_2OCH_3$

(ix) $(CH_3)_3N$ and $CH_3CH_2CH_2NH_2$

(x) H_3N—[benzene ring]—$COCH_3$ and [benzene ring]—$NHCOCH_3$

Sol.

(i) The spectrum of C_6H_5–CH_2–CH=CH_2 shows a medium intensity C=C stretching band near 1640 cm^{-1} and intense trans–CH wagging and CH_2 wagging absorptions near 990 and 910 cm^{-1} respectively. These bands will not be observed in the spectrum of C_6H_5–$CH_2CH_2CH_3$ which exhibits the characteristic C–H symmetric bending absorption for the methyl group near 1380 cm^{-1}.

(ii) The infrared absorption near 1640–1600 cm^{-1} due to C=C stretching in trans-stilbene remains inactive (symmetry forbidden) because the stretching of C–φ band produces no change in the dipole moment of the molecule. In cis-stilbene, however, a medium intensity band for C=C stretching absorption near 1640–1600 cm^{-1} appears because C–φ stretching vibration produces a net change in the dipole character of the molecule.

(iii) The spectrum of CH_3–C≡CH exhibits a strong and sharp band near 3300 cm^{-1} due to ≡C–H stretching vibration and a strong broad band near 680–610 cm^{-1} due to ≡C–H out-of-plane bending absorption.

Both these bands will not be observed in the spectrum of C_6H_6C≡N.

(iv) The OH group in salicylic acid is involved in intramolecular hydrogen bonding and hence the value of OH–stretching bonded absorption near 3400–3200 cm^{-1} remains almost the same at all

dilutions whereas the OH group in p-hydroxybenzoic acid is involved in intermolecular hydrogen bonding and consequently studying the compound in dilute solutions will cause the low frequency, broad, intense OH (bonded) absorption to diminish and high frequency sharp rather weak OH (free) band of unbonded hydroxy group to appear.

(v) The compound CH_3CH_2CHO can be distinguished from CH_3COCH_3 by the presence of

(a) Weak C–H stretching absorption of the CHO group in the region 2830–2695 cm^{-1} which often appears as a doublet due to Fermi resonance.

(b) Weak C–H out-of-plane bending absorption in the region 975 to 780 cm^{-1}.

(vi) The presence of p-OMe group (+ M group) in p-methoxyacetophenone assists the mesomeric shift to decrease the bond order of C=O bond leading to lower C=O stretching frequency. A p-NO_2 group (–M effect) on the other hand tends to oppose these trends and thus the C=O stretching frequency in p-nitroacetophenone is higher than in p-methoxyacetophenone.

(vii) The normal value of carbonyl absorption in esters (alkyl substituted saturated esters) appears in the range 1750–1735 cm^{-1}. This value is lowered to 1725 cm^{-1} in methyl benzoate because the carbonyl group is conjugated with phenyl group and is raised to 1770 cm^{-1} in phenyl acetate because an electron withdrawing phenyl group is attached to the single bonded oxygen which stiffens the C=O bond.

(viii) The spectrum of CH_3CH_2COCl exhibits an intense C=O stretching absorption at 1800 cm^{-1} whereas the spectrum pertaining to $ClCH_2CH_2–O–CH_3$ shows intense C–O stretching absorptions in the range from 1300–1000 cm^{-1}.

(ix) The spectrum of n-propylamine exhibits two N–H stretching bands; one near 3400–3300 cm^{-1} due to N–H asymmetric stretching and the other near 3330–3250 cm^{-1} due to N–H symmetric stretching vibration. These N–H stretching bands will not be observed in the spectrum of t-butylamine.

(x) The spectrum of p-aminoacetophenone exhibits two N–H stretching absorptions in the range 3500–3300 cm^{-1} whereas multiple N–H stretching bands in the range from 3300–3120 cm^{-1} will appear in the spectrum of acetanilide.

Study Problems

1. Absorption of infrared light occurs only if the dipole moment of the molecule is different in two vibrational states. Justify.

2. What do you mean by coupled vibrations? How they originate?

3. Explain that the vibrational degrees of freedom of a non-linear polyatomic molecule is $3n - 6$, where n is the number of atoms in the molecule.

4. Describe the factors influencing vibrational frequencies in the IR spectra.

5. The stretching frequencies of C=C and C=O occur at higher frequencies than C–C and C–O stretching frequencies respectively. Explain.

6. Explain the importance of IR spectroscopy in fingerprint region.

7. What is the basic requirement for a vibration to be infrared active. Explain taking a suitable example.

8. How will you determine the orientation of groups in disubstituted benzenes with the help of IR spectra.

9. Define and illustrate Fermi resonance, giving one example.

10. How will you determine E and Z isomers with the help of IR spectroscopy.

11. How would the IR spectra of the following compounds differ in the 4000–1600 cm^{-1} region:

(a)　　　　　　　　(b)　　　　　　　　(c)
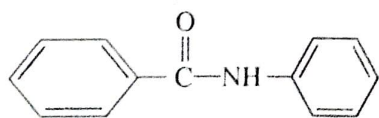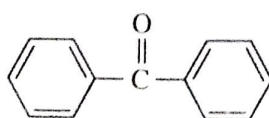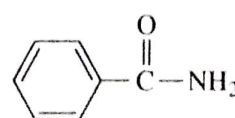
12. Discuss, with suitable examples, the inductive, resonance and ring size effect in carbonyl stretching frequencies.

The diffusion of blood alcohol through the lung occurs into the blow of breath which is subjected to IR spectroscopy in the O-H stretching region. The test is useful for the determination of the alcohol level in the breath and therefore, in the blood.

■ EXERCISES AND PROBLEMS

1. Placed below are the infrared spectra of thirteen compounds, (Fig. 3.43-3.49). In some of these spectra, either the main functional group is identified (by marking some of the corresponding bands in the high frequency region), or some significant bands are located. Analyse the other bands to confirm the assignments and comment on the overall structural features.

[Hint]
No characteristic absorption in the functional group region. The band ~2950 cm^{-1} is sp^3 C-H stretch. The band ~720 cm^{-1} is -(CH$_2$)$_n$- n ⩾ 4.

[Hint]
* No characteristic absorption in the functional group region.
* sp^3 C-H stretch is weak.
* C-X bond is indicated.

Fig. 3.43

Spectrum 3 labels: TRANSMITTANCE %; Olefinic C - H stretch (~ 3080 cm^{-1}); ~ 2950 cm^{-1}; C=C stretch; C = C - H bending (~ 900, 1000 cm^{-1}); CH$_2$ rock ~ 722 cm^{-1}

[Hint]
* Presence of unsaturation.
* Presence of - (CH$_2$)$_n$ - n ≥ 4.

Spectrum 4 labels: TRANSMITTANCE %; Olefinic C-H stretch; C=C stretch; C= C-H bending around 700 cm^{-1}

[Hint]
*Presence of unsaturation.
* Position of C=C-H bending will indicate the type of alkene.

Frequency (cm^{-1})
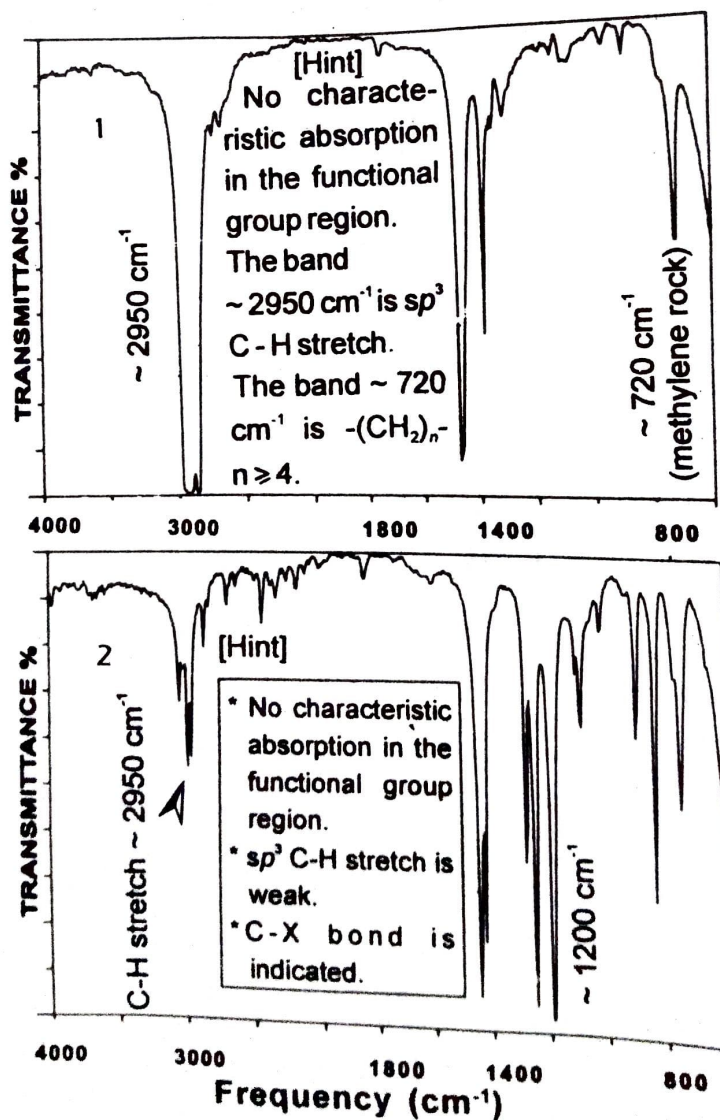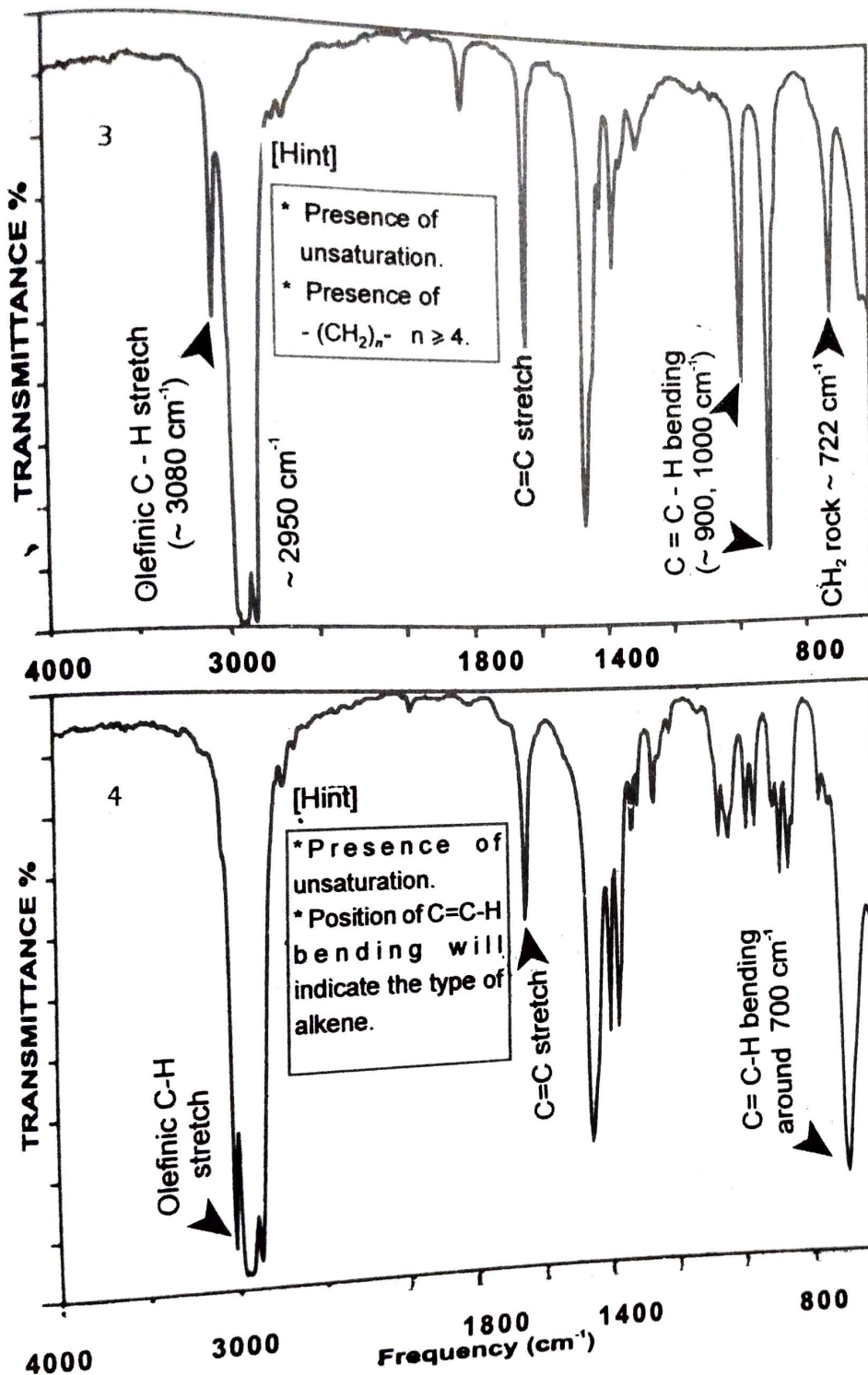
Fig. 3.44

2. An organic compound $C_8C_8O_2$ gives the infrared spectrum shown in Figure 3.50. Comment on the structural features in the compound.

3. Comment briefly on the stretching frequencies of the following bonds:

	Bond	Frequency Range, cm^{-1}
Alkyl	C—H	2853-2962
Alcohol	O — H	3590-3650

	Bond	Frequency Range, cm^{-1}
Amine	N — H	3300-3500
	C ≡ C	2100-2260
	C ≡ N	2220-2260
	C = C	1620-1680
	C = O	1690-1750

5

~3440 cm^{-1}

~1720 cm^{-1}

[Hint]

*Intense C=O band
*A rather intense overtone 3440cm^{-1} of C=O stretch

6

C-H stretch ~ 2950 cm^{-1}

~1715 cm^{-1}

[Hint]

*Apart from C=O band no other structural feature can be recognised.

Frequency (cm^{-1})

Fig. 3.45

Spectrum 7 labels:
- above 3000 cm⁻¹
- 2800, 2720 cm⁻¹ doublet
- 1700 cm⁻¹ conjugated C=O

[Hint]
*Aromatic C-H stretch
*Aldehydic C-H stretch
(doublet due to Fermi
resonance)
*Intense C=O stretch
*Check aromatic substitution
type.

TRANSMITTANCE %

4000   3000   1800   1400   800

Spectrum 8:

[Hint]
The compound does not
seem to be aromatic
there being no aromatic
C-H stretch above 3000
cm⁻¹ There are,
however, lot many strong
bands ~1400 - 1600 cm⁻¹
and below 900 cm⁻¹.

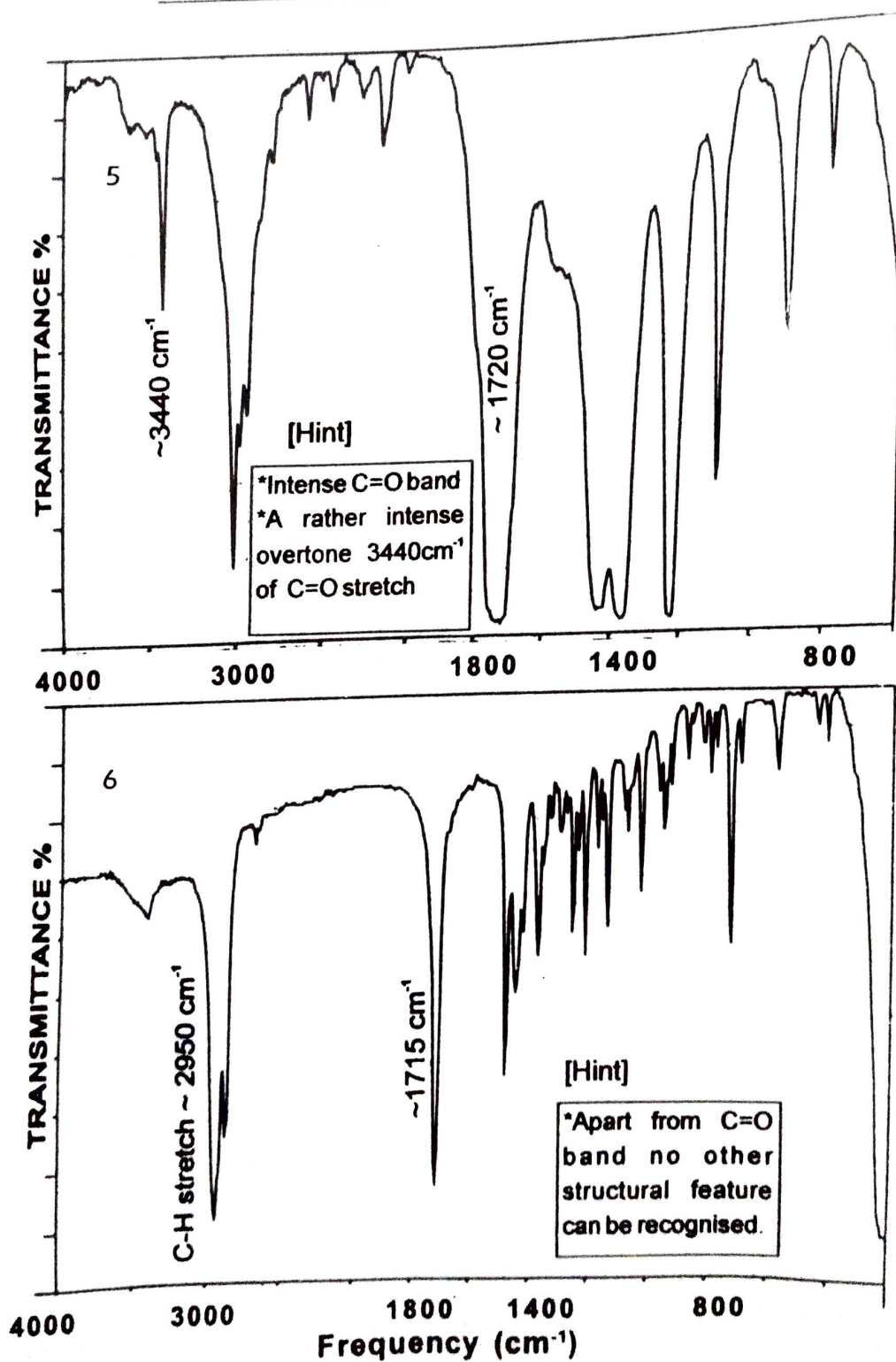◄ O-C stretch

TRANSMITTANCE %

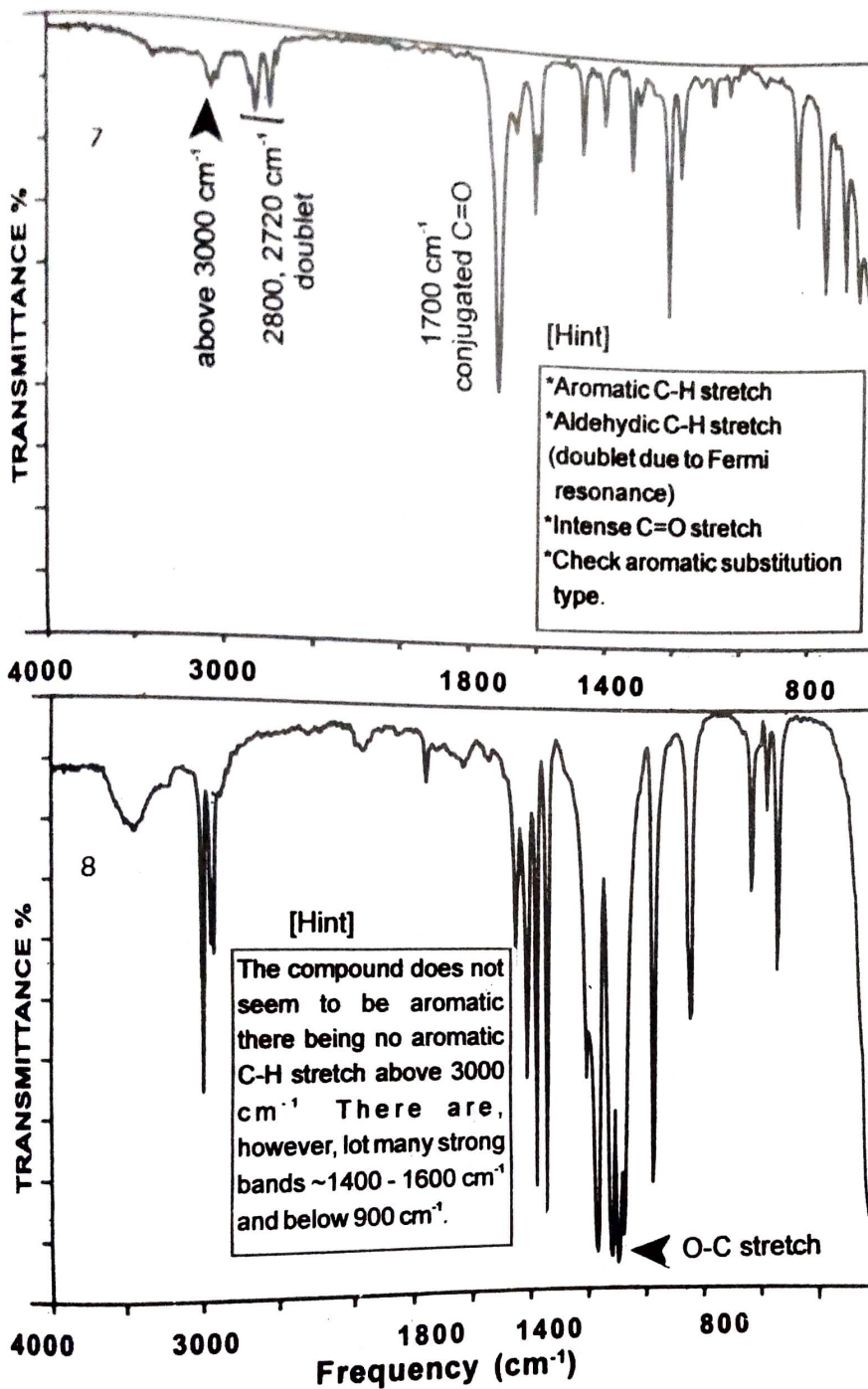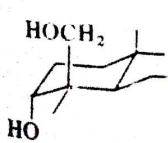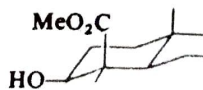4000   3000   1800 1400   800

Frequency (cm⁻¹)

Fig. 3.46

4. Comment on the indicated O—H and C=O stretching vibrations for the stereoisomeric pairs: I, 3641 and II, 3629 and 3550 cm⁻¹; III, 3548 and 1709 cm⁻¹ and IV, 3635 and 1723 cm⁻¹.
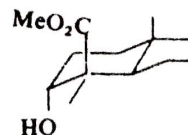

HOCH₂ ... HO (I)

HOCH₂ ... HO (II)

MeO₂C ... HO (III)

MeO₂C ... HO (IV)

TRANSMITTANCE %

9

bonded O-H stretch

C-H stretch

O-C stretch

[Hint]

The compound seems to be an aliphatic hydrogen bonded alcohol, with C-O stretch ~1020 cm^{-1} it may have -CH$_2$OH moiety.

4000   3000   1800   1400   800

TRANSMITTANCE %

10

bonded O-H stretch

C-H stretch

O-C stretch

CH$_2$ rock ~ 722 cm^{-1}

[Hint]

Saturated long chain primary alcohol [CH$_2$ rock ~720 cm^{-1} (CH$_2$), $n > 4$]

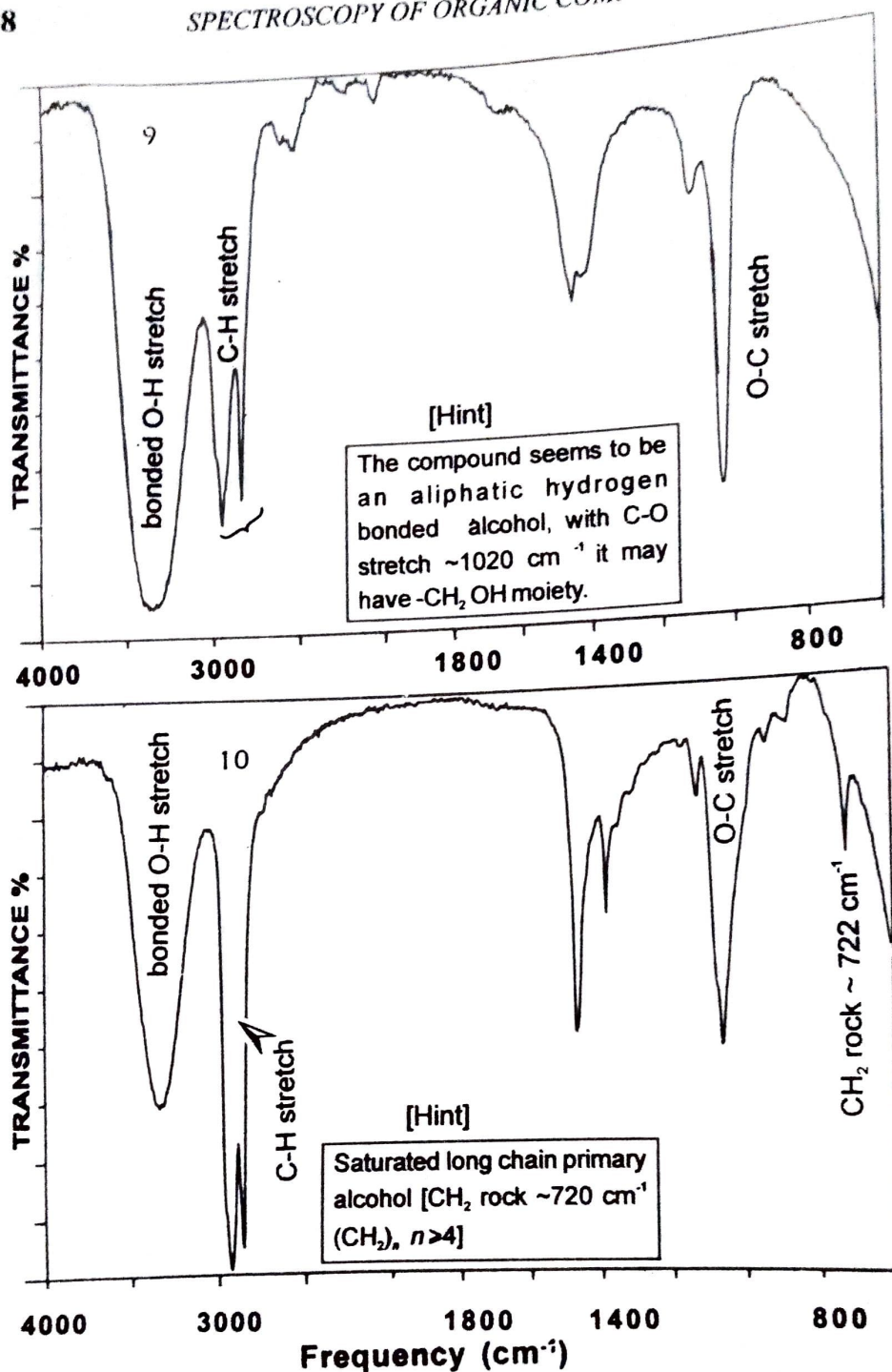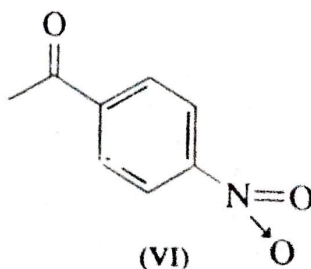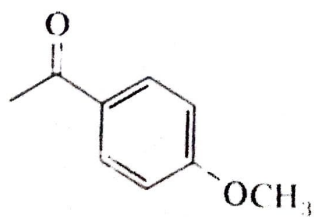4000   3000   1800   1400   800

Frequency (cm^{-1})

Fig. 3.47

5. Which out of compounds (V and VI) is expected to show a lower C=O stretching frequency?

(V)

(VI)

Spectrum 11: TRANSMITTANCE % vs frequency — labeled: broad O-H stretch superimposed upon C-H stretch (-COOH group); Intense C=O stretch. X-axis: 4000, 3000, 1800, 1400, 800.

Spectrum 12: TRANSMITTANCE %

[Hint]
*The compound looks like aromatic (bands ~1400, 1500 and 1600 cm^{-1} and below ~900 cm^{-1}.
*It may be monosubstituted benzene derivative.

C=O stretch (1683 cm^{-1})

X-axis: 4000, 3000, 1700, 1400, 800
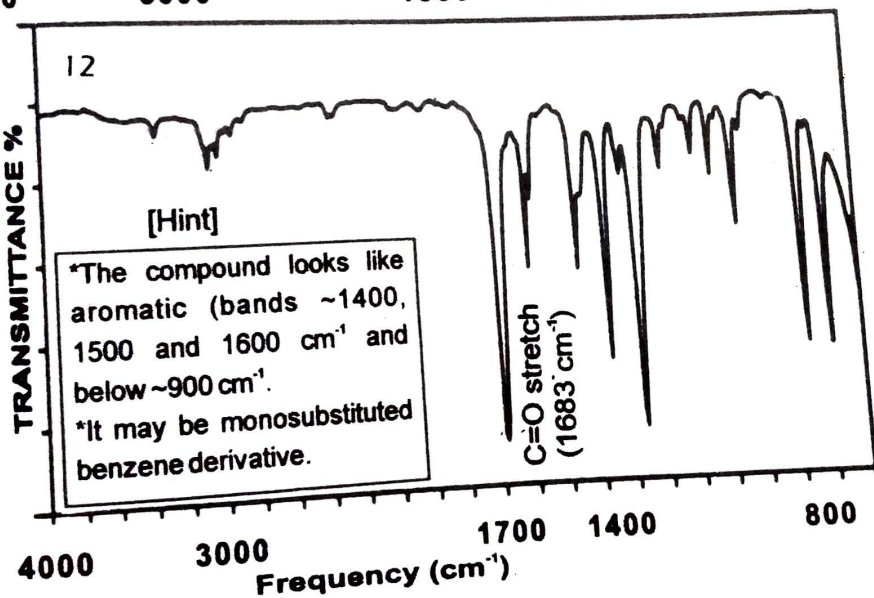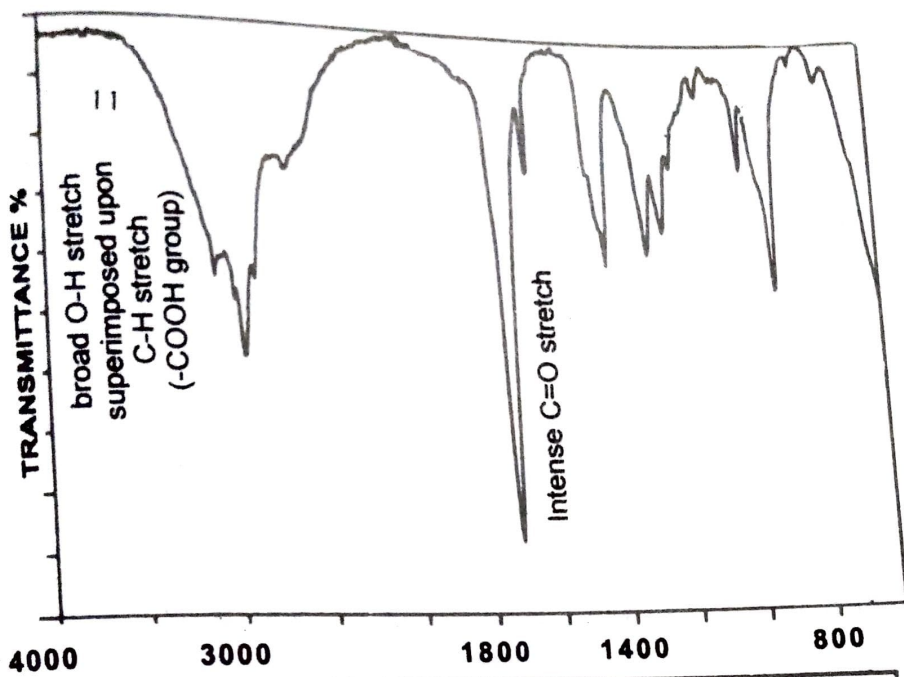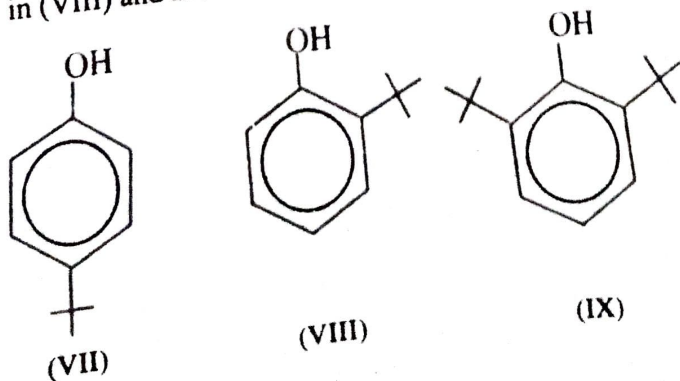
Frequency (cm^{-1})

Fig. 3.48

6. Esters of o-chlorobenzoic acid show two C=O stretching frequencies. Explain.

7. In the substituted phenols the O—H stretching is at 3608 cm^{-1} in (VII), at 3605 and 3643 cm^{-1} in (VIII) and at 3643 cm^{-1} in (IX). Explain.
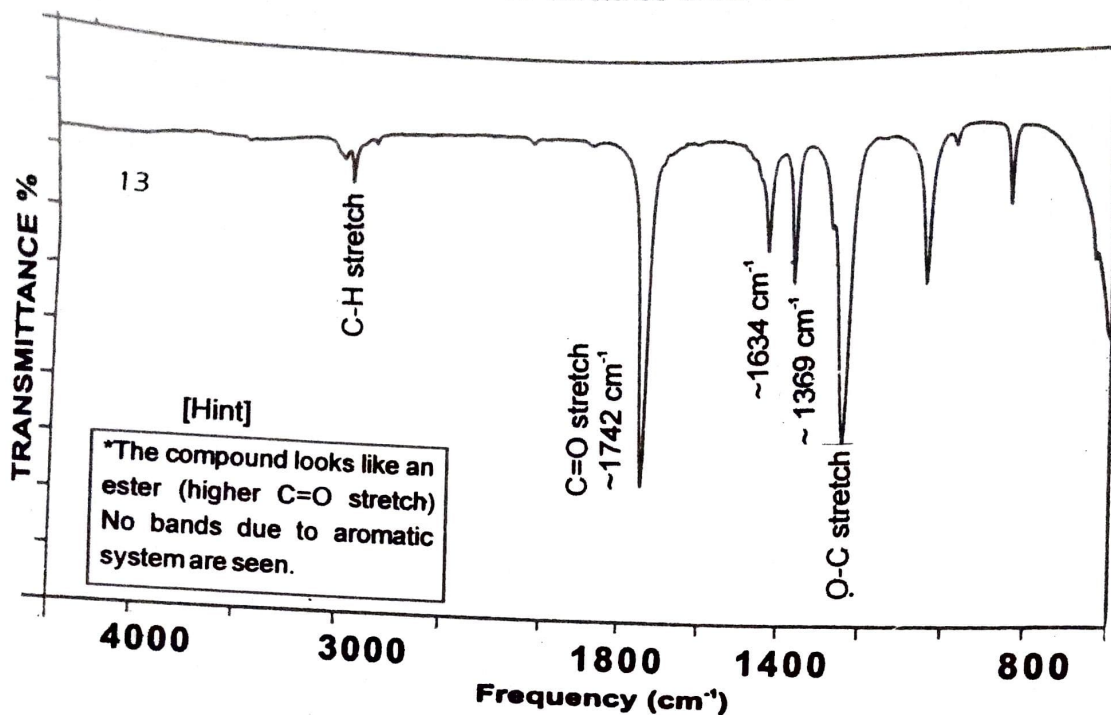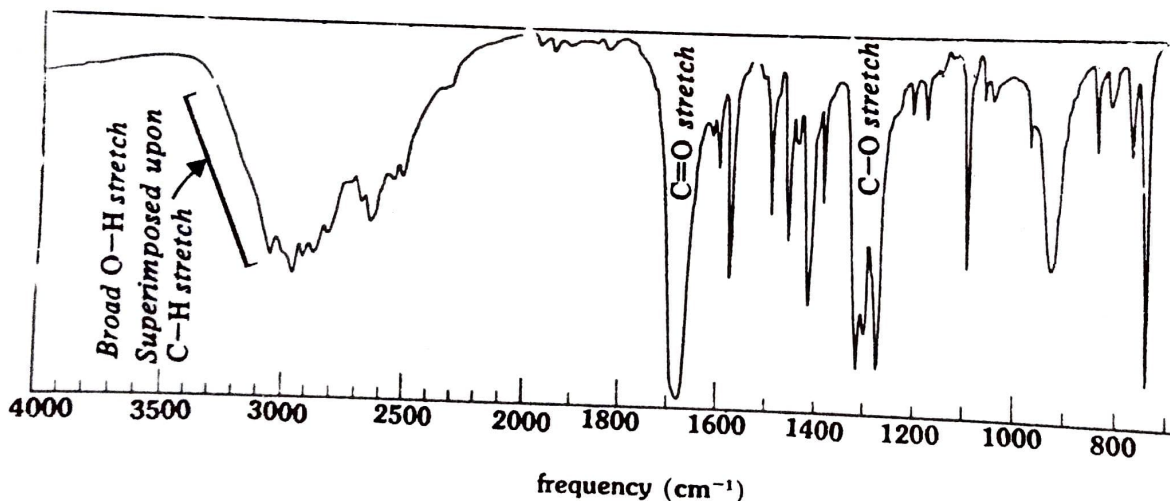

(VII)   (VIII)   (IX)

Fig. 3.49

The spectrum is labelled with: 13, C-H stretch, C=O stretch ~1742 cm^{-1}, ~1634 cm^{-1}, ~1369 cm^{-1}, O-C stretch.

[Hint]
*The compound looks like an ester (higher C=O stretch) No bands due to aromatic system are seen.

TRANSMITTANCE %

Frequency (cm^{-1})

Fig. 3.50

The spectrum is labelled with: Broad O—H stretch Superimposed upon C—H stretch, C=O stretch, C—O stretch.

frequency (cm^{-1})

8. 2-Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies at 1692 and 1658 cm^{-1}. Explain.

9. O-Nitrophenol has an O—H band at 3200 cm^{-1} in KBr pellet as well as in CHCl$_3$ solution, whereas in the *para* isomer the values are different in the two media (pellet 3330; CHCl$_3$ solution 3520 cm^{-1}). Explain by writing structures and their effect on their volatility.

10. In the infrared spectra of two compounds (Fig. 3.51), the bands due to functional groups have been marked, identify these bands.
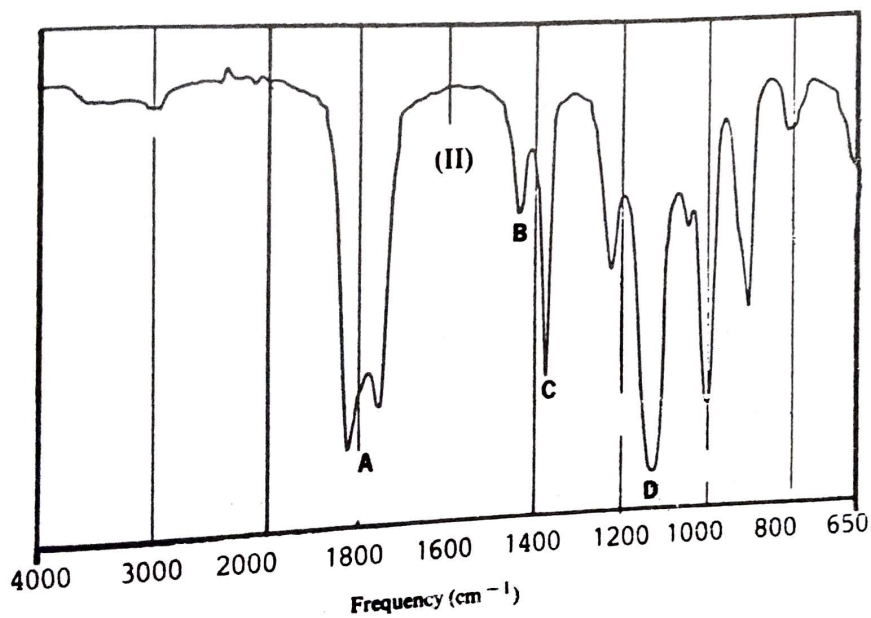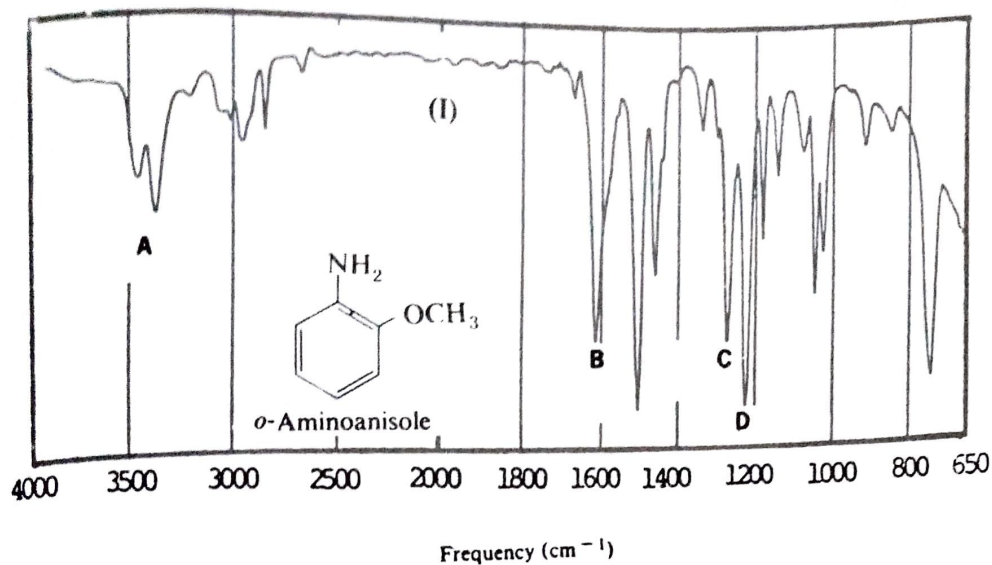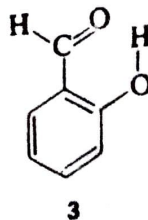
(I)

NH$_2$

OCH$_3$

o-Aminoanisole

A   B   C   D

4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 650

Frequency (cm^{-1})

(II)

A   B   C   D

4000 3000 2000 1800 1600 1400 1200 1000 800 650
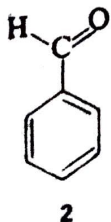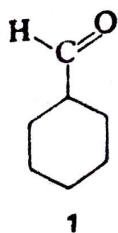
Frequency (cm^{-1})

Fig. 3.51

11. Predict the frequency shift of the carbonyl absorption in the aldehydes 1-3.

1

2

3

12. An acyl group is readily detected from the infrared spectroscopy since the C=O stretching frequency varies with the functional group, *i.e.*, with G. From the follow-

ing trends in the strong carbonyl stretching absorption peak in the 1700 cm^{-1} region, identify a particular acid derivative in each case.

$$O$$
$$||$$
$$R - C - G$$
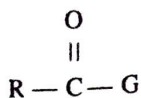
(i) 1,700–1,815 cm^{-1} (5.65–5.51 μ)
(ii) 1,740–1,790 cm^{-1} and 1,800–1,850 cm^{-1} [two bands]
(iii) 1,720–1,750 cm^{-1}
(iv) 1,630–1,690 cm^{-1}

13. Certain acyl compounds, *e.g.,* carboxylic acids, aldehydes and amides have further distinctive features other than explained in exercise 15 above. Explain.

14. Infrared absorption due to carbonyl stretching occurs at higher frequencies than stretching of the carbon-carbon double bond. Explain.

15. An unsaturated hydrocarbon containing a vinylidene ($>C=CH_2$) double bond displays the infrared spectrum shown in Figure 3.52, I. The spectral changes on its dihydroxylation with O_sO_4 and subsequent rupture of σ bond with periodic acid to give a ketone are presented in figures II and III. Assign the bands in each spectrum to respective functional groups.

■ ANSWERS TO THE PROBLEMS

1. *Spectrum 1.* It displays a strong aliphatic C—H stretch around 2950 cm^{-1} and C—H bending of methyl and methylene groups around 1380 and 1465 cm^{-1}. The methyl C—H band at 1380 cm^{-1} is not split into a doublet, thus isopropyl or tertiary butyl moieties are absent. This together with a strong methylene rock at 720 cm^{-1} shows that the compound is a straight chain saturated hydrocarbon. The compound is dodecane.

Spectrum 2. The spectrum displays bands for aliphatic C—H stretch (rather weak), and C—H bending of methylene group around 1450 cm^{-1}. There is no C—H bending of the methyl group (The region from 1300-1400 cm^{-1} being blank). The compound is 1,2-dibromoethane.

Spectrum 3. The compound typically shows the presence of unsaturation. The nature of double bond can be assessed form the C—H bending vibrations which are located around 1000 and 900 cm^{-1} (vinyl double bond). There is a methylene rocking band around 720 cm^{-1}. The compound is thus a long chain alkene, with terminal unsaturation. The compound is 1-tetradecene. Note the typical overtone band around 1825 cm^{-1}.

Spectrum 4. The compound is unsaturated. The presence of C—H bending at 700 cm^{-1} shows the compound to contain *cis*-disubstituted double bond. The compound is *cis*-2-hexene.

Spectrum 5. It is a carbonyl compound. An inspection of the methyl and methylene C—H bending region shows that the band below 1400 cm^{-1} is more intense than the one above 1400 cm^{-1}. This shows the presence of a methyl group on a carbonyl. The compound is acetone.

Spectrum 6. It represents a saturated ketone, whose C=O stretch at around 1715 cm^{-1} is suggestive of either an acyclic ketone, a six-membered ring ketone or an eleven or
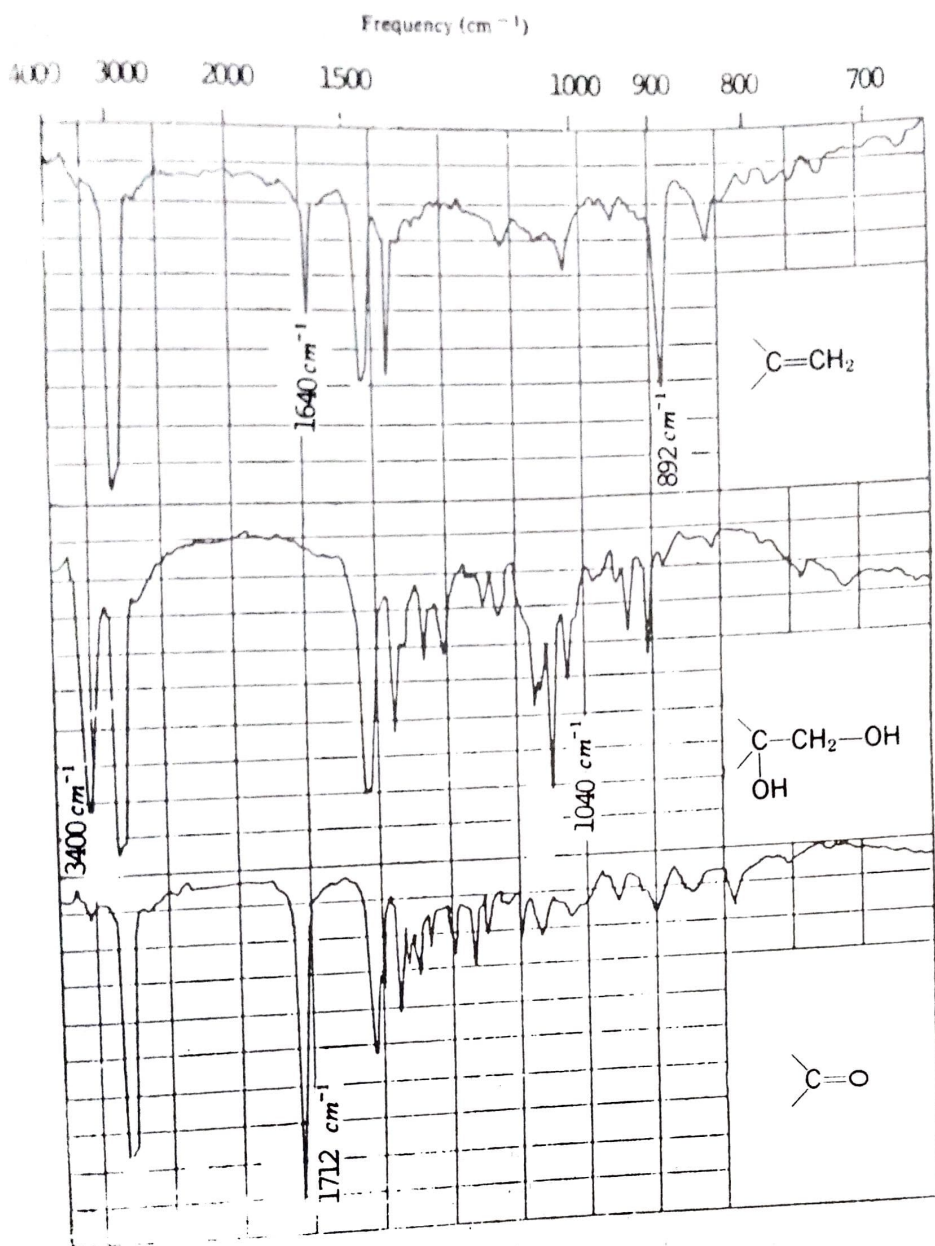
Frequency (cm⁻¹)

400   3000   2000   1500   1000   900   800   700

1640 cm⁻¹

892 cm⁻¹

⟩C=CH₂

3400 cm⁻¹

1040 cm⁻¹

⟩C—CH₂—OH
⎮
OH

1712 cm⁻¹

⟩C=O

Fig. 3.52

higher membered ring ketone. 7-10-Membered ring ketones show their C=O stretch around 1702 cm⁻¹ while 5,4 and 3-membered ring ketones show higher C=O stretchings at 1745, 1780 and 1825 cm⁻¹ respectively. The compound is cyclododecanone.

Spectrum 7. The presence of aromatic C—H stretch above 3000⁻¹, aldehydic C—H stretch near 2700 and 2800 cm⁻¹ and C=O stretch around 1700 cm⁻¹ and typical out of the plane C—H bendings show that the compound is a monosubstituted benzene derivative. The compound is benzaldehyde.

Spectrum 8. The compound represents metaldeyde, *i.e.,* the tetramer of acetaldehyde. The C—O stretching region between 1000-1200 cm⁻¹ is indeed full of strong bands.

metaldehyde → heat → acetaldehyde
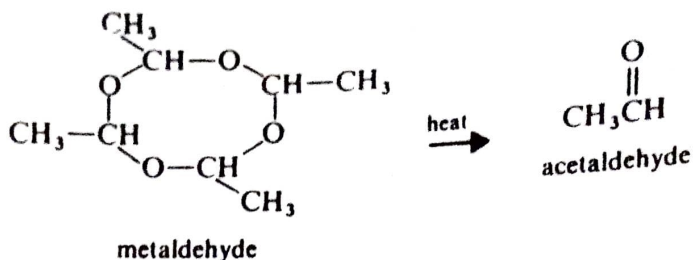
Spectrum 9. The spectrum is of an alcohol as evident from strong O—H and C—O stretchings. The compound is methyl alcohol.

Spectrum 10. There is a strong O—H stretch, and this coupled with C—O stretch at 1025 cm^{-1}, shows it to be a primary alcohol. The compound is l-decanol.

Spectrum 11. The spectrum shows typical and broad O—H stretch which is superimposed upon C—H stretch. This coupled with C=O stretch around 1720 cm^{-1} shows that the compound is a carboxylic acid. There is unsaturation in the compound as shown by the presence of C=C stretch around 1625 cm^{-1}. The C—H bendings around 900 cm^{-1} (s) and 975 cm^{-1} show the presence of vinyl double bond. The compound is 6-heptenoic acid.

Spectrum 12. The spectrum shows aromatic C—H stretch above 3000 cm^{-1} and also aliphatic C—H stretch below 3000 cm^{-1}. The C=O stretch 1683 cm^{-1} is at lower frequency than the normal C=O stretch which is around 1725 çm^{-1}. This is probably due to its conjugation with the phenyl group. The presence of C - - - C ring stretchings and out of plane C—H bendings are typical of a monosubstituted benzene. The compound is acetophenone.

Spectrum 13. The C—H stretch is weak, however, it cannot be aromatic since its position is below 3000 cm^{-1}, it is therefore assigned to aliphatic C—H stretch. The presence of C=O stretch (1742 cm^{-1}) along with C—O stretch 1240 cm^{-1} shows the compound to be a saturated ester. A shrewed eye will detect that in the methyl, methylene C—H bending region of the two bands at 1434 and 1369 cm^{-1}, the band at lower frequency is more intense. This shows the presence of CH$_3$—C=O moiety (Fig. 3.38). The compound is methyl acetate.

2. Strong broad O—H stretch is centred at around 3000 cm^{-1} and superimposed upon the region of C—H stretch. This coupled with the presence of strong C=O stretch around 1690 cm^{-1} confirms the presence of a conjugated —COOH group and accounts for both the oxygen atoms. The presence of combination bands, aromatic C=C stretch around 1400, 1500 and 1600 cm^{-1} and strong C—H bending at 735 cm^{-1} further shows that the aromatic substitution type is *ortho*-disubstituted benzene. The compound is *O*-toluic acid.

o-Toluic acid
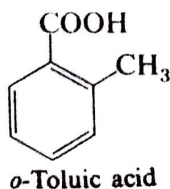
3. The stretching frequency of a bond and therefore, its position in an infrared spectrum is related to two factors; the masses of the bonded atoms — light atoms vibrate at higher frequencies than heavier ones — and the relative stiffness of the bond. Triple

bonds being stiffer, vibrate at higher frequencies than double bonds and double bonds are stiffer and thus vibrate at higher frequencies than single bonds. The stretching frequencies of groups involving hydrogen, *i.e.*, a light atom such as C—H, N—H and O—H all occur at relatively high frequencies. As expected, the triple bonds vibrate at higher frequencies than double bonds.

4. In these stereoisomeric pairs of compounds I and II and III and IV only one member from each pair permits hydrogen bonding leading to lowering in the O—H and C=O stretchings.
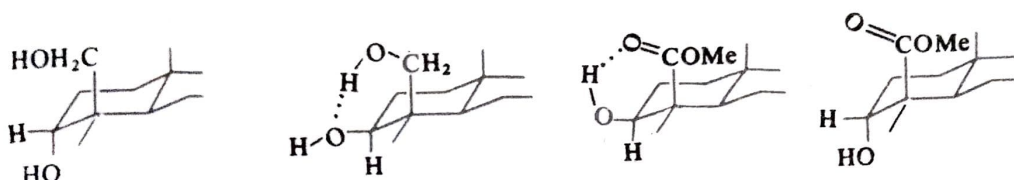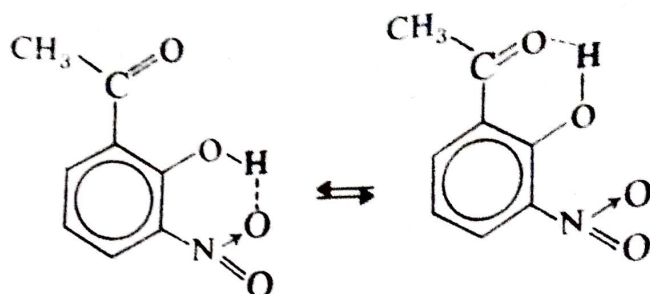

5. The presence of *p*-OMe group (a + *M* group) in V assists the mesomeric shift to decrease the bond order of C=O bond leading to lower C=O stretching frequency. A *p*-NO$_2$ (—M group) tends to oppose these trends and thus in (VI) the C=O stretching frequency is higher than V.

6. In *O*-chlorobenzoic acid esters the field effect shifts the C=O frequency in the rotational isomer (VII) and not in the isomer (VIII). Normally both the isomers are present, so that two C=O stretching absorptions are observed.
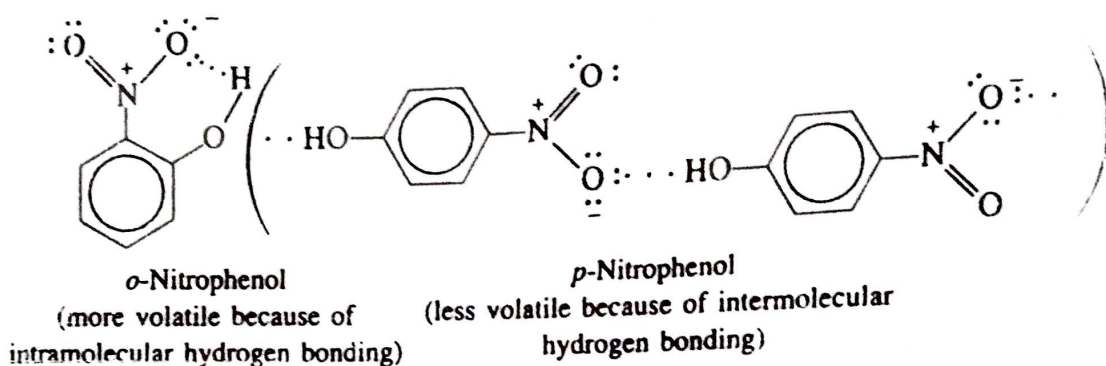

(VII)   (VIII)
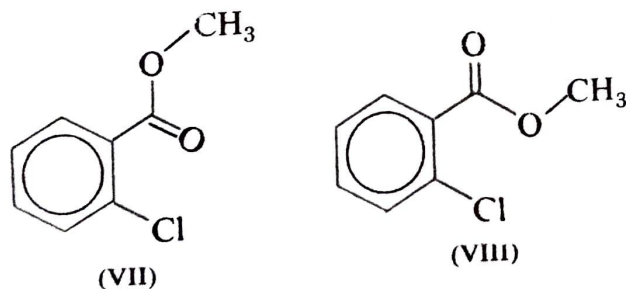
7. In *p-t* butylphenol (VII) only a single hydroxyl frequency is seen at 3608 cm^{-1} due to associated OH group. In the *O*-isomer (VIII), bands are seen at both 3605 and 3643 cm^{-1} showing that in some molecules there is association whereas in others the OH is not hydrogen bonded due to crowding by *t*-butyl group. In 2.6 di-*t*-butyl phenol (IX) only a single hydroxyl frequency is seen at 3643 cm^{-1}, since two different molecules are not able to approach close enough to form an intermolecular hydrogen bond.

8. Due to competing hydrogen bond formation and therefore as a result of the equilibrium shown below. The structure with free carbonyl shows the normal conjugated C=O stretch, however, on association with the OH group the C=O stretch is further shifted to lower frequency.
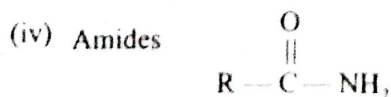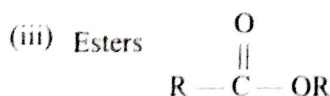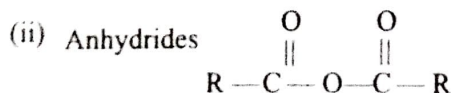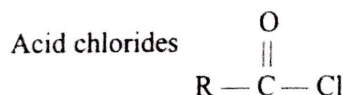
9.   2-hydroxy-3-nitroacetophenone

o-Nitrophenol
(more volatile because of
intramolecular hydrogen bonding)

p-Nitrophenol
(less volatile because of intermolecular
hydrogen bonding)

10. In spectrum (I), Figure 3.51, A is NH stretch (coupled vibrations); B is NH bend, C is C—N stretch and D is O—C stretch. In spectrum (II), A is the coupled C=O stretch and the high frequency points to a carboxylic acid anhydride; B and C is C—H bend of CH₃— Ċ=O moiety and D is O—C stretch. The compound is acetic anhydride.

11. Cyclohexane carboxaldehyde 1, being saturated will absorb around 1730 cm⁻¹. In benzaldehyde 2, the absorption will be shifted to lower frequency (1700 cm⁻¹) due to conjugation. In salicylaldehyde 3, the internal (chelated) hydrogen bonding causes a further large frequency shift to around 1666 cm⁻¹.

12. (i)   Acid chlorides

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl$$

(ii) Anhydrides

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - O - \overset{\overset{\displaystyle O}{\|}}{C} - R$$

(iii) Esters

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OR$$

(iv) Amides

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2$$

13. Carboxylic acids show a strong and broad O—H stretching frequency in the region 2,500 to 3,000 cm⁻¹, which is absent in esters. Furthermore, carboxylic acids show a C—O stretching frequency at ~1,250 cm⁻¹, whereas the C—O stretching in esters normally occurs as two relatively strong bands in the region 1,050 to 1,300 cm⁻¹. Aldehydes and ketones show no absorption in this broad region, thus they are readily

distinguishable from carboxylic acids and esters. Amides display N—H stretching in the 3,050 to 3,540 cm^{-1} region and show another strong absorption band in the 1,600 to 1,645 cm^{-1} region due to N—H bending.

14. This is explained in terms of the π bond stretch of the C=O bond, which is considerably stronger than the π bond in C=C.

15. The changes from an alkene (C=C stretch 1640 cm^{-1}, C—H bend 892 cm^{-1}) to a diol (OH stretch 3400 cm^{-1} C—O stretch 1040 cm^{-1}) and finally to a ketone C=O stretch (1712 cm^{-1}) are marked on the spectra.

▉ SUMMARY

1. The infrared region from 4000-650 cm^{-1} is useful or structural information of organic compounds. This region is split into two parts, 4000-1300 cm^{-1}, the high frequency part, *i.e.*, the functional group region and the low frequency part 1300-650 cm^{-1}, the fingerprint region.

2. Most of the functional groups give absorption bands in the high frequency part of the spectrum, which, therefore has a small number of bands. The fingerprint region contains a large number of bands and is rich in detail. This part is used for compound comparison.

3. As most organic compounds contain alkane residues, therefore, the strong aliphatic C—H stretch centred around 2925 cm^{-1} and the medium intensity bands for their C—H bendings around 1465 (CH_3, —CH_2) and 1380 cm^{-1} (CH_3) are generally present in an infrared spectrum (Fig. 3.7). Aromatic and olefinic C—H stretch is above 3000 cm^{-1}.

   To assist the student in his understanding, the main regions, where most of the common functional groups absorb are shown in thick lines with respect to three aliphatic bands, *i.e.*, C—H stretch (2925 cm^{-1}) and C—H bend (—CH_3, —CH_2—, 1465 and —CH_3 1380 cm^{-1}). However, the absence of these absorption bands due to the absence of alkyl residues does not offer any difficulty to assign bands to the presence of other functional groups.

4. The absorption of functional groups on the higher (left hand side) and lower (right hand side) frequency side of the main aliphatic C—H stretch are presented in Fig. 3.53. Among the prominent bands on the higher frequency side of this band mention may be made of O—H stretching band which is used to recognise the presence of alcohols and phenols. The value of O—H stretching frequency is used gainfully to detect hydrogen bonded ($\sim$ 3400 cm^{-1}) or free hydroxyl groups ($\sim$ 3600 cm^{-1}). The N—H stretchings occur around the same region. However, N—H absorptions are much sharper (weak tendency to form hydrogen bonds), weaker in intensity and in dilute solutions never give rise to absorptions as high as the free O—H groups (*i.e.* 3600 cm^{-1}).

   A carboxylic acid is very easy to recognise because of the special shape of the broad bonded O—H stretch which lies across the aliphatic C—H stretch (Fig. 3.25). Primary amines and amides show two bands (coupled N—H stretchings) and can thus be distinguished from their secondary counterparts which normally show one band; in tertiary systems since there is no H on N, these bands are absent.