

scanned, a large number of questions come to our mind viz.

- Which group/groups can be present in the compound?
- What environments are influencing it?
- What type is the carbon skeleton in the compound?
- Is the compound aromatic? If so, what type of substitution?

Some of the important families giving characteristic absorptions and the environmental effects on them are discussed below:

3.11 A Hydrocarbons

These compounds are made up of carbon and hydrogen only. Hydrocarbons may be saturated and unsaturated aliphatics; cyclics or aromatics.

3.11 A₁ Alkanes and alkyl residues

The alkane residues are detected from C—H stretching and C—H deformation absorptions. As C—H does not take part in hydrogen bonding, its absorption position is little effected by chemical environments. Since most of the organic compounds possess alkanes residue, C—H absorption bands in a spectrum are of little diagnostic value. Commonly two C—H stretching absorption bands appear just below 3000 cm^{-1} ; one for symmetrical and the other for asymmetrical vibrational frequencies. The group of bands corresponding to C—H def. is characteristic of alkyl group provided it is not under some electrical influence.

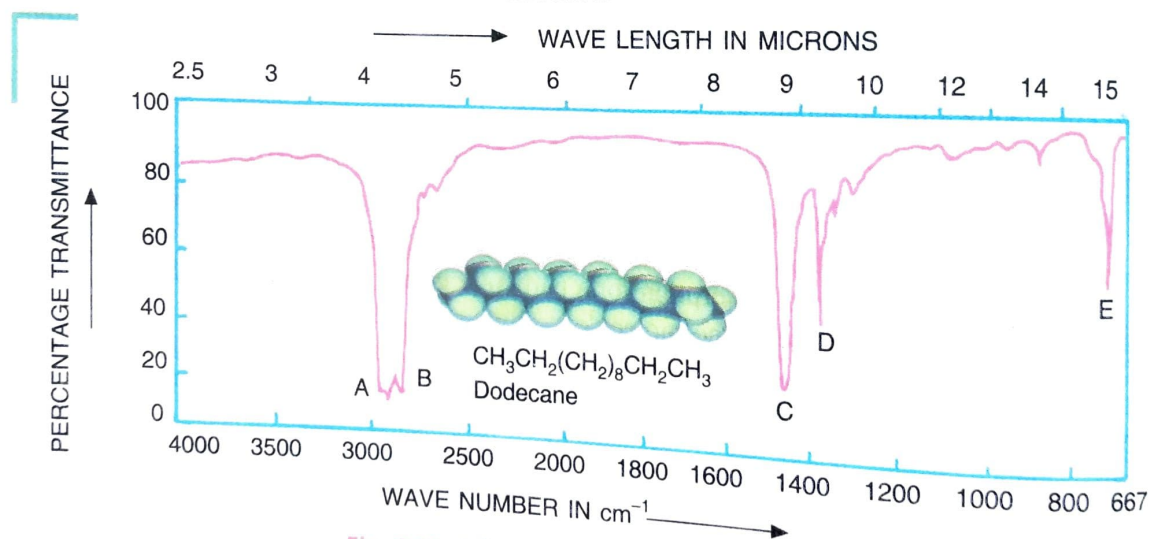


Fig. 3.21. Infra-red spectrum of Dodecane.

Courtesy: Sadtler Research Laboratories, Philadelphia

Positions of some characteristic absorptions

- A = 2962 cm^{-1} ; C—H Str
- B = 2872 cm^{-1} ; C—H Str in CH_3
- C = 1465 cm^{-1} ; C—H_{def}
- D = 1450 cm^{-1} ; C—H def in CH_2
- E = 772 cm^{-1} ; CH_2 (Rocking)

Positions of some characteristic absorptions

- A = 2941 cm^{-1} ; C—H Str.
- B = 2880 cm^{-1} ; C—H Str. in methyl/methylene
- C = 1450 cm^{-1} ; C—H def.
- D = 1372 cm^{-1} ; C—H def. in CH_3

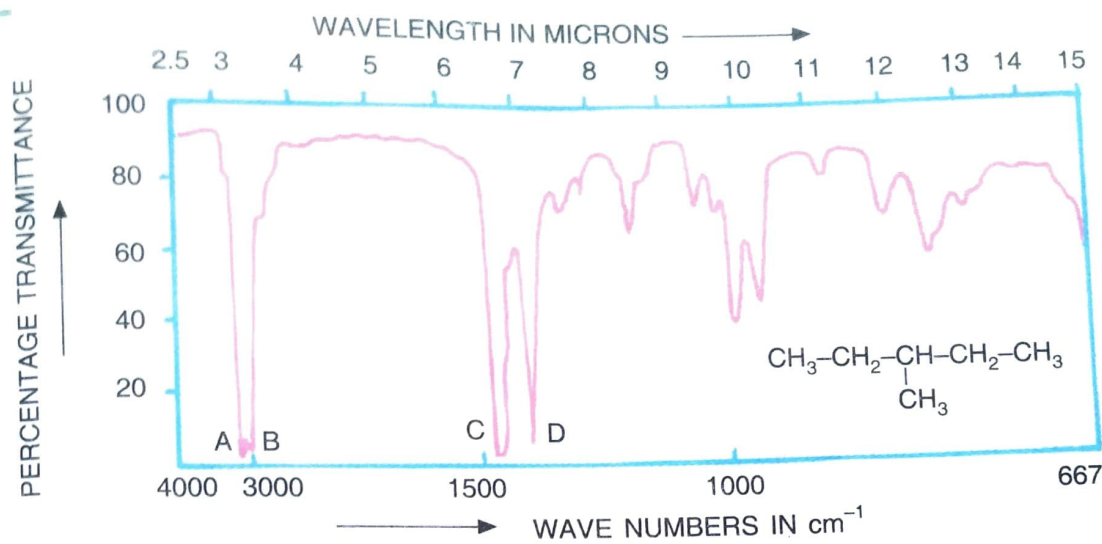


Fig. 3.22. Infra-red spectrum of 3-methyl pentane.

The various C—H bending vibrations in alkanes appear in the region $1485\text{-}1340\text{ cm}^{-1}$. Vibrational absorptions for C—H bonds are much different from C—C bonds due to the large mass differences. C—C linkages are less characteristic and appear as weak bands in the region $1300\text{-}800\text{ cm}^{-1}$. Spectra of isoalkanes differ from those of *n*-alkanes in the region $1500\text{-}700\text{ cm}^{-1}$.

In gem dimethyl [$-\text{C}(\text{CH}_3)_2$], a doublet appears at about 1380 cm^{-1} . An absorption band in the range of $1395\text{-}1385\text{ cm}^{-1}$ appears for $-\text{C}(\text{CH}_3)_2$ group. For aldehydes ($-\text{CHO}$), two weak C—H str* absorptions appear between $2900\text{-}2820\text{ cm}^{-1}$ and $2775\text{ - }2700\text{ cm}^{-1}$.

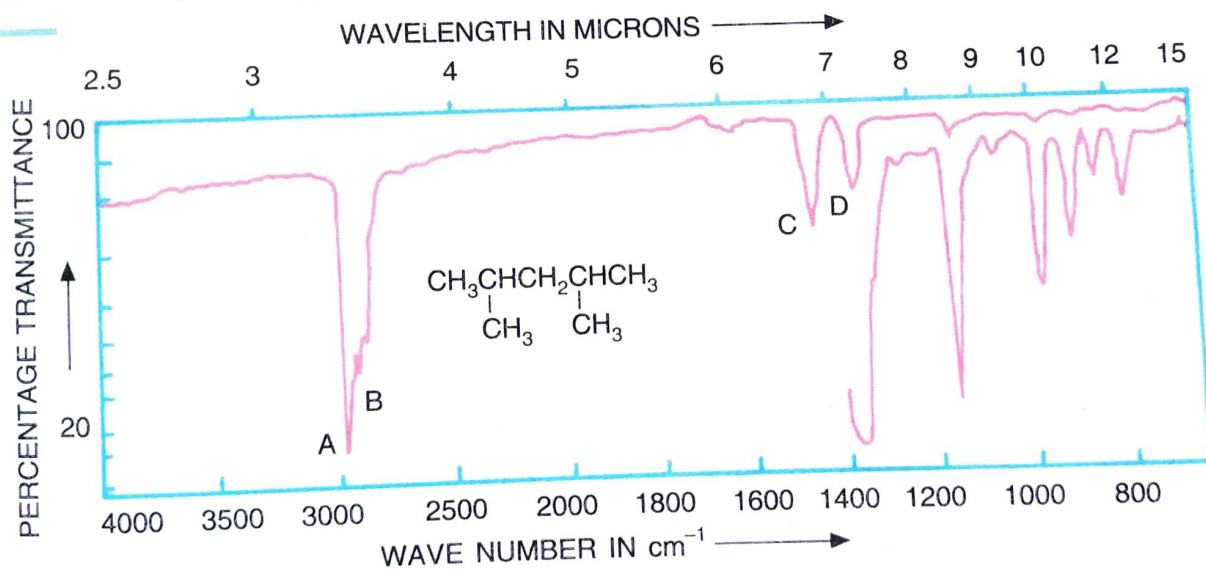


Fig. 3.23. Infra-red spectrum of 2, 4-dimethyl pentane.

Courtesy: Sadtler Research Laboratories, Philadelphia.

Positions of some characteristic absorptions

- A = 2962 cm^{-1} C—H str
- B = 2872 cm^{-1} C—H str in CH_3, CH_2
- C = 1465 cm^{-1} C—H def
- D = 1375 cm^{-1} C—H def (gem dimethyl)

For molecules containing $-\text{OCH}_3, -\text{N}(\text{CH}_3), \text{O}-\text{CH}_2-\text{O}$ etc., C—H str absorption appears below 3000 cm^{-1} .

Table T₃-1.

Group	Type of vibration	Region in cm^{-1} and intensity
C—H	C—H str	2960-2850 (m, s)
	C—H def	1485-1340 (w)
C—C	C—C str	1300-800 (w)
—CH ₂ —	C—H def	1485-1440 (m)
—CH ₃	C—H def	1470-1430 (m)
—C(CH ₃) ₂	C—H def	~1380 (m)
Gem dimethyl		~1365 (s) doublet
—C(CH ₃) ₃	C—H def	1395-1385 (m)
Tert. Butyl		

3.11 A₂ Alkenes

In alkenes (olefines), C—H str absorption band appears in the region 3100-3000 cm^{-1} . Conjugation of double bond with an aromatic ring shows C=C str near 1625 cm^{-1} .

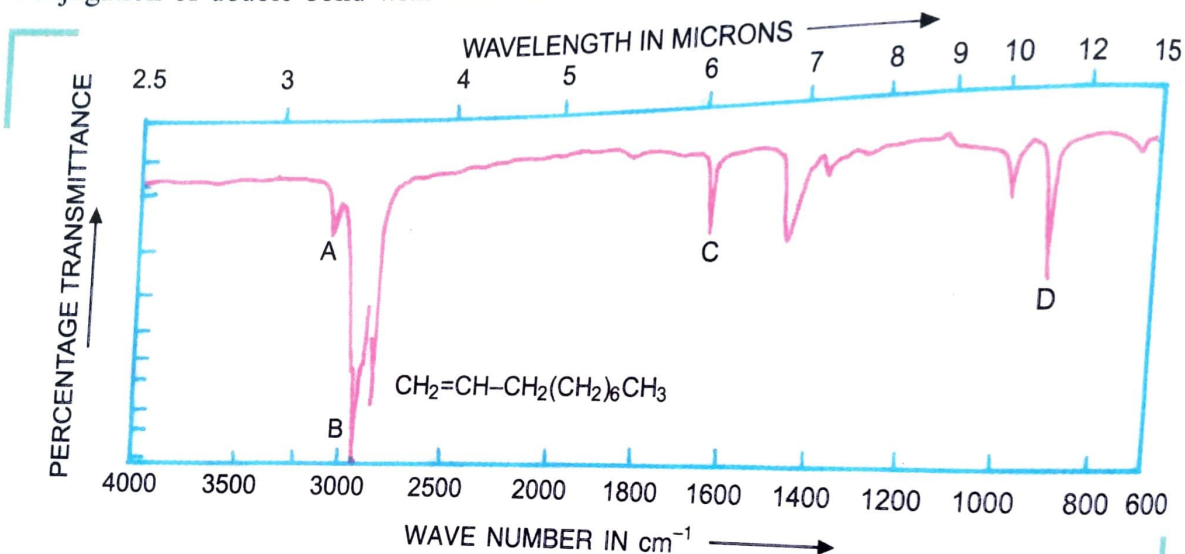


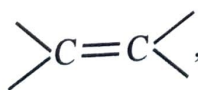
Fig. 3.24. Infra-red spectrum of 1-Decene.

Courtesy. Sadtler Research Laboratories, Philadelphia.

Positions of some characteristic absorptions

- (i) A = 3049 cm^{-1} C—H str in olefins
 B = 2960 - 2850 C—H str in CH_3 , CH_2
 C = 1645 cm^{-1} C=C str
 D = 986 cm^{-1} C—H def out of plane
 E = 720 cm^{-1} Methylene rocking

For trans alkenes, C—H def comes around 970 cm^{-1} and for the corresponding cis isomer, it appears at about 700 cm^{-1} (not much identified). This helps in distinguishing cis and trans alkenes. Conjugated dienes which form a symmetrical molecule as butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) shows one band near 1600 cm^{-1} (C=C stretching). Similar absorptions for molecules without centre of symmetry as 1, 3 Pentadiene appear in the region 1650-1600 cm^{-1} . Cumulative double bonds such as C=C=C shows strong absorption band around 2000-1900 cm^{-1} . For a symmetrical alkene,



, absorption is Raman active due to molecular symmetry.

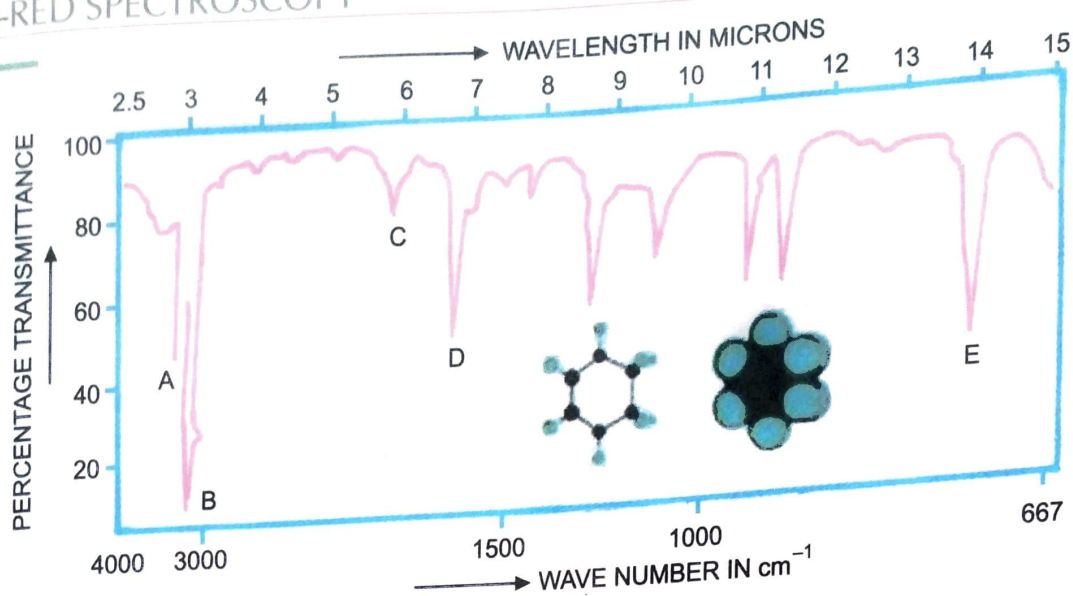


Fig. 3.25. Infra-red spectrum of Cyclohexene.

Positions of some characteristic absorptions

- | | |
|---------------------------|----------------------------|
| A = 3033 cm ⁻¹ | =C—H str |
| B = 2940 cm ⁻¹ | C—H str in CH ₂ |
| C = 1640 cm ⁻¹ | C=C str |
| D = 1435 cm ⁻¹ | C—H def in CH ₂ |
| E = 721 cm ⁻¹ | C—H def. (cis isomer). |

Table T₃-2. Alkenes

Group	Type of vibration	Region in cm ⁻¹ and intensity
Alkenes	>C=C-H str	3100-3000 (<i>m</i>)
Monosubstituted	C—H str	3090-3075 (<i>m</i>)
	C—H def	3040-3010 (<i>m</i>) 700 (<i>s</i>) 915-905 (<i>s</i>)
Disubstituted (Trans)	C—H str	3040-3010 (<i>m</i>)
	C—H def	970-960 (<i>s</i>)
Disubstituted (cis)	C=C str	~1675 (<i>m</i>)
	C—H str	3040-3010 (<i>m</i>)
Trisubstituted	C—H def	~700 (<i>s</i>)
	C=C str	~1660 (<i>m</i>)
	C—H str	3040-3010 (<i>m</i>)
Tetra substituted	C—H def	850-790 (<i>s</i>)
	C=C str	~1670 (<i>m</i>)
Disubstituted (gem)	C=C str	~1670 (<i>m</i>)
	C—H str	3095-3075 (<i>m</i>)
Non-conjugated diene	C—H def	895-875 (<i>s</i>)
	C=C str	~1670 (<i>m</i>)
Conjugated diene	C=C str	1650-1600 (<i>v</i>)
	C=C str	~1600 (<i>w</i>) ~1650 (<i>w</i>)

3.11 A₃ Alkynes

In acetylenes, a strong band for $\text{—C}\equiv\text{C—H}$ str appears at about 3300 cm^{-1} and a weak $\text{C}\equiv\text{C}$ str occurs at about 2200 cm^{-1} . For mono-substituted acetylenes, C—H stretching appears at about 3300 cm^{-1} . This band is strong and narrow and can be distinguished from the hydrogen bonded O—H and N—H stretching occurring in the same region. C—H bending for acetylenes and mono-substituted acetylenes occur at $650\text{--}610\text{ cm}^{-1}$.

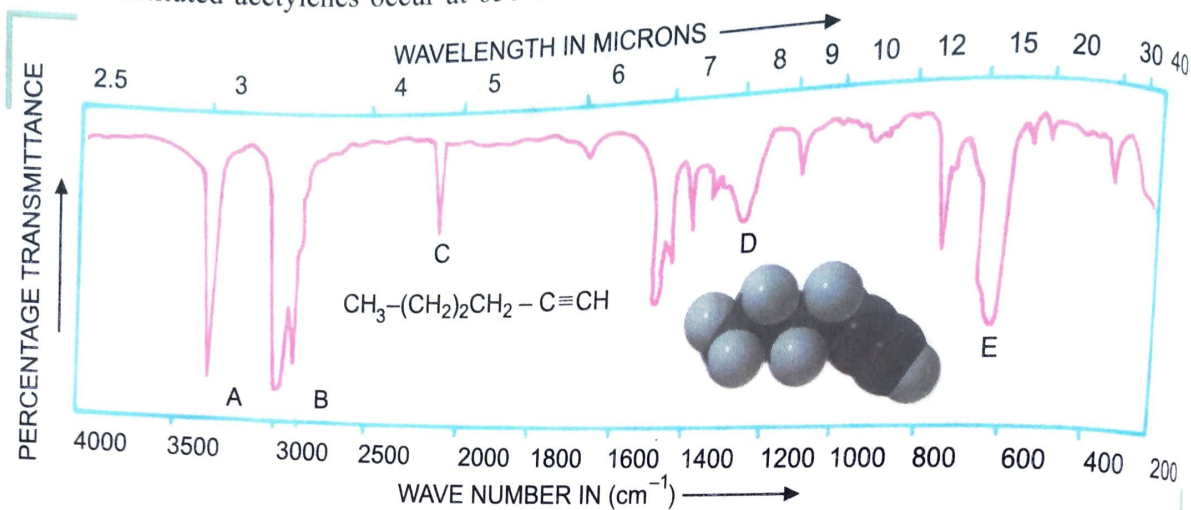


Fig. 3.26. Infra-red spectrum of 1-Hexyne.

Courtesy: Sadtler Research Laboratories, Philadelphia.

Positions of some characteristic absorptions

A = 3268 cm^{-1}	$\equiv\text{C—H}$ str
B = $2940\text{--}2860$	C—H str in CH_3, CH_2
C = 2110 cm^{-1}	$\text{C}\equiv\text{C}$ str
D = 1247 cm^{-1}	$\equiv\text{C—H}$ def (overtone)
E = 630 cm^{-1}	$\equiv\text{C—H}$ def (Fundamental)

3.11 A₄ Cycloalkanes

In cycloalkanes, the value of C—H str increases with the increasing angle of strain in the ring. The asymmetric CH_2 stretching vibrations for cyclopropane is between $3100\text{--}2919\text{ cm}^{-1}$ and that for cyclohexane is 2950 cm^{-1} . With increasing strain in the ring, C—H bending also shows an increase. For example, C—H bending in cyclopentane is at 1455 cm^{-1} while that in cyclohexane is at 1442 cm^{-1} .

Table T₃—3.

Alkynes and Cycloalkanes

Group	Type of vibration	Region in cm^{-1} and intensity
Alkyne	$\text{C}\equiv\text{C—H}$ str	~ 3300 (s)
Monosubstituted	C—H def	$650\text{--}610$ (s)
	$\text{C}\equiv\text{C}$ str	$650\text{--}610$ (s)
Disubstituted	$\text{C}\equiv\text{C}$ str	$2140\text{--}2100$ (m)
	C=C str	$2260\text{--}2200$ (w)
Cycloalkanes	C—H str	$2000\text{--}1900$ (m)
	C—H str	$3100\text{--}2920$ (m)

Its value changes with the change in the angle of strain in the ring. The C—H str. absorption for cyclopropane occurs at a higher wave number as compared to that in cyclohexane.

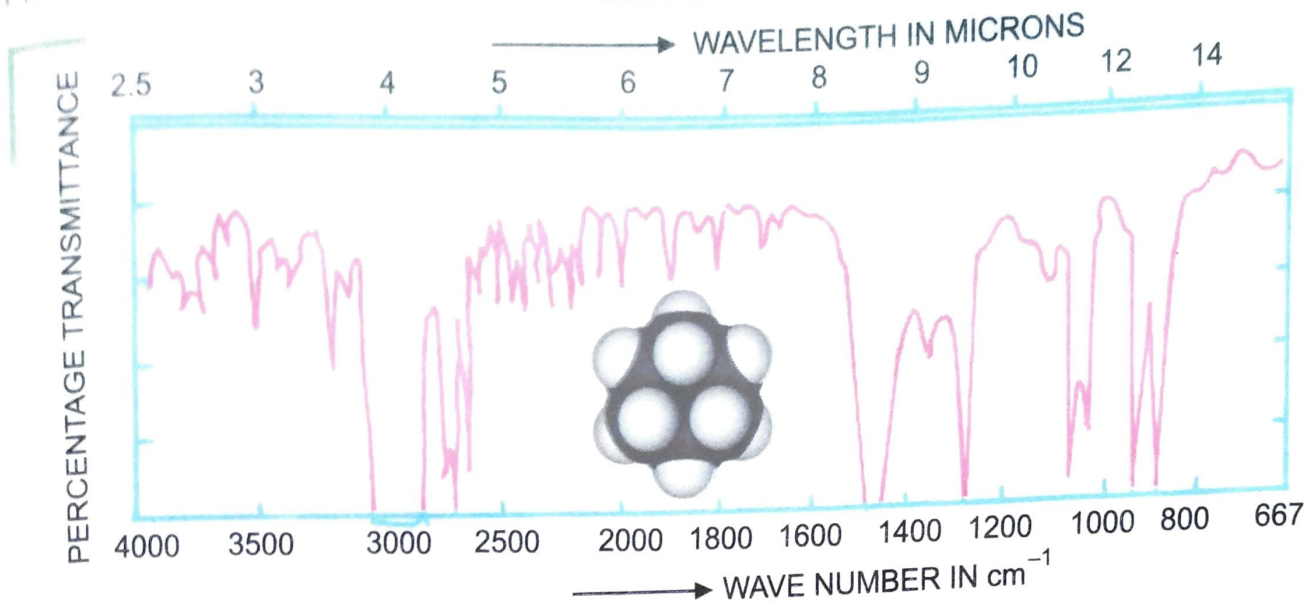


Fig. 3.27. Infra-red spectrum of cyclohexane.

Note. Such a spectrum (cyclohexane) is important as a finger print and can be used for comparison.

3.11 A₅ Aromatic Hydrocarbons

In aromatic hydrocarbons, a variable C—H stretching absorption occurs in the region 3050-3000 cm⁻¹; C=C str at 1650-1450 cm⁻¹ and C—H def vibrations at 900-700 cm⁻¹. For aromatic compounds, the most characteristic C=C stretching bands are at 1600 cm⁻¹, 1580 cm⁻¹, 1500 cm⁻¹ and 1450 cm⁻¹ (*m*). If there is no absorption in this region, it is a fair proof that the compound is not aromatic. Monosubstituted benzene can be easily recognised by bands (i) 710-690 cm⁻¹ (*s*) and at 770-730 cm⁻¹ (*s*). Metasubstituted benzene usually shows two bands (i) 710-690 cm⁻¹ (*m*) and (ii) 800-750 cm⁻¹ (*m*). Ortho and para substituted benzenes show one band each at 770-735 cm⁻¹ (*v, s*) and at 840-800 cm⁻¹ (*m*) respectively.

Table T₃-4. Aromatic Compounds

Group	Type of vibration	Region in cm ⁻¹ and intensity
Aromatic hydrocarbons	Ar—H str	3050-3000 (<i>v</i>)
	C=C str	~1600 (<i>v</i>)
		~1580 (<i>v</i>)
		~1500 (<i>m</i>)
		~1450 (<i>m</i>)
Monosubstituted	C—H def	900-700 (<i>m</i>)
	C—H def	(i) 710-690 (<i>s</i>) (ii) 770-730 (<i>s</i>)
Disubstituted (meta)	C—H def	(i) 710-690 (<i>m</i>) (ii) 800-750 (<i>m</i>)
Disubstituted (ortho)	C—C def	770-735 (<i>v, s</i>)
Disubstituted (para)	C—H def	840-800 (<i>m</i>)

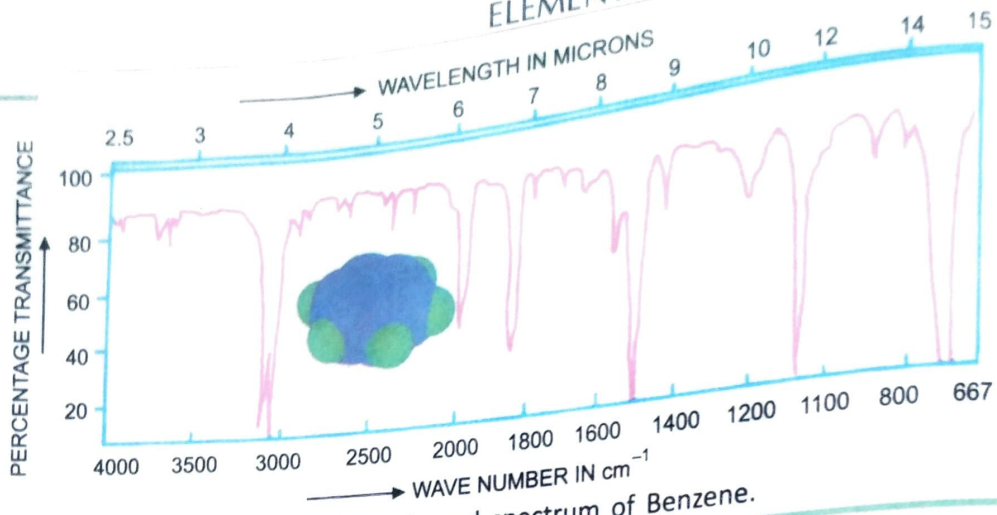


Fig. 3.28. Infra-red spectrum of Benzene.

Exercise. Mark the various bands in the Infra-red spectrum which are most characteristic of benzene.

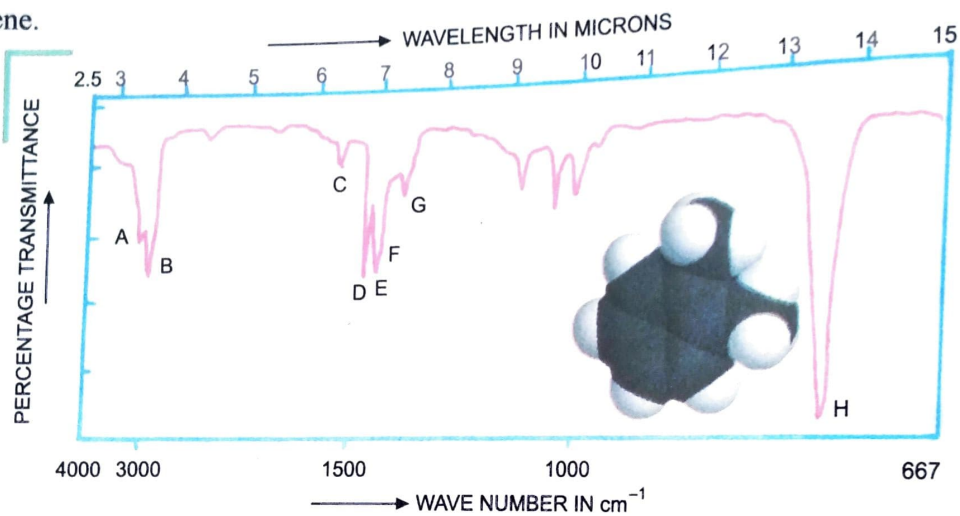


Fig. 3.29. Infra-red spectrum of ortho-Xylene.

Positions of some characteristic absorptions

- | | |
|--|-------------------------------|
| A = 3020 cm^{-1} ; | =C—H str in olefins/aromatics |
| B = 2941 cm^{-1} ; | C—H str |
| C, D, E, F = 1606, 1495, 1460, 1450 cm^{-1} ; | C=C str in aromatic nuclei. |
| G = 1375 cm^{-1} ; | C—H def in methyl |
| H = 745 cm^{-1} ; | ortho-disubstituted benzenes |

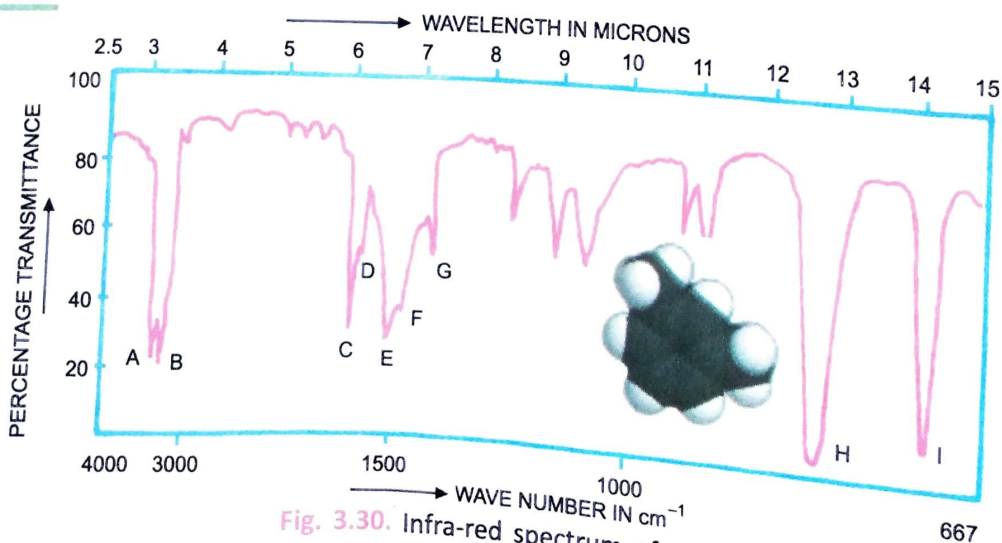


Fig. 3.30. Infra-red spectrum of meta-Xylene.

Positions of some characteristic absorptions

- | | |
|--|-------------------------------|
| A = 3030 cm^{-1} ; | C—H str in olefines/aromatics |
| B = 2940 cm^{-1} ; | C—H str |
| C, D, E, F = 1610, 1585, 1492, 1455 cm^{-1} ; | C=C str in aromatic nuclei. |
| G = 1370 cm^{-1} ; | C—H def in methyl |
| H and I = 770 cm^{-1} ; | meta-disubstituted benzene |

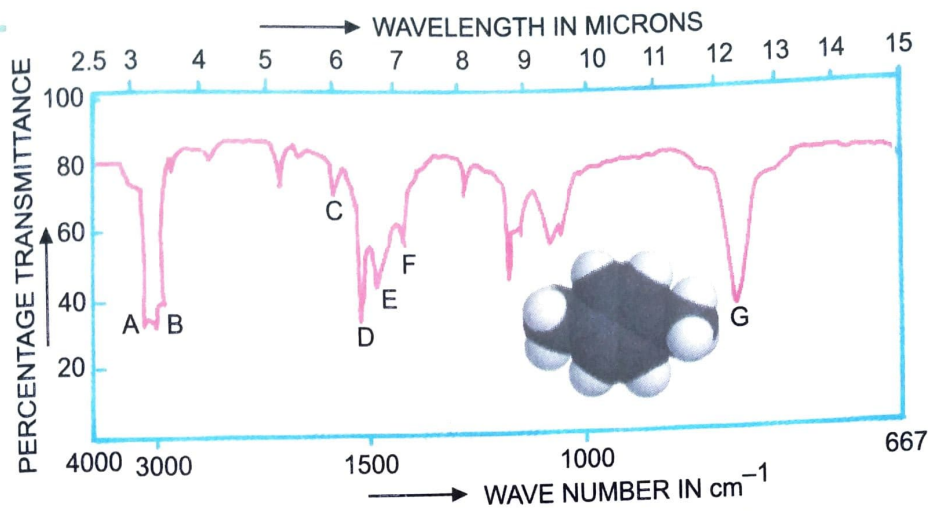


Fig. 3.31. Infra-red spectrum of para- Xylene.

Positions of some characteristic absorptions

- | | |
|---|-------------------------------|
| A = 3030 cm^{-1} ; | =C—H str in olefins/aromatics |
| B = 2940 cm^{-1} ; | C—H str in methyl |
| C, D, E = 1624, 1510, 1450 cm^{-1} ; | C=C str in aromatic nuclei |
| F = 1370 cm^{-1} ; | C—H def |
| G = 802 cm^{-1} ; | Para-disubstituted benzene |

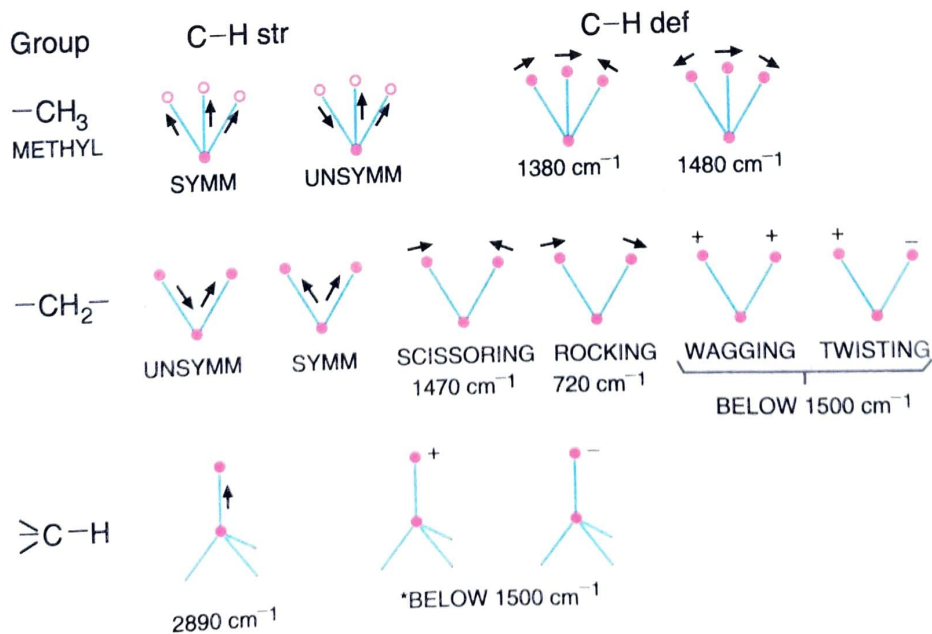
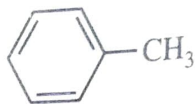


Fig. 3.32. Representation of C—H str and C—H def vibration for

—CH₃, —CH₂— and C—H groups.

(+) and (-) signs indicate vibrations perpendicular to the plane of the paper.

EXAMPLE 6. Write the various infra-red bands in the case of toluene.

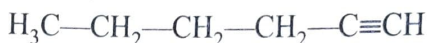


SOLUTION. Some of its important Infra-red bands are :

- | | |
|--|--|
| (i) Ar—H str | ~3030 cm^{-1} |
| (ii) C—H str in CH_3 — | 2850-2960 cm^{-1} |
| (iii) C = C str | ~1600 cm^{-1} , ~1580 cm^{-1} , ~1460 cm^{-1} |
| (iv) C—H bending for monosubstituted benzene | = 730 – 770 cm^{-1} . |

EXAMPLE 7. Describe the various infra-red bands in case of 1-Hexyne.

SOLUTION. The structure of 1-Hexyne is

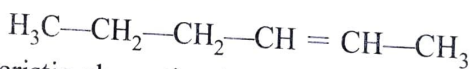


Some of its important absorption bands in Infra-red spectroscopy are :

- | | |
|---|--------------------------------|
| (i) $\equiv\text{C}-\text{H}$ str | ~ 3300 cm^{-1} |
| (ii) C—H str in CH_2 and CH_3 | ~ 2860 – 2950 cm^{-1} |
| (iii) $\text{C}\equiv\text{C}$ str | ~ 2100 cm^{-1} |
| (iv) C—H bending | ~ 1465 cm^{-1} |

EXAMPLE 8. Describe the various characteristic absorption bands in case of 2-Hexene in the Infra-red spectroscopy.

SOLUTION. The structure of 2-Hexene is



Some of its important characteristic absorption bands are :

- | | |
|---|--------------------------------|
| (i) C—H str in alkenes | ~ 3050 cm^{-1} |
| (ii) C—H str in CH_2 and CH_3 | ~ 2860 – 2950 cm^{-1} |
| (iii) C = C str | ~ 1680 cm^{-1} |
| (iv) C—H bending | ~ 1460 cm^{-1} |
| (v) $-\text{CH}=\text{CH}_2$ (for cis, trans) | 700 – 970 cm^{-1} |

PROBLEM P₃-1. An Infra-red spectrum of a hydrocarbon containing 10 per cent hydrogen gave two bands (i) 3295 cm^{-1} and (ii) 625 cm^{-1} alongwith a weak absorption band near 2130 cm^{-1} . What is the probable structure of the compound ?

PROBLEM P₃-2. The Infra-red spectrum of the hydrocarbon containing 14.3 per cent hydrogen gave the following absorption bands :

(i) 3.32-3.29 μ (m), (ii) 10.40 μ (s) and (iii) 5.96 μ (m). What is the probable structure of the compound? Also tell the geometry of this compound.

3.11 B Halogen Compounds

In the halogen compounds, the C—H stretching shifts to higher wave number due to the $-I$ effect of the halogen atom. Due to the $-I$ (inductive) effect of halogen, C—H part of the molecule becomes rich in s-component and hence force constant increases. Greater the electronegativity of the halogen atom, greater is the value of C—H stretching. C—X bonds show lower values of absorption frequencies as compared to C—H bond due to the decreased force constant and increase in the reduced mass. C—X str (X = Cl, Br, I) absorption lies between 800-500 cm^{-1} while in the case of C—F bond, stretching vibrations occur in the region 1400-1000 cm^{-1} .

Bromides and chlorides are best detected by their mass spectra. The asymmetric C—H stretching vibrations of —CH₃ group in CH₃X occur above 3000 cm⁻¹ which is also the region for aromatic and unsaturated compounds.

C—H stretching shifts to higher frequencies in dihalogen and trihalogen derivatives. The detection of halogen by this technique is not reliable as most of the absorptions occur below 650 cm⁻¹.

Table T₃—5. Halogen Compounds

Group	Type of vibration	Region in cm ⁻¹ and intensity
C—Cl	C—Cl str	800-600 (s)
C—Br	C—Br str	600-500 (s)
C—I	C—I str	~ 500 (s)
C—F	C—F str	1400-1000 (s)

The Infra-red spectrum of chlorobenzene is shown below :

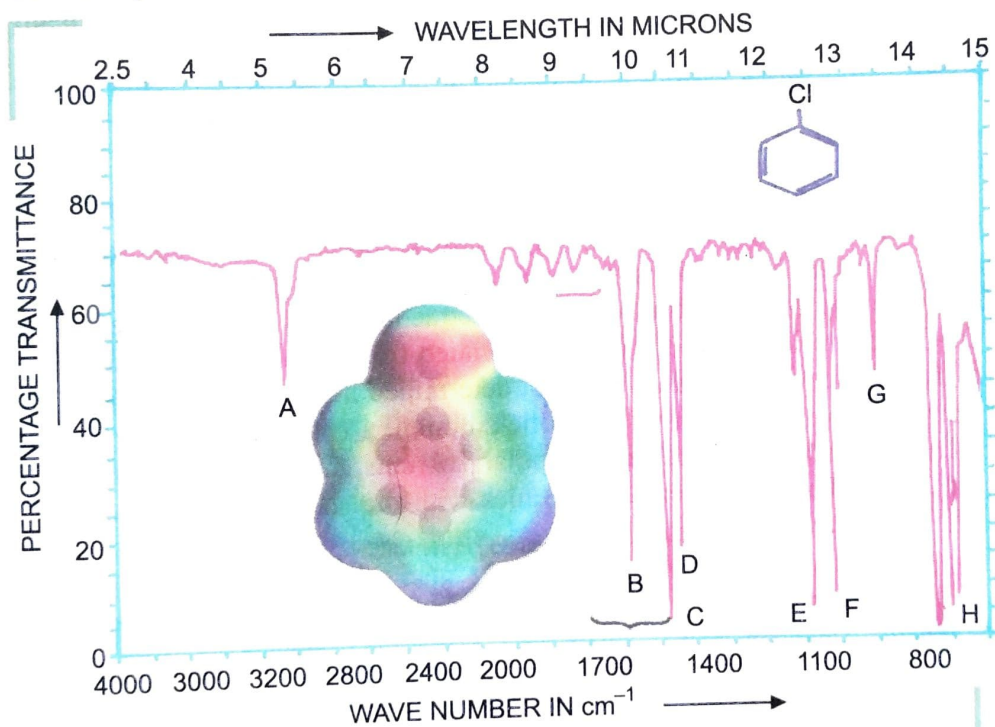


Fig. 3.33. Infra-red spectrum of chlorobenzene.

Positions of some characteristic absorptions

A = 3072 cm⁻¹

B = 1584 cm⁻¹

C = 1478 cm⁻¹

D = 1446

G and H 735 cm⁻¹, 702 cm⁻¹

C—H str (Aromatic)

C=C str

C=C str

C=C str of benzene

C—Cl str

The infra-red spectrum of 2-Bromopropane is shown below :

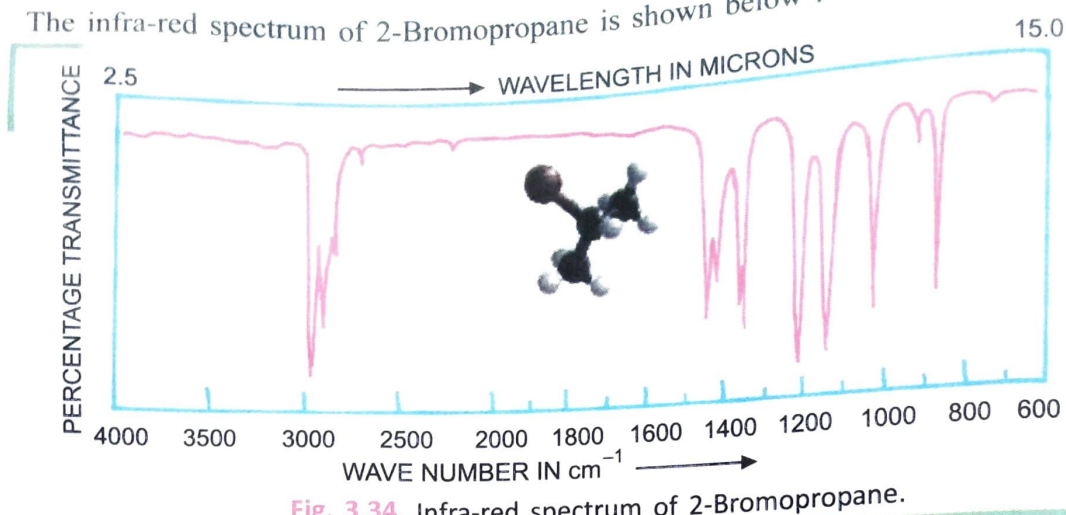


Fig. 3.34. Infra-red spectrum of 2-Bromopropane.

EXERCISE: (Write characteristic absorption peaks of 2-Bromopropane yourself)

In this spectrum, C—H bending vibration of a methyl group is seen as a doublet as two methyl groups are present on the same carbon atom.

3.11 C Alcohols And Phenols

Alcohols and phenols exhibit an excellent property of hydrogen bonding. Due to this reason, O—H stretching bands for such compounds are normally recorded in dilute solutions of the sample in non-associating solvents. A variable sharp band appears in the region $3700\text{--}3500\text{ cm}^{-1}$, when a spectrum of a dilute solution of alcohol in carbon tetrachloride is scanned. Because of its high intensity, the O—H absorption band can be differentiated from the overtones and the combination bands of this region. Spectra for alcohols are best determined in the vapour phase. If the spectrum is taken with increased concentration of alcoholic solution, a sharp band disappears and a broad band at lower frequency appears instead. In polar solvents, O—H str appears at lower wave number due to the association of alcohol molecules with the solvent molecules.

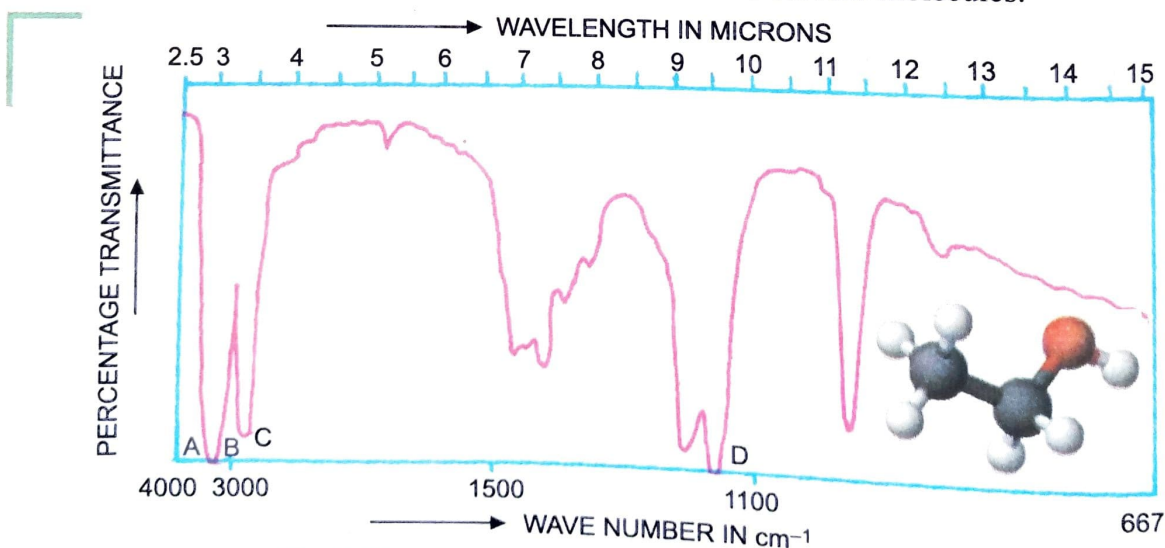


Fig. 3.35. Infra-red spectrum of Ethanol as a film.

Positions of some characteristic absorptions

A = 3330 cm^{-1}	O—H str (hydrogen bonded)
B = 2996 cm^{-1}	C—H str
C = 2924 cm^{-1}	C—H str
D = 1050 cm^{-1}	C—O str (for primary alcohols)

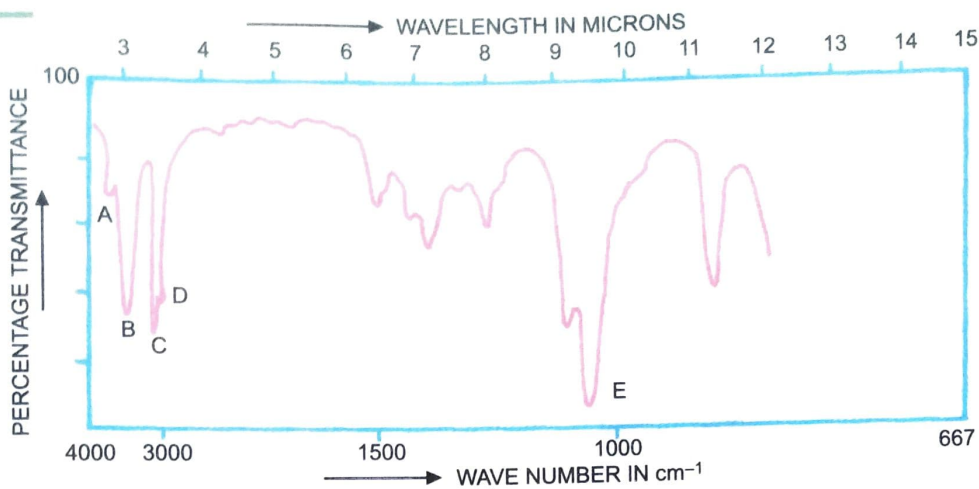


Fig. 3.36. Infra-red spectrum of Ethanol in carbon tetrachloride.

EXERCISE. Mark the various bands in the Infra-red spectrum which are most characteristic of ethanol.

Primary, secondary and tertiary alcohols can be frequently classified from the bands for the coupling vibrations, *i.e.*, C—O str and O—H bending. Primary alcohols show a strong band near 1050 cm^{-1} and secondary alcohols near 1100 cm^{-1} in addition to another strong band at $1350\text{--}1260\text{ cm}^{-1}$. Tertiary alcohols can be distinguished due to the appearance of strong band at 1200 cm^{-1} and another at $1410\text{--}1310\text{ cm}^{-1}$. The strong absorption observed in the spectra of hydroxy derivatives between $1250\text{--}1000\text{ cm}^{-1}$ was assigned to a characteristic absorption of >C—OH group.

The frequency range ($3640\text{--}3600\text{ cm}^{-1}$) decreases alongwith band intensities in the order, primary > secondary > tertiary. It can be expected on the basis of +I effect. In concentrated solution or in the solid state, the O—H str absorption band becomes broader and sharper and occurs at lower wave number. **Thus, the absorption maximum for O—H stretching depends upon concentration, nature of the solvent and temperature.** In case, an alcohol is branched heavily in the α -position, the absorption band corresponds to the free O—H group. In intermolecular hydrogen bonded molecules, absorption shifts are concentration dependent. The O—H stretching absorption band appears at $3570\text{--}3450\text{ cm}^{-1}$ in compounds which show intramolecular hydrogen bonding. For such molecules, there is no absorption shift on diluting the sample. For chelate molecules such as mono-carboxylic acids existing as dimers, hydrogen bonded structure is stabilised by resonance. Thus, O—H str absorption appears as a broad band between $3000\text{--}2500\text{ cm}^{-1}$.

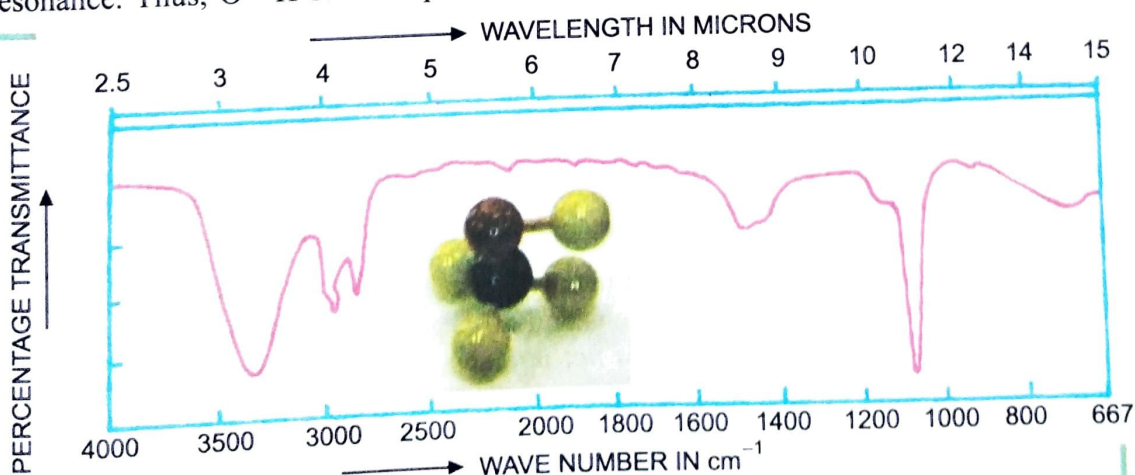


Fig. 3.37. Infra-red spectrum of Methanol.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of methanol.

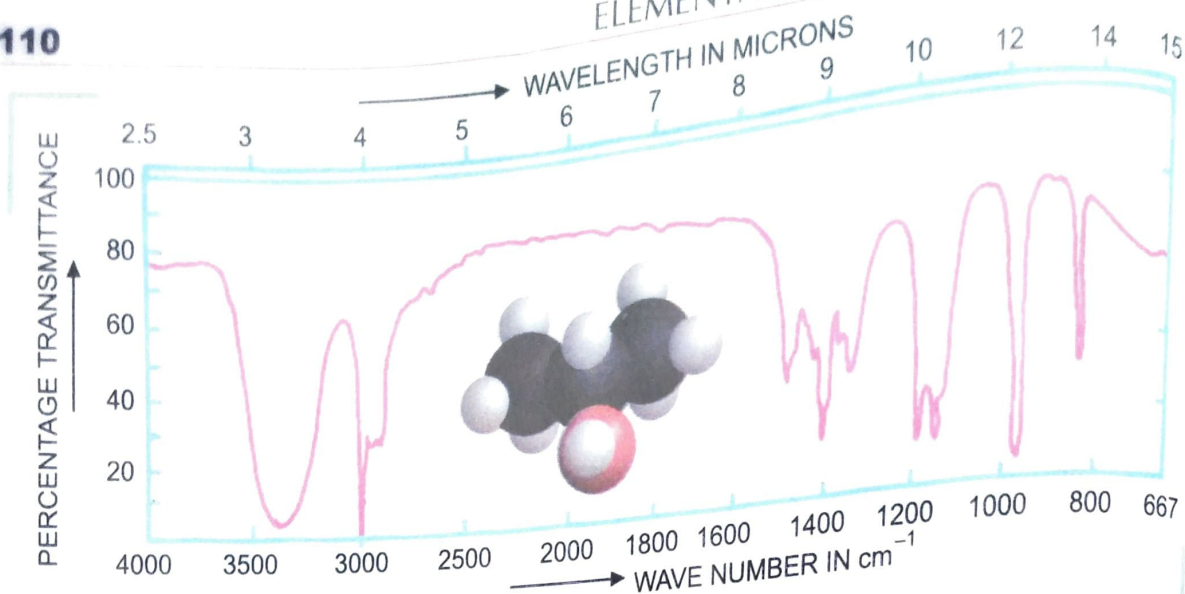


Fig. 3.38. Infra-red spectrum of Propan-2-ol.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of propan-2-ol.

The axial or the equatorial position of the O—H group in cyclohexanols can also be detected. The frequency of the axial hydroxyl group is higher than that of the equatorial. This can be explained by repulsion between the groups in the 1, 3 positions of the cyclohexane ring, hindering the vibration of the oxygen atom responsible for the increase in force constant of the O—H bond. It may be noted that in equatorial O—H groups, the motions are less restrained. Consider the case of 1, 2, cyclohexane diols (chair form). In cis-form, one of the two OH groups is axial and the other is equatorial while in the trans-form, both are either axial or equatorial. In trans 1, 2 cyclohexane diol, the distance OH.....O calculated for axial conformation (*a, a*) is about 3.3 Å and for equatorial conformation, (*e, e*), it is 2.34 Å. The spectra for trans 1, 3, cyclohexane diol shows a band for bonded OH at 3602 cm^{-1} . Clearly, the molecule exists in equatorial conformation which is energetically more favoured.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of 2-methyl cyclohexanol.

In phenols, the frequency of the free O—H str lies near 3600 cm^{-1} . In addition to the usual band for O—H str, phenols show characteristic strong C—O str band near 1200 cm^{-1} and another at 1410-1300 cm^{-1} . Phenols form intermolecular hydrogen bonds more readily than alcohols. Hydroxyl group in the associated form absorbs at 3500-3300 cm^{-1} . As in alcohols, the value of frequency shift in phenols provides information as regards the strength of the hydrogen bonds and also the type of association. It was shown that in concentrated solutions, meta and para substituted monoalkyl phenols form polymeric associations and absorption occurs near 3322 cm^{-1} (bonded region). *The strength of the hydrogen bond is not influenced by the nature or the volume of the substituents in these positions (e.g., substituent group may be methyl or the tertiary butyl).* Compared with alcohols, phenol can be classified as sterically hindered, partially hindered and normal. If the phenol is substituted in the ortho positions, it is said to be sterically hindered and we cannot expect

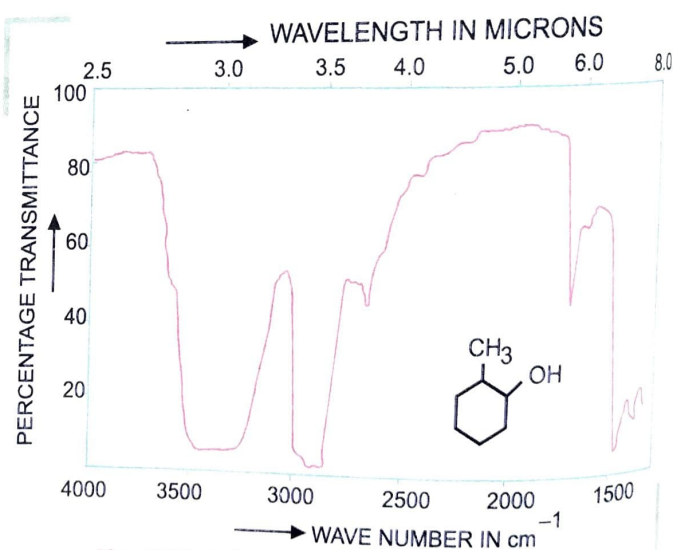


Fig. 3.39. Infra-red spectrum of 2 methyl

Absorption shifts to higher wave-number on dilution.

Absorption shift on dilution.

absorption in the bonded region. Thus, the spectrum for such a compound shows a strong band corresponding to free hydroxyl group near 3640 cm^{-1} . If a single alkyl group is present in the ortho position in phenol, the absorption shows a slight downward shift. Spectra of ortho substituted phenols (capable of forming hydrogen bonds with —OH group), show a free OH band along with another band arising from intramolecularly bonded O—H group. In such a case, bonded O—H band has a lower frequency of absorption. Di and poly hydroxylic phenols with adjacent O—H groups form intramolecular hydrogen bonds. Catechol in dilute solution shows two bands at 3610 cm^{-1} (due to free O—H group) and another at 3570 cm^{-1} (due to intramolecularly bonded O—H group).

Table T₃—6. Alcohols and Phenols

Group	Type of Vibrations	Region in cm^{-1} and intensity
Alcohols		
Free O—H group	O—H str	3700-3500 (v, sh)
Intermolecular hydrogen bonded OH* (Polymeric association)	O—H str	3400-3200 (v, b)
Intramolecular hydrogen bonded OH**	O—H str	3570-3450 (v, sh)
Chelate compounds	O—H str	3000-2500 (w, b)
Primary alcohols	C—O str	(i) 1350-1260 (s) (ii) ~1050 (s)
Secondary alcohols	C—O str	(i) 1350-1260 (s) (ii) ~ 1100 (s)
Tertiary alcohols	C—O str	(i) 1400-1310 (s) (ii) ~ 1150 (s)
Cis-1, 2 cyclohexanediol	O—H str	(i) 3626 (free) (ii) 3600 (bonded)
Phenols	C—O str	(i) ~1200 (s) (ii) 1410-1300 (s)

PROBLEM P₃-3. An organic compound (Molecular weight = 108) gave the following peaks in its Infra-red spectrum :

3401 cm^{-1} (s, b); 3077 cm^{-1} (w), 2899 cm^{-1} , 1499 cm^{-1} (w, sh) and 1456 cm^{-1} , (m, sh). With alkaline potassium permanganate, it is oxidised to an acid. It gives a negative test with ferric chloride solution.

The infra-red spectrum of Phenol is given below :

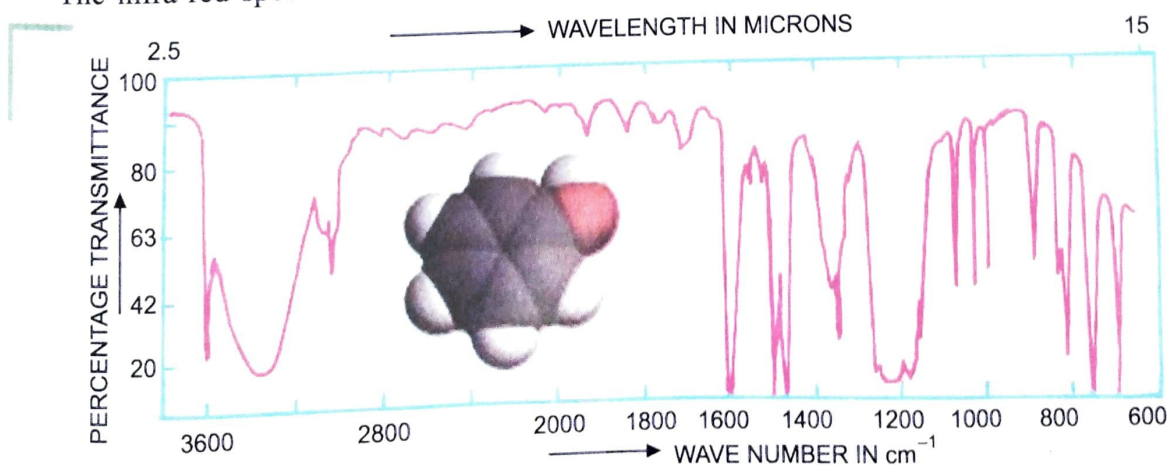


Fig. 3.40. Infra-red spectrum of Phenol. (Courtesy : Research laboratories, Division of Bio-Rad Laboratories)

EXERCISE. Explain some important characteristic absorptions in the above spectrum.

The Infra-red spectrum of Benzyl alcohol is shown below :

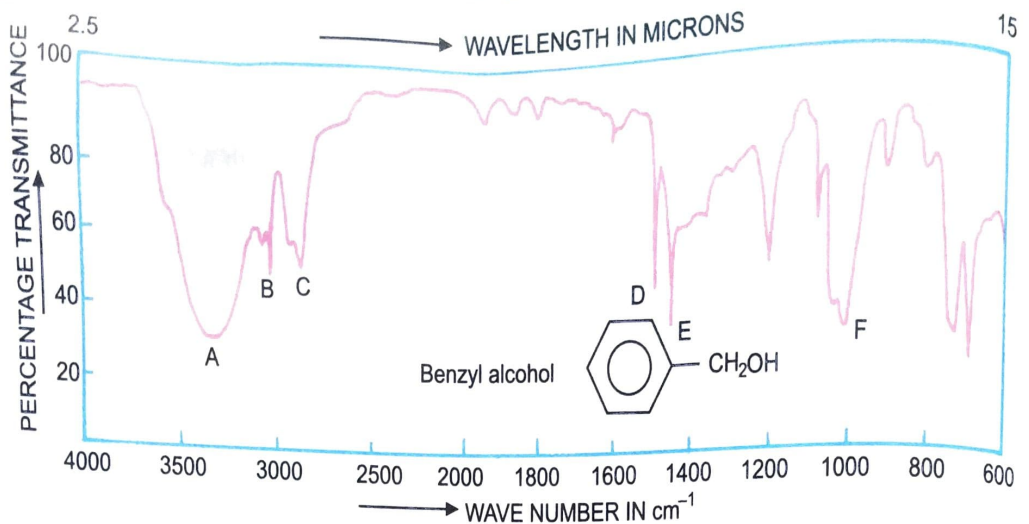


Fig. 3.41. Infrared spectrum of Benzyl alcohol. (Courtesy : Sadtler Research Laboratories)

Positions of some characteristic absorptions

A = 3330 cm^{-1}	O—H str (broad, H-bonding)
B = 3100 – 3000 cm^{-1}	C—H str (Aromatic)
C = 2980 – 2840 cm^{-1}	C—H str (in methylene)
D, E = 1580, 1460 cm^{-1}	C=C str (Aromatic)
F = 1017 cm^{-1}	C—O str (1° -alcohol)

The Infra-red spectrum of *p*-cresol is given below :

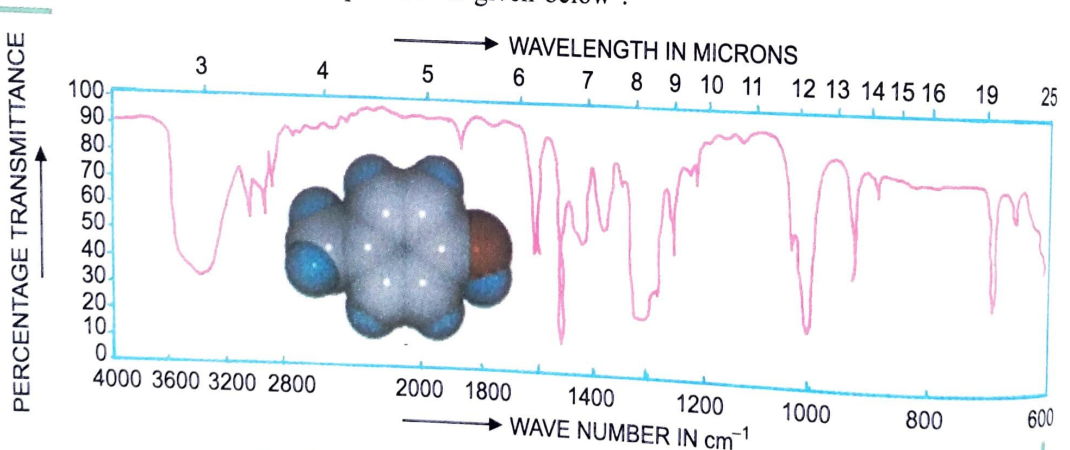


Fig. 3.42. Infra-red spectrum of *p*-cresol (liquid-neat)

EXERCISE. Mark some important characteristic absorptions in the above spectrum.

3.11 D Ethers

Ethers are derivatives of alcohols and show characteristic C—O—C bands. Since the masses of C—C and C—O are comparable, their force constants are quite close. But due to the large difference in their dipole-moments, the C—O bonds are stronger as compared to C—C bonds. Ethers show only one characteristic band in the region 1300-1050 cm^{-1} . The identification of ether in an unknown compound is difficult in presence of another oxygenated compound because many

other strong bands appear in the same region. Saturated aliphatic ethers show a strong band in the region $1150-1070\text{ cm}^{-1}$ for asymmetric C—O—C stretching and another at 940 cm^{-1} for symmetrical stretching. The C—O—C absorption spectrum of higher members lie in the broader region $1250-1070\text{ cm}^{-1}$. Keto ethers and esters are difficult to distinguish since both are identified for the values of C = O stretching and C—O stretching.

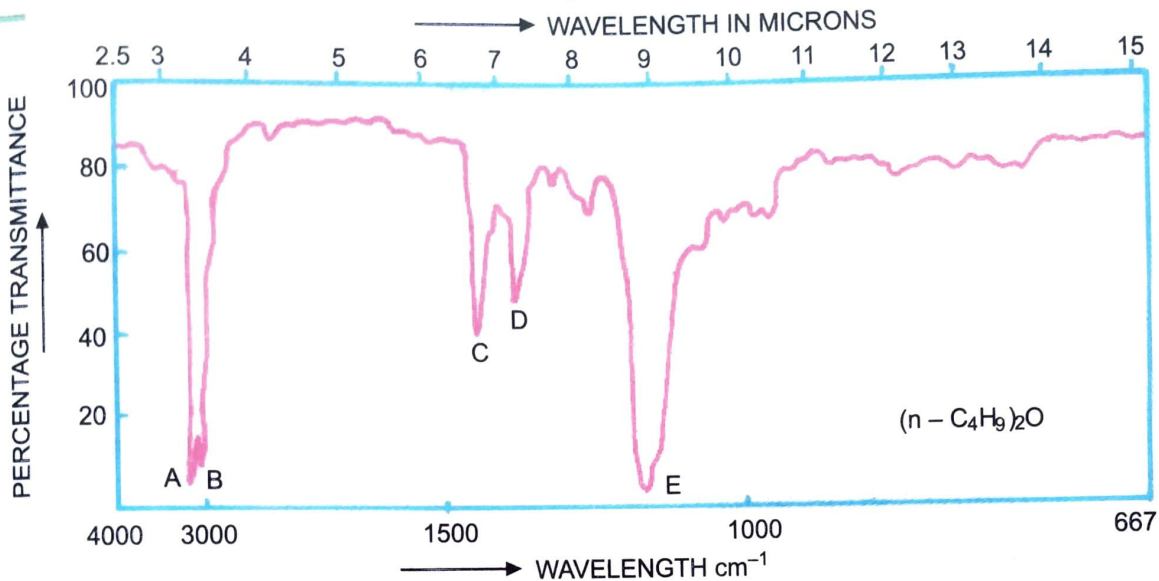


Fig. 3.43. Infra-red spectrum of di-*n*-butyl ether.

Positions of some characteristic absorptions

- A = 2960 cm^{-1} C—H str in methyl
- B = 2880 cm^{-1} C—H str
- C = 1462 cm^{-1} C—H def methyl/methylene.
- D = 1372 cm^{-1} C—H def in methyl.
- E = 1124 cm^{-1} C—O str in C—O—C group

Table T₃-7. Ethers

Group	Type of vibrations	Region in cm^{-1} and intensity
	C—O str	$1150-1070$ (s)
C—O—CH_3	C—H str	$2850-2810$ (m)
	C—O str	~ 1250 (s) ~ 910 (s) ~ 800 (s)
C=C—O—C	C—O str	$1070-1020$ (s) $1270-1200$ (s)

The Infra-red spectrum of Phenetole is given below :

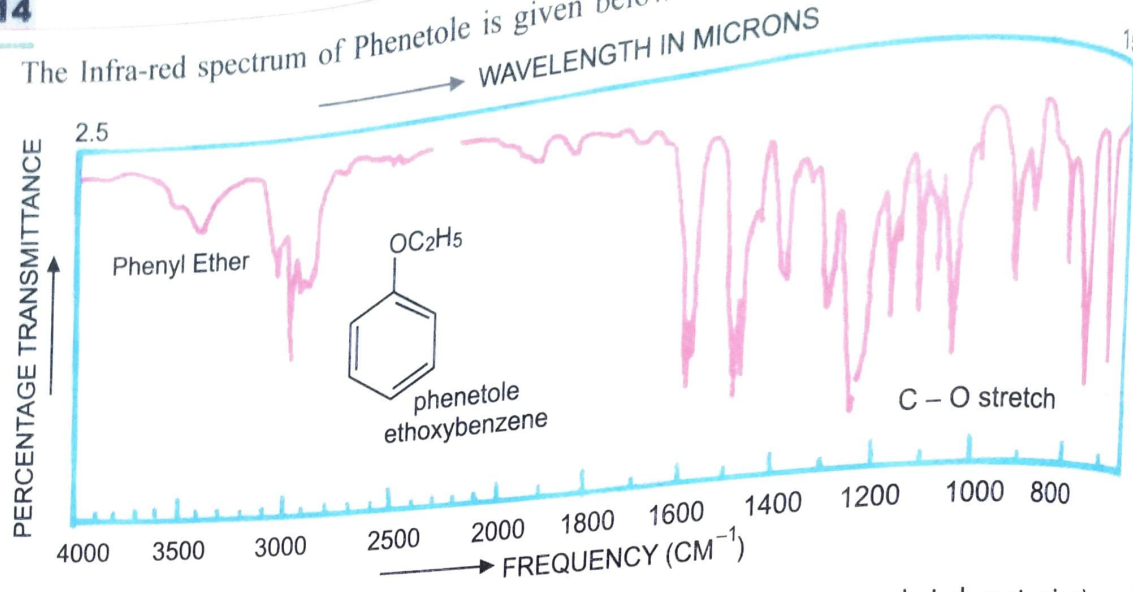
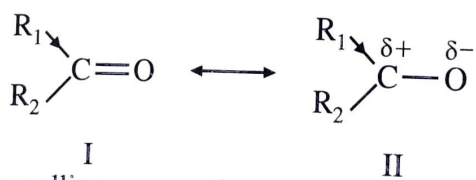


Fig. 3.44. Infra-red spectrum of Phenetole. (Courtesy : Sadtler Research Laboratories)

Mark some important characteristic absorptions in the above spectrum.

3.11 E Carbonyl Compounds

The appearance of a strong band in the spectrum between $1650-1950\text{ cm}^{-1}$ shows the presence of a carbonyl group in the compound. It is due to $\text{C}=\text{O}$ str and is the most representative type of vibration localised in an individual bond. After detecting the carbonyl group, the next step is to examine other peaks in the spectrum for the determination of the exact functional group viz. aldehyde, ketone, ester, amide, quinone etc. Greater the number of peaks in the spectrum, easier becomes the detection. The frequency of absorption due to the carbonyl group depends mainly on the force constant which in turn depends upon inductive effect, conjugative effect, field effect and steric effects. All these effects operate simultaneously. A carbonyl compound can be written in the following two forms :



If R_1 and R_2 are electron repelling groups, the structure II is favoured, the force constant (also bond order) is lowered and absorption occurs at lower wave number. If R_1 or/and R_2 is/are electron withdrawing group/groups, then under its/their influence, the structure I is favoured. Clearly, the force constant for structure I is more and hence absorption occurs at higher wave number. The position of absorption is also sensitive to unsaturation. $\text{C}=\text{O}$ stretching for α, β -unsaturated ketones occurs at a lower frequency as compared to its saturated analogue. Aryl ketones show $\text{C}=\text{O}$ stretching absorption at a lower wave number as compared to aliphatic ketones. The position is raised with the decrease in the size of the ring.

3.11 E₁ Aldehydes and Ketones

Due to the large +I effect operating in ketones as compared to that in aldehydes, the latter usually absorb at higher wave number as compared to the former. The $\text{C}=\text{O}$ stretching absorption for formaldehyde (HCHO), acetaldehyde (CH_3CHO) and acetone (CH_3COCH_3) are $1750, 1745$ and 1718 cm^{-1} respectively. Aldehydes can be easily distinguished from ketones due to the presence of two weak $\text{C}-\text{H}$ str (asymm. and symm.) absorption bands—one near 2820 cm^{-1} and the other near 2720 cm^{-1} .

Usually, the band at higher wave number is not observed if there is another C—H str due to some other part of the molecule. Ketones exist in equilibrium with their enolic forms. The enolic form can be detected by a broad band in the bonded O—H region and another at a very low C=O stretching frequency. Lower the value of the carbonyl frequency, greater is the enolic content in equilibrium. In case of some electron withdrawing groups which also cause α , β -unsaturation, viz., alkenyl, alkynyl, aryl etc., the conjugative effect dominates over inductive effect and the result is the net decrease in the wave number of carbonyl absorption.

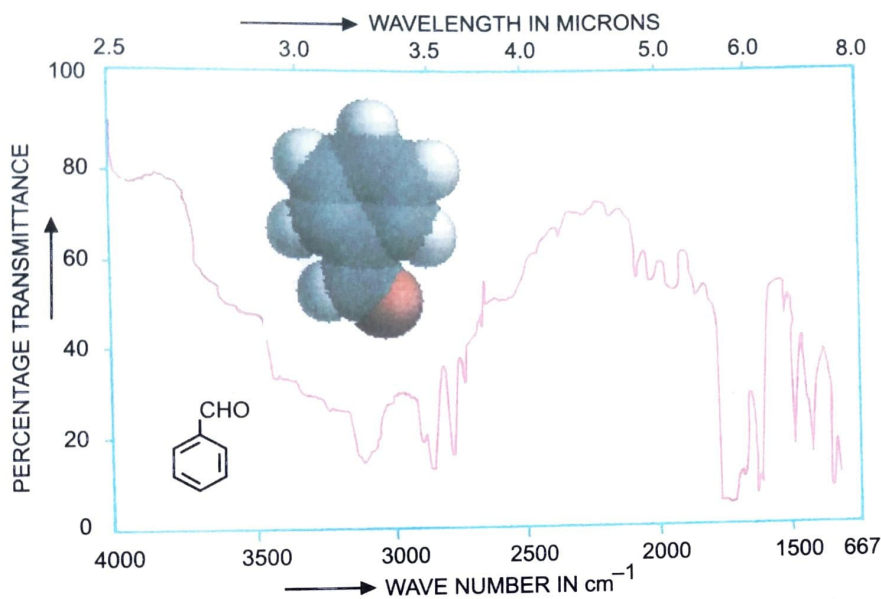
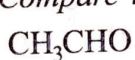


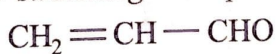
Fig. 3.45. Infra-red spectrum of Benzaldehyde (higher).

EXERCISE. Mark some characteristic absorptions in the Infra-red spectrum of Benzaldehyde.

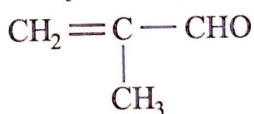
EXAMPLE. Compare the $\nu_{\text{C=O}}$ stretching absorption in the following compounds:



(I) 1745 cm^{-1}



(II) 1723 cm^{-1}



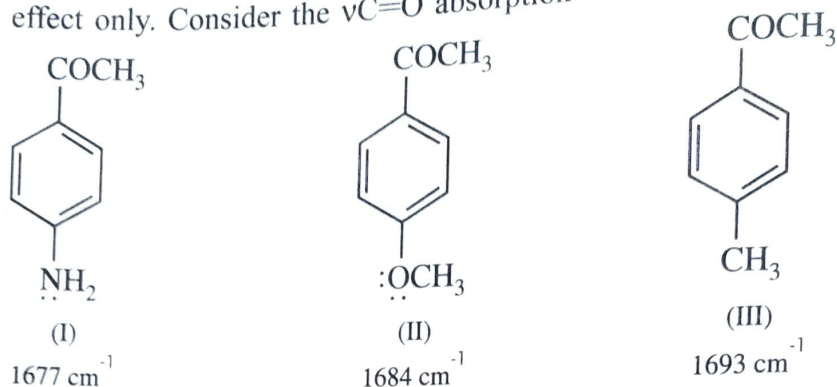
(III) 1702 cm^{-1}

In II, conjugative effect dominates over $-I$ effect and absorption occurs at a low wave number. In III, both conjugative and $+I$ effect (due CH_3 group) operate in the same direction and help in still lowering the wave number of absorption.

In cyclic ketones, $\nu_{\text{C=O}}$ absorption increases as the size of the ring decreases (ring strain increases). Cyclopropanone shows carbonyl absorption at 1855 cm^{-1} . Cyclobutanone at 1788 cm^{-1} and cyclopentanone at 1746 cm^{-1} . Cyclohexanone absorbs at almost the same wave number at which acyclic saturated ketones absorb. A rise in $\nu_{\text{C=O}}$ with decrease in the ring size is due to the changes in the state of hybridisation in small rings. As the ring size decreases, the ring bonds become enriched in p -component and C=O bond acquires greater s -character. Hence, force constant for C=O bond increases and also the wave number of absorption rises. With α , β -unsaturation, the said absorption frequency is lowered by about 30 cm^{-1} . Consider the spectra of cyclohexanone and 2-cyclopentenone. Due to α , β -unsaturation in 2-cyclopentenone, the downward shift corresponding to cyclopentenone is to the extent of nearly 30 cm^{-1} and both absorb at nearly the same wave number.

The $\nu_{\text{C=O}}$ absorption for aryl ketones is lower than that in alkyl ketones reaching a minimum value in p -N, N-dimethyl amino benzophenone. In aryl alkyl ketone, the $+I$ effect due to alkyl

group has an additional effect besides conjugation of C=O with the ring. $\nu_{\text{C=O}}$ absorptions in these compounds occur near 1690 cm^{-1} . For ortho and para substituted ketones, frequency shift is due to inductive effect only. In meta substituted compounds, frequency shift is due to conjugative effects play a significant role. Consider the $\nu_{\text{C=O}}$ absorption in the following compounds.



In (I) and (II) the lone pair of electrons on nitrogen and oxygen atom are involved in conjugation with the ring. The electron pair on nitrogen atom is more labile and is more readily available for conjugation with the ring. These groups (NH_2 , $-\text{OCH}_3$) facilitate conjugation by the electron release and hence $\nu_{\text{C=O}}$ absorption occurs at a lower wave number. In III, methyl group in para position causes +I effect and brings down the absorption to occur at 1693 cm^{-1} .

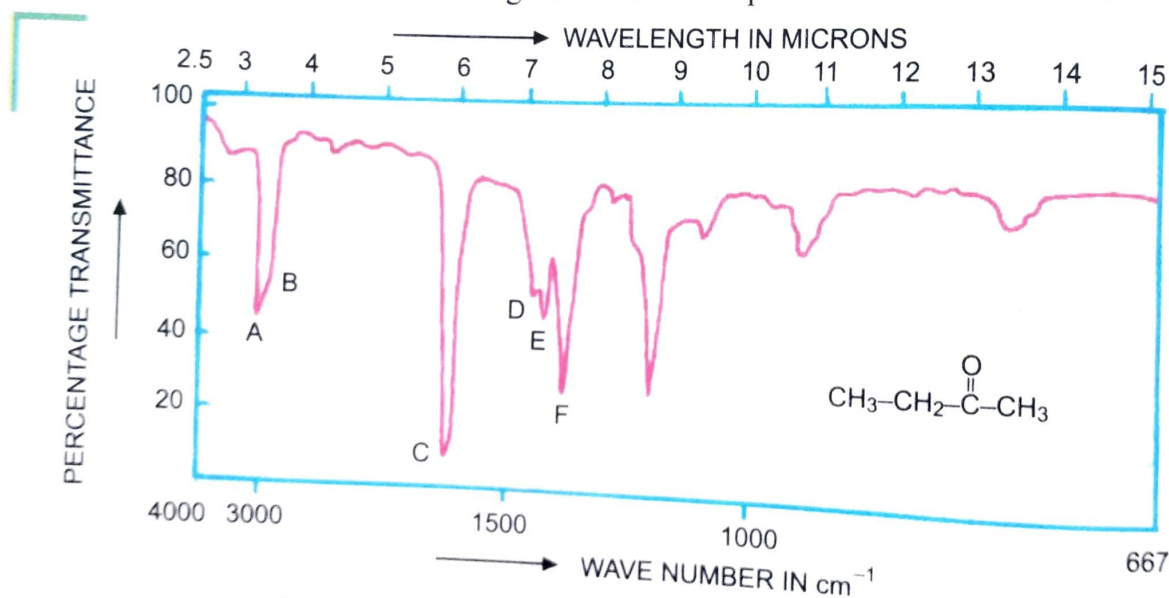


Fig. 3.46. Infra-red spectrum of Ethyl methyl ketone.

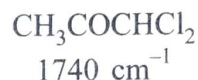
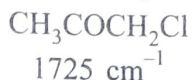
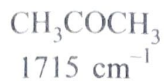
Positions of some characteristic absorptions

- | | |
|---------------------------|------------------------------|
| A = 3002 cm^{-1} | C—H str in methyl/methylene. |
| B = 2940 cm^{-1} | C—H str |
| C = 1715 cm^{-1} | C = O str |
| D = 1450 cm^{-1} | C—H def in methyl/methylene |
| E = 1406 cm^{-1} | C—H def in $-\text{CH}_2-$ |
| F = 1360 cm^{-1} | C—H def in $-\text{CH}_3$. |

In α -chloro and α -bromo ketones, the $\nu_{\text{C=O}}$ absorption is about 20 cm^{-1} higher than the corresponding non-halogenated compound. The electro-negative halogen atom changes the electron distribution in C = O group by -I effect and field effect.

* Field effect is the electrostatic effect which is transmitted...

Note the $\nu\text{C} = \text{O}$ absorption in the following compounds taken in the liquid phase.



The spectra of α -halogenated cyclic ketones are particularly interesting in establishing the configuration of the halogen atom. In α -halogeno-cyclohexanone, the equatorial halogen atom is practically eclipsed by the carbonyl group which has a trigonal geometry. If halogen atom is axial, then it must be in the staggered position relative to the carbonyl oxygen atom. In a conformation in which halogen atom is equatorial, the almost parallel dipole of $\text{C}-\text{X}^{**}$ and $\text{C} = \text{O}$ bonds result in the rise of $\nu\text{C} = \text{O}$ absorption by 20 cm^{-1} whereas no shift in the $\nu\text{C} = \text{O}$ absorption is caused when halogen is in the axial position. Consider the spectra of cis and trans 2-bromo-4-tert butyl cyclohexanone. The bulky tert butyl group must be in the equatorial position.

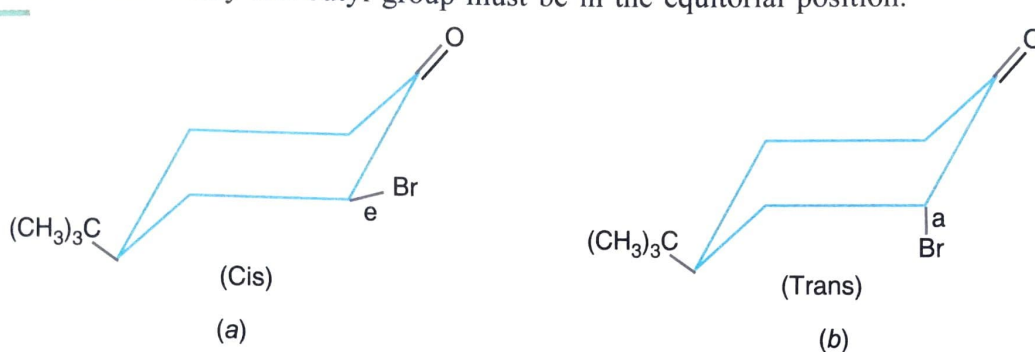
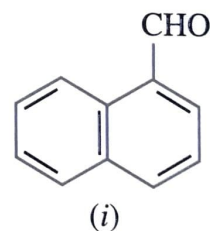


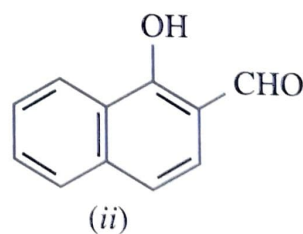
Fig. 3.46 (a). 2-Bromo-4-tert. butyl Cyclohexanone.

When bromine atom is equatorial, it (form *a*) becomes cis and $\nu\text{C} = \text{O}$ absorption is raised by about 20 cm^{-1} . When bromine atom is axial (form *b*), the configuration is trans which does not show any $\nu\text{C} = \text{O}$ shift from the normal value.

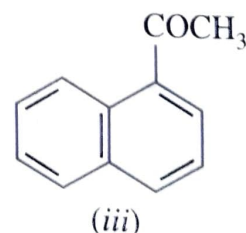
$\nu\text{C} = \text{O}$ 1700 cm^{-1} , lowering is due to conjugation of $\text{C}=\text{O}^*$ with the ring.



$\nu\text{C} = \text{O}$ 1651 cm^{-1} , lowering is due to conjugation as well as intramolecular hydrogen bonding.



$\nu\text{C} = \text{O}$ 1685 cm^{-1} , lowering is due to conjugation of $\text{C} = \text{O}$ with the ring.

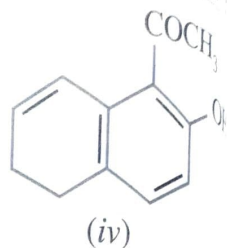


* Field effect is the electrostatic effect which is transmitted through space.

* Normal value of $\nu\text{C} = \text{C}$ absorption is more for aldehydes as compared to the corresponding ketones.

** X is a halogen atom.

$\nu_{C=O}$ 1625 cm^{-1} , lowering is due to conjugation as well as intramolecular hydrogen bonding.



In hydroxy aldehydes and ketones, intramolecular hydrogen bonding lowers the $\nu_{C=O}$ and ν_{O-H} absorptions. In saturated hydroxy ketones, the intra-molecular hydrogen bonds give a strong O—H band in the region 3400-3200 cm^{-1} . Note the $\nu_{C=O}$ absorptions in the compound (Fig. 3.47).

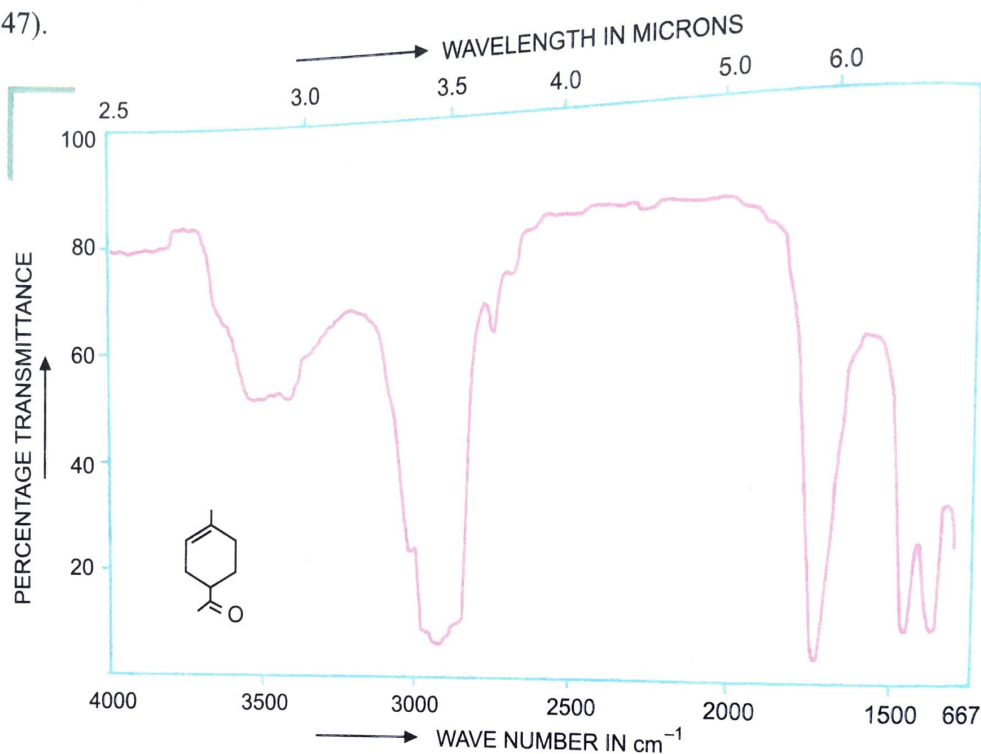


Fig. 3.47. Infra-red spectrum of 1-acetyl-4 methylcyclo-hex 3-ene.

EXERCISE. Mark some characteristic absorptions in the Infra-red spectrum of 1-acetyl-4 methylcyclohex - 3e.

We know that β -diketones exist as a mixture of ketonic and enolic forms in equilibrium with each other. The enolic form is stabilised by resonance.



For enolic form, $\nu_{C=O}$ absorption band appears in the region 1640-1580 cm^{-1} which is much lower than that for conjugated ketones. This much lowering is due to the intra-molecular hydrogen bonding stabilised by resonance. Acetyl acetone absorbs in the ketonic form at 1725 cm^{-1} and in the enolic form at 1630 cm^{-1} . Quantitative studies of these forms are possible from the peak intensities.

Quinones are a special case of α, β -unsaturated ketones. For this class of compounds, characteristic frequencies of absorption due to $C=O$ stretching and $C=C$ stretching lie in the region 1695 to 1587 cm^{-1} . *p*-quinones with two carbonyl groups in the same ring absorb in the range 1680-1660 cm^{-1} . Presence of electron repelling groups (+I effect) lowers the frequency of absorption while the presence of electron attracting group (-I effect) increases the force constant and hence raises the wavenumber of absorption.

EXAMPLE 9. Distinguish between the following two isomers of the molecular formula, C_3H_6O



SOLUTION.



- (i) $\nu C=O$ str $1740-1720\text{ cm}^{-1}$,
 (ii) $\nu C-H$ str $\sim 2720\text{ cm}^{-1}$ (For CHO)
 (iii) $\nu C-H$ str $\sim 3000\text{ cm}^{-1}$



- (i) $\nu C=O$ str $\sim 1715\text{ cm}^{-1}$
 (ii) $\nu C-H$ str $2960-2850\text{ cm}^{-1}$

PROBLEM P₃-4

Molecular formula— C_3H_6O

- (i) UV: λ_{max} 292 nm, ϵ_{max} 21.
 (ii) I.R. (i) 2720 cm^{-1} (w) (ii) 1738 cm^{-1} (s)

Determine the structure of the compound.

Table T₃-8. Aldehydes and Ketones

Group	Types of vibration	Region in cm^{-1} and intensity
Saturated aldehydes	$C=O$ str	$1740-1720$ (s)
HCHO	$C=O$ str	1750 (s)
CH_3CHO	$C=O$ str	1745 (s)
α, β -Unsaturated (aliphatic)	$C=O$ str	$1705-1680$ (s)
Aryl aldehyde	$C=O$ str	$1715-1690$ (s)
All aldehydes	$C-H^*$ str	(i) $2900-2820$ (w) (ii) $2770-2700$ (w) (iii) $1640-1550$ (s)
Saturated ketones	$C=O$ str	$1725-1700$ (s)
α, β -Unsaturated ketones	$C=O$ str	$1685-1665$ (s)
Cyclopropanone	$C=O$ str	~ 1855 (s)
Cyclobutanone	$C=O$ str	~ 1788 (s)
Cyclopentanone	$C=O$ str	~ 1746 (s)
Cyclohexanone	$C=O$ str	$1725-1705$ (s)
α, β -Unsaturated (Five membered)	$C=O$ str	$1725-1710$ (s)
α, β -Unsaturated (Six membered)	$C=O$ str	$1680-1665$ (s)
Aryl ketones	$C=O$ str	$1670-1660$ (s)
Diaryl ketones	$C=O$ str	$1700-1680$ (s)
β -diketones	$C=O$ str	(i) ~ 1725 (s) ketonic (ii) $1640-1580\text{ cm}^{-1}$ (enolic)
<i>p</i> -quinones	$C=O$ str	$1680-1660$ (s)
Hydroxy*aldehydes and ketones in which hydrogen bonding is possible	$C=O$ str	$\sim 1630^{**}$ (s)

* For aldehydes, two $C-H$ str bands may be noted; especially the one which appears at a lower wave number.

* $\nu O-H$ absorption gives a broad band near $3400-3200\text{ cm}^{-1}$.

** $\nu C=O$ absorption is sufficiently lower since intramolecular hydrogen bonded structure is stabilised by resonance.

Note the various regions of absorptions for C—H, \equiv C—H, = C—H, N—H, and O—H stretching frequencies in Fig. 3.48.

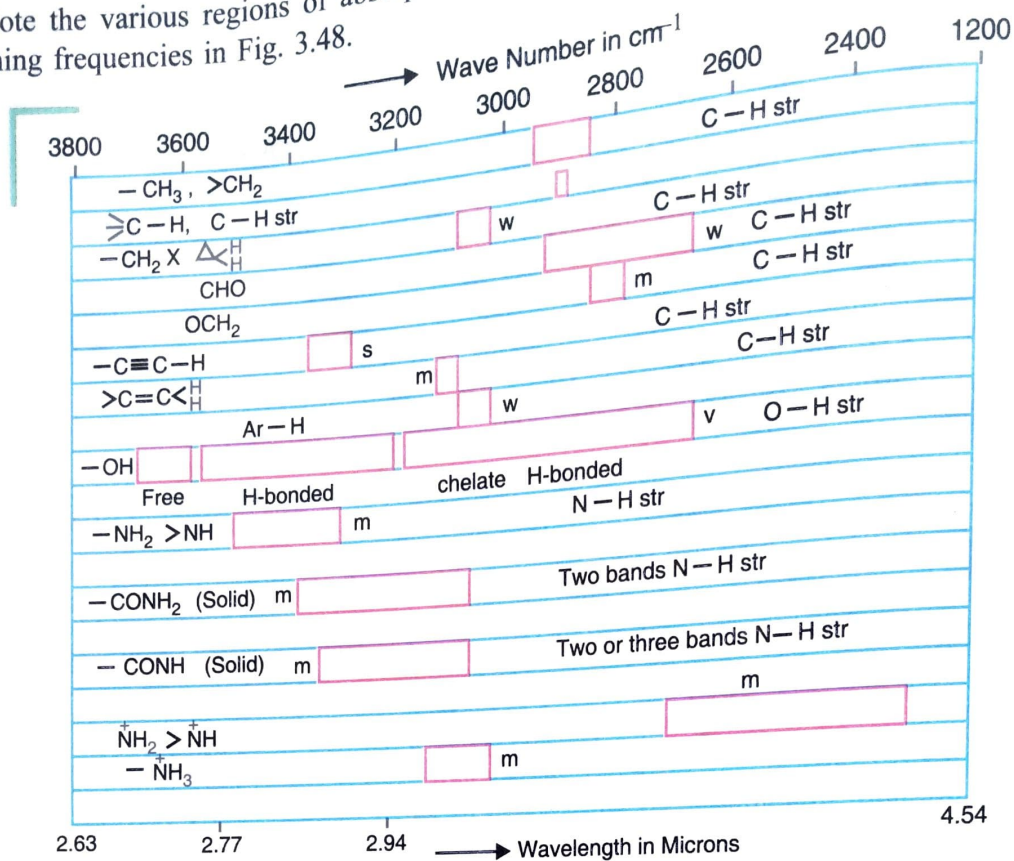


Fig. 3.48. Regions of absorptions for single bond hydrogen stretching frequencies.

Note the various regions of absorptions for C=C, C \equiv C, C \equiv N, C=C stretching frequencies and also N—H bending frequencies in Fig. 3.49.

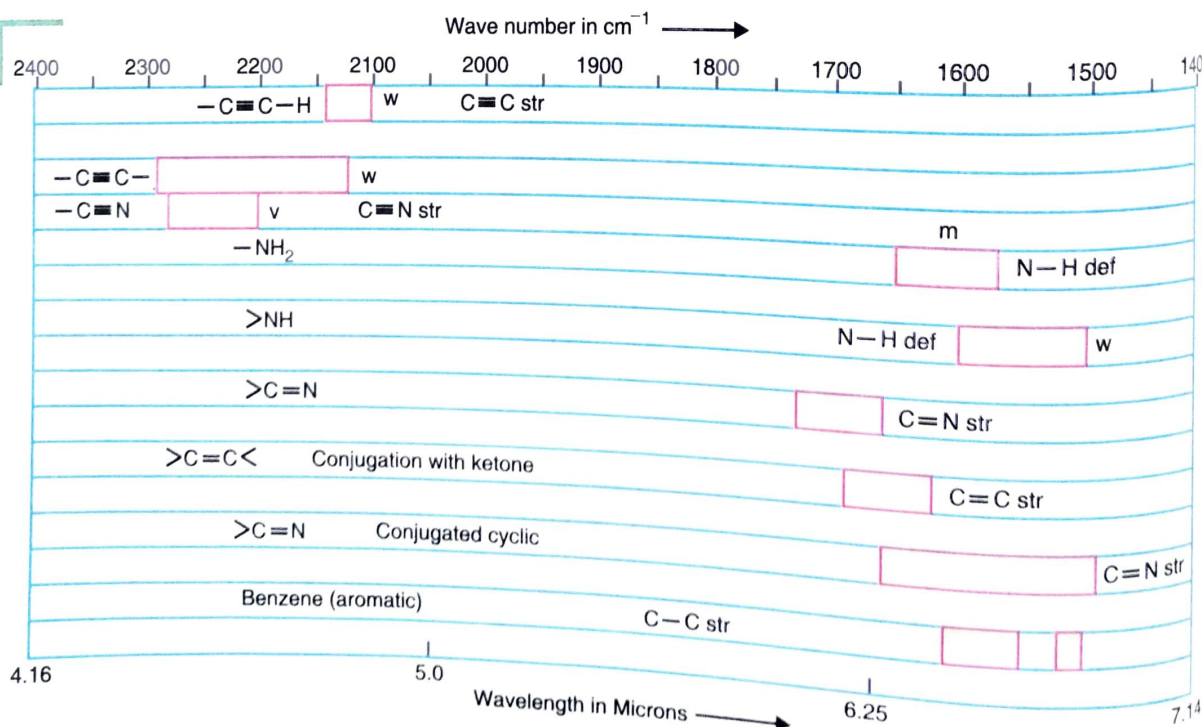


Fig. 3.49. Regions of absorption for (i) stretching frequencies of double and triple bonds and (ii) N—H bending frequencies.

Write important regions of absorption for:

- (i) $\equiv \text{C}-\text{H}$ str for acetylenic compounds
- (ii) $\text{C}-\text{H}$ str in aldehydes
- (iii) $\text{O}-\text{H}$ str for free and bonded alcohols
- (iv) $\text{O}-\text{H}$ str for carboxylic acids
- (v) $\text{N}-\text{H}$ str for primary and secondary amines/amides

Write important regions of absorption for:

- (i) $\text{C}=\text{C}$ str when the double bond is in conjugation with the carbonyl group.
- (ii) $\text{C}=\text{C}$ str in aromatic compounds,
- (iii) $\text{C}\equiv\text{C}$ str in acetylenes,
- (iv) $\text{C}\equiv\text{N}$ str in nitriles,
- (v) $\text{N}-\text{H}$ def (bending) in case of primary and secondary amines and amides.

Note the various regions of absorption for $\text{C}=\text{O}$ stretching frequencies in Fig. 3.50.

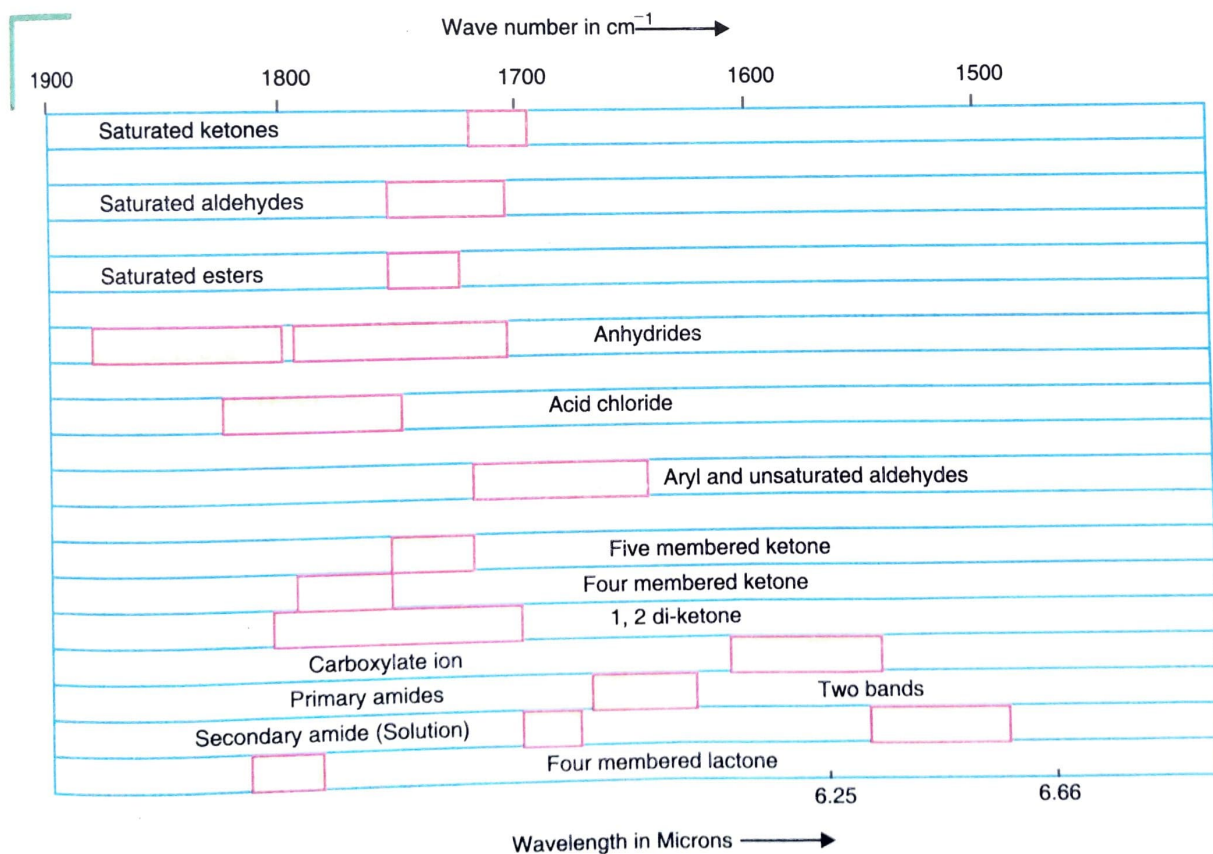


Fig. 3.50. Regions of absorption for the stretching frequencies of carbonyl group.

Write important regions of absorption for:

- (i) $\text{C}=\text{O}$ str. in anhydrides (two bands are observed; one is usually intense and the other is medium).

- (ii) C = O str in esters (the presence of an ester is confirmed by C—O str in the fingerprint region).
- (iii) C = O str in aldehydes (saturated and unsaturated). The presence is confirmed by C—H str at about 2720 cm^{-1} .
- (iv) C = O str in amides (primary and secondary). The presence is confirmed if there is absorption in the N—H str region.

Infra-red spectra of some more carbonyl compounds

(i) **Butanal:** The Infra-red spectrum of Butanal is given below:

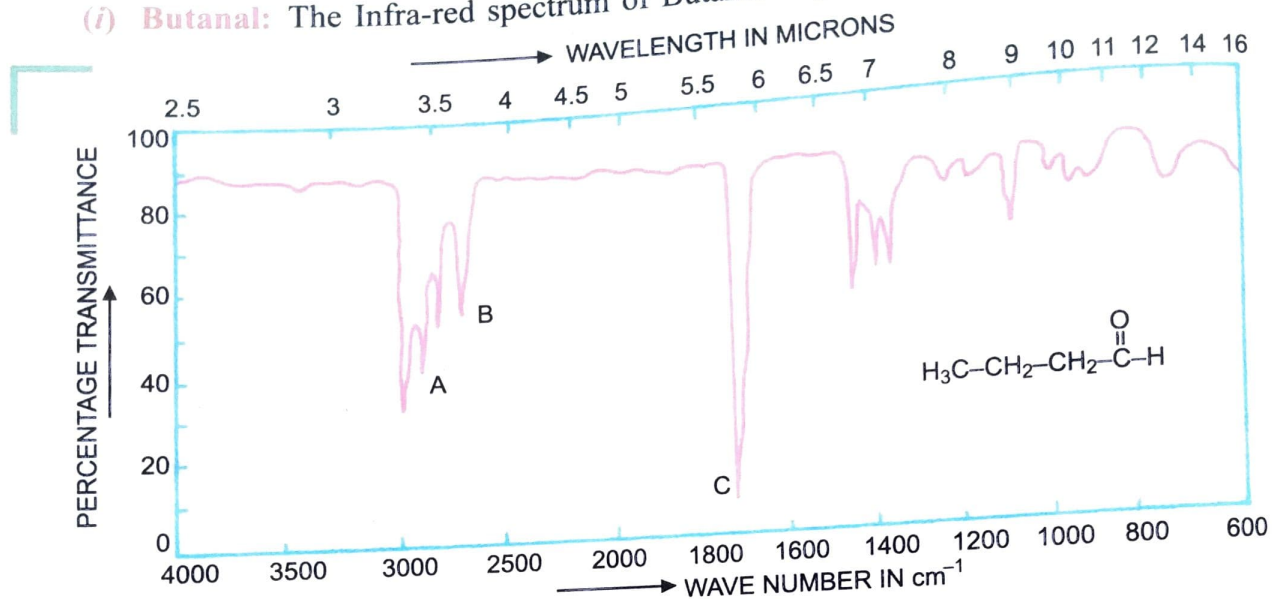


Fig. 3.51. Infra-red spectrum of Butanal.

Positions of some characteristic absorptions.

- | | |
|---------------------------|---|
| A = 2820 cm^{-1} | C — H str (in methyl) |
| B = 2715 cm^{-1} | C — H str (characteristic of aldehydes) |
| C = 1720 cm^{-1} | C = O str (due to aldehydes) |

(ii) **Hexan-2-one:** The Infra-red spectrum of Hexan-2-one is given below:

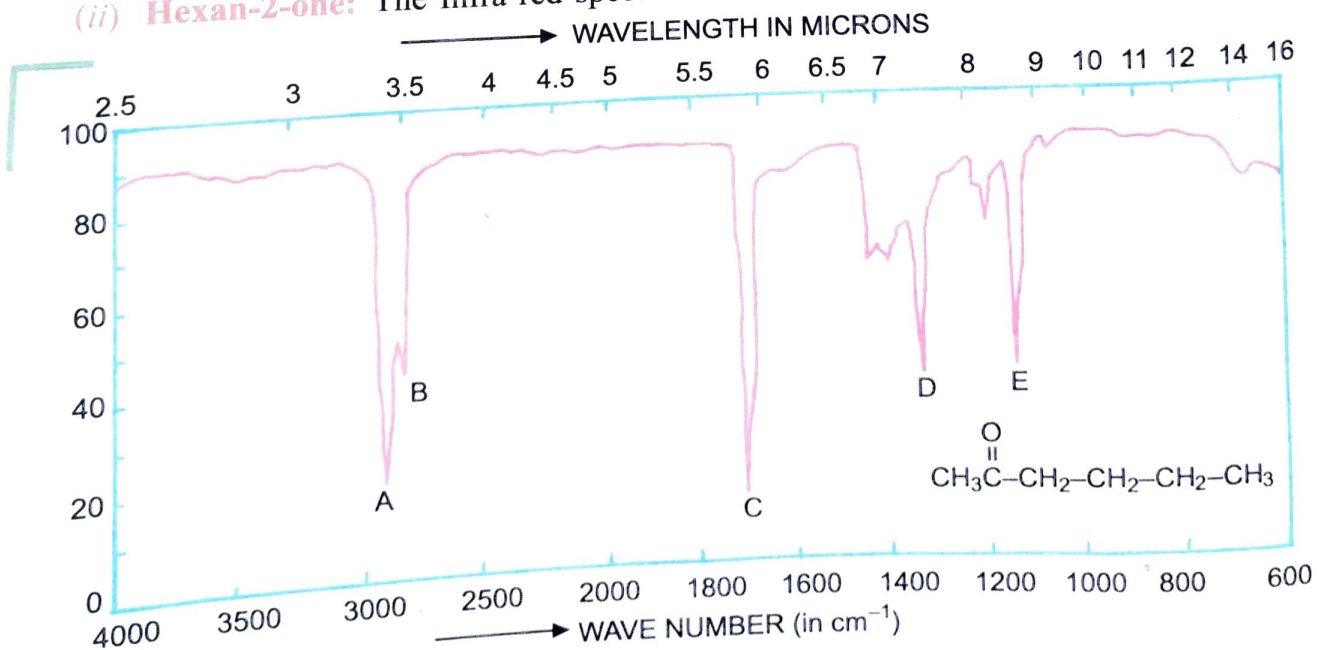


Fig. 3.52. Infra-red spectrum of Hexan-2-one.

Mark some important absorption positions characteristic of Hexan-2-one.